



JIAQI WU

THERMOELECTRIC MATERIALS WITH HIGH SURFACE AREA FOR
THE APPLICATION OF THERMOELECTRIC PROMOTION OF
CATALYSIS

School of Aerospace, Transport and Manufacturing
Manufacturing

PhD

Academic Year: 2019 - 2023

Supervisor: Dr Zhaorong Huang
Associate Supervisor: Dr Glenn Leighton
Jun 2023



School of Aerospace, Transport and Manufacturing

PhD
Academic Year 2019 - 2023

JIAQI WU

THERMOELECTRIC MATERIALS WITH HIGH SURFACE AREA FOR
THE APPLICATION OF THERMOELECTRIC PROMOTION OF
CATALYSIS

Supervisor: Dr Zhaorong Huang
Associate Supervisor: Dr Glenn Leighton
Jun 2023

This thesis is submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy
(NB. Remove if the degree award is based solely on examination of the thesis)

© Cranfield University 2023. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.

Academic integrity declaration

I declare that:

- the thesis submitted has been written by me alone.
- the thesis submitted has not been previously submitted to this university or any other.
- that all content, including primary and/or secondary data, is true to the best of my knowledge.
- that all quotations and references have been duly acknowledged according to the requirements of academic research.

I understand that to knowingly submit work in violation of the above statement will be considered by examiners as academic misconduct.

Abstract

Thermoelectric materials have been used for generating electricity from a temperature difference and noiseless cooling from electricity for several decades, but their application in the field of catalysis is still in its infancy. In fact, only a few years ago my supervisor and his colleagues used thermoelectric materials as a catalyst support and promoter for the first time in the world, and discovered that a Seebeck voltage can increase the catalytic activity by several tens to hundreds of times, and called this effect thermoelectric promotion of catalysis (TEPOC), or thermoelectrocatalysis. This effect has since been confirmed by other people in the world. This work aims to investigate other fundamental aspects of the application of thermoelectric materials for catalysis promotion, e.g., how to combine high surface area porous structure, how to achieve highest possible temperature difference in a given reaction chamber, and whether it is possible to use other thermoelectric materials which can work at high temperatures, for the thermoelectric promotion of catalysis.

Numerical modelling has been used to simulate the transient thermal behaviors of thermoelectric materials in a custom-made reaction chamber during a typical chemical reaction run, and the modelling results were used to guide the sample design. Firstly, thicker sample was found to generate higher Seebeck voltage. Secondly, stacked samples were found to have the similar promotional effect as if it is one single sample. The second point also enables the sample to be consisted of a dense bulk and porous surface sample, so that both the high Seebeck voltage and high surface area for the sample could be achieved for a stacked sample.

Sol-gel technique and the addition of polymer particles to thermoelectric powders have been used to obtain porous high surface area thermoelectric materials. Their microstructural and thermal transport properties have been

characterized and their effect for the application of TEPOC on the reverse water-gas shift (RWGS) reactions has been investigated. Generally speaking, the porous sample has a much higher (>10 times) surface area than their non-porous counterparts, but possesses much lower Seebeck coefficient. This leads to a modest improvement of catalysis promotion as compared to the non-porous ones. The previously observed TEPOC dynamic rate equation, i.e., the linearity between the promotional ratio and the Seebeck voltage, was proved to be effective for porous thermoelectric materials.

A new Figure of merit for thermoelectric materials for the application of TEPOC, has been proposed as S/κ , here S is the Seebeck coefficient and κ the thermal conductivity of the thermoelectric material. This Figure of merit is different from the usual dimensionless Figure of merit ZT which is best for the indication of energy conversion efficiency. A comprehensive literature survey has been carried out and it was found out that among all the non-single crystal thermoelectric materials, the previously used BiCuSeO have the highest S/κ , and another oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ systems which are stable at very high temperatures also have a high S/κ . Following this, thermoelectric $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples were prepared and applied in CO_2 hydrogenation reactions. The results reveal a strong enhancement in Seebeck coefficient by doping Tb into $\text{Ca}_3\text{Co}_4\text{O}_9$, while $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples showed excellent stability at the range of 373K-1073K. A highest CO_2 conversion of 64% was obtained from $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples at 700K and inlet gas ratio $\text{H}_2:\text{CO}_2=3:1$.

In summary, the high catalytic activity of porous BiCuSeO samples demonstrates the great potential of combining high porosity with the thermoelectric materials in the application of TEPOC. In the meantime, the use of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ enables higher temperature range in the field of TEPOC application.

Keywords

Thermoelectric promotion of catalysis; porosity; BiCuSeO; $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$; thermoelectric effect

Acknowledgements

I would like to begin by expressing my deepest gratitude to my advisor, Dr Zhaorong Huang, for his invaluable guidance, unwavering support, and immense patience throughout my doctoral journey. His expertise, insightful feedback, and constructive criticism have been indispensable in shaping the trajectory of my research and enhancing the quality of this thesis.

I am also indebted to my collaborators, Professor Michael J. Reece and Dr. Kan Chen from School of Engineering and Materials Science, Queen Mary University of London, for their contribution in characterizing the thermoelectric properties of my samples as well as Dr. Richard Tuley and Dr. Cevriye Koz from European Thermodynamics Ltd., for their kindly help with sample preparation and characterization.

My sincere thanks go to the faculty members and staff at Surface Engineering and Precision Centre, specifically Dr. Christopher Shaw, Mr Tim Pryor and Mr Andrew Stallard, for providing me with a nurturing academic environment, state-of-the-art facilities, and access to invaluable resources. I am also grateful to Drs. Tracey Roberts, Sunera Athauda for their efforts in sample characterization.

I would like to extend my heartfelt appreciation to all the participants who generously volunteered their time and shared their experiences for the purpose of this research. Without their cooperation and willingness to contribute, this study would not have been possible.

At last, I am deeply grateful to my family for their unconditional love, unwavering belief in me, and constant encouragement. Their sacrifices, understanding, and unwavering support have been the bedrock of my success. I am forever indebted to them.

Table of Contents

Academic integrity declaration	i
Abstract.....	ii
Acknowledgements	v
List of Figures	ix
List of Tables	xv
List of Equations	xvi
List of Abbreviations.....	xviii
1 Introduction	1
1.1 Brief Background.....	1
1.2 Aim and Objectives	2
1.3 Thesis Structure	3
2 Literature Review	4
2.1 Literature Review on Thermoelectricity	4
2.1.1 Thermoelectric Effects	4
2.1.2 Means for Increasing Thermoelectricity	5
2.1.3 Applications for Thermoelectricity	19
2.1.4 Research Progress of Thermoelectric Materials	21
2.1.5 Fabrication methods of Thermoelectric Material BiCuSeO	23
2.1.6 Survey of thermoelectric materials for TEPOC application	25
2.2 Literature Review on Catalysis	33
2.2.1 Catalyst Components and Their Functions.....	34
2.2.2 Reverse Water Gas Shift (RWGS) reaction - one of the most popular research topics in the field of catalysis	40
2.2.3 The Improvement of Catalytic Activity.....	46
3 Methods for Materials Processing and Characterizations	57
3.1 Introduction.....	57
3.2 Thermoelectric samples preparation	57
3.2.1 Synthesis of BiCuSeO powder through Flux method.....	57
3.2.2 Preparing nano-porous BiCuSeO samples through Sol-Gel method.....	58
3.2.3 Methods for obtaining porous/nano-porous/non-porous BiCuSeO samples	59
3.2.4 Preparation of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples	60
3.3 Characterization Methods.....	61

3.3.1 Microstructure Characterizations	61
3.3.2 Thermoelectric properties	63
3.3.3 Experimental Set-up for Catalytic Chemical Reactions.....	64
4 Characterization of porous/non-porous BiCuSeO	67
4.1 Introduction.....	67
4.2 Result and discussion	67
4.2.1 The XRD analysis of porous/non-porous BiCuSeO prepared by Flux method and Spark plasma sintering.....	67
4.2.2 The XRD analysis of BiCuSeO prepared by Sol-Gel method ..	68
4.2.3 BET surface area measurement results	81
4.2.4 The surface morphology of BiCuSeO samples	82
4.2.5 Band gap	96
4.3 Conclusion.....	98
5 Simulation and experimental verification of temperature distribution of thermoelectric samples under reaction conditions.....	99
5.1 Introduction.....	99
5.2 Result and discussion	100
5.2.1 3D modelling and heating process.....	100
5.2.2 The establishment of a simplified 3D model and implement of finite element simulation	102
5.2.3 Meshing	104
5.2.4 The setting of loading conditions and solution	109
5.2.5 The temperature distribution of the TE sample under simulated and experimental heating conditions	113
5.3 Conclusion.....	119
6 Effect of sample thickness and porosity on the catalytic activity of BiCuSeO	120
6.1 Introduction.....	120
6.2 Result and discussion	120
6.2.1 The characterization of porous and non-porous BiCuSeO samples	120
6.2.2 Initial test on 4mm bulk BiCuSeO sample under TE and RTE conditions	124
6.2.3 The effect of sample thickness on the catalytic activity of BiCuSeO samples	126
6.2.4 The use of stacked sample in CO ₂ hydrogenation reactions ..	129

6.2.5 The effect of porosity on the thermoelectric properties of stacked BiCuSeO samples	132
6.2.6 The effect of porosity on the CO ₂ conversion and CO selectivity	135
6.3 Conclusion.....	138
7 Thermoelectric Ca _{2.6} Tb _{0.4} Co ₄ O ₉ for the CO ₂ mitigation reactions	140
7.1 Introduction.....	140
7.2 Result and discussion	141
7.2.1 Microstructural characterization of Ca _{2.6} Tb _{0.4} Co ₄ O ₉ samples.....	141
7.2.2 The effect of sample thickness on the catalytic activity of Ca _{2.6} Tb _{0.4} Co ₄ O ₉	144
7.2.3 High CH ₄ selectivity under Reduced Thermoelectric condition	152
7.2.4 The effect of inlet gas ratio H ₂ :CO ₂ on the catalytic activities of Ca _{2.6} Tb _{0.4} Co ₄ O ₉ under Reduced Thermoelectric condition	158
7.3 Conclusion.....	161
8 Conclusions	163
9 Recommendations for Future Work	166
10 REFERENCES	168

List of Figures

Figure 2-1 Schematic of (a) Seebeck effect; (b) Peltier effect and (c) Thomson effect	4
Figure 2-2 Schematic representation of the density of electron states of the valence band of pure PbTe (dashed line). The figure of merit ZT is optimized when the Fermi energy E_F of the holes in the band falls in the energy range ER of the distortion (Heremans et al., 2008)	8
Figure 2-3 (a) Pisarenko relation between Seebeck coefficient and carrier concentration; (b) Properties of $\text{Pb}_{0.98}\text{Tl}_{0.02}\text{Te}$ with different content (Zhang et al., 2012)	10
Figure 2-4 (a) Schematic of the alignment of the valence band (VB) and conduction band (CB) energies of SrTe precipitates in the PbTe matrix at above 300K, with the changes of (b) carrier mobility μ and (c) ZT value of different PbTe–SrTe samples doped with 1% Na ₂ Te and a control sample containing no SrTe (Biswas et al., 2011)	11
Figure 2-5 (a) Mg doping increased the band gap width of SnTe; (b) The thermoelectric Figure of merit ZT in Mg (2-10 at. %) alloying SnTe samples	12
Figure 2-6 (a) all-scale hierarchical architectures, and (b) cumulative distribution function of lattice thermal conductivity	13
Figure 2-7 (a) Crystal structure diagram of $\text{AgPb}_{18}\text{SbTe}_{20}$ (LAST); (b) schematic of the charge balance in LAST; (c) The nanostructure of Ag-Sb-riched nano dots under TEM; (d) Thermoelectric Figure of merit ZT of LAST with the increase of temperature	14
Figure 2-8 (a) TEM image of mesoscale grains; (b) Platelet-like and spherical nanoscale precipitates; (c) Grain size distribution histogram; (d) Size distribution histogram of SrTe nanoparticles; (e) High-magnification lattice image depicting some perpendicular or parallel platelet-like precipitates; (f) Platelet-like precipitates along only one direction (Wu et al., 2015)	15
Figure 2-9 (a) Maximum achievable ZT values; (b) ZT as a function of temperature (Biswas, 2012)	16
Figure 2-10 (a) Schematic of lone pairs in Sb-containing compounds and (b) the thermal conductivity of AgSbTe_2 , AgBiSe_2 , of single-crystal PbTe, and of the chalcopyrite compound AgInTe_2 (Morelli et al., 2008)	18

Figure 2-11 (a) the atomic structure of BiCuSeO compounds; (b) Figure -of-merit ZT of typical current thermoelectric materials.....	19
Figure 2-12 integrating thermoelectrics into vehicles for improved fuel efficiency (C. B. Vining, 2009).....	20
Figure 2-13 Current state-of-the-art bulk thermoelectric materials: the Figure-of-merit ZT as a function of temperature and year (Tan et al., 2016).....	22
Figure 2-14 Geometric and electronic structures of single/dual-atom, cluster and bulk metal materials. (Hou <i>et al.</i> , 2020).....	35
Figure 2-15 The Cu ⁰ active site near the Cu-FeO _x interface (Guo <i>et al.</i> , 2020)	42
Figure 2-16 Schematic of the RWGS reaction over Pt/CeO ₂ (Goguet <i>et al.</i> , 2004)	43
Figure 2-17 Schematic of the RWGS reaction on Pd/Al ₂ O ₃ (Wang <i>et al.</i> , 2015)	45
Figure 2-18 Schematic of Supported Ru/CeO ₂ for CO ₂ reduction and the increase of CO Selectivity (Aitbekova <i>et al.</i> , 2018)	47
Figure 2-19 Steady-state effect of applied current on the rate of ethylene oxidation Broken lines are constant enhancement factor lines	50
Figure 2-20 Schematic of a metal catalyst electrode particle supported on Y2O3-doped ZrO2 (YSZ), an O2- conductor, under open-circuit conditions (top) and upon application of an anodic (positive) current showing the backspillover-formed double layer at the metal-gas interface (bottom). (Yiokari et al., 2000; Vayenas et al., 2001; Papadakis et al., 1996)	52
Figure 2-21 Monolithic electrochemical promotion reactor (Souentie <i>et al.</i> , 2009)	53
Figure 2-22 Schematic of energy bands and Fermi levels for TE materials (Achour <i>et al.</i> , AEnM, 2018).....	54
Figure 2-23 The reaction rate in a log scale as a function of increasing Seebeck voltage (Achour <i>et al.</i> , ACS Catal., 2018)	55
Figure 3-1 (a) and (b) the raw materials in the crucible; (c) BiCuSeO samples after calcination	58
Figure 3-2 (a) Schematic and (b) actual picture of the reaction chamber	65

Figure 4-1 XRD patterns of non-porous samples BCSO @Flux and BCSO @SPSed; porous samples BCSO @10wt% PS, BCSO @15wt% PS and BCSO @20wt% PS.....	68
Figure 4-2 XRD patterns of the gels which were calcined at 500°C, 530°C, 570°C and 600°C, the BiCuSeO phase only generated at the gel sample which calcined at around 570°C.....	70
Figure 4-3 XRD patterns of the gels calcined under 530°C - 570°C, a relatively pure BiCuSeO phase was obtained from the gel which calcined under 550°C (i.e. sample 1d)	71
Figure 4-4 XRD patterns of the Sol-Gel method BiCuSeO samples calcined under heating ramp rates of 6°C/min, 4°C/min and 2°C/min, BiCuSeO phase tend to be generated at lower heating ramp rate.....	73
Figure 4-5 XRD patterns of calcined gel samples, with different molar ratio of $n(\text{NA}):n(\text{M}^{n+})=10:1$, $15:1$ and $20:1$ in their gel formula, the highest proportion of BiCuSeO phase was observed on sample with $n(\text{NA}):n(\text{M}^{n+})=20:1$	75
Figure 4-6 XRD patterns of the calcined samples with molar ratio of $n(\text{CA}):n(\text{M}^{n+})=0.5:1$, $1:1$, $2:1$ and $3:1$, the optimal ratio among these results is $n(\text{CA}):n(\text{M}^{n+})=1:1$	77
Figure 4-7 XRD patterns of the calcined samples with molar ratio of $n(\text{EG})$: ..	79
Figure 4-8 More secondary phases appear on the XRD patterns of dip-coated or drop-coated BiCuSeO samples rather than sample BCSO @50wt% Gel	80
Figure 4-9 The isotherm of samples (a) BCSO @20wt% PS and (b) BCSO @50wt% Gel	82
Figure 4-10 The surface morphology of porous BiCuSeO samples at 200X..	84
Figure 4-11 Statistic of pore diameter distribution.....	86
Figure 4-12 Pore diameter distributions of (a) BCSO @20wt% PS 0.53MPa, (b) BCSO @20wt% PS 1.07MPa, and (c) BCSO @20wt% PS 1.60MPa.....	88
Figure 4-13 Pore area measurement using imageJ	89
Figure 4-14 5000X SEM images for porous BiCuSeO samples pressed under pressures (a) 0.53MPa; (b) 1.07MPa; (c) 1.60MPa.....	92
Figure 4-15 Compositional analysis of porous BiCuSeO samples surface	94

Figure 4-16 5000X SEM images for porous BiCuSeO samples with PS additions (a) 10wt%; (b) 15wt%; (c) 20wt%.....	95
Figure 4-17 Band gap measurement result of BiCuSeO under different sintering conditions	97
Figure 5-1 Diagram of the analysis process.....	99
Figure 5-2 3D model of reaction chamber.....	100
Figure 5-3 The Time-Temperature curve during the heating process for finite element simulation	101
Figure 5-4 Sectional view of the simplified model of the reaction chamber with TE sample	103
Figure 5-5 Meshing diagram of (a) The reaction rig with TE sample inside and (b) the enlarged TE sample.....	105
Figure 5-6 (a) Schematic diagram of the location of four probes (b) the final temperatures at these four probes changed slightly with the meshing condition.....	107
Figure 5-7 The temperatures at four specific positions on the TE sample was lower under a dwelling time of 20 mins, but kept stable when dwelling time range from 30 mins to 60 mins.....	111
Figure 5-8 The simplified heating process	112
Figure 5-9 The temperature distribution of (a) 4mm and (b) 10mm TE sample at heating temperature of 750°C	114
Figure 5-10 The temperature difference ΔT at (a) the center and (b) the edge of 2mm, 4mm, 6mm, 8mm and 10mm TE samples.....	115
Figure 5-11 The schematic of the thermocouples within the reaction chamber	117
Figure 5-12 The values of simulated and experimental measured temperatures of 2mm (a), (b); 4mm (c), (d) and 6mm (e), (f) BiCuSeO samples are very close.....	119
Figure 6-1 (a) thermal conductivity, (b) electrical conductivity, (c) Seebeck coefficient and (d) ZT value as a function of temperature for porous/non-porous BiCuSeO samples	121
Figure 6-2 XRD patterns of the newly prepared non-porous sample BCSO @Flux and porous sample BCSO @50wt% Gel before being used for chemical reaction	122

Figure 6-3 The BiCuSeO samples BCSO @Flux and BCSO @50wt% Gel decomposed severely after applied in catalytic chemical reactions at 450°C for 10 hours, but it was more stable at 400°C after over 100 hours	123
Figure 6-4 The (a) CO ₂ conversion and (b) CO selectivity as a function of T _h for samples hereinafter.....	125
Figure 6-5 the Seebeck voltage as a function of T _h for samples BCSO 6B @1:1, BCSO 4B @1:1 and BCSO 2B @1:1	127
Figure 6-6 The relationship between (a) T _h - CO ₂ Conversion, (b) T _h - CO Selectivity and (c) -eV/k _b T _h - ln (Y) for samples BCSO 6B @4:1, BCSO 4B @4:1 and BCSO 2B @4:1	128
Figure 6-7 The (a) CO ₂ conversion, (b) Seebeck voltage V, and (c) CO selectivity as a function of T _h for samples BCSO 4B + 2B @1:1 and BCSO 6B@1:1	131
Figure 6-8 Schematic diagram for the stacked BCSO sample	133
Figure 6-9 The (a) Seebeck voltage and (b) Seebeck coefficient as a function of T _h for samples BCSO 4B+2P, BCSO 4B+2B, BCSO 2B+2P and BCSO 2B+2B	134
Figure 6-10 CO ₂ conversion as a function of (a) temperature T _h and (B) Seebeck voltage V for samples BCSO 4B + 2P @1:1, BCSO 4B + 2B @1:1, BCSO 2B + 2P @1:1 and BCSO 2B + 2B @1:1	135
Figure 6-11 CO selectivity as a function of Th for BCSO 4B + 2P @1:1, BCSO 4B + 2B @1:1, BCSO 2B + 2P @1:1 and BCSO 2B + 2B @1:1.....	138
Figure 7-1 XRD pattern of Ca ₃ Co ₄ O ₉ and Ca _{2.6} Tb _{0.4} Co ₄ O ₉ samples	141
Figure 7-2 (a) thermal conductivity and (b) Seebeck coefficient of Ca ₃ Co ₄ O ₉ and Ca _{2.6} Tb _{0.4} Co ₄ O ₉ samples.....	143
Figure 7-3 DSC and TG analysis of Ca _{2.6} Tb _{0.4} Co ₄ O ₉ sample.....	143
Figure 7-4 The relationship between (a) T _h and CO ₂ conversion; (b) Seebeck voltage V and CO ₂ conversion; (c) T _h and CO selectivity.....	145
Figure 7-5 The calculated TEC for RWGS (a) with methanization and (b) without methanization (U. R. Bajirao, 2012)	149
Figure 7-6 The CO ₂ conversion as a function of (a) T _h and (b) V; and the CO selectivity as a function of (c) T _h for 4mm and 6mm CTCO samples at H ₂ :CO ₂ =1:1 and 3:1	151

Figure 7-7 The CO ₂ conversion as a function of (a) T _h and (b) V for 2mm and 4mm CTCO samples under TE and RTE conditions	153
Figure 7-8 The relationship between (a) T _h – CO KPA; (b) T _h – CH ₄ KPA; (c) V – CO KPA; and (d) V – CH ₄ KPA for 2mm and 4mm CTCO samples under TE and RTE conditions	155
Figure 7-9 The CO selectivity as a function of T _h for 2mm and 4mm CTCO samples under TE and RTE conditions	157
Figure 7-10 The (a) CO ₂ conversion; (b) CO selectivity; (c) CO KPA and (d) CH ₄ KPA as a function of T _h	159

List of Tables

Table 2-1 Thermoelectric properties and a new Figure of merit S/k of thermoelectric materials	27
Table 4-1 Gel formula for the Sol-Gel method and calcination procedure	69
Table 4-2 The BET surface area of non-porous sample BCSO @Flux and they other porous samples.....	82
Table 4-3 Surface porosity measurement results.....	90
Table 5-1 The simulation time nodes and their correlation temperature	101
Table 5-2 The dimensions of the main part of the model	103
Table 5-3 The meshing parameters for the simplified model	104
Table 5-4 the quality check results under different meshing conditions, better average element quality were obtained from model 3, 4 and 5	106
Table 5-5 Thermo-physical properties of the materials that used for the simulation	108
Table 5-6 The recorded hot surface temperatures of TE sample at step sizes of 0.5, 1, 2, 3 and 4 minutes, P1-P7 represent seven stages during the heating process and were pointed out in Figure 5-8	112
Table 6-1 The combination of stacked BCSO sample refer to Figure 6-8....	133
Table 7-1 Room temperature electrical conductivity for $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ prepared using SPS and SSR	142
Table 7-2 The preset temperatures of hot plate during heating process and the corresponding T_h , ΔT , V and S	147
Table 7-3 The temperature T_h and the corresponding ΔT and V of 2mm and 4mm samples CTCO samples under TE and RTE conditions.....	156

List of Equations

Equation 2-1	5
Equation 2-2	5
Equation 2-3	5
Equation 2-4	6
Equation 2-5	6
Equation 2-6	7
Equation 2-7	8
Equation 2-8	8
Equation 2-9	12
Equation 2-10	17
Equation 2-11	26
Equation 2-12	37
Equation 2-13	40
Equation 2-14	40
Equation 2-15	40
Equation 2-16	41
Equation 2-17	41
Equation 2-18	42
Equation 2-19	42
Equation 2-20	42
Equation 2-21	43
Equation 2-22	43
Equation 2-23	43
Equation 2-24	43
Equation 2-25	43
Equation 2-26	49

Equation 2-27	49
Equation 2-28	49
Equation 2-29	50
Equation 2-30	50
Equation 2-31	55
Equation 2-32	56
Equation 3-1	63
Equation 3-2	63
Equation 3-3	64
Equation 3-4	66
Equation 3-5	66
Equation 4-1	75
Equation 4-2	88
Equation 6-1	127
Equation 6-2	129

List of Abbreviations

BCSO	BiCuSeO
BET	Brunauer–Emmett–Teller
CCO	$\text{Ca}_3\text{Co}_4\text{O}_9$
CTCO	$\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive Spectroscopy
EPOC	Electrochemical Promotion of Catalysis
GC	Gas Chromatography
NEMCA	Non-Faradaic Electrochemical Modification of Catalytic Activity
RTE	Reduced Thermoelectric
RWGS	Reverse Water Gas Shift
TCD	Thermal Conductivity Detector
TE	Thermoelectric
TEC	Thermodynamic Equilibrium Conversion
TEPOC	Thermoelectric Promotion of Catalysis
TG	Thermogravimetry
SEM	Scanning Electron Microscopy
SPS	Spark Plasma Sintering
SSR	Solid-State Reaction
UV-Vis	Ultraviolet–Visible
XRD	X-Ray Diffraction
ZT	Figure of Merit

1 Introduction

1.1 Brief Background

Catalysts are used in more than 95% of industrial chemical processes because they can increase the reaction rate, reduce the operational temperature, or improve the yield of a desired product. It is highly desirable to be able to control the catalytic activity of a reactor under operation, particularly for operations under dynamic conditions. Generally, this can be achieved by adjusting the particle size of the active component in-situ, or introducing promotional species onto the catalyst surface by applying an external small current or voltage to metal catalysts supported on a solid state electrolyte through electrochemical promotion of catalysis, also called Non-Faradaic Electrochemical Modification of Catalytic Activity (NEMCA). NEMCA has proved to be an excellent research technique, but its large-scale industrial use has been limited mainly due to the low efficiency of the catalytic materials (which are often expensive noble metals), because a continuous film is required to maintain electrical conductivity, and also there is a need to maintain electrical connection under often harsh chemical reaction conditions.

Given the swift expansion of energy needs and exacerbation of pollution, there is growing awareness of the requisite for exploring novel energy conversion technologies and developing more eco-friendly and efficacious catalysts. Thermoelectric (TE) devices have been used for generating electricity from heat and silent cooling from electricity for many years. Recently, a new concept named Thermoelectric Promotion of Catalysis (TEPOC) was presented to indicate the process in which a thermoelectric material is utilized to enhance the performance of a catalyst in a chemical reaction. In the TEPOC process, the thermoelectric material acts as a catalyst support and promoter. It converts a temperature difference into an electrical potential difference, which promotes the chemical reaction. This can accelerate the reaction rate, change the selectivity of the reaction, and even activate the reaction at lower temperatures.

As thermoelectric materials can also be used alone-without any other noble metal catalysts, the above effect can also be termed as thermoelectrocatalysis. TEPOC and thermoelectrocatalysis are interchangeable in this thesis.

TEPOC effect was first reported on the CO₂ hydrogenation by a TE material BiCuSeO (A.Achour *et al.*, 2018). The generality of the suggested mechanism based on the work function change by the Seebeck voltage indicates that TEPOC could be applied to many different catalytic chemical processes. Indeed, several other groups in the world have since applied TEPOC to other applications, such as enhanced hydrogen peroxide generation for environmental disinfection (Lin *et al.*, 2021), and selective oxyfunctionalization of hydrocarbons by waste heat (Jaeho *et al.*, 2022). In both cases, a temperature difference across the thermoelectric material Bi₂Te₃, was the key for the increased generation of hydrogen peroxide. As a result, a high H₂O₂ generation rate was obtained and these were explained by the TEPOC model. Much more potential applications in the fields such as energy conversion, chemical synthesis, and environmental remediation can be envisaged, but generally speaking, TEPOC is still in the early stages of its development.

Generally speaking, any chemical reaction depends on the total surface area and its temperature. In order to further improve the TEPOC effect, this project aims to increase the total area at the reaction surface by creating porosity in the thermoelectric materials. A number of approaches were adopted in order to increase the temperature of the reaction surface in the specifically fabricated reaction chamber, in order to further improve the TEPOC effect.

1.2 Aim and Objectives

The aim of the project is to develop high surface area thermoelectric materials to work at highest possible temperature difference in a particular reaction chamber, in order to optimize the TEPOC effect. To achieve this aim, the following objectives will be fulfilled:

- 1: Numerical modelling of the current reaction rig for TEPOC in order to achieve the highest possible temperature difference.
- 2: Development of TE materials with high surface area, by introducing hierarchical porosity, nano-porosity and nano-structuring into the thermoelectric materials BiCuSeO.
- 3: To verify that high surface area can improve the TEPOC effect.
- 4: Exploration of TEPOC with high temperature TE materials.

1.3 Thesis Structure

This thesis is divided into eight chapters, of which this is the first. Each chapter is briefly described below. After providing a literature review on thermoelectric materials and catalyst (Chapter 2), Chapter 3 discusses the methods used in this project, followed by the details of preparation and characterization of thermoelectric materials in Chapters 4. The 3D modeling of thermoelectric sample and reaction chamber, the simulation and experimental verification of temperature distribution of thermoelectric samples under heating condition are presented in Chapters 5. The investigation of TEPOC, such as BiCuSeO with high surface area and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ on CO_2 hydrogenation reactions, can be found in Chapters 6 and 7, respectively. This dissertation finishes with Chapter 8 which summarizes the main conclusions of this work as well as recommendations for further studies in Chapter 9.

2 Literature Review

2.1 Literature Review on Thermoelectricity

Thermoelectric materials are a type of material with the ability to convert heat energy into electrical energy, and vice versa, through a phenomenon called the thermoelectric effect. Thermoelectric materials have various applications, particularly in energy harvesting and temperature control systems. They can be used to convert waste heat, such as from industrial processes or vehicle exhaust, into electricity, improving energy efficiency. They also find application in portable power generation, cooling electronic devices, and even in space exploration, where they provide reliable power in extreme temperature environments. In this chapter, the fundamental mechanism and application for thermoelectricity will be exemplified, as well as the introduction on thermoelectric materials.

2.1.1 Thermoelectric Effects

Seebeck, Peltier, and Thomson effects are all related phenomena that occur in thermoelectric materials. The schematic of these three effects are listed in Figure 2-1.

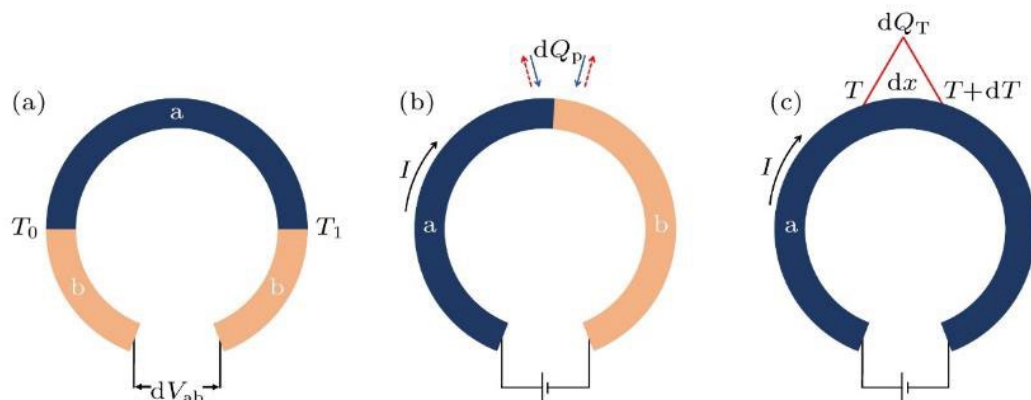


Figure 2-1 Schematic of (a) Seebeck effect; (b) Peltier effect and (c) Thomson effect

The Seebeck effect was first observed in 1821, which refers to the generation of an electric voltage when there is a temperature difference across a junction of two different materials a and b (Martin *et al.*, 2010). This effect occurs due to the difference in the behavior of charge carriers (electrons or vacancies) in the

two materials. The temperature difference ΔT leads to the diffusion of charge carriers, creating a potential difference or voltage, named Seebeck voltage V_{ab} .

$$V_{ab} = S_{AB} \cdot \Delta T \quad \text{Equation 2-1}$$

where S_{AB} is called Seebeck coefficient between the two materials A and B (Martin *et al.*, 2010).

The Peltier effect is considered as the reverse process to the Seebeck effect (L. Onsager, 1931). It describes the phenomenon where an electric current flowing through a junction of two dissimilar materials a and b leads to the absorption or release of heat at the junction, resulting in a temperature difference. Then heat change Q_P at the junction is depending on the direction of the current (i.e. I in Figure 2-1b), and expressed as

$$Q_P = \Pi \cdot I \quad \text{Equation 2-2}$$

where Π is the Peltier coefficient, I is current flow.

The Thomson effect (J. D. Goddard, 2011), which named after the Scottish physicist William Thomson (also known as Lord Kelvin), described the relationship between Seebeck effect and Peltier effect. It refer to the phenomenon where a temperature difference is produced in a conductor when an electric current flows through it. This effect occurs due to the interaction between the temperature difference and the behavior of charge carriers (usually electrons) within the conductor. The Thomson coefficient τ could be calculated as

$$\tau = Q_T / (I \cdot \Delta T) \quad \text{Equation 2-3}$$

where Q_T is the heat absorption or release rate. While a positive Thomson coefficient indicates heat absorption.

2.1.2 Means for Increasing Thermoelectricity

In the past century, a relatively complete theoretical model of thermoelectricity was established by German physicist E. Altenkirch. It has been pointed out that thermoelectric properties of materials can be characterized by the dimensionless thermoelectric Figure of merit ZT (Ioffe *et al.*, 1959). Materials

with high ZT values exhibits superior thermoelectric conversion efficiency. The ZT value can be calculated as,

$$ZT = S^2 \sigma T / (\kappa_l + \kappa_e) \quad \text{Equation 2-4}$$

where S is Seebeck coefficient, T is the absolute temperature; σ is the electrical conductivity of the material; $(\kappa_l + \kappa_e)$ represent the sum of the lattice thermal conductivity (κ_l) (related to the heat carried by phonons) and the carrier thermal conductivity (κ_e) (related to the heat carried by electrons). Besides, there is a liner relationship between the thermoelectric Figure of merit ZT and the energy conversion efficiency of material. From Equation 2-4, it can be concluded that a thermoelectric material with a high ZT value must have both a high Seebeck coefficient, high electrical conductivity and low thermal conductivity, where the thermoelectric properties of the material was directly determined by these important parameters. Therefore, it is important to achieve independent or cooperative regulation between these three parameters, then the material which has a higher thermoelectric Figure of merit ZT in a wider temperature range can be obtained in the future. For now, there are two commonly used methods to increase the thermoelectric Figure of merit ZT: one of which is to reduce the thermal conductivity (Zhao *et al.*, 2012), and the other is to increase the power factor PF ($PF = S^2 \sigma$) (Biswas *et al.*, 2011; Heremans *et al.*, 2008). However, the difficulty in improving the thermoelectric Figure of merit ZT is that the Seebeck coefficient, electrical conductivity, and thermal conductivity of the thermoelectric material are not unrelated, they are all depend on the electronic structure and the carrier transport characteristics of the material. For example, the electrical conductivity σ can be described as,

$$\sigma = qn\mu \quad \text{Equation 2-5}$$

where q is the electric charge of a charge carrier, n is the charge carrier concentration and μ represent the charge carrier mobility. Besides, the carrier thermal conductivity κ_e is related to the electrical conductivity σ according to the Wiedemann-Franz's law,

$$\kappa_e = L\sigma T$$

Equation 2-6

where L is the Lorentz number and it adopts the close-to-constant Sommerfeld value of $2.44 \times 10^{-8} \text{ W} \cdot \Omega \cdot \text{K}^{-2}$, T stand for the working temperature of the thermoelectric material. Since the Seebeck coefficient s , electrical conductivity σ and thermal conductivity ($\kappa_l + \kappa_e$) are intimately linked, which complicates optimization and typically requires a compromise. One common application of the thermoelectric materials is semiconductor cooler (also known as thermoelectric cooler) which has the advantages of high efficiency, environmental friendly and low maintenance, etc. (Kroon *et al.*, 2016).

2.1.2.1 Increase Seebeck coefficient

Among those thermoelectric materials with the multi-energy-band structure, there are some differences in the dispersion relationship and symmetry within different energy bands. It is proved that the Seebeck coefficient can be adjusted through changing the energy difference between the energy bands by tuning the doping and composition. The aim of this method is to converge the valence (or conduction) bands to achieve high valley degeneracy, as multiple charge carrying valleys can increase the effective mass (Mahan, 1998; DiSalvo, 1999) and therefore improve thermoelectric properties of the material with a slightly decrease in carrier mobility. Thus a new kind of thermoelectric materials with both high Seebeck coefficient and high electrical conductivity can be obtained (Pei *et al.*, 2011). For example, Pr dopant in $\beta\text{-Zn}_4\text{Sb}_3$ could effectively improve its thermoelectric properties (Dresselhaus *et al.*, 2007), the addition of Pr results in the state density resonance, it also doubled the carrier effective mass of $\beta\text{-Zn}_4\text{Sb}_3$ and increased the Seebeck coefficient by 40-50 $\mu\text{V/K}$.

Besides, the Seebeck coefficient can be enhanced through a distortion of the electronic density of states (DOS). According to Equation 2-4, it can be seen that increasing the Seebeck coefficient can directly affect the ZT value. Heremans *et al.* obtained the TI-doped PbTe ingot material and found that the addition of TI causes the DOS near the Fermi level in PbTe to protrude, as shown in Figure 2-2.

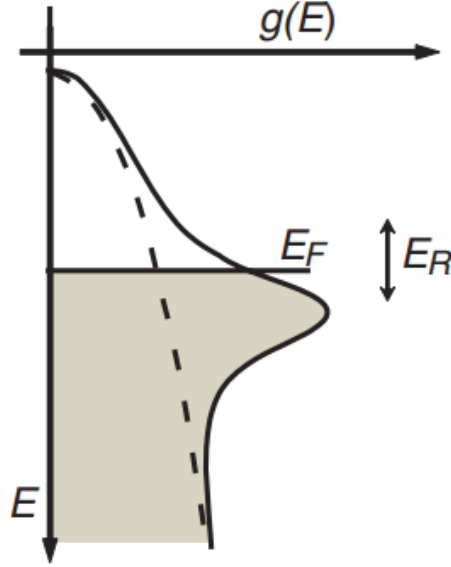


Figure 2-2 Schematic representation of the density of electron states of the valence band of pure PbTe (dashed line). The figure of merit ZT is optimized when the Fermi energy E_F of the holes in the band falls in the energy range E_R of the distortion (Heremans et al., 2008)

The effect of this local increase in DOS on Seebeck coefficient S is given by the Mott expression (Cutler *et al.*, 1969). As shown in Equation 2-7, S depends on the energy derivative of the energy-dependent electrical conductivity $\sigma(E)=n(E)q\mu(E)$ taken at the Fermi energy E_F ,

$$S = \frac{\pi^2}{3} \frac{k_B}{q} k_B T \left\{ \frac{d[\ln(\sigma(E))]}{dE} \right\}_{E=E_F} \quad \text{Equation 2-7}$$

$$= \frac{\pi^2}{3} \frac{k_B}{q} k_B T \left\{ \frac{1}{n} \frac{dn(E)}{dE} + \frac{1}{\mu} \frac{d\mu(E)}{dE} \right\}_{E=E_F}$$

where $n(E)=g(E)f(E)$, $n(E)$ represent the carrier density at the energy level E , $f(E)$ is the Fermi function, q the carrier charge, $\mu(E)$ is the mobility, and $g(E)$ is calculated as,

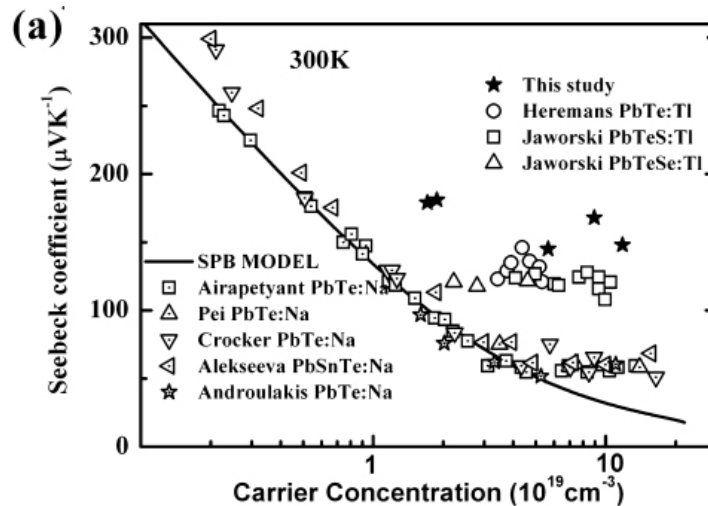
$$g(E) = \frac{(m_d^*)^{3/2} \sqrt{2E}}{\hbar^3 \pi^2} \quad \text{Equation 2-8}$$

where m_d^* is the effective mass.

Equation 2-7 reveals that there are two common ways to increase the Seebeck coefficient S : (i) increasing the energy-dependence of $\mu(E)$, for example, by a

scattering mechanism that strongly depends on the energy of the charge carriers; (ii) increasing the energy-dependence of $n(E)$, i.e. increase the value of $g(E)$. It can be seen from Figure 2-2 that the integral of the energy near the Fermi level increases with the widening of the DOS curve, thereby improving the $g(E)$ value. Many research were carried out to maximize the Seebeck coefficient of traditional thermoelectric materials.

The TI-doped PbTe prepared by ball milling with rapid hot pressing process was investigated (Zhang *et al.*, 2012), as shown in Figure 2-3a. Results shows that the grain size of the material is significantly reduced after the ball milling and hot pressing process, while the grain boundary scattering reduces the thermal conductivity of the material compared to the ingot. A PbTe thermoelectric material with a ZT of about 1.7 was obtained (Figure 2-3b) (Zhang *et al.*, 2012). In addition, the sample was likely to soften at a temperature above 673 K, which mainly due to higher vacancies, dislocations, and bond deformation in the sample. The addition of Si nanoparticles strengthened the mechanical property so the sample could stand higher temperature of 770K. The Al-doped PbSe was prepared and investigated as well, an n-type PbSe thermoelectric materials with a ZT value of 1.3 at 850 K was obtained. It can be concluded that the high ZT value is achieved by a combination of high Seebeck coefficient and low thermal conductivity, while the high Seebeck coefficient is possibly caused by the resonant states in the conduction band after Al dopant.



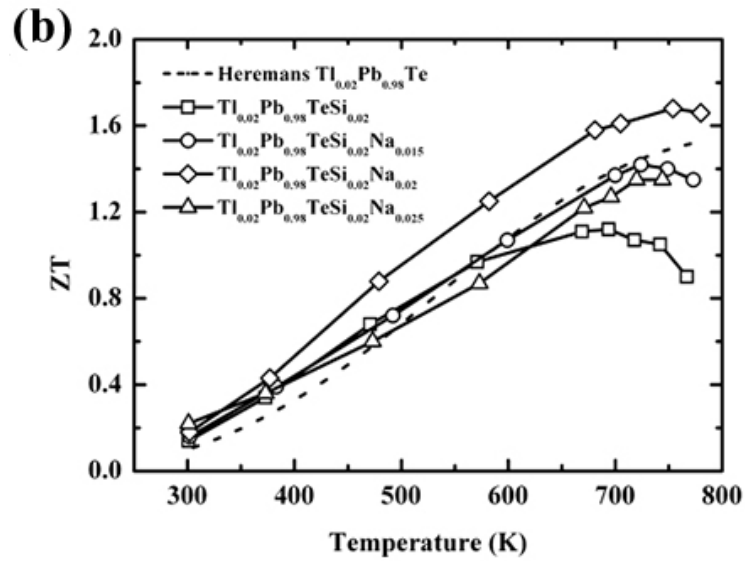


Figure 2-3 (a) Pisarenko relation between Seebeck coefficient and carrier concentration; (b) Properties of $\text{Pb}_{0.98}\text{Tl}_{0.02}\text{Te}$ with different content (Zhang et al., 2012)

The first band alignment example is the introduction of the SrTe phase in the PbTe matrix, see Figure 2-4a. The insertion of SrTe nanocrystals in PbTe matrix was considered not affect the hole scattering due to two reasons: (1) the three dimensional crystallographic alignment of SrTe and PbTe; (2) a small difference in energy levels of the valence bands between these two materials. Figure 2-4b shows the changes of carrier mobility μ with different SrTe contents in PbTe. It can be seen that with the increase of SrTe content, μ decreased significantly with the temperature, but it was less affected by SrTe content. Figure 2-4c shows the ZT value of PbTe / SrTe as a function of temperature. Result shows that by controlling the carrier mobility, and a thermoelectric Figure of merit ZT 1.7 was achieved (Biswas *et al.*, 2011).

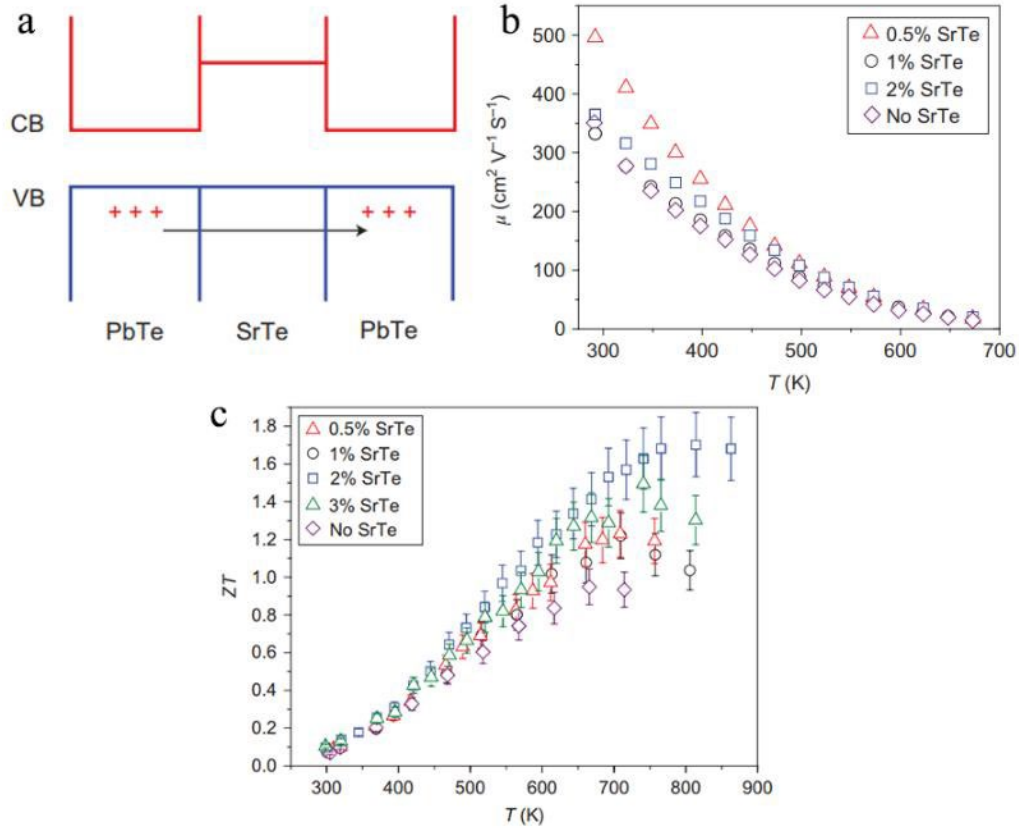


Figure 2-4 (a) Schematic of the alignment of the valence band (VB) and conduction band (CB) energies of SrTe precipitates in the PbTe matrix at above 300K, with the changes of (b) carrier mobility μ and (c) ZT value of different PbTe–SrTe samples doped with 1% Na₂Te and a control sample containing no SrTe (Biswas *et al.*, 2011)

Equation 2-8 suggested that the methods which increases the effective mass m^*_d could also improve $n(E)$, such as energy level resonances and the increase of DOS near the Fermi surface, and finally lead to the raise of Seebeck coefficient. It was also reported that the energy level resonance formed by TI increased the ZT value of PbTe to 1.5 (Heremans *et al.*, 2008). Pei *et al.* have prepared a p-type PbTe materials with high doping levels of Na. They observed a high hole concentration in the p-type PbTe samples with heavy effective mass, which leading to a high DOS near the Fermi level and a large Seebeck coefficient and high ZT value of 1.4 at 750 K. The addition of Mg into SnTe was also found to exhibit high Seebeck coefficient with a controlled hole concentration. As shown in Figure 2-5a (Banik *et al.*, 2015), the Mg dopant

optimize the electronic band structure SnTe of by increasing its band gap, and leads to a decrease in the energy separation between its light and heavy hole valence bands. Therefore, the contribution of the heavy holes valence band was improved, results in a significant improvement in the Seebeck coefficient in Mg-doped SnTe. Finally, a maximum thermoelectric Figure of merit ZT of 1.2 can be achieved at 860 K (Figure 2-5b).

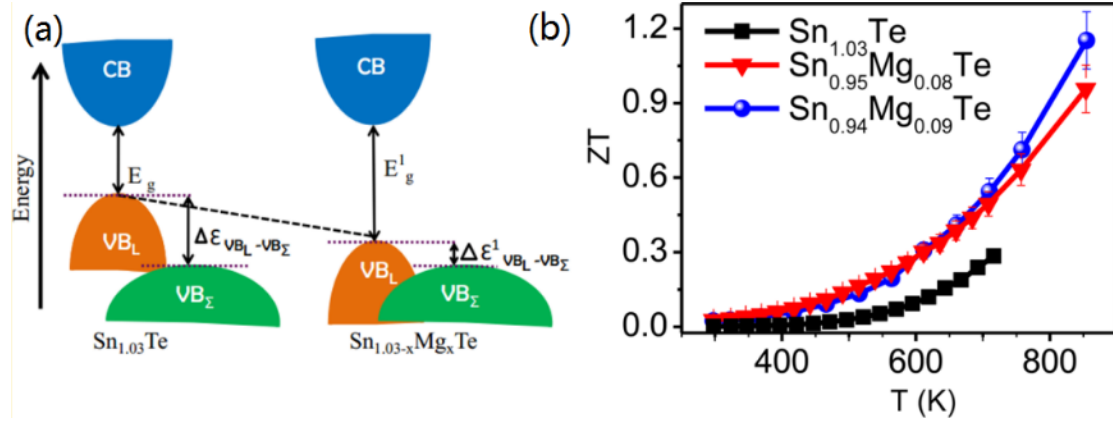


Figure 2-5 (a) Mg doping increased the band gap width of SnTe; (b) The thermoelectric Figure of merit ZT in Mg (2-10 at. %) alloying SnTe samples

2.1.2.2 Reduce thermal conductivity

Various methods were explored to reduce the thermal conductivity to improve the ZT value of thermoelectric materials since the mid-1990s. The thermal conductivity can be divided into two parts, the carrier thermal conductivity κ_e and the lattice thermal conductivity κ_l . However, the decrease of carrier thermal conductivity will simultaneously leads to the change of power factor according to Wiedemann-Franz's law. Therefore, the most effective way to optimize the thermal conductivity is to manipulate the independent parameter κ_l , which is not determined by the electronic structure of the material.

From the correlation of thermoelectric parameters, it is known that κ_l is mainly determined as,

$$\kappa_l = \frac{1}{3} C_v \cdot v \cdot l \quad \text{Equation 2-9}$$

where C_v is the specific heat capacity, v is the phonon transmission speed, and l is the mean free path (MFP) of the phonon. The phonon MFP changes with

different wavelengths and are distributed from the atomic scale to the micron scale. When the size of the defect in the material is close to the phonon MFP, these defect will have a significant influence on the scattering of phonon.

Figure 2-6a is a schematic diagram of phonon scattering on the atomic-scale, nano-scale and micro-scale defects (Zhao *et al.*, 2014). The atomic-scale defects are generally composed of atomic point defects caused by doping, the nano-scale defects are considered to be nano-deposited phases. While the micro-scale defects are mainly formed near the grain boundary. If one of these defects has occurred in a material, it will leads to the scattering of phonons and effectively reduce the κ_l of the material. Figure 2-6b shows the distribution of the accumulated percentage of κ_l in related with the phonon MFP at different scale ranges. It can be seen from the Figure that in both 300K and 600K, the κ_l was accumulated to as high as 80% on the nanometer scale. Hence nanostructures can significantly reduce the thermal conductivity of the material lattice.

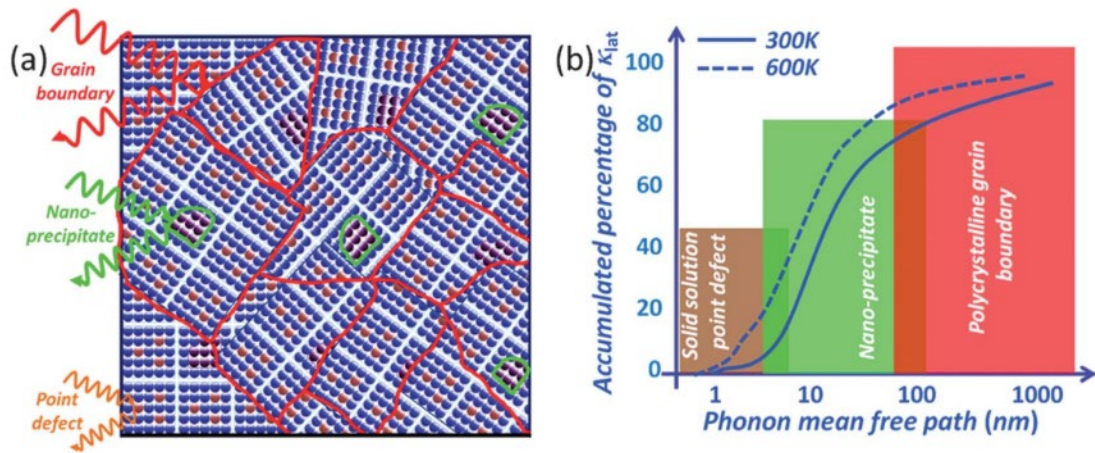


Figure 2-6 (a) all-scale hierarchical architectures, and (b) cumulative distribution function of lattice thermal conductivity

The crystal structure of a typical thermoelectric material $\text{AgPb}_{18}\text{SbTe}_{20}$ (LAST) is shown in Figure 2-7a (Hsu *et al.*, 2004). The material LAST can be regarded as co-doping of Ag and Sb in PbTe or a solid solution formed by PbTe and AgSbTe_2 . Figure 2-7b (Zhao *et al.*, 2015) exhibits the schematic of the charge balance after four Pb^{2+} were replaced by two pairs of Ag^+ and Sb^{3+} . Although

the charge balance is formed among the elements, but a nano-sized region (Figure 2-7c) was occurred in the sample at the same time, and it is found to be an Ag-Sb-rich phase (Quarez *et al.*, 2005). Further research suggested that the nanostructure LAST perform an extremely low κ of $0.8 \text{ Wm}^{-1}\text{K}^{-1}$, and the thermoelectric Figure of merit ZT reaches about 2.2 at a temperature of 823K (Figure 2-7d). This study indicates that both atomic-scale defects and nano-scale precipitates were observed in the LAST, which have a huge impact on its thermoelectric properties. The LAST with ZT value of 1.54 at 723K was prepared by ball milling and spark plasma sintering afterwards (Li *et al.*, 2013). The results reveals that the thermoelectric Figure of merit ZT of LAST can be increased by 50% through repeating the milling and SPS processes, and the electrical conductivity and thermopower of LAST could be enhanced due to refined grains and from nanostructuring method.

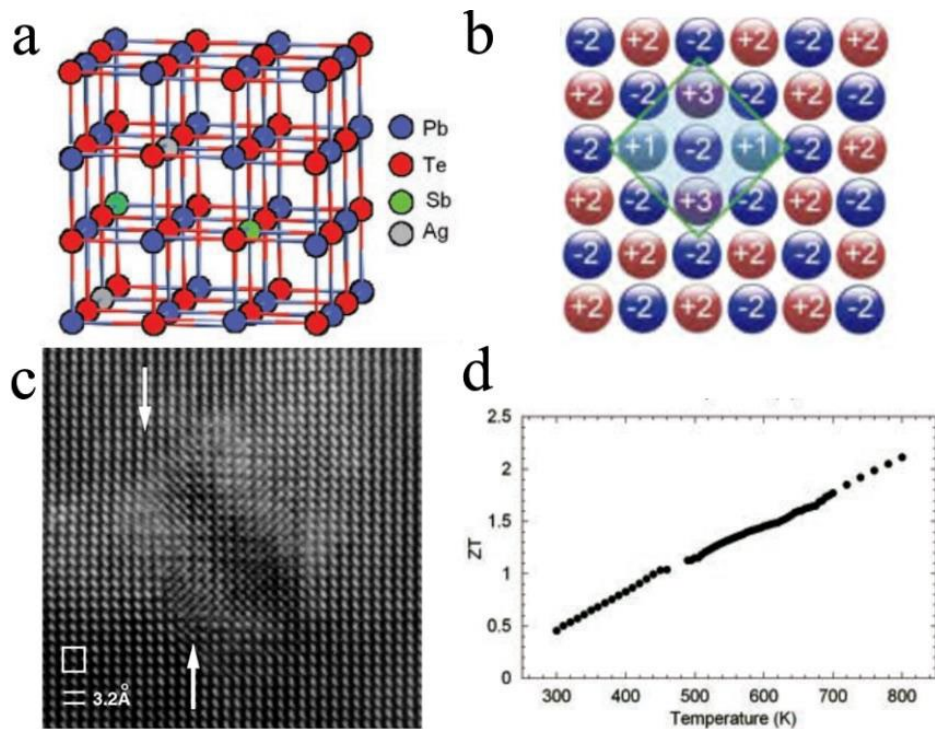


Figure 2-7 (a) Crystal structure diagram of AgPb₁₈SbTe₂₀ (LAST); (b) schematic of the charge balance in LAST; (c) The nanostructure of Ag-Sb-rich nano dots under TEM; (d) Thermoelectric Figure of merit ZT of LAST with the increase of temperature

The other way to produce nano-deposited phases is to form a limited or infinite

solid solution. In the case of limited solid solution, a supersaturated second phase B is introduced into the matrix A. Then the second phase B would precipitate from the matrix A while the solid solution limit was exceeded during the cooling process. In the case of infinite solid solution, the nanostructured phase B was separated from matrix A within the process of spinodal decomposition. There are several typical compound systems with such characteristics which include PbTe-PbS and PbSe-PbS, etc (Wu *et al.*, 2014; Wu *et al.*, 2015). The nanostructure of PbTe-4SrTe-2Na are shown in Figure 2-8, this material is characterized by a layered microstructure with defects at the atomic, nanometer and micron scales, so that all of the phonons with different wavebands can be scattered, which significantly reduces the κ_l of the material. Figure 2-8a, b and e represent micro-scale, nano-scale and atomic-scale structure of the sample, respectively. The size distribution histogram of the grain and SrTe nanoparticles are shown in Figure 2-8c and 2-8d.

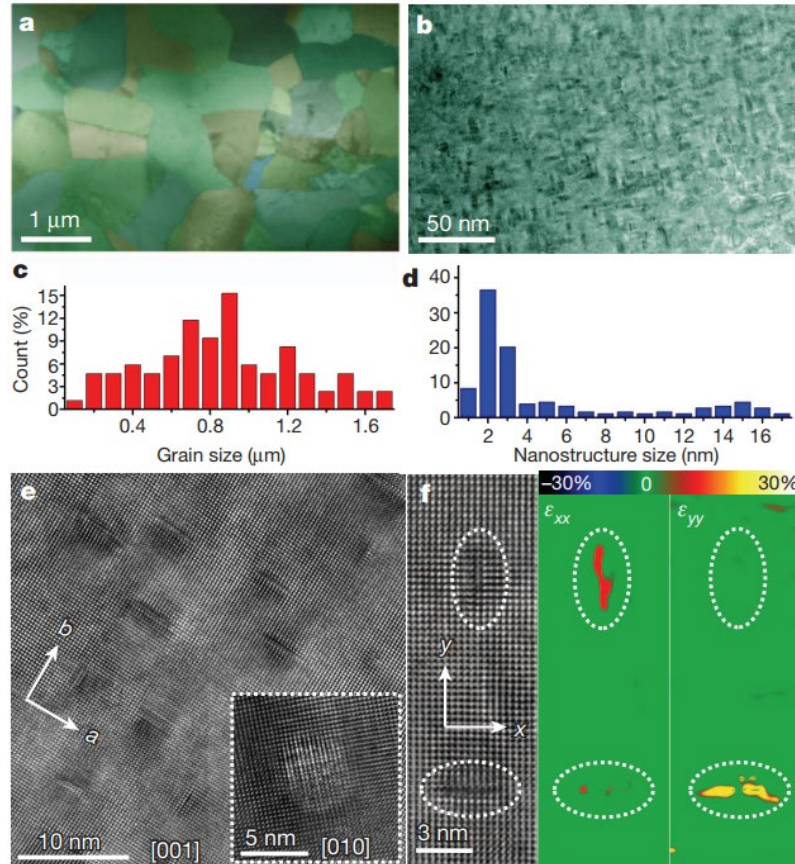


Figure 2-8 (a) TEM image of mesoscale grains; (b) Platelet-like and spherical nanoscale precipitates; (c) Grain size distribution histogram; (d)

Size distribution histogram of SrTe nanoparticles; (e) High-magnification lattice image depicting some perpendicular or parallel platelet-like precipitates; (f) Platelet-like precipitates along only one direction (Wu et al., 2015)

The ZT values of PbTe-4SrTe-2Na samples with different microstructure are shown in Figure 2-9. It can be seen that the maximum thermoelectric Figure of merit ZT of Na-doped sample is 1.1, and the ZT value of the ingot sample added with SrTe increased to 1.7. By integrating the effects of atomic-scale alloy doping, endotaxial nanostructuring, and mesoscale grain-boundary control. The maximum phonon scattering can be achieved at high temperatures and the ZT value can be increased (from 1.7 to 2.2 at 915K) beyond the value possible with nanostructuring alone, suggesting an ideal prospect for multiscale hierarchical architecture in bulk thermoelectric materials.

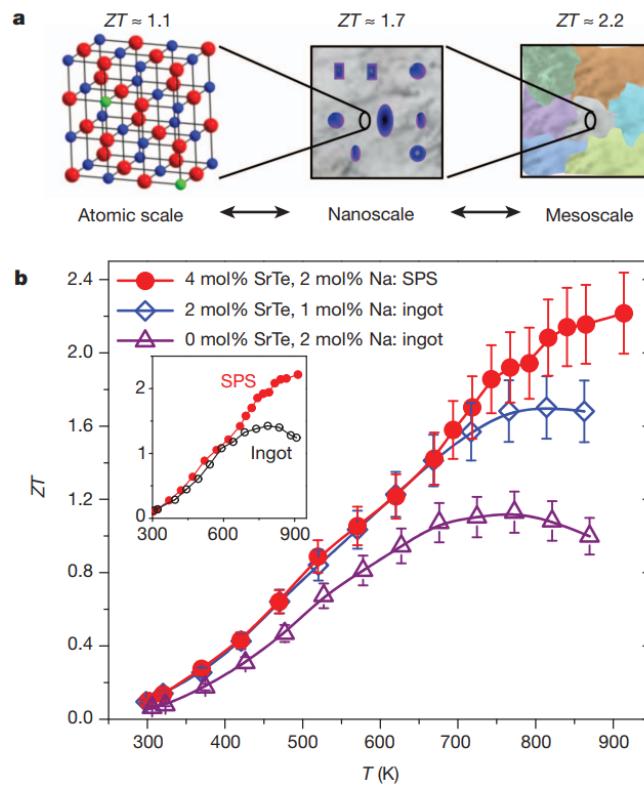


Figure 2-9 (a) Maximum achievable ZT values; (b) ZT as a function of temperature (Biswas, 2012)

2.1.2.3 Use of materials with low intrinsic thermal conductivity

Higher ZT value can be obtained by the application of nanostructures to the

thermoelectric material, but some other problems such as the low stability of nanophases at high temperatures should be taken into consideration. Based on this, the use of materials with low intrinsic thermal conductivity can minimize the risks when the materials are exposure to high temperature. The materials that have been found to have low intrinsic thermal conductivity include Zintl compounds (Gascoin *et al.*, 2005), Cu-Sb-Se, Cu₂Se (Liu *et al.*, 2012), Cu₂S, Cu-Fe-Se (Skoug *et al.*, 2011), Ag₉TiTe₅, AgSbTe, AgBiTe (Kurosaki *et al.*, 2005), BiCuSeO (Zhao *et al.*, 2014) and SnSe (Zhao *et al.*, 2014).

Due to the complex crystal structure or large molecular weight, most of the Zintl compounds performed a relatively low thermal conductivity. For example, the relative molecular mass of Yb₁₄MnSb₁₁ is 3783.088, which is 10 times that of a typical thermoelectric material PbTe (Brown *et al.*, 2006). The large molecular mass leads to a low thermal conductivity of the material: 0.8Wm⁻¹K⁻¹ at room temperature, and 0.7Wm⁻¹K⁻¹ at 1200K. Another example of Zintl compounds is Ag₉TiTe₅ (Kurosaki *et al.*, 2005), it exhibits a complex crystal structure and the low elastic modulus, indicating that the chemical bond of the material is weak. Thus it is less conductive for the phonons. The thermal conductivity of Ag₉TiTe₅ is maintained at about 0.25Wm⁻¹K⁻¹ from room temperature to 650K, and the ZT value of the material could reach 1.25 at 673K.

Non-resonant effects can cause low thermal conductivity as well. The non-resonant effect means that a phonon is driven away from the equilibrium position by external factors. Greater non-resonant energy would be generated as the phonon is further away from the equilibrium position. The Grüneisen constant γ can be used to measure the strength of the non-resonant effect,

$$\gamma = \frac{3\beta BV_m}{C_v} \quad \text{Equation 2-10}$$

where β is the bulk thermal expansion coefficient, B is the isothermal bulk modulus, C_v is the volumetric heat capacity, V_m is the molar volume.

A typical thermoelectric materials with non-resonant effects is PbTe (Korkosz *et al.*, 2014). The room temperature thermal conductivity of PbTe is between

1.0~2.0 Wm⁻¹K⁻¹, and its Grüneisen constant γ is about 1.4, which is relatively larger compared to other thermoelectric materials. Research indicates that the Pb atom is likely to deviate from the equilibrium position at room temperature, while the distance between Pb atoms and equilibrium position increase with temperature rising, hence the thermoelectric properties was improved due to the non-resonant effects of Pb atoms (Girard *et al.*, 2010; He *et al.*, 2012). In addition, Sb and Bi containing compounds were proved to have low intrinsic thermal conductivity. This is caused by the special electronic structure of Sb and Bi atoms, as shown in Figure 2-10. It was found in Figure 2-10a that there are lone pair electrons in the outermost layer of the Sb nucleus, these isolated electrons will have an unbalanced effect on the transmission of phonons, the non-resonant effects result in low heat transmission properties in Sb and Sb-containing compounds (Jovovic *et al.*, 2008). Bi and Sb have similar electronic structures, thereby Bi-containing compounds should also perform large Grüneisen constants γ and low thermal conductivity. It can be seen in Figure 2-10b (Morelli *et al.*, 2008) that AgSbTe₂ and AgBiSe₂ exhibit extremely low thermal conductivity, far less than that of PbTe.

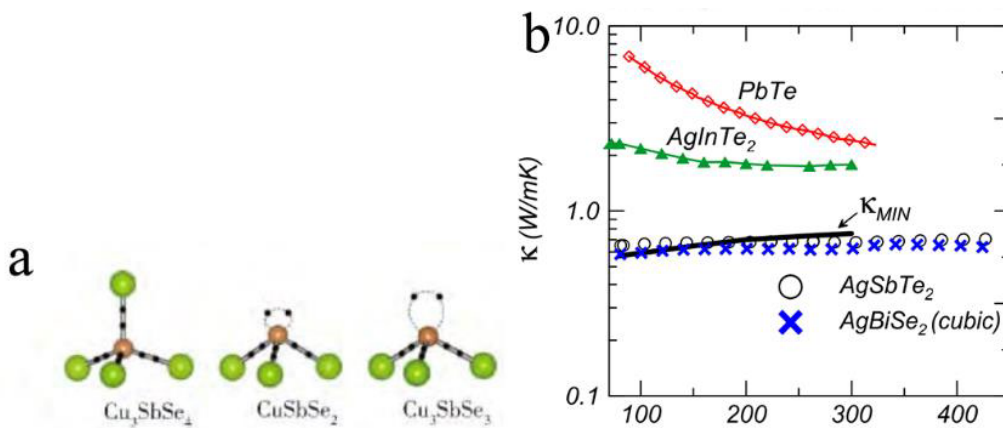


Figure 2-10 (a) Schematic of lone pairs in Sb-containing compounds and (b) the thermal conductivity of AgSbTe₂, AgBiSe₂, of single-crystal PbTe, and of the chalcopyrite compound AgInTe₂ (Morelli *et al.*, 2008)

The last kind of materials with intrinsically low thermal conductivity were called anisotropic materials, such as BiCuSeO compounds. The thermoelectric

properties of BiCuSeO was first reported in 2010, the atomic structure is shown in Figure 2-11a (Zhao *et al.*, 2010). It was found that undoped BiCuSeO displayed a moderate power factor, combined with low thermal conductivity ($\sim 0.60 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature, and $0.40 \text{ Wm}^{-1}\text{K}^{-1}$ at 923K) and appropriate ZT value of 0.45 at 923K (Zhao *et al.*, 2010), suggesting its potential in thermoelectric field. Subsequent modification methods for BiCuSeO include doping of bivalent elements (Mg, Ca, Sr, Ba, and Pb) at the Bi site (Barreateau *et al.*, 2012; Li *et al.*, 2013), Cu deficiencies (Liu *et al.*, 2011), microstructure design, band gap tuning (Liu *et al.*, 2011), and improving carrier mobility through 3D modulation doping (Pei *et al.*, 2014), etc. The maximum ZT value of 1.5 (Liu *et al.*, 2016) was achieved after several years since BiCuSeO was originally reported with the ZT value of 0.76 in 2010. It is shown in Figure 2-11b (Zhao *et al.*, 2014) that BiCuSeO display better ZT values than those of Half-Heusler, SiGe alloy and Zintl phase compounds in the temperature range of 800-1000K. Moreover, BiCuSeO perform better chemical and thermal stability, and its thermoelectric performance are expected to improve after further parameter optimization, content designation and microstructure adjustment.

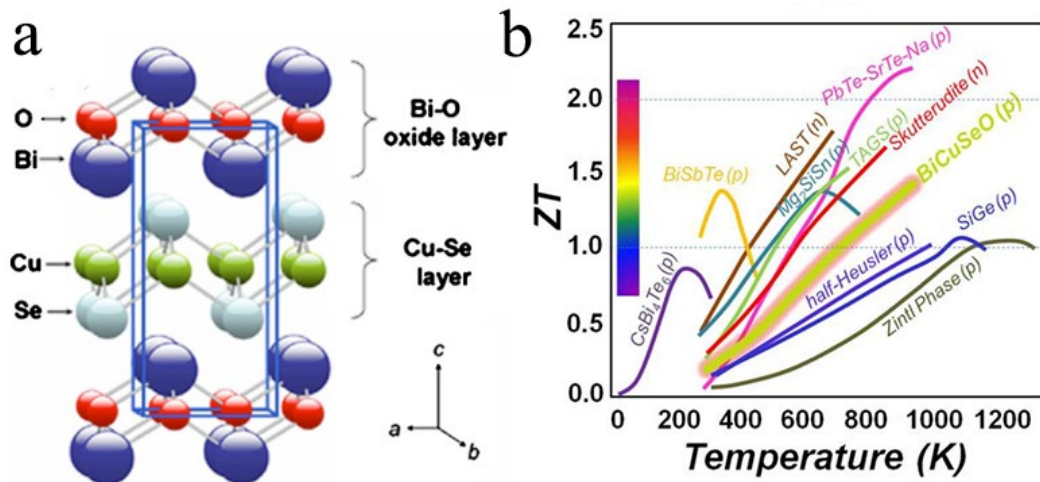


Figure 2-11 (a) the atomic structure of BiCuSeO compounds; (b) Figure - of-merit ZT of typical current thermoelectric materials

2.1.3 Applications for Thermoelectricity

The Seebeck effect and Peltier effect have laid the foundation for the

application of thermoelectric materials. Hence the thermoelectric devices are mainly divided into two categories: the thermoelectric power generation devices which based on the Seebeck effect and thermoelectric refrigeration which based on the Peltier effect.

As early as the 1960s, the thermoelectric generator (TEG) was used for artificial satellites in USA. Since then, thermoelectric power generation devices have been widely used in the aerospace field. A typical example of thermoelectric power generator is the Multi-mission Radioisotope Thermoelectric Generator (MMRTG) on the Mars Rover “Curiosity” launched in 2011. Unlike the previous Mars Rover which applied solar cell technology, the energy generation efficiency of thermoelectric generator would not be affected by sand storms and dust tornadoes on Mars. Therefore, thermoelectric power generation device show greater potential as an advanced aerospace application with stability, safety and reliability.

In addition to applications in the aerospace field, thermoelectric conversion devices can also be useful in daily life. It was mentioned in a program named ‘FreedomCar’ from the US Department of Energy that the vehicle waste heat could be redirected to a TEG to produce electricity and thus improve overall utilization rate of fossil fuels. As shown in Figure 2-12, TEGs have been equipped on BMW 530i in order to realize the waste heat recovery (C. B. Vining, 2009).



Figure 2-12 integrating thermoelectrics into vehicles for improved fuel efficiency (C. B. Vining, 2009)

In recent years, it has been proposed that thermoelectric devices can be combined with other forms of energy conversion. And these combinations could improve the overall conversion efficiency of the device. For example, an energy device with a CuInGaSe₂ (CIGS) photovoltaic (PV) cell connected to an active energy-harvesting device (thermoelectric generator (TEG)) was reported to present a record-high efficiency of 22% at a cool-side temperature below 5°C, which shows potential for high-efficiency energy-harvesting applications (Hsueh *et al.*, 2014).

Compared to the typical compressor-based refrigerator, the thermoelectric cooler has many outstanding advantages, such as noiseless, simply constructed, easy to carry, high cooling speed, long service life, and conveniently managed temperature control, etc. But thermoelectric coolers are still difficult to replace traditional refrigeration appliances due to low conversion efficiency. The main reason for this is that the thermoelectric Figure of merit of thermoelectric materials is generally low. Thereby improving the thermoelectric Figure of merit has always been the primary goal of thermoelectric materials research.

2.1.4 Research Progress of Thermoelectric Materials

Many materials have been explored and considered useful to generate thermoelectricity, including metals, ceramics and ultimately semiconductors. In the 1950s, A.F. Ioffe proposed that the dimensionless thermoelectric Figure of merit ZT could be used as an important index to evaluate the conversion efficiency of thermoelectric materials (Ioffe *et al.*, 1959). This laid the theoretical foundation for the thermoelectric effect and greatly accelerated the development of thermoelectric materials with high Figure of merit ZT . The initial thermoelectric materials such as Bismuth telluride and its alloys, lead telluride and its alloys, and silicon-germanium alloys have been extensively studied since then. In the early 1990s, G. Slack proposed that idealized thermoelectric materials should have the characteristics of "lattice glass-electronic crystals"

(PGEC), and related research of PGEC has become the most important and representative direction in the field of thermoelectric materials in recent years. The characteristics of PGEC indicate that the thermoelectric material should have both glass-like thermal conductivity and crystal-like electrical conductivity. Theoretical predictions also show that nano-scaled materials exhibit greatly improvement in thermoelectric performance. Thus more and more articles based on this theory to predict and improve the thermoelectric properties of materials have been published. At the same time, several bulk PGEC thermoelectric materials with complex crystal structures and excellent thermoelectric properties have been discovered, such as skutterudites (Nolas *et al.*, 1999), Ge clathrates filled with Sr atoms (Iversen *et al.*, 2000), and Zintl phase structures (Kauzlarich *et al.*, 2007). These recent advances in the field of thermoelectricity are expected to make thermoelectric materials more conversion efficient. In addition, artificial superlattices, Bi nanowires and quantum well systems, films, carbon nanotubes, cat's-eye-like structures, etc. all show potential for improving the properties of thermoelectric materials. Figure 2-13 shows the development history of several key thermoelectric materials and their thermoelectric merit values at different temperatures.

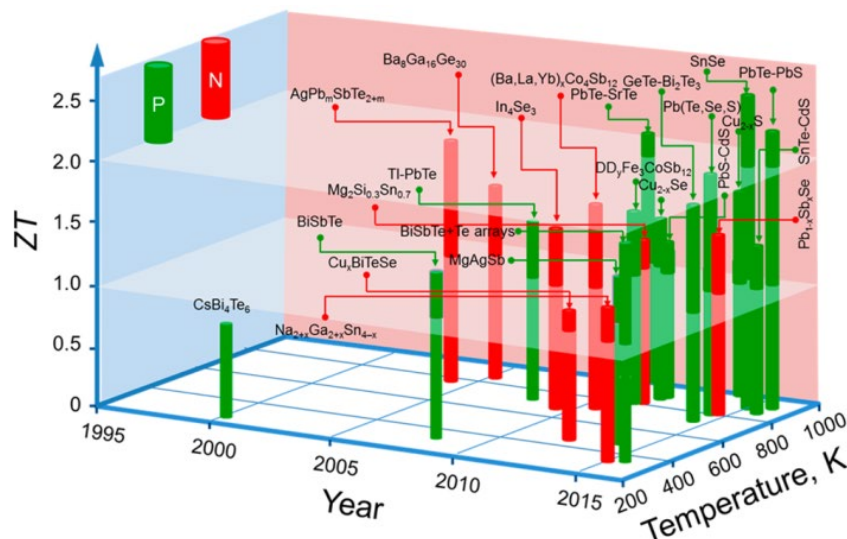


Figure 2-13 Current state-of-the-art bulk thermoelectric materials: the Figure-of-merit ZT as a function of temperature and year (Tan et al., 2016)

Great achievements have been achieved with both n-type and p-type materials with the greatest ZTs around or above 2, especially since the year 2010 (Biswas *et al.*, 2012). Traditional thermoelectric materials, namely, bismuth telluride (Poudel *et al.*, 2008) and lead chalcogenides (Biswas *et al.*, 2011) remain the top performing ones in their respective working temperature region and attract strong attention. On the other hand, because of concerns of the scarceness of tellurium and the perceived toxicity of lead in lead chalcogenides, researchers also explore the possibility of Te- and Pb-free compounds, among which MgAgSb (Zhao *et al.*, 2014), skutterudites (Qui *et al.*, 2011) and copper and tin chalcogenides (Liu *et al.*, 2012; Zhao *et al.*, 2014) appear as most promising. Particularly, single crystalline SnSe, a simple binary compound containing no toxic or scarce elements, displays an excitingly record high ZT of ~ 2.6 at 923 K along the b axis of the room-temperature orthorhombic unit cell. (Zhang *et al.*, 2020) This can be achieved because of the giant anharmonic and anisotropic bonding of SnSe which gives rise to an extremely low thermal conductivity (Zhao *et al.*, 2014). Thus, the search for new compounds with intriguing physical properties is a necessary activity to achieve high thermoelectric performance in addition to optimizing the known systems. Although in the past decade breakthroughs have been constantly made in the thermoelectric field, systematic and in-depth analysis and new perspectives on the applied approaches and concepts are valuable.

2.1.5 Fabrication methods of Thermoelectric Material BiCuSeO

The preparation methods of BiCuSeO compounds include two-step high-temperature solid-phase reaction method, mechanical alloying method and self-propagating high-temperature synthesis method. In order to obtain dense bulk materials, the hot press sintering (HPS) or spark plasma sintering (SPS) are applied to BiCuSeO compounds above.

2.1.5.1 High temperature solid phase reaction method

High-temperature solid-phase reaction method is widely used to produce

BiCuSeO compounds. The first step is to mix the Bi, Cu, Se, Bi₂O₃ powders in proportion. Generally, the powders were ball milled together, and the ball mill tank was evacuated in order to ensure that the raw materials won't oxidize during the high-speed ball milling process. A small amount of BiCuSeO phase has formed after ball milling, but there are still a lot of unreacted raw materials left. The objective of ball milling is to fully mix the raw materials and refine the particles of powder, which can be used in the subsequent step of heat treatment (Li, 2012). In the second step, the ball milled powder was sealed in a vacuum quartz tube, and the tube was put in a muffle furnace for high temperature reaction. As the grains of the product obtained by high temperature solid phase reaction are relatively coarse, the product needs to be further ball milled to refine its grains.

2.1.5.2 Mechanical alloying

Mechanical alloying is a method of obtaining a solid alloy by high-speed ball milling or grinding. The mechanical alloying method has attracted wide attention due to its short cycle, low energy consumption and simple process. It has also been used in the preparation process BiCuSeO (Wu *et al.*, 2015): Bi, Cu, Se and Bi₂O₃ powder were weighed in proportion (the mole ratio was 1:3:3:1). Milling was performed at 500 rpm for several times with a ball-to-material ratio of 20:1, and a single-phase BiCuSeO powder is obtained. The high-speed ball milling process will refine the grains and introduce a large amount of Cu vacancies, thereby greatly increasing the vacancy concentration and improving the electrical performance of material. By extending the ball milling time and increasing the ball milling strength, it can further refine the grains, increase the carrier concentration, enhance phonon scattering and further improve the thermoelectric performance. Recently, the effect of synthesis processes on the thermoelectric properties of BiCuSeO was systematically investigated (Feng *et al.*, 2018). High energy ball milling was performed at 300 or 400 rpm in argon atmosphere for 2 h, 4 h, 6 h, 8 h and 12 h, respectively. Results shows that the optimum process parameters are: 400 rpm for ball milling speed, 16 h for ball

milling time, 873 K for sintering temperature, 50 MPa for sintering pressure. The corresponding maximum power factor reached $0.31 \text{ mWm}^{-1}\text{K}^{-2}$ and the highest ZT value reached 0.62 for the produced BiCuSeO.

2.1.5.3 Self-propagating high-temperature synthesis (SHS)

Self-propagating high-temperature synthesis is a particular method which rely on the self-heating and self-reacting between reactants to get the products. Once the reaction is triggered by external energy, it will continue unless the reaction is complete. This technique is mainly used in the preparation of compounds with complex composition, especially suitable for intermetallic compounds and refractory compounds. It is referred that a sodium doped BiCuSeO was prepared by SHS (Lan *et al.*, 2017). The sample exhibits optimized power factor and lower thermal conductivity, result in a higher ZT value of 0.70 at 873 K for $\text{Bi}_{0.85}\text{Na}_{0.15}\text{CuSeO}$, which is about 100% higher than that of the pristine BiCuSeO.

2.1.5.4 Sol-gel method

The sol-gel method uses compound with high chemical activity component as a precursor, these precursors form a stable sol system through chemical reactions such as hydrolysis and condensation. The gel is obtained by polymerize and gelation, which can be dried and sintered to produce bulk materials. Sol-gel method was firstly reported in the synthesis of BiCuSeO in 2017. In this paper, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$, Se powders were quantitatively dissolved in citric acid ($\text{C}_6\text{H}_8\text{O}_7$) and ethylene glycol ($\text{C}_2\text{H}_8\text{O}_2$), The solution was heated to 95°C and stirred to allow the polymerization reaction to occur. The high purity of BiCuSeO could be confirmed by XRD as a result (Bhaskar *et al.*, 2017).

2.1.6 Survey of thermoelectric materials for TEPOC application

Generally speaking, the Figure of merit, ZT, is a crucial parameter for assessing the energy conversion efficiency of a thermoelectric materials. However, for TEPOC application, the best Figure of merit for TE may no longer be the ZT.

Firstly, as TE is in an open circuit configuration in this application, no electrical current is involved, hence the electrical conductivity may no longer as important as in the closed circuit configuration for TEG and Peltier cooling devices. Secondly, the change of activation energy for chemical reactions is linearly proportional to the change of the surface energy, which itself is linearly proportional to the Seebeck voltage. Hence, we define the amount of the Seebeck voltage per unit of heat loss as the new Figure of merit for the TE for TEPOC application.

$$\text{Figure of merit} = V/Q = (-S \cdot \Delta T) / (-\kappa \cdot \Delta T) = S/\kappa \quad \text{Equation 2-11}$$

where V is the Seebeck voltage, Q is the heat flux, ΔT represent the temperature difference across the material, S and κ are the Seebeck coefficient and thermal conductivity, respectively. Generally speaking, optimization in the dimensionless Figure of merit ZT or power factor $S^2\sigma$ do not necessarily lead to the optimization of S/κ .

The data presented in the table below includes the majority of thermoelectric properties of surveyed thermoelectric materials. These reported data could be used to evaluate the feasibility of various thermoelectric materials for TEPOC applications.

Table 2-1 Thermoelectric properties and a new Figure of merit S/k of thermoelectric materials

Materials	Dopant	Temperature (K)	ZT	κ (W·m ⁻¹ ·K ⁻¹)	σ (S·cm ⁻¹)	S (μV·K ⁻¹)	new FOM S/ κ	Ref.
BiCuSeO	Sr	873	0.75	0.64	100	225	352	Zhao, 2010
BiCuSeO	Ca	773	0.80	0.63	130	225	357	Li, 2013
BiCuSeO	Ba	923	1.10	0.48	190	180	375	Li, 2012
BiCuSeO	Pb	823	1.14	0.53	135	222	419	Lan,2013
BiCuSeO	Pb,Ba	873	1.05	0.66	170	190	289	Feng, 2018
BiCuSeO	Ca, Pb	873	1.50	0.52	170	210	404	Liu, 2016
BiCuSeO	Mg,Pb	750	1.19	0.70	320	180	257	Sun, 2017
BiCuSeO	Cs	680	0.66	0.34	25	370	1088	Achour, 2018
BiCuSeO	none	923	0.45	0.32	14	425	1328	Zhao, 2014
BiCu _{1-x} SeO	Cu vac	923	0.81	0.50	50	275	550	Liu,2011
Bi _{1-x} Ba _x SeO	Ba	923	1.40	0.68	250	200	294	Pei, 2014
Bi _{0.975} Cu _{0.975} SeO	Dual vac	750	0.60	0.36	4700	300	833	Li, 2015
Bi _{1.04} Cu _{1.05} Se _{0.99} 10%Ag	+ Ag	850	0.01	0.60	10	-55	-92	Zhang, 2018
Ca ₃ Co ₄ O ₉	Cr	1000	0.16	2.19	100	185	85	Prasoetsopha, 2014
Ca ₃ Co ₄ O ₉	Sm	1000	0.15	1.60	85	220	138	Cha, 2018.
Ca ₃ Co ₄ O ₉	Tb	1000	0.73	1.30	112	320	246	Saini,2017
Ca ₃ Co ₄ O ₉	K	1000	0.22	1.30	98	170	131	Wang, 2018
Ca ₃ Co ₄ O ₉	Cd	1000	0.35	1.50	120	210	140	Butt, 2014
Ca ₃ Co ₄ O ₉	Sr	1000	0.22	1.80	100	180	100	Delorme, 2011
Ca ₃ Co ₄ O ₉	Na, W co	1000	0.21	1.34	61	210	157	Hira, 2018
Ca ₃ Co ₄ O ₉	La, Fe co	1000	0.32	1.30	82	225	173	Butt, 2014

Ca ₃ Co ₄ O ₉	NCO, nano	BCCO	1000	0.34	1.79	97	250	140	Bittner, 2019
Na _x CoO ₂	Ag, Au		1000	0.4	2.75	284	230	84	Ito, 2008
Na _x CoO ₂	Ni		1073						Park, 2012
NaCoO ₂	Cu		1000			190	470		Park, 2006
Na _x CoO ₂	K,Sr,Y, Nd, Sm, Yb		1000	0.5	1.60	273	160	100	Nagira, 2003
Bi ₂ Ca ₂ Co ₂ O ₉	Na		900			50	205		Karakaya, 2018
Bi ₂ Ca ₂ Co ₂ O ₉	K		1000	0.31					Gao, 2015
Bi ₂ Ca ₂ Co ₂ O ₉	Pb, La		1000						Hao, 2010
ZnO	Al		1073	0.34	2.00	260	-145	-73	Nam, 2012
ZnO	Ni		1000	0.09	7.00	33	-420	-60	Colder, 2011
ZnO	Al, Ni		773	0.06	8.00	900	-90	-11	Zhang, 2016
ZnO	Ga		1273	0.25	7.00	-110	-80	-11	Jung, 2012
SrTiO ₃	La,Nb,Sm,Gd,Dy		1073	0.2-0.28	3.00	170-220	-200	-67	Liu, 2013
SrTiO ₃	La,Nb,Sm,Gd,Dy		973	0.37	4.00	100	-290	-73	Park, 2014
SrTiO ₃	Gd		1023	0.37	3.00		-275	-92	Li, 2014
SrTiO ₃	Nb		1023	0.39	3.20	250	-220	-69	Zhang, 2015
SrTiO ₃	Nb, Nd		1073	0.32	3.00	300	-170	-57	Chen, 2018
CaMnO ₃	Dy,Ho,Er,Yb		1000	0.15-0.2	1.70		-155	-91	Wang, 2008
CaMnO ₃	W		1073	0.16	2.00		-150	-75	Thiel, 2013
CaMnO ₃	Y,Dy codopant		800	0.18	1.85		-120	-65	Seo, 2017
CaMnO ₃	Pr,Yb codopants		973	0.24	2.00		-200	-100	Li, 2018

In ₂ O ₃	Sn, Al	1200	0.15	3.00	110	-90	-30	Bittner, 2019
In ₂ O ₃	Ge, Mn, Zn	1200	0.08	10.00	880	-180	-18	Bittner, 2019
P-type Zintle								
Yb ₁₄ MnSb ₁₁		1200	1.02	0.71	178	185	261	Brown, 2006
	Al	1200	1.28	0.50	153	240	480	Toberer, 2008
	Sc	1200	1.02	0.68	158	230	338	Grebenkemper, 2016
	Y	1200	1.01	0.80	135	225	281	Grebenkemper, 2016
Yb ₁₄ MnSb ₁₁		1075	1.03	0.70	113	240	343	Hu, 2015
Sr ₁₄ MgBi ₁₁		1075	0.71	1.45	485	140	97	Tan, 2017
Ca ₅ Al ₂ Sb ₆	Na	1050	0.61	0.70	111	200	286	Toberer, 2010
Yb ₉ Mn _{4.2} Sb ₉		1000	0.74	0.56	126	190	339	Bux, 2014
CaZn ₂ Sb ₂	Na, Mg	800	0.85	0.80	160	240	300	Wood, 2018
EuZn ₂ Sb ₂	Cd	650	1.05	1.40	623	190	136	Zhang, 2010
YbCd ₂ Sb ₂	Mn	650	1.13	0.70	181	235	336	Guo, 2011
YbCd ₂ Sb ₂	Zn	700	1.22	1.10	593	180	164	Wang, 2009
YbCd ₂ Sb ₂	Mg	650	1.06	0.59	332	225	381	Cao, 2016
CaMg ₂ Bi ₂	Na	850	0.88	1.25	308	200	160	Shuai, 2016
CaMg ₂ Bi ₂	Yb	850	0.96	1.10	305	200	182	Shuai, 2016
Eu _{0.5-x} Yb _{0.5-x} Mg ₂ Bi ₂	Ca	850	1.26	0.92	292	215	234	Shuai, 2016
Mg ₃ Sb ₂	Na	750	0.58	0.59	26	400	678	Bhardwaj, 2013
N-type Zintle								
Mg ₃ Sb ₂	Te	700	0.61					Wang, 2019
Mg ₃ Sb ₂	Bi, Te	700	1.59	0.56	186	-260	-464	Zhang, 2017
Mg ₃ Sb ₂	Nb, Bi, Te	700	1.52	0.85	236	-280	-329	Shuai, 2017
Mg ₃ Sb ₂	Mn, Bi, Te	700	1.71	0.80	222	-300	-375	Chen, 2018

Mg ₃ Sb ₂	Bi,Te	700	1.45	0.73	168	-300	-411	Shuai, 2018
P-type half-Heusler								
FeNb _{0.88} Hf _{0.12} Sb		1200	1.45	4.20	885	240	57	Fu, 2015
FeNb _{0.86} Zr _{0.14} Sb		1050	0.80	7.00	1043	210	30	Fu, 2015
FeNb _{0.95} Ti _{0.05} Sb		973	0.70	6.50	686	270	42	He, 2016
FeNb _{0.8} Ti _{0.2} Sb		973	1.10	4.50	1325	200	44	He, 2016
ZrCoBi _{0.65} Sb _{0.15} Sn _{0.20}		973	1.42	2.62	751	225	86	Zhu, 2018
Hf _{0.44} Zr _{0.44} Ti _{0.12} CoSb _{0.8} Sn _{0.2}		973	1.00	2.80	520	232	83	He, 2015
N-type half-Heusler								
TiNiSn		775	0.40	4.00	384	-250	-63	Muta, 2009
Ti _{0.5} Zr _{0.5} NiSn		900	0.55	7.00	1019	-180	-26	Kimura, 2009
Ti _{0.5} Hf _{0.5} NiSn		900	0.48	4.00	608	-240	-60	Kimura, 2009
Ti _{0.5} Zr _{0.25} Hf _{0.25} NiSn _{0.998} Sb _{0.002}		700	1.50	2.90	689	-300	-103	Shutoh, 2005
Hf _{0.6} Zr _{0.4} Hf _{0.25} NiSn _{0.995} Sb _{0.005}		900	1.20	3.50	971	-220	-63	Chen, 2015
NbCoSb _{0.8} Sn _{0.2}		973	0.56	3.80	582	-190	-50	Huang, 2017
(Zr _{0.4} Hf _{0.6}) _{0.88} Nb _{0.12} CoSb		1173	0.99	3.10	612	-210	-68	Liu, 2018
N-type GeSi alloy								
Si _{0.8} Ge _{0.2}	P	1073	1.84	0.93	196	-284	-305	Basu, 2014
	P	1173	1.30	2.90	531	-240	-83	Wang, 2008
	Sb	1000	0.67	3.00	99	-450	-150	Wang, 2015
	P,SiC	1173	1.72	2.00	366	-280	-140	Bathula, 2017
	P,Mg ₂ Si	1173	1.27	2.80	258	-340	-121	Nozariasbmarz, 2016
	P, FeSi ₂	1173	1.18	2.80	445	-250	-89	Nozariasbmarz, 2016
	P, WSi ₂	1173	1.16	2.40	727	-220	-92	Mackey, 2015
P-type GeSi alloy								

Si _{0.8} Ge _{0.2}	B	1173	1.22	2.00	388	230	115	Bathula, 2015
	B	1073	0.96	2.50	302	270	108	Joshi, 2008
	Ga	1073	0.52					Lin, 2013
	B,Y2O3	1073	1.81	1.90	406	310	163	Ahmad, 2016
	B,CrSi2	1073	0.65	2.80	236	300	107	Zamanipour, 2012
	B,YSi2	1073	0.53	3.20	314	230	72	Wongprakarn, 2017
	B,WSi2	1173	0.66	3.40	306	240	71	Mackey, 2015
PbSe _{0.85} -PbTe _{0.15}	Na, Cd	900	1.65	0.89	250	250	281	Tan, 2019
AgPb ₁₈ SbTe ₂₀		800	2.10	1.10	200	-370	-336	Hsu, 2004
BiSbTe Nanocryst	nano crystal	373	1.40	1.00	850	210	210	Poudel, 2008
PbTe	Tl	773	1.50	1.00	168	340	340	Heremans, 2008
Mg ₂ Si _{1-x} Sn _x	x=0.5	800	1.20	2.15	605	-230	-107	Liu, 2012
PbSe	Na	923	0.90	1.00	150	270	270	Zhao, 2012
CsBi ₄ Te ₆	SbI3	300	0.60	1.28	1000	160	125	Chung, 2000
Bi ₂ (Te _{0.9} Se _{0.1}) ₃	Cu	375	1.10	1.45	1100	-200	-138	Wang, 2013
Co ₄ Sb ₁₂	Ba,La,Yb	800	1.50	2.60	1385	-190	-73	Shi, 2011
MgAg _{0.965} Sb _{0.99}	Ni	500	1.40	0.80	463	220	275	Zhao, 2014
GeTe	Pb, Bi	773	1.80	1.40	447	270	193	Wu, 2014
PbTe	Se, S	800	2.00	1.10	390	265	241	Korkosz, 2014
PbTe-PbS	Na	923	2.30	0.85	339	250	294	Wu, 2015
SnTe	In, Cd	923	1.10	1.40	417	200	143	Tan, 2015
PbSe	Sb	923	1.30	1.05	257	-240	-229	Lee, 2014
SnSE								
SnSe SC	Single Crystal	900	2.60	0.35	80	350	1000	Zhao, 2014

SnSe nanoporous	porous	823	1.70	0.25	50	330	1320	Shi, 2018
SnSe alloy	Na	773	0.80	0.40	40	300	750	Chere, 2016
SnSe CNT	CNT	773	0.96	0.40	60	300	750	Chu, 2018
SnSe Poly	Na, (Pure)	783	3.10	0.25	110	300	1200	Zhou, 2021
SnSe poly		380		0.15		668	4453	Serrano-Sanchez, 2015
SnSe	Br	773	2.80	0.25	40	-480	-1920	Chang, 2018

According to the new Figure of merit S/κ , BiCuSeO appears to be the most appropriate TE material for TEPOC applications, as it shows a maximum value of $1328 \mu\text{V}\cdot\text{m}\cdot\text{W}^{-1}$ (Zhao *et al.*, 2014). However, due to its temperature instability, the working temperature for BiCuSeO should be below 500°C , ideally even lower than 400°C . At high temperatures another oxide $\text{Ca}_3\text{Co}_4\text{O}_9$ (Butt *et al.*, 2014; Lin *et al.*, 2015; Prasertsopha *et al.*, 2013) appears to have a high new Figure of merit S/κ . It is stable at up to 1000 K, comparatively low thermal conductivity ($1.3\text{-}1.8 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and pretty good Seebeck coefficient ($120\text{-}180 \mu\text{V}\cdot\text{K}^{-1}$), making it a promising material for TEPOC applications at high temperatures. Particularly, the doping of Tb further improve thermoelectric properties of $\text{Ca}_3\text{Co}_4\text{O}_9$, resulting in a desirable Seebeck coefficient of $320 \mu\text{V}\cdot\text{K}^{-1}$ and Figure of merit S/κ of $246 \mu\text{V}\cdot\text{m}\cdot\text{W}^{-1}$ at 1000K for $\text{Ca}_{3-x}\text{Tb}_x\text{Co}_4\text{O}_9$ (Saini *et al.*, 2017). Therefore, this project will investigate BiCuSeO and $\text{Ca}_{3-x}\text{Tb}_x\text{Co}_4\text{O}_9$ TE materials for TEPOC applications.

2.2 Literature Review on Catalysis

Catalysis is the process of increasing the rate of a chemical reaction by introducing a substance known as a catalyst. The catalyst usually lowers the activation energy required for the reaction to occur, making it easier for the reactants to come together and react (Rothenberg, 2017). This results in a faster reaction rate, higher reaction yield, and lower energy requirements compared to the same reaction taking place without a catalyst. Catalysts are widely used in industrial and laboratory processes to improve reaction efficiencies and enable the synthesis of valuable products that would be difficult or impossible to produce without them (Roduner, 2014). In a catalytic chemical reaction, the catalyst provides an alternative pathway for the reaction to occur, with a lower activation energy. This alternative pathway allows the reactants to more easily bond and break apart, which results in an overall faster reaction rate for the system. By providing a specific pathway for the reaction to take place, a catalyst can help to control which products are formed, leading to

higher yields of a desired product and lower amounts of unwanted byproducts (Tanimu *et al.*, 2017). Finding the right catalyst for a chemical reaction is often a complex task, since there isn't always a simple "matching" of a particular catalyst with a particular reaction. Many factors such as the desired reaction pathway, product selectivity, and stability of the catalyst under the reaction conditions should be taken into consideration.

2.2.1 Catalyst Components and Their Functions

A catalyst is defined as a substance that changes the reaction rate but does not change the total standard Gibbs free energy of the reaction, while its composition, chemical properties and weight doesn't change during the reaction, and they are highly selective for chemical reactions. Normally, the catalyst can be divided into three interrelated components: active component, catalyst supports and promoter.

2.2.1.1 The classification of catalysts

2.2.1.1.1 Metal Catalysts

Metal catalysts are an important class of industrial catalysts, they can be divided into five categories:

- (1) Single-site metal catalysts, such as electrolytic silver catalysts, molten iron catalysts, platinum mesh catalysts. These single-site metal catalysts were manufactured in the form of skeleton catalysts, wire-mesh catalysts and catalyst particles, etc. For example, nickel skeleton catalysts are the most commonly used in the hydrogenation reaction, while platinum wire is one of the best catalysts for the ammoxidation process;
- (2) Metal alloy catalysts, most of which are binary metal catalysts. Including three main categories: the first type is a bimetallic system consist of Group VIII and Group IB elements, such as Ni-Cu and Pd-Au, they are widely used in the hydrogenolysis, hydrogenation and dehydrogenation of hydrocarbons; the second is binary alloy of group IB elements, such as Au-Ag and Cu-Au; the third type is binary alloy of group VIII elements, such as Pt-Ir and Pt-Fe. It is worth

mention that the noble metal Pt-based metal catalysts present excellent catalytic performance in petroleum refining and automobile exhaust treatment, but its high cost brings a lot of restrictions. Thus looking for alternatives to Pt-based catalysts becomes a global research topic.

(3) Supported metal catalysts, such as Pt-Re/Al₂O₃ catalysts and Ni/Al₂O₃ catalysts, studies have shown that supported metal catalysts combine the advantages of inorganic heterogeneous catalysts and metal-organic complex catalysts. It not only has high activity, selectivity and stability, but also easy to recycle and reuse. Currently the selection of support to maximize its catalytic properties and improve the bonding strength between the catalyst and the support are the research priorities for supported metal catalysts.

(4) Metal cluster catalyst. When the size of solid catalyst has decreased to atomic level and form a cluster, the utilization of metal atoms can reach to a high level and the catalysts will exhibit amazing molecularlike behaviors due to their similar electronic structures (Figure 2-14) (Hou *et al.*, 2020). It has been proved to be a promising catalyst.

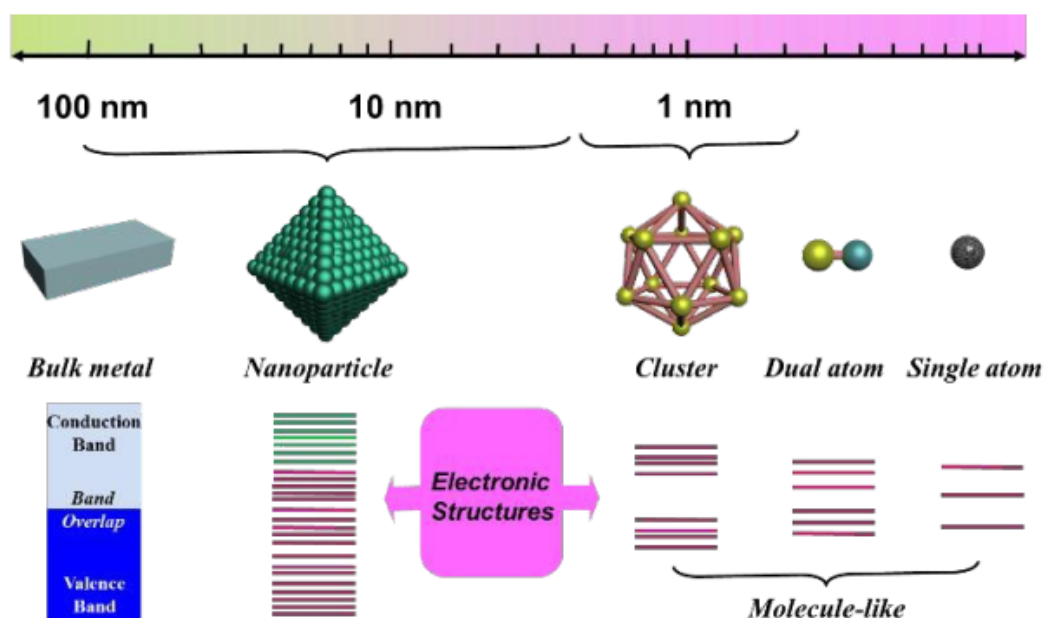


Figure 2-14 Geometric and electronic structures of single/dual-atom, cluster and bulk metal materials. (Hou *et al.*, 2020)

However, current metal cluster catalysts face the problem of unstable structures

with a low-porosity and ultralow metal loading (generally < 1 wt%), as a result of lacking anchoring groups of supports or the relatively weak interactions between the metals and hosts, thus rational design and fabrication of suitable supports is required.

(5) Intermetallic compound catalysts, such as LaNi_5 . Since the metal compounds are outstanding in terms of electrical conductivity, stability and other physical and chemical properties, and many of these compounds having a high affinity to hydrogen and oxygen, the intermetallic compound catalysts are suitable as a substitute for noble metal catalysts.

2.2.1.1.2 Metal Oxide Catalysts

Most of metal oxide catalysts are complex oxides, that is, multi-component oxides. For example, $\text{VO}_5\text{-MoO}_3$, $\text{Bi}_2\text{O}_3\text{-MoO}_3$ (Iordanova *et al.*, 1994), $\text{TiO}_2\text{-V}_2\text{O}_5\text{-P}_2\text{O}_5$ (Titlbach *et al.*, 2012), $\text{V}_2\text{O}_5\text{-MoO}_3\text{-Al}_2\text{O}_3$ (Meng *et al.*, 2014). The structure of metal oxide catalysts are complex, multiple phases will coexist in this complex system. Normally at least one of the components is transition metal oxide, and there may be interactions between these components. Transition metal oxide catalysts are non-stoichiometric compounds, the negative or positive ion vacancies in them became specific active centers during the catalytic process, and then the reactants can be activated by electron transfer at these active centers.

Metal oxide catalysts are applicable for reactions such as selective oxidation of hydrocarbons. These are strong exothermic reactions, so the effective heat and mass transfer is necessary to the catalysts.

2.2.1.1.3 Complex Catalysts

Complex catalysts are able to activate reactant molecules through coordination. The catalyst could be in a dissolved state or a solid state, the component of complex catalysts could be a common compound or complex. The catalytic process including homogeneous complex catalysis and heterogeneous complex catalysis. And the research of complex catalysis aimed at the activation of some small molecules, such as CO , H_2 , O_2 , C_2H_4 , C_3H_6 , etc.

An important feature of complex catalysis is that the active center of the catalyst and the reaction system kept connecting through a chemical bond during the reaction. The catalytic active center took effect by changing the coordination number or coordination group, at least one reaction molecule enters the coordination state and is activated, then at least one reactant molecule enters the coordination state and is activated, thereby promoting the reaction. The complex catalysis are usually carried out under mild reaction conditions, the reaction temperature is about 100-200°C, and the reaction pressure varies from standard atmospheric pressure to 20×10^5 Pa (Chen *et al.*, 2019). However, an obvious disadvantage of complex catalysis is that the homogeneous complex catalysts are difficult to recover, thus it is necessary to discover the methods to solidify the homogeneous complex catalyst.

2.2.1.1.4 Molecular Sieve Catalysts

Molecular sieves are crystalline aluminosilicates with a uniform pore structure. The molecular sieve contains a large amount of crystal water, which can be removed by vaporization when heated, so it is also called zeolite. A manmade zeolite is also called molecular sieve. Their chemical composition can be expressed as:



where M represent a metal (Ca、Na、K、Ba、Sr) cation, n is the valence of M, x is the number of molecules of AlO_2 , y is the number of molecules of SiO_2 , z is the number of molecules of water. Since the AlO_2 is negatively charged, the presence of metal cations can keep the molecular sieve electrically neutral. When $n=1$, the number of M cations is equal to that of Al, if $n=2$, the number of M cations is half of Al.

Commonly used molecular sieves can be divided into four types: A type molecular sieve, such as natrolite; X-type and Y-type molecular sieve, such as faujasite; mordenite; Zeolite Socony Mobil (ZSM)-5 composite molecular sieve, etc. Molecular sieves can present significant activity and selectivity for the acid-base catalytic reactions, which are widely used in petroleum processing, gas-

liquid separation, drying, dehydration and other industrial processing.

2.2.1.1.5 Acid-Base Catalysts

The acid-based catalyst has the ability to activate the reactant and transform it into a transition state, and is proved to occupy an important position in petroleum and petrochemical industry. Chemical reactions such as catalytic cracking of hydrocarbons, alkylation of aromatics and olefins, polymerization of olefins or diolefins, and catalytic dehydration of alcohols are all affected by acid catalysts. Although a large amount of acid-base catalysts are used in industrial processing, they can be distinguished according to their acidity, namely proton acid-base (also known as Brønsted acid-base, referred to as B-acid, B-base) catalysts and Lewis acid-base (referred to as L-acid, L-alkali) catalysts. The acid catalysts are able to emit protons or electron pairs while the alkaline catalysts accept protons or electron pairs.

2.2.1.2 Catalyst Supports

The initial purpose of introducing catalyst supports is to reduce the consumption of precious catalyst materials (e.g. Pt, Pd, Au). By dispersing catalyst materials on the surface area of substance with large volume, the use of monolith materials are avoided. Another purpose of using the support material is to improve the wear resistance and impact strength of the catalyst. Therefore, some natural materials (e.g. pumice, diatomite, quartz) with appropriate mechanical properties was used as the original catalyst support. Subsequent research result indicated that the catalyst supports not only improve the mechanical properties of the catalytically active component, but also affect their catalytic performance through chemical reaction. Nowadays synthetic materials with less impurities and better performance has gradually replaced natural materials and widely used as industrial catalyst supports. The materials used for catalyst supports need to meet the following requirements:

(1) The materials should have sufficient mechanical strength to withstand the thermal shock during the catalytic reaction. For gaseous reactants, it is also required to have good wear resistance.

(2) The materials should have large surface area and appropriate pore structure, so as to be able to carry more active components and improve the catalytic efficiency.

(3) The materials should be stable and have the ability to withstand corrosion of active substances, reactants and reaction products.

(4) The materials shouldn't contain ingredient that is harmful to the catalyst.

(5) The materials should provide relatively high thermal conductivity.

(6) The materials should be low cost, eco-friendly and easily to produce.

Generally, the application of catalyst support is to improve the mechanical properties of whole catalyst. However, there are complex interactions generated between the active component and the catalyst supports in most cases, and the effect of these interactions on the catalytic performance has not yet been explained. In other words, the selection of support materials for specific catalysts and catalytic reactions brings a lot of possibilities to the study of catalyst supports.

2.2.1.3 Catalyst Promoters

In general, catalyst promoters are considered as those components which significantly enhance the catalytic performance with less content in the catalyst (usually less than one-tenth of the total amount). After introducing the catalyst promoters, the chemical composition, crystal structure, ion valence, acidity and surface area of catalyst was significantly changed, thereby affecting its activity or selectivity. The effects of catalyst promoter on catalyst can be concluded as follow:

(1) Catalyst promoters are able to adjust the electronic structure of the active center in some catalysts, thus the catalytic activity is improved.

(2) Sometimes the grains inside the catalyst grow during the catalytic process and that could deteriorate the catalytic activity (Feng *et al.*, 2015). The addition of catalyst promoters stabilize the structure of the catalyst and inhibit the grain growth.

(3) Catalyst promoters can enlarge the proportion and distribution of the specific

active component on the catalyst surface and enhance the selectivity of the catalyst to the reaction.

(4) Some catalyst promoters can accelerate the production of intermediates in stepwise chemical reactions.

2.2.2 Reverse Water Gas Shift (RWGS) reaction - one of the most popular research topics in the field of catalysis

CO₂ is the ultimate product of many fossil fuel combustion processes, and catalytic conversion of CO₂ to CO (an important intermediate in C1 chemistry) is a key step in the economical utilization of CO₂ and carbon cycling. Thus the reverse water gas shift (RWGS) reaction that involves the conversion of carbon dioxide (CO₂) and hydrogen (H₂) into carbon monoxide (CO) and water (H₂O) is increasingly being valued. The basic equation for RWGS reaction is



Due to the exothermic nature of the RWGS reaction, high temperatures are more favorable for the generation of products, resulting in higher CO₂ conversion. As the reaction temperature decreases, the exothermic CO₂ methanization and CO methanization (i.e. Equation 2-14 and 2-15) reactions become increasingly dominant.



A decrease in the proportion of CO in the product is disadvantageous for further conversion into high value-added chemicals and fuels. In addition, the chemical equilibrium of the RWGS reaction is independent of reaction pressure, but high pressure can accelerate the CO₂ or CO methanization reactions (Su *et al.*, 2016). Therefore, the high energy consumption at high temperatures and serious methanization side reactions at low temperatures poses a significant challenge in selecting the reaction conditions.

2.2.2.1 Brief introduction of the mechanism of RWGS reaction

In recent years, in-situ infrared spectroscopy, isotope labeling tests and density

functional theory (DFT) calculations were used to track the substances that adsorbed on the catalyst surface, leading to a clearer explanation of the mechanism of the RWGS reaction. There are mainly two reported mechanisms for the RWGS reaction: redox mechanism and associative mechanism (Kattel *et al.*, 2016; Cao *et al.*, 2016; Kim *et al.*, 2012).

2.2.2.1.1 Redox mechanism

In the redox mechanism, the key to the catalytic activity is the presence of recyclable redox sites on the surface of the catalyst, which mainly include two types: (a) variably valent metal sites and (b) oxygen vacancies on the oxide surface.

For metallic redox sites such as Cu, the oxidation-reduction process roughly proceeds as follows (Guo *et al.*, 2020):



A dynamic simulation on the surface RWGS reaction of Cu-based catalysts was also carried out, the simulation result suggested that the adsorption and dissociation of CO₂ on Cu site (Equation 2-16) is the rate-determining step. Guo *et al.* have further investigated the RWGS reaction by using Cu-Cr₂O₃-Fe₂O₃ as catalyst, a series of *in situ* characterizations proves that active surface oxygen species are mostly correlated to the hydroxyl that located near the Cu-FeO_x interface and Cu⁰ is the main active site, as shown in Figure 2-15. (Guo *et al.*, 2020)

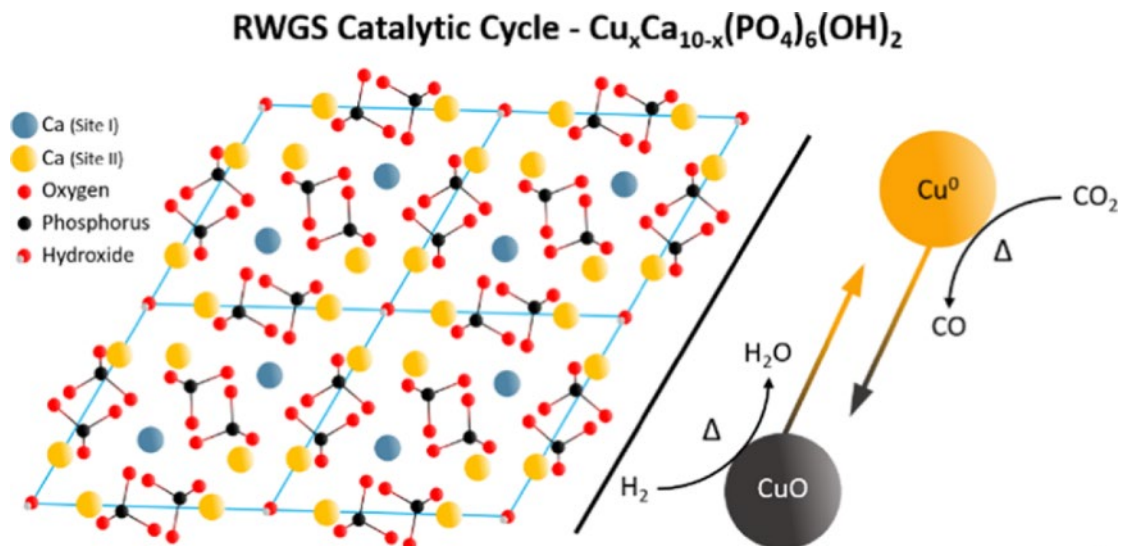


Figure 2-15 The Cu^0 active site near the Cu-FeO_x interface (Guo *et al.*, 2020)

Besides, the RWGS reaction using the Au/CeO_2 (Liu *et al.*, 2013) and Au/TiO_2 (Bobadilla *et al.*, 2018) catalysts were observed to be consistent with the redox mechanism. While CO_2 was adsorbed on oxygen vacancies (Ov) on reducible oxides such as CeO_2 or TiO_2 and dissociates to produce CO, followed by the reduction of oxygen species and regeneration of oxygen vacancies, ultimately completing the entire oxidation-reduction process. The elementary reaction steps involved can be concluded as follows, where * denotes an adsorbed species (Kim *et al.*, 2012).



2.2.2.1.2 Associative mechanism

The associative mechanism can be explained by a widely known model of the WGS reaction (Amadeo *et al.*, 1995; Kim *et al.*, 2012). The process of CO_2 reduction usually involves the formation of C-H bonds and the generation of carbon intermediates, which are then further transformed or decomposed into the final product CO. Depending on the types of intermediates formed, they can be mainly classified into formate pathway and carboxylate pathway.

In terms of the formate pathway, the reaction goes in the order of,





The asterisk (*) is often used in catalytic chemical reactions as a symbol to denote the catalytic species or surface. It is used to distinguish the catalytic species from the reactants and products in the reaction equation. For carboxylate pathway, the HCOO^* in Equation 2-22 and 2-23 is replaced by COOH^* . Goguet *et al.* performed steady-state isotopic transient kinetic analysis (SSITKA) experiments to dynamically detect the adsorbed species on Pt/CeO₂ catalyst surface. The formate, carbonyl, and carbonate species were simultaneously recognized on the catalytic surface (Figure 2-16, Goguet *et al.*, 2004), indicating that the RWGS reaction involves multiple key intermediates and has a complex and varying reaction pathway that often exhibits high similarity.

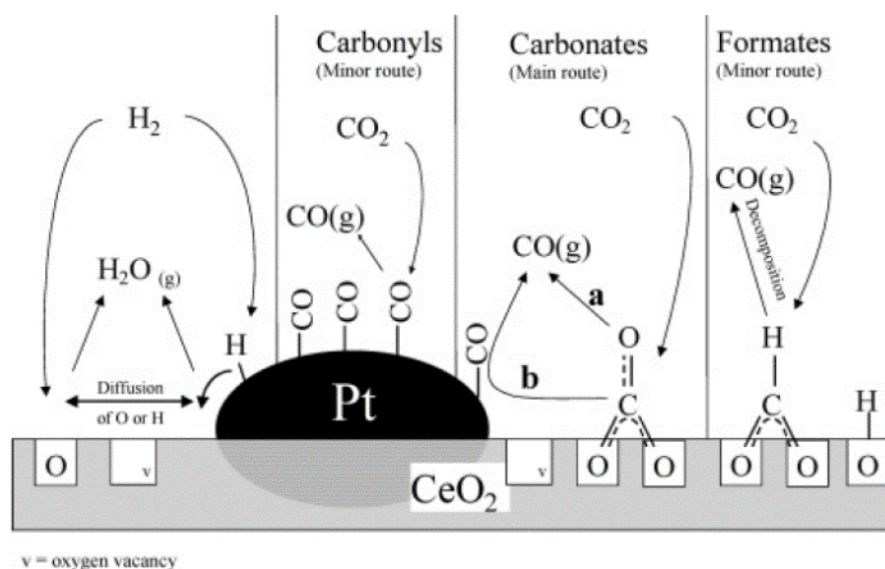


Figure 2-16 Schematic of the RWGS reaction over Pt/CeO₂ (Goguet *et al.*, 2004)

2.2.2.2 Commonly used catalysts for RWGS reaction

The endothermic nature of the RWGS reaction signified a high working

temperature of its catalyst. However, high temperature will also accelerate the oxidation and other deactivation of catalyst. Working at low temperature helps reduce energy consumption, but it is also difficult to achieve high CO₂ conversion rates and CO selectivity. Therefore, the modification of catalyst for RWGS reaction should focus on both high-temperature stability and low-temperature high-efficiency. Currently, the RWGS catalyst system mainly includes three categories: supported metal catalysts, oxide catalysts (mixed oxides, spinels, and perovskites), and carbide catalysts.

2.2.2.2.1 Supported Metal Catalyst

Supported metal catalysts have been widely studied due to their synergistic catalytic effect between metal sites and oxide supports in converting CO₂ and dissociating H₂, exhibiting excellent catalytic performance. In the supported metal catalyst system, the electronic properties and geometric structures of the metal and support will significantly affect the catalyst performance. Generally, supported metal catalysts can be divided into two categories: supported noble metal catalysts and supported non-noble metal catalysts. Noble metals mainly include Pt, Pd, Au, Ru, and Rh, while non-noble metals include Cu, Ni, Fe, and Co, and commonly used supports include Al₂O₃, SiO₂, CeO₂, TiO₂, ZrO₂, and MoO₃.

Noble metal catalysts shows excellent activity, selectivity, unique d-orbital electron properties, and usually play a critical role in efficient conversion of CO₂ (Kim *et al.*, 2012). As shown in the Figure 2-17, Wang *et al.* demonstrated that Pd/Al₂O₃ catalysts do not directly dissociate CO₂. Pd metal is responsible for the dissociation of H₂, while hydroxyl groups on the Al₂O₃ support react with CO₂ to form bicarbonates, afterwards the bicarbonates react with dissociated H species which close to the Pd particles and finally produce CO (Wang *et al.*, 2015).

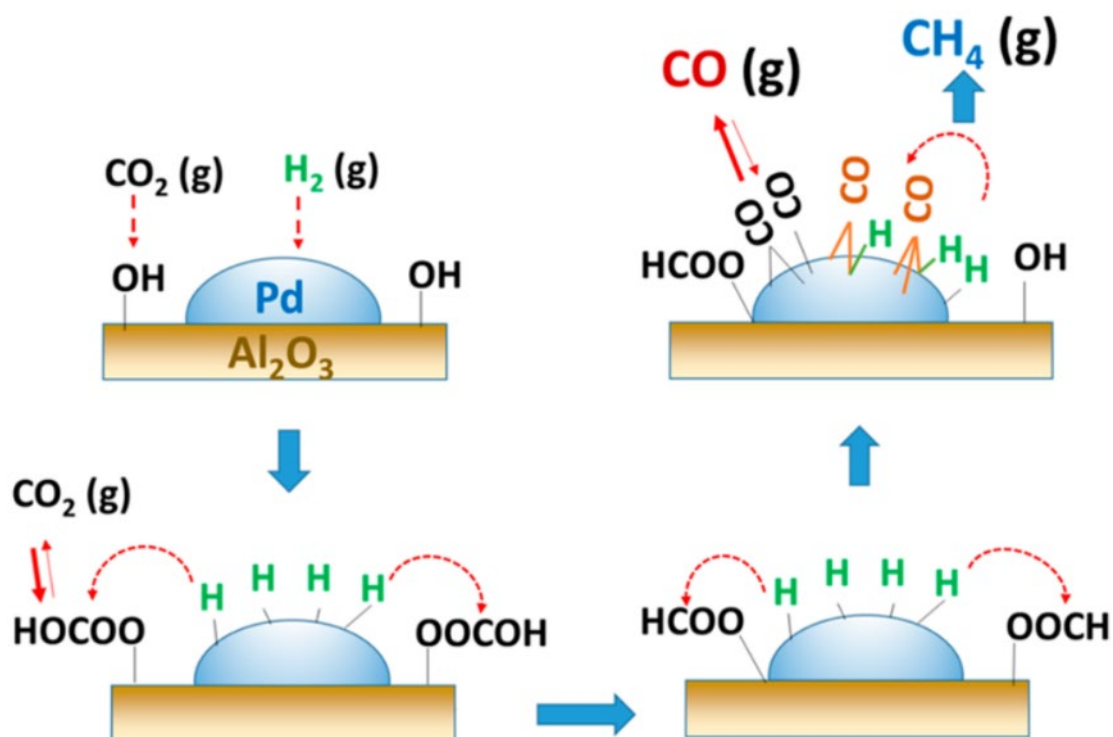


Figure 2-17 Schematic of the RWGS reaction on Pd/Al₂O₃ (Wang *et al.*, 2015)

Besides, Chen *et al.* have studied the effects of noble metal Au, Pt, Ir and their particle sizes on the evolution of main intermediates through DFT simulations. The results indicate that Au nanoparticles exhibit weak ability for C-O bond scission in the RWGS reactions but high CO selectivity, whereas Ir nanoparticles is more favorable for C-O bond scission and result in high CH₄ selectivity. (Chen *et al.*, 2003)

Non-noble metal catalysts (including Cu, Ni, Fe, Co, etc.) have been widely used due to their low cost and high feasibility for modification. For example, Cu-based catalysts exhibit excellent CO selectivity under 400°C, but the low Hüttig temperature of Cu results in poor thermal stability, making them prone to deactivated at temperatures over 350°C (Zhai *et al.*, 2008). Therefore it is necessary to combining them with suitable carriers (such as CeO₂, Al₂O₃, TiO₂ and ZnO) or promoters (Fe, Zn, etc.) to enhance the high-temperature anti-sintering and anti-oxidation capabilities of Cu-based catalysts (Zhou *et al.*, 2017; Kattel *et al.*, 2016; Chen *et al.*, 2004), and thereby regulating the reaction pathways and product selectivity.

2.2.2.2.2 Metal Oxide Catalyst

The metal oxide catalysts utilized for RWGS reactions mainly include solid solutions (such as CeZrOx, InCeOx, etc.), spinels (AB₂O₄ structure, such as ZnAl₂O₄, ZnCr₂O₄, etc.), and perovskite (ABO₃ structure, such as BaZrO₃, etc.). Compared with supported noble metal catalysts, oxide catalysts have advantages such as high thermal stability, high oxygen storage capacity, high concentration of oxygen vacancies, low cost, and weak dissociation ability of H₂, which guarantees high CO selectivity (Wang *et al.*, 2016; Park *et al.*, 2000; Park *et al.*, 2001; Daza *et al.*, 2014). More importantly, oxide catalysts are highly adjustable. By doping or changing the elements of A-site and B-site in spinels and perovskite catalysts, their geometric structure and electronic properties could be tuned *in-situ* (Li *et al.*, 2019; Su *et al.*, 2019). However, the unignorable disadvantage of metal oxide catalysts are their fairly poor ability to dissociate H₂, therefore hinder the improvement of catalytic activity.

2.2.2.2.3 Transition Metal Carbide Catalyst

Transition metal carbides perform similar electronic properties to noble metals, but stronger ability of H₂ dissociation and much lower costs than noble metals. These carbides include MoC (or Mo₂C), WC, TiC, VC, etc., among which MoC and Mo₂C has been extensively studied. Gao et al. reported an excellent RWGS reaction performance of α-MoC and β-Mo₂C nanowires. A CO₂ conversion of 27% and a CO selectivity of 100% were attained under 600°C and a H₂/CO₂ ratio of 1:1. Moreover, the CO₂ conversion rate exceeded 60% while maintaining the 100% CO selectivity at the H₂/CO₂ ratio of 4:1 (Gao *et al.*, 2016). The main drawback of transition metal carbide is that they get oxidized and deactivated easily at temperatures higher than 500°C, especially under oxidation conditions, which restricts their further industrial applications.

2.2.3 The Improvement of Catalytic Activity

2.2.3.1 Modifications of Catalyst

The modification of catalyst depends on the reaction environment, conditions,

and product requirements, etc. Taking the RWGS reaction as an example, the following methods are often used:

2.2.3.1.1 Enhance the Metal-Substrate Interactions

The RWGS reaction usually performed at the metal-support interface. Therefore, the catalyst activity and selectivity can be improved by adjusting the interaction between the metal and the support. Aitbekova et al. induced the redispersion of Ru on CeO₂ support by using a pre-heat treatment, as shown in Figure 2-18. In situ X-ray absorption spectroscopy (XAS) analysis proved that stable RuOx species were produced on the CeO₂ support surface after the redispersion, which significantly promoted the CO selectivity (Aitbekova *et al.*, 2018).

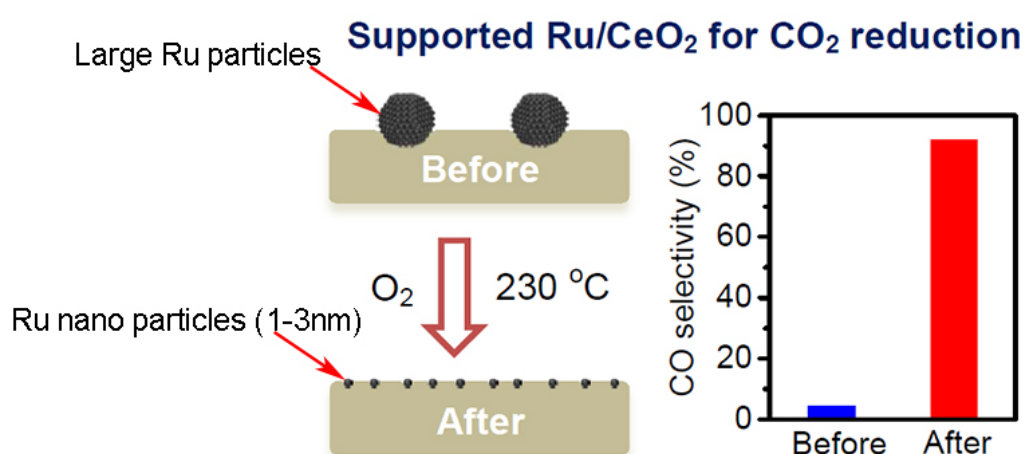


Figure 2-18 Schematic of Supported Ru/CeO₂ for CO₂ reduction and the increase of CO Selectivity (Aitbekova *et al.*, 2018)

For supported metal catalysts, the change of metal particle size can affect the surface chemical states of metals and thus the adsorption capability of reactants and intermediates. Li et al. introduced Ir particles with different sizes on CeO₂ and achieved a strong interactions between sub-nano-sized (<1 nm) Ir particles and CeO₂ support, which dramatically improve the CO selectivity from 12% to 100% in CO₂ hydrogenation reaction (Li *et al.*, 2017).

2.2.3.1.2 Addition of Catalyst Promoter

Alkali metal and transition metal are commonly added as the catalyst promoter.

They alter the interface structures and produce a great deal of active sites, thereby changing the adsorption of intermediate species and increasing CO₂ conversion. For example, the added Cu in the Cr₂O₃-Fe₂O₃ catalyst led to the generation of Cu⁰ on the newly-formed Cu-Fe₃O₄ interface, where the Cu⁰ provided active sites for H₂ dissociation and promoted the reduction of nearby surface oxygen species through hydrogen spillover, thus accelerating the CO₂ hydrogenation reaction (Zhu *et al.*, 2020). For the RWGS reaction, the addition of alkali metal promoter K enhance the overall electronic properties, these metal sites on the other hand alter the reaction pathway and facilitate the CO₂ adsorption (Yang *et al.*, 2017). Besides, the addition of transition metal such as Cu, Fe produces new active sites and interface structures, thus increases RWGS reaction rate (Consuelo *et al.*, 2016; Rubin *et al.*, 2018).

2.2.3.1.3 Formation of Bimetallic Catalysts

Bimetallic catalysts are catalysts that contain two different metallic elements in the active site. The two metals have different electronic properties and can interact in various ways, leading to improved catalytic performance compared to monometallic catalysts. A series of DFT simulation on the RWGS reactions catalyzed by Ni and Re-doped Ni were carried out (Yuan *et al.*, 2018), it was concluded that the doping of Re lowering the activation barrier of C-O bond cleavage due to the strong affinity of Re to oxygen, which proves that it is more favorable for product CO. However, it is worth noting that the product selectivity is correlated with electronic properties of the catalyst support as well. Porosoff *et al.* have investigated the catalytic performance of PtCo, PtNi and PdNi supported by CeO₂ or Al₂O₃ in RWGS reactions, the results indicating that catalyst PtNi/CeO₂ displayed the highest catalytic activity but was more inclined to produce CH₄, while catalyst PtCo/Al₂O₃ exhibited a significantly high CO selectivity (Porosoff *et al.*, 2013).

2.2.3.2 NEMCA -the Electrical Enhancement of Catalytic Activity

2.2.3.2.1 The Research Process of NEMCA Effects

Non-Faradaic electrochemical modification of catalytic activity (NEMCA) is a

newly founded technology that could significantly improve the efficiency of the catalytic process. Which means that the catalytic activity and selectivity of metal catalysts can be altered dramatically and reversibly by adjusting the applied current or potential at the catalyst surface. The impact of electricity on catalytic performance was realized since the 1950s, and then controlled modification of the electronic and concomitant catalytic properties became an important research goal. In 1981, a special phenomenon was observed by M. Stoukides, he found that when external voltages are applied to a solid electrolyte (YSZ) cell, the selectivity of ethylene oxidation on polycrystalline silver can be affected obviously through electrochemical oxygen pumping. The increase in the rate of C_2H_4O production can exceed the rate of O^{2-} pumping over 400 times, indicating a dramatic change in the properties of the silver catalyst (M. Stoukides, 1981).

Afterwards a simple model was proposed by M. Stoukides to explain this phenomenon, and two parameters was introduced: reaction rate enhancement factor ρ and Faradaic enhancement factor Λ :

$$\rho = \frac{r}{r_0} \quad \text{Equation 2-26}$$

$$\Lambda = \frac{\Delta r}{\frac{i}{2F}} \quad \text{Equation 2-27}$$

where $\Delta r = r - r_0$, r_0 is the catalytic reaction rate without electrochemical enhancement, r is the catalytic reaction rate after electrochemical enhancement, i is the current and F is the Faraday constant. Generally after the catalyst is electrochemically enhanced, $\rho \neq 1$ and $|\Lambda| > 1$ (M. Stoukides, 1981). One year later, they proposed that the order of magnitude of the enhancement factor Λ can be estimated from:

$$\Lambda = 2Fr_0/I_0 \quad \text{Equation 2-28}$$

where I_0 is the exchange current of the catalyst-solid electrolyte interface (Stoukides et al., 1982).

The concept of NEMCA was first proposed by S. Bebelis and C. G. Vayenas, they conducted a deep oxidation of ethylene to CO₂ in a Solid Oxide Fuel Cell (SOFC) membrane reactor and found that the steady-state increase in the catalytic reaction rate Δr is typically 10⁴-10⁵ higher than the rate of O²⁻ transport to the catalyst surface (Figure 2-19). In 1988, C. G. Vayenas *et al.* proved that the spillover (O²⁻) would produce or consume at the boundaries between the solid electrolyte-catalyst-gas three phases during the reaction, which causes an increase or decrease in the catalyst work function $e\Phi$. And they found that:

$$e\Delta\Phi = e\Delta V_{WR} \quad \text{Equation 2-29}$$

where $e\Delta V_{WR}$ is the overpotential measured between the solid electrolyte/catalyst and the metal reference electrode (R).

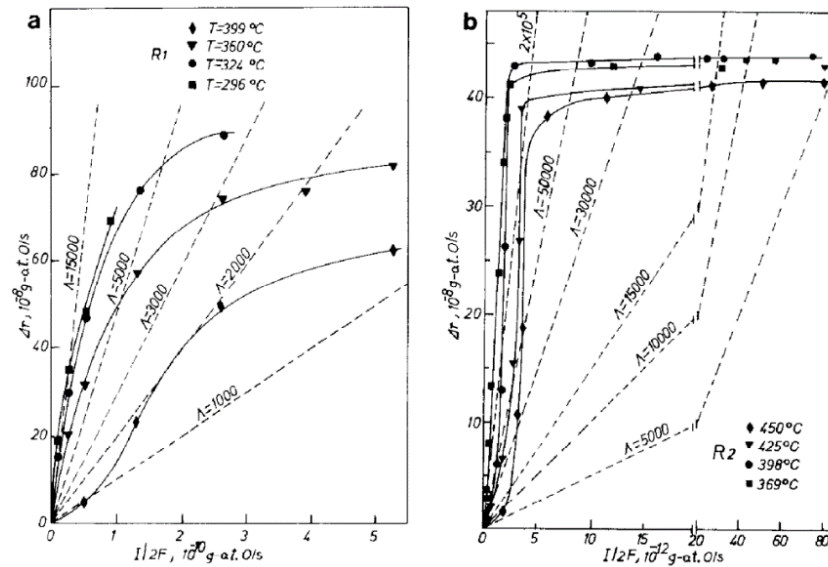


Figure 2-19 Steady-state effect of applied current on the rate of ethylene oxidation Broken lines are constant enhancement factor lines

Then C. G. Vayenas *et al.* investigated NEMCA effect within a work function ranges from 0.3 eV to 1 eV and suggested that the rates of catalytic reactions depend exponentially on the catalyst work function, it can be conclude as:

$$\ln(r/r_0) = \alpha e(\Phi - \Phi^*)/k_B T \quad \text{Equation 2-30}$$

where r_0 is the regular catalytic rate, α and Φ^* are reaction- and catalyst-specific constants. The value of $|\alpha|$ is typically between 0.2 and 1. When $\alpha > 1$ indicates that the chemical reaction is electrophilic, otherwise the reaction is

electrophobic (Vayenas *et al.*, 1990).

In 1991, Vayenas *et al.* used hydroxide ion (OH^-) as a spillover on the Pt/ β - Al_2O_3 fuel cell, and observed the NEMCA effect during the C_2H_4 oxidation reaction. It's also the first time to prove that the NEMCA effect could be induced by another ion instead of O^{2-} . In 1994, Neophytides *et al.* reported that an effect similar to NEMCA could be observed in aqueous solution at ambient temperatures. Their experiments were carried out in aqueous KOH with dispersed platinum/graphite electrode and they found that the rate of H_2 oxidation is increased by 500% due to the application of a positive potential of 1-2V on Pt electrode. They considered hydroxide ion as the spillover and found that each hydroxide ion in the catalytic system lead to the oxidation of about 20 H_2 atoms. In 2007, Beck *et al.* pointed out that the catalytic reaction is not just conducted on the three-phase interface area when the NEMCA effect occurs (Beck *et al.*, 2017). At the same time, Levia predicted that the coverage of spillovers on the catalyst surface is linearly related to the potential difference at the metal-solid electrolyte interface. As of 2011, more than 100 chemical reactions have been proved to be promoted by NEMCA effect (Vayenas *et al.*, 2011).

2.2.3.2.2 Double layer model of NEMCA

Soon after the term of NEMCA was proposed, a theoretical model of a double-layered structure was proposed to explain the NEMCA effect. As shown in Figure 2-20, a metal catalyst electrode particle (grey zone) is supported on Y_2O_3 -doped ZrO_2 (YSZ) (white rectangle), an O^{2-} conductor, while different kinds of spillover-formed double layer structure are depicted and compared. Result indicates that electrochemical promotion is caused by the electrochemically controlled migration of spillover from the solid electrolyte onto the gas-exposed electrode surface. These migrations are accompanied by the compensating charge of spillover in the metal and establish an overall neutral double layer on the gas-exposed catalyst surface (Papadakis *et al.*, 1996; Yiokari *et al.*, 2000). This double layer structure is suggested to have an impact

on the chemical absorption and catalytic performance of the catalyst (Vayenas *et al.*, 2001).

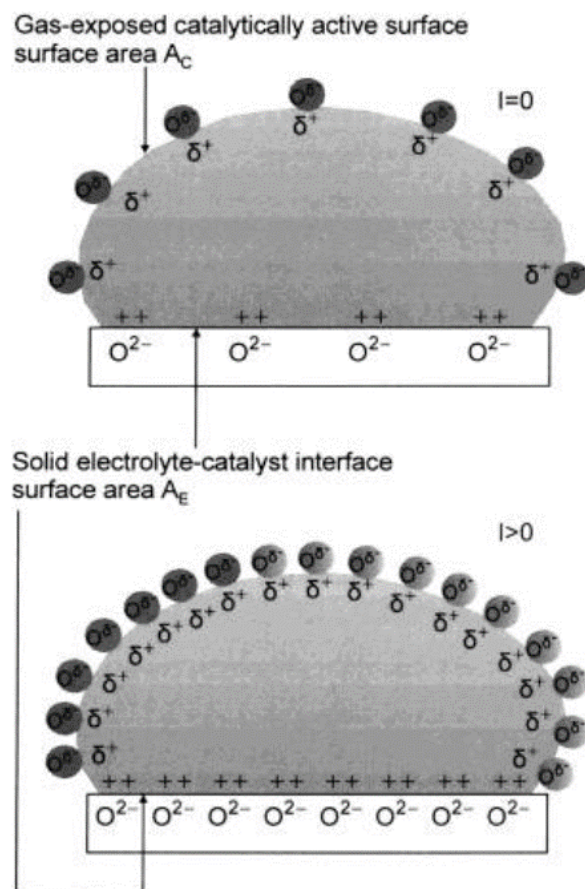


Figure 2-20 Schematic of a metal catalyst electrode particle supported on Y2O3-doped ZrO2 (YSZ), an O₂⁻ conductor, under open-circuit conditions (top) and upon application of an anodic (positive) current showing the backspillover-formed double layer at the metal-gas interface (bottom). (Yiokari *et al.*, 2000; Vayenas *et al.*, 2001; Papadakis *et al.*, 1996)

2.2.3.2.3 The Application of NEMCA effects

(1) Proton exchange membrane

Proton exchange membrane (PEM) is a commonly used organic membrane proton electrolyte material for low-temperature fuel cells. It performs high hydrogen ion conductivity at lower temperatures. In 2005, Li *et al.* proposed a method to synthesize ammonia gas from hydrogen and nitrogen at standard atmospheric pressure utilizing PEM with the help of NEMCA effects (Li *et al.* 2005). Moreover, Sapountzi *et al.* studied the conversion of CO to CO₂ in PEM

fuel cell reactor and found that the efficiency of electrochemical promotion depends strongly on the anodic electrocatalyst (Pt or Au), CO concentration, operating temperature and the presence of oxygen, while the electropromotion effect were found to be much higher in CO-rich anode environments (Sapountzi *et al.* 2009). This phenomenon indicates that the application of NEMCA effect has advantage in the elimination of CO in PEM fuel cell.

(2) EPOC Reactor

In order to maximize the utilize of the NEMCA effect, S. Balomenou of the C.G. Vayenas research group proposed a strategy to combine EPOC reactor unit to produce an enhanced fuel cell reactor, called Monolithic Electropromoted Reactor (MEPR). In 2009, Souentie *et al.* investigated the reduction of NO by C₂H₄ in high excess of O₂ a MEPR with 22 Rh/YSZ/Pt parallel plate elements, the MEPR is shown in Figure 2-21 (Souentie *et al.*, 2009). It was found that the selective catalytic reduction (SCR) of NO can be electropromoted by 450% with near 100% selectivity to N₂, and the oxidation rate of C₂H₄ is enhanced up to 900% with Faradaic efficiency.

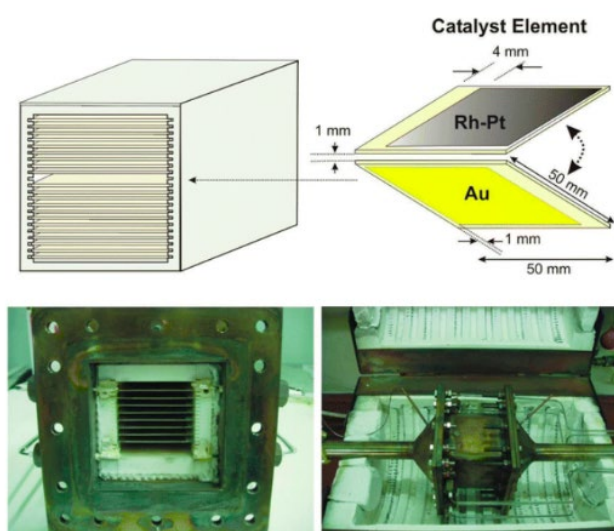


Figure 2-21 Monolithic electrochemical promotion reactor (Souentie *et al.*, 2009)

2.2.3.3 Thermoelectric promotion of catalysis (TEPOC)

Thermoelectric promotion of catalysis is a novel approach to enhance the efficiency of catalytic reactions. It exhibits the utilization of Seebeck voltage

generated by thermoelectric materials, which promotes the catalytic reaction. The concept of TEPOC is still relatively new, and there has been significant interest in exploring its potential as a method to optimize catalytic reactions. In 2018, Achour *et al.* reports on an innovative application of a thermoelectric material, BiCuSeO, as both a catalyst support and promoter for CO₂ hydrogenation and Ethylene oxidation reactions (Achour *et al.*, AEnM, 2018; Achour *et al.*, ACS Catal., 2018). The authors propose that using thermoelectric materials can shift the Fermi level and work function of a catalyst, and therefore exponentially increasing the catalytic activity of catalyst particle which deposited on its surface, as plotted in Figure 2-22.

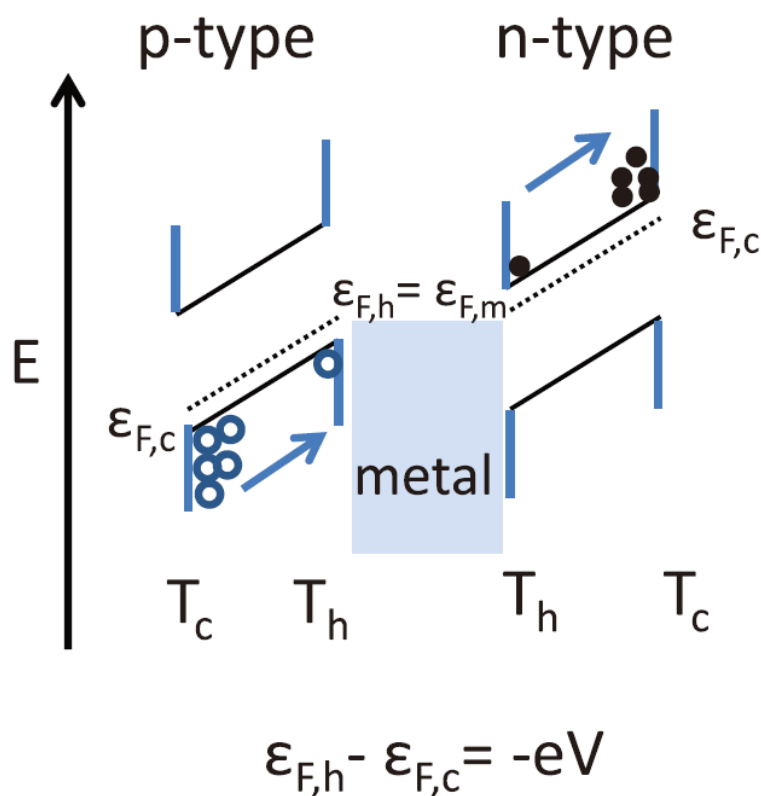


Figure 2-22 Schematic of energy bands and Fermi levels for TE materials (Achour *et al.*, AEnM, 2018)

It was found that the thermoelectric Seebeck voltage has made a contribution to the dramatically rising of CO₂ conversion rate and CO selectivity for CO₂ hydrogenation, indicating that thermoelectric effects can not only increase the reaction rate but also alter chemical equilibrium. Furthermore, the results reveal

that the thermoelectric promotion of catalysis allowed BiCuSeO oxide itself to have high catalytic activity for CO₂ hydrogenation. For the Ethylene oxidation experiments, a linear relationship between the logarithm of the reaction rate and the thermoelectric Seebeck voltage was also observed (Figure 2-23, Achour *et al.*, ACS Catal., 2018).

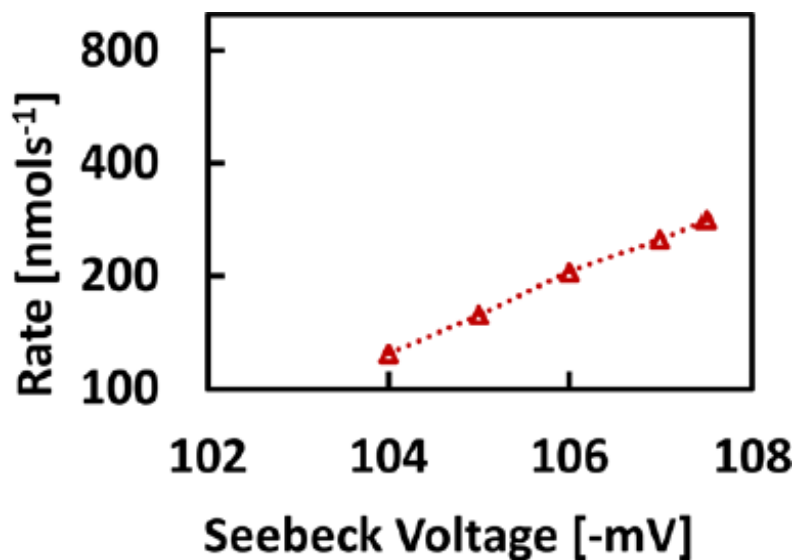


Figure 2-23 The reaction rate in a log scale as a function of increasing Seebeck voltage (Achour *et al.*, ACS Catal., 2018)

The basic equation for TEPOC (Achour *et al.*, AEnM, 2018) derives from Equation 2-30, which can be summarised as,

$$\ln(Y/Y_0) = -\gamma eV/k_b T_h \quad \text{Equation 2-31}$$

Here, γ is a constant, to be determined by experiment. Y represent the conversion of reactant at a specific temperature T_h , Y_0 is the conversion obtained when Seebeck voltage V equals zero. For the p-type TE material BiCuSeO, the Seebeck voltage at hot surface is negative, so $-\gamma eV$ is positive. The ratio Y/Y_0 can be calculated by introducing the γ obtained above and the corresponding V and T_h values into Equation 2-31. By calculating Y/Y_0 for each conditions, the improvement of conversion with a Seebeck voltage over without a Seebeck voltage could be clearly seen.

From Arrhenius law, we have $Y_0 = B \cdot A_s \cdot \exp(-E_a/k_b T_h)$, here B is a constant, A_s is the surface area, and E_a the activation energy of the reaction without the

TEPOC effect. Thus a generalized rate equation could be written as

$$Y = B \cdot A_s \cdot \exp(-(E_a + \gamma eV)/k_b T_h) \quad \text{Equation 2-32}$$

One of the objectives of this project is to confirm the validity of the above two equations (Equation 2-31 and Equation 2-32) still valid for porous thermoelectric materials used in a chemical reaction. In the next few chapters, we will apply porous structure to the surface of TE samples, then catalyze the CO₂ hydrogenation reactions by using these porous samples. After obtaining data for relevant variables such as Seebeck coefficient, conversion rate, reaction temperature, etc., we will substitute them into the above two formulas to validate their feasibility.

3 Methods for Materials Processing and Characterizations

3.1 Introduction

In this chapter, a description of materials and methods used in this project is given. The first subchapter aimed at the preparation of porous and non-porous thermoelectric material BiCuSeO, the preparation process for $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ is also presented. The techniques used to characterise these materials are listed in the second subchapter. At last, the schematic of reaction chamber for conducting the catalytic chemical reaction are presented.

3.2 Thermoelectric samples preparation

3.2.1 Synthesis of BiCuSeO powder through Flux method

The initial step in the experiment is the synthesis of BiCuSeO compound powder. High purity commercially purchased Bi_2O_3 , Cu, Bi, and Se powders were weighed stoichiometrically and hand-mixed in an agate mortar for 2 hours. The mixed powder were then placed in a cylindrical alumina crucible and covered with B_2O_3 powder, as shown in Figure 3-1a and 3-1b. The powders in the crucible were uniformly compacted to minimize the air in the powder gaps. The calcination process was conducted in a box furnace for 10 hours at 600°C in air. The resulting reaction products (Figure 3-1c) were ground into powders in a mortar, a model D5005 X-Ray Diffractometer from Siemens was used to analyze the composition of the powder. After the desired BiCuSeO phase and its high purity was certified by XRD, the obtained powder would be subsequently utilized to produce porous and non-porous BiCuSeO samples.

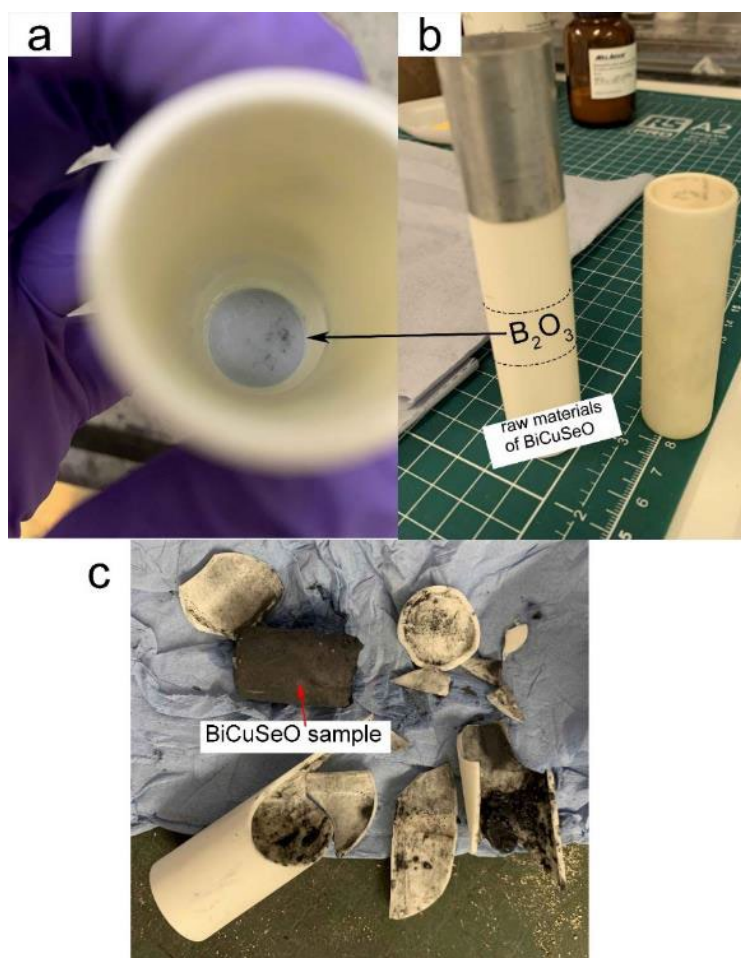


Figure 3-1 (a) and (b) the raw materials in the crucible; (c) BiCuSeO samples after calcination

3.2.2 Preparing nano-porous BiCuSeO samples through Sol-Gel method

The Bi(NO₃)₃, Cu(NO₃)₂, Se and Citric Acid (CA) powder were stoichiometrically weighed with an analytical balance. The Se powder was first put into a beaker, an appropriate amount of Nitric Acid (NA) was added to dissolve the Se, then the solution was heated to 50°C and stirred vigorously with a magnetic stirrer, a light yellow clarified solution could be obtained after several minutes, indicating that the Se powder had been completely dissolved. On the other hand, Bi(NO₃)₃, Cu(NO₃)₂ and Citric Acid powder were dissolved into 30ml distilled water to get a bluish transparent solution and 36-72ml of Ethylene Glycol (EG) was added at the same time. The above two solutions were mixed, then heated to 90°C and stirred to mix it thoroughly. A light blue gel was formed

within 3 hours, it was then put into an oven and dehydrated under 80°C for 8 hours to get a dry bluish gel. In a tube furnace, the dry gel was put into a round shallow crucible and calcined at 550°C for 10 hours. Finally a blackish BiCuSeO powder was prepared, followed by phase identification using XRD.

3.2.3 Methods for obtaining porous/nano-porous/non-porous BiCuSeO samples

For non-porous samples, the BiCuSeO powder obtained from flux method was directly cold-pressed under pressure of 1.07MPa to form $\Phi 20\text{mm} \times 2\text{mm}$ pellets and subsequently sintered in a tube furnace under 650°C for 10 hours in Argon atmosphere with heating and cooling ramp rate of 1°C/min, this sample was named as BCSO @Flux. Besides, spark plasma sintering (SPS) was applied to maximize its thermoelectric properties and density. The dimension of SPSed sample is $\Phi 20\text{mm}$ pellet with a thickness of 2mm and this sample was named as BCSO @SPSed. The sintering was conducted in vacuum with a vacuum degree of about 15Pa. The temperature was controlled at 630°C under a heating rate of 50K/min, the holding time was 5 minutes and the sintering pressure was 50MPa.

In terms of porous samples, the sol-gel method provides an approach to obtain nano-porosity, but a significant drawback of it is the difficulty in controlling the surface area or porosity. The basic idea is to dip the bulk non-porous BiCuSeO sample into the Bi, Cu, Se contained gel (Chapter 3.2.2) and drop the gel onto the surface of non-porous BiCuSeO sample to form a thin gel layer at the sample surface, they were then calcined in the tube furnace at 550°C for 12 hours to form porous coating and named as BCSO @Dip coating and BCSO @Drop coating. Their composition and surface structure were discussed in Chapter 4.2.2 and 4.2.3.

Moreover, the BiCuSeO powder produced by Flux method (Chapter 3.2.1) was mixed with dry bluish gel (Chapter 3.2.2) in a weight ratio of 1:1 to form nano-porous structure, the mixed powder was ball milled for 12 hours and cold

pressed into a $\Phi 20\text{mm} \times 2\text{mm}$ sample under a pressure of 1.07MPa. At last, a porous sample could be obtained after calcined in the tube furnace (550°C , 12hrs), which was named as BCSO @50wt% Gel.

In order to obtain the desired porosity, polystyrene (PS) was chosen to introduce a hierarchical porosity to BiCuSeO sample. During the preparation process, the BiCuSeO powder was mixed with 10 wt%, 15 wt% and 20 wt% of PS particles of grain size $\leq 155\mu\text{m}$, respectively. The mixture was then milled in a ball milling machine for 12 hours and cold-pressed into $\Phi 20\text{mm} \times 2\text{mm}$ pellets, these sample were then named as BCSO @10wt% PS, BCSO @15wt% PS and BCSO @20wt% PS, respectively. Moreover, three continuous cold-press pressure 0.53MPa, 1.07MPa and 1.60MPa were chosen for preparing BCSO @10wt% PS, BCSO @15wt% PS and BCSO @20wt% PS samples, their surface morphology was characterized and compared in Chapter 4.2.4. At last, all of the samples above were sintered in a tube furnace in Argon. They were first heated to 300°C and kept for 2 hours to eliminate the internal PS and maintained at 650°C for 10 hours afterwards to generate the porous structure.

3.2.4 Preparation of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples

Thermoelectric samples of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ were prepared by solid state reaction and spark plasma sintering methods. For solid state reaction method, stoichiometric amounts of Calcium oxide (CaO, Alfa Aesar, 99.9%), Cobalt oxide (Co_3O_4 , Alfa Aesar, 99.7%) were mixed together to obtain a homogenous powder to produce $\text{Ca}_3\text{Co}_4\text{O}_9$. Besides, Terbium oxide (Tb_4O_7 , Alfa Aesar, 99.9%) were used for the preparation of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$. The resulting powder was then calcined twice at 973 K for 20 hours with intermediate grinding steps. After being pulverized, the powder was compressed using a cold pressing machine under a pressure of 15 MPa, resulting in $\Phi 20\text{mm} \times 2\text{mm}$ pellets. These pellets underwent sintering at a temperature of 1173 K for 20 hours, and the process of re-pelletizing and

sintering was repeated twice. Finally, the sintered pellets were polished for characterization experiments.

In terms of spark plasma sintering method, those pulverized powder described in the paragraph above was weighed and consolidated using a Spark Plasma Sintering (SPS) technique (HP-D- 25/1, manufactured by FCT Systeme GmbH, Frankenblick, Germany). The SPS processing conditions were adopted from the published reports (Lin et al., 2015; Saini et al., 2017; Shimonishi et al., 2019), which were: at 1073 K and 50 MPa pressure with dwell time of 5 minutes under vacuum, the heating ramp rate is 50 K/min. The densities of the samples were measured using the Archimedes method.

The SPS processing and density measurement were carried out by Dr. Cevriye Koz from European Thermodynamics Ltd., UK.

3.3 Characterization Methods

3.3.1 Microstructure Characterizations

3.3.1.1 X-Ray Diffraction

The X-ray Diffraction (XRD) is an analytical technique for providing detailed information about the structure of crystalline substances. A primary use of this tool is the characterization and identification of compounds based on their diffraction pattern. In this research, XRD (Siemens D5005) scans were carried out at 40 kV with a Cu K α X-ray source at a 2 θ range of 20° - 70° with a step size of 0.06°. Crystalline structures were identified and evaluated using a XRD Evaluation software and compared to Joint Committee on Powder Diffraction Standards (JCPDS) patterns.

3.3.1.2 Scanning Electron Microscopy

The microstructural investigations were carried out using a scanning electron microscope (SEM) (Philips, FEI XL30 SFEG). The SEM is equipped with Energy Dispersive X-Ray Spectroscopy (EDS) to detect and quantify elements from Beryllium upwards. Also, it is important to note that the EDS measures

elements present to a depth of several micrometers into the samples. The ImageJ software was used to determine the pore size distribution of porous TE samples.

3.3.1.3 Thermogravimetric and Differential Scanning Calorimetry

The combination of differential scanning calorimetry (DSC) and thermogravimetry (TG) is used to determine the oxidation and the decomposition properties of the bulk pieces of materials in an argon or air atmosphere. This method is based on the simultaneous measurement of the heat flux and mass change during oxidation or reduction. The DSC signal reflects the heat flux from the sample to the instrument chamber and was compared to the heat flow of an alumina crucible as a reference. The TG signal analyses the mass change as a function of temperature to determine characteristics of the materials e.g., decomposition points.

3.3.1.4 Ultraviolet–visible spectroscopy

Ultraviolet–visible (UV-Vis) spectroscopy (Jasco, V-670) is a useful analytical technique in chemistry and materials science that examines the interaction of molecules with ultraviolet and visible light. This technique measures the absorption of light as a function of wavelength, which provides information about the electronic structure of molecules and materials. UV-Vis spectroscopy is commonly used in chemical analysis, quality control, and research to study the properties of molecules and materials. In terms of the procedure of UV-Vis test, a reference sample is measured in the same way as the target sample to account for any background absorption at first, the sample is then measured and the data is analysed to determine the absorbance at each wavelength.

3.3.1.5 Brunauer–Emmett–Teller (BET) Surface Area measurement

BET surface area measurement is a common analytical technique used in chemistry and materials science to determine the surface area of a solid material, typically a porous or powdered substance. The technique is based on the Brunauer-Emmett-Teller (BET) theory, which states that the amount of gas molecules adsorbed by a solid surface is proportional to its surface area. In this

thesis, a BET measuring instrument (model: 3P meso 112/222) was used. During BET surface area measurement, a gas, typically nitrogen or carbon dioxide, is adsorbed onto the surface of a material at different pressures, and the amount of gas adsorbed is measured using specialized equipment. The data obtained from the measurements is then used to calculate the material's surface area using the BET equation (Brunauer *et al.*, 1940) which may be written as

$$n^a = \frac{n_m^a C p}{(p^{0-p}) [1 + (C - 1) (p/p^0)]} \quad \text{Equation 3-1}$$

where n^a is the amount of gas adsorbed at a pressure p , n_m^a is the amount of the gas required to form a monolayer on the surface of the adsorbent, p^0 is the saturation vapour pressure of the adsorbate at the adsorption temperature and C is a parameter given by the equation

$$C = A \exp \left[\frac{E_1 - E_L}{RT} \right] \quad \text{Equation 3-2}$$

where E_1 is the mean enthalpy of adsorption of the first layer and E_L the enthalpy of liquefaction of the adsorbate. The quantities R and T have their usual significance.

3.3.2 Thermoelectric properties

3.3.2.1 Seebeck Coefficient and Electric Resistivity

Seebeck coefficient and electrical resistivity were measured simultaneously by using a LSR-3 Linseis for BiCuSeO samples at range of a 300 K - 723 K and for $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples at 300 K - 973 K. These systems have a primary heating chamber. The sample is vertically placed in between two platinum electrodes in the chamber, which serve as the current electrodes for the four- point resistivity measurements. The two contacting thermocouples measure the temperature difference by determining the temperature of the sample at two different points. The generated Seebeck voltage is determined between two electrodes which is the same as for measuring temperature

difference. The electrical resistivity is measured by means of the standard four-probe techniques. A constant current is applied to the electrodes while the voltage generated across the sample is measured by two contacting electrodes.

3.3.2.2 Thermal Conductivity

The thermal diffusivity (D) is determined by using a LFA-457 Netzsch laser flash method under a continuous argon flow. By using an infrared detector, the temperature increase is measured versus time. The thermal conductivity (κ) could be calculated by the equation below,

$$\kappa = D \cdot \rho \cdot C_p \quad \text{Equation 3-3}$$

where ρ is the sample density and C_p is specific heat capacity that is almost constant in condensed matter. The sample density was determined using the Archimedes method, while the specific heat (C_p) was determined using a differential scanning calorimeter (DSC) instrument.

The Seebeck coefficient, electrical resistivity and thermal diffusivity measurements were carried out by the group of Prof. Mike Reece of School of Engineering and Materials Science, Queen Mary University of London, UK.

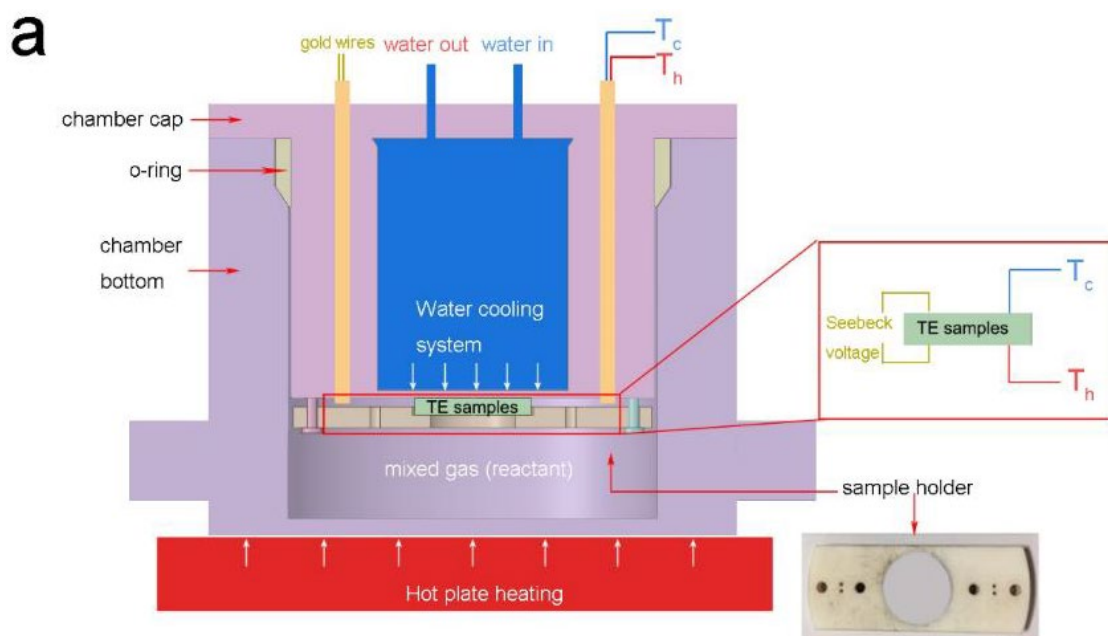
3.3.3 Experimental Set-up for Catalytic Chemical Reactions

3.3.3.1 Reaction Chamber

Chemical reactions were performed in a single chamber reactor. The schematic and actual pictures of the reaction chamber are shown in Figure 3-2. The reactor consisted of a stainless-steel cylinder of 40 cm³, capped with a cover plate and tightened with O-ring and screws (M5 x 25mm, RS). The cover plate was cooled with continuous running water. Gold wires (Agar Scientific, Ø 0.2 mm) were used to connect the sample and a digital voltage meter. The Seebeck voltage between the bottom hot and upper cold surfaces could be read directly on the screen of the digital voltage meter. The temperatures (cold T_c and hot T_h sides) were measured with K-type thermocouples (Ø 0.25mm, TC Direct) placed onto the sample surfaces with a high temperature tape. Gold wires and thermocouples were led out of the reactor chamber through two four-holes

alumina tubes (Omegatite 350). A high temperature hot plate 1500F model (HP99YX, Wenesco, Inc.) with a temperature controller was used to heating the reaction chamber.

The reaction chamber was directly placed on the top of hotplate with connection to the water cooling system by two pipes. A disc sample pellet was placed into a pre-designed ceramic (MACOR) holder (Figure 3-2a) and attached to the cooling surface of the cover plate for normal thermoelectric effect experiments, so that its top side (T_c) was always below 373 K (Figure 3-2a). The bottom side of TE sample faces toward the hot bottom of the reaction chamber, and is surrounded by the reactant mixed gas.



Reaction chamber

Figure 3-2 (a) Schematic and (b) actual picture of the reaction chamber

3.3.3.2 Catalytic Activity Experiment

The catalytic activity measurements for different catalysts were carried out in the reaction chamber described above. A set of three gas mass flow controllers (MKS, 1679B Series, Unit UFC-1100) were used to control the gas composition and flowrate. The reaction reactants and products were continuously monitored using an online Gas Chromatograph (GC8340, CE instruments). The gas chromatograph (GC) is equipped with a Thermal Conductivity Detector (TCD) and two columns, the manipulation were performed using the TotalChrom Workstation (Version 6.2.1 for Windows) data system. Each experiment was repeated for three cycles to test the stability and reproducibility. At each temperature, the catalyst was allowed to reach a steady state for at least 30 minutes and then three injections were performed for GC measurements. The average of three GC measurements at each temperature is recorded.

For the CO₂ hydrogenation reaction, the reactants were BOC standards of H₂ supplied as a 30% mixture in He, 3% CO₂ mixture in He, and the gases were mixed with helium gas (BOC, 99.996%) to obtain the desired concentrations. The inlet gas ratio were set as H₂: CO₂ = 1:1 and 4:1 for BiCuSeO samples to investigate their catalyst activities, while they were H₂: CO₂ = 1:1, 3:1 and 5:1 for Ca₃Co₄O₉ and Ca_{2.6}Tb_{0.4}Co₄O₉ samples. All samples were tested at an overall flow rate of 100 ml · min⁻¹. The conversion of CO₂ and the selectivity of CO and CH₄ were evaluated from the outlet carbon percentage values obtained by the gas analysis. Because the reaction product water vapour could not be detected by GC, thus the CO₂ conversion, and the selectivity of product X (X=CO, CH₄) can be calculated as:

$$\text{CO}_2 \text{ Conversion (\%)} = (\text{CO (KPA)} + \text{CH}_4 \text{ (KPA)}) / (\text{CO (KPA)} + \text{CH}_4 \text{ (KPA)} + \text{CO}_2 \text{ (KPA)}) * 100 \quad \text{Equation 3-4}$$

$$\text{X Selectivity (\%)} = \text{X (KPA)} / (\text{CO (KPA)} + \text{CH}_4 \text{ (KPA)}) * 100 \quad \text{Equation 3-5}$$

Here, CO₂ (KPA), CO (KPA) and CH₄ (KPA) stand for the partial pressure of CO₂, CO and CH₄ within the outlet gas, which could be identified and calculated from GC data.

4 Characterization of porous/non-porous BiCuSeO

4.1 Introduction

In chapter 3.2, non-porous BiCuSeO samples were prepared by conventional sintering and spark plasma sintering (which were named as BCSO @Flux and BCSO @SPSed), while the porous samples were obtained by mixing flux method BiCuSeO powder with 50wt% BiCuSeO gel or 10 wt%, 15wt% and 20wt% polystyrene (which were named as BCSO @50wt% Gel, BCSO @10wt% PS, BCSO @15wt% PS and BCSO @20wt% PS, respectively). In this chapter, the characterization of the above-mentioned samples was reported. The optimal molar ratio of the reactants Nitric Acid, Citric Acid and Ethylene Glycol to the total metal cations M^{n+} for BiCuSeO preparation was obtained as $n(\text{Nitric Acid}): n(\text{Citric Acid}): n(\text{Ethylene Glycol}): n(M^{n+}) = 20:1:1:1$ (which corresponding to sample 1d, highlighted in Table 4-1). Furthermore, the microstructure and surface area of porous BCSO have been investigated systematically, the highest surface porosity of 37.3% was achieved from sample BCSO @ 20wt% PS 0.53MPa.

4.2 Result and discussion

4.2.1 The XRD analysis of porous/non-porous BiCuSeO prepared by Flux method and Spark plasma sintering

Figure 4-1 shows the XRD patterns of the porous/non-porous BiCuSeO samples prepared by conventional sintering and the SPS. From the figure, it can be seen that the diffraction peaks of all samples mostly match with the standard card of BiCuSeO (PDF#45-0296), indicating that these samples are mainly comprised of BiCuSeO. A small characteristic peak of Bi_4Se_3 can be observed at $2\theta=28.7$ in the XRD patterns of all samples except BCSO @SPSed, while a small CuSe peak occurs in sample BCSO @SPSed at $2\theta=28$.

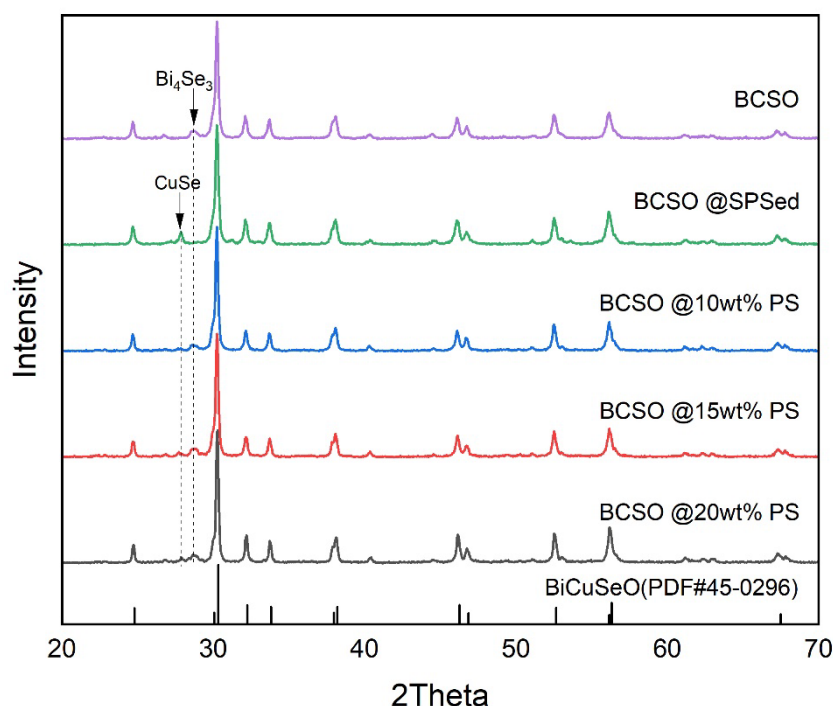


Figure 4-1 XRD patterns of non-porous samples BCSO @Flux and BCSO @SPSed; porous samples BCSO @10wt% PS, BCSO @15wt% PS and BCSO @20wt% PS

4.2.2 The XRD analysis of BiCuSeO prepared by Sol-Gel method

Related studies have shown that the structure of gels can be controlled by changing the type of chelating agent and solvent, pH value of solution, and concentration of chelating agent (Bhaskar *et al.*, 2017). Owens *et al.* compared the structural characteristics of gels made up of different chelating agents, and the results showed that as the molecular weight of the chelating agent increased, the porosity of the product porous material decreased, as well as the pore size (Owens *et al.*, 2016). The main reason is that the increasing of molecular weight of the chelating agent strengthen the viscosity of the sol system, leading to a decrease in the rate of sol-gel polymerization reaction and the diffusion of the solvent. In the meantime, the changes in solvent concentration of the sol system also have a significant impact on the pore structure of the product. When the solvent concentration is low, the pores in the porous material tend to exist in isolation, with the increase of solvent concentration, a large number of interconnected continuous pore channels are

formed in the material, resulting in a high porosity.

Table 4-1 Gel formula for the Sol-Gel method and calcination procedure

	Sample No.	n(NA): n(M ⁿ⁺)	n(CA): n(M ⁿ⁺)	n(EG): n(CA)	Calcine Temp.(°C)	Heating Ramp Rate (°C/min)	Dwelling Time(h)
Different Calcine Temperature Figure 4-2, 4-3	1a	20	1	1	500	2	10
	1b	20	1	1	530	2	10
	1c	20	1	1	540	2	10
	1d	20	1	1	550	2	10
	1e	20	1	1	560	2	10
	1f	20	1	1	570	2	10
	1g	20	1	1	600	2	10
Different Heating Ramp Rate Figure 4-4	1d	20	1	1	550	2	10
	2a	20	1	1	550	4	10
	2b	20	1	1	550	6	10
Different ratio of Nitric Acid to metal cation Figure 4-5	3a	10	1	1	550	2	10
	3b	15	1	1	550	2	10
	1d	20	1	1	550	2	10
Different ratio of Citric Acid to metal cation Figure 4-6	4a	20	0.5	1	550	2	10
	1d	20	1	1	550	2	10
	4b	20	2	1	550	2	10
	4c	20	3	1	550	2	10
Different ratio of Ethylene Glycol to metal cation Figure 4-7	5a	20	1	0	550	2	10
	1d	20	1	1	550	2	10
	5b	20	1	2	550	2	10

In order to investigate the impact of the gel formula and the calcination conditions on the composition of the products, different control experiments were designed, where n(NA), n(CA), n(EG) and n(Mⁿ⁺) in Table 4-1 represent the mole number of Nitric Acid, Citric Acid and Ethylene Glycol and the sum of

metal cations (i.e. Bi^{3+} and Cu^{2+}), the calcination temperature and heating ramp rate were the controlled variables. The gel formula and calcination procedure of a series of samples that prepared by the Sol-Gel method are listed in Table 4-1.

4.2.2.1 The effect of calcination temperature on the composition of the Sol-Gel product

The effect of calcination temperature on the composition of the product was investigated at the earliest stage. In order to narrow the calcination temperature within the range of 500°C - 600°C , the dried gel were calcined at 500°C , 530°C , 570°C and 600°C separately (corresponding to samples 1a, 1b, 1f and 1g in Table 4-1). The XRD patterns of the calcined samples are shown in Figure 4-2.

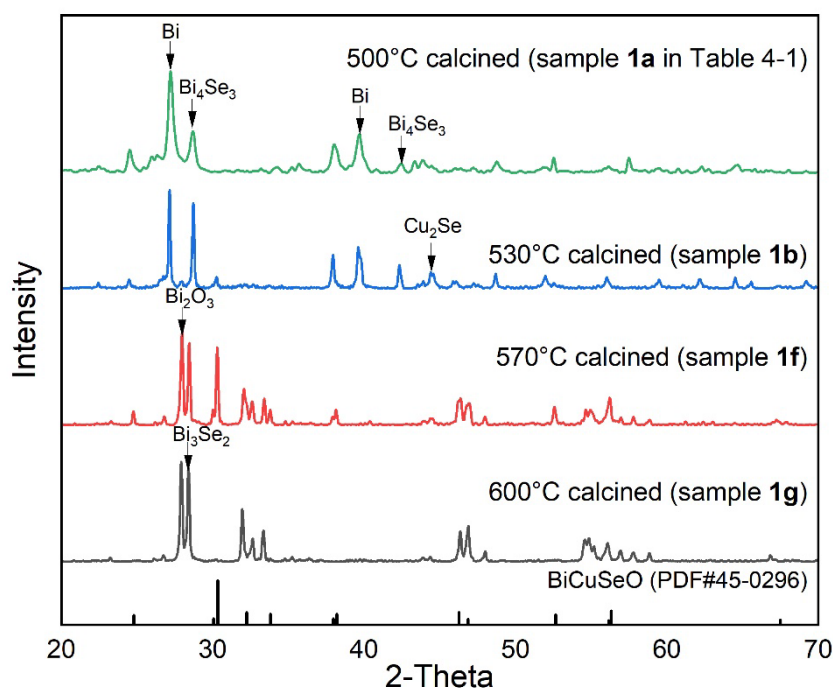


Figure 4-2 XRD patterns of the gels which were calcined at 500°C , 530°C , 570°C and 600°C , the BiCuSeO phase only generated at the gel sample which calcined at around 570°C

It can be seen in Figure 4-2 that the peaks of the target phase BiCuSeO (PDF #45-0296) are shown on the curve of sample 1b and 1f at a 2θ of 30.5 , but no peak occurs at the same position on the other two curves. In addition, the XRD pattern show that the calcined samples are consist of more than one phases.

For the calcined samples 1a and 1b, the secondary phases are mainly Bi and Bi_4Se_3 (corresponding to peaks at $2\theta=27.1$ and $2\theta=28.7$, respectively). While a small peak of Cu_2Se can be seen at $2\theta=44.4$, and its intensity is about 5%-20% of the highest peak. The overall pattern of sample 1a showed more and lower peaks, indicating that the calcination product is more unstable under 500°C . In terms of the samples 1f and 1g, the calcination products consist of Bi_2O_3 and Bi_3Se_2 (corresponding to peaks at $2\theta=28$ and $2\theta=28.7$, respectively). On the contrary, the Cu_2Se peak was unseeable on these curves. The results of the above four samples reveal that the target phase BiCuSeO occurs in samples 1b and 1f, while the intensity of characteristic peak of BiCuSeO phase is significantly larger in sample 1f than 1b, thus it can be inferred that BiCuSeO phase could form under a temperature range of 530°C - 570°C .

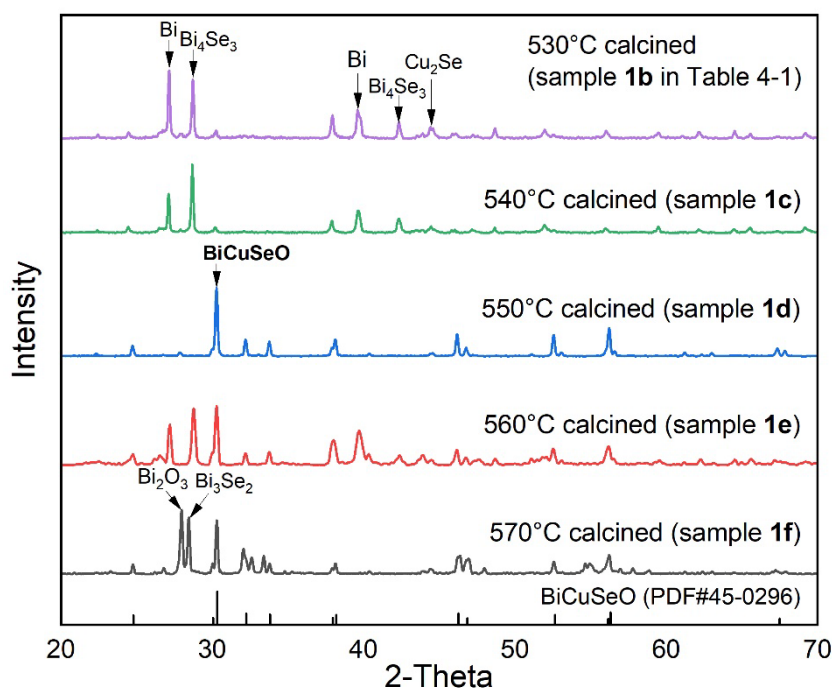


Figure 4-3 XRD patterns of the gels calcined under 530°C - 570°C , a relatively pure BiCuSeO phase was obtained from the gel which calcined under 550°C (i.e. sample 1d)

In the subsequent experiments, 540°C , 550°C and 560°C (corresponding to samples 1c, 1d and 1e) were chosen as the calcination temperature and the XRD pattern of the products were plotted in Figure 4-3. The characteristic peaks

at $2\theta=30.2$ of BiCuSeO phase (JCPD No. 45-0296) can be seen in these curves, among which the characteristic peaks of BiCuSeO phase for samples 1b and 1c are very small, but those peaks on the other three pattern are much higher. Further analysis of the composition of these calcination products shows that samples 1b and 1c are consist of Bi, Bi₄Se₃ and Cu₂Se, corresponding to the characteristic peaks at $2\theta=27.1$, 28.7 and 44.4 , with a faint BiCuSeO peak at $2\theta=30.2$. For samples 1b and 1c, a comparison between the intensity of peaks of BiCuSeO and secondary phases Bi and Bi₄Se₃ reveals that BiCuSeO was barely formed at a temperature below 540°C . The main difference between these two samples is the intensity of Bi and Bi₄Se₃ peaks, a higher intensity of Bi peak and lower intensity of Bi₄Se₃ peak could be obtained at lower temperatures, which can be verified by comparing the intensity of the characteristic peaks at $2\theta=27.1$ and $2\theta=28.7$ in Figure 4-3. In respect of the characteristic peak of BiCuSeO at $2\theta=30.2$, it is the highest among all the peaks in patterns of sample 1d, 1e and 1f, while the secondary phases include Bi (or Bi₂O₃), Bi₄Se₃, and Bi₃Se₂. It is worth noting that the secondary phases are Bi and Bi₄Se₃ for those samples which calcined at a temperature below 560°C . Whereas Bi₂O₃ and Bi₃Se₂ were formed as the secondary phase instead of Bi and Bi₄Se₃ on pattern of sample 1f, and similar results can be seen in Figure 4-3, The characteristic peaks of Bi₂O₃ and Bi₃Se₂ at $2\theta=28.7$ and $2\theta=28$ also appeared in the XRD pattern of the sample 1g. It can be deduced that some solid-state reactions occurred within the sample when the calcination temperature was higher than 560°C , result in the change of secondary phase. It is demonstrated that in Bi-Se binary system (Okamoto *et al.*, 1994), the composition of Bi_xSe_y binary compound changes slightly with the temperature and percentage of Se. Hence there is a possibility that Bi₄Se₃ phase would transform into Bi₃Se₂ phase at higher calcination temperature because the latter is more stable, Hasanova et al. has also proved that the standard molar entropy of Bi₃Se₂ is much less than that of Bi₄Se₃ (Hasanova *et al.*, 2021). Besides, the Bi₂O₃ phase might be generated from the oxidation of Bi at high

temperatures.

Among all the samples discussed above, for the sample calcined at 550°C, the amount of peaks of secondary phases is the least, and the intensity of peaks of secondary phases are much smaller than that of BiCuSeO peak. This indicates that the BiCuSeO phase is most likely to be stable at 550°C. Meanwhile, the characteristic peak of Cu₂Se can be observed on the patterns of the other samples except the sample 1d, which also indicates that BiCuSeO phase might be unstable to exist at these temperatures and partially decomposed into Bi-Se and Cu-Se binary compounds. Based on the results, the preparation process of single-phase BiCuSeO through Sol-Gel method will be further investigate at a calcination temperature of 550°C.

4.2.2.2 The effect of heating ramp rate on the composition

Figure 4-4 shows the XRD patterns of the samples calcined under a same temperature and dwelling time, and heating ramp rates of 6°C/min, 4°C/min and 2°C/min, corresponding to samples 2a, 2b and 1d in Table 4-1, respectively.

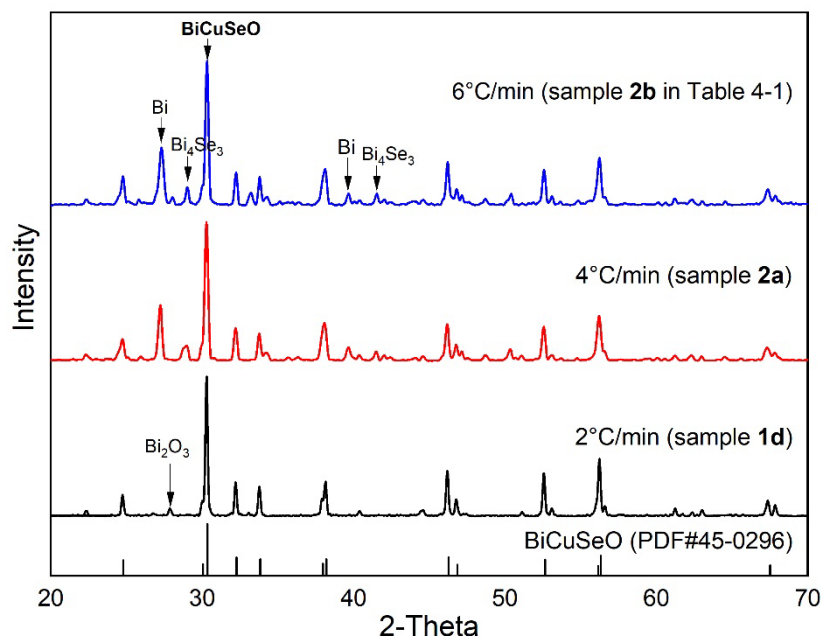


Figure 4-4 XRD patterns of the Sol-Gel method BiCuSeO samples calcined under heating ramp rates of 6°C/min, 4°C/min and 2°C/min, BiCuSeO phase tend to be generated at lower heating ramp rate

It can be seen that the characteristic peaks of BiCuSeO phase appear in the XRD pattern of all three samples. For samples 2a and 2b, the characteristic peak of Bi phase can also be observed at $2\theta=27.1$ and its intensity is about 1/3 of the highest peak. Moreover, two small peaks are observed at $2\theta=28.7$ and $2\theta=33$ in the sample 2b, and these two peaks were considered belong to Bi_2O_3 . The difference between XRD patterns of sample 2a and 2b is small, which suggests that the composition of the calcination product does not change significantly during the decrease of the heating ramp rate from $6^\circ\text{C}/\text{min}$ to $4^\circ\text{C}/\text{min}$.

The formation of the secondary phases Bi and Bi_2O_3 may be due to the fact that the organic component in the gel starts to decompose at about 200°C during the calcination process, while the formation temperature of the BiCuSeO phase is higher than 400°C . Under the higher heating rate, the temperature in the tube furnace rises rapidly, and the time interval for the furnace temperature to rise from 200°C to 400°C is not sufficient so that the decomposition of organic component could not be carried out completely. While the BiCuSeO phase was formed at a temperature above 400°C , a certain amount of organic component would decompose in the meantime. The gas-phase products of decomposition might have an effect on the environment inside the furnace during calcination and therefore affect the stability BiCuSeO phase, which eventually lead to the formation of secondary phases.

In terms of sample 1d, a very small peak of Bi was seen at $2\theta=27.1$ in addition to the characteristic peaks of the target phase BiCuSeO, thus it is believed that when the heating ramp rate is decreased to $2^\circ\text{C}/\text{min}$, the generating of secondary phase was inhibited. Hence, $2^\circ\text{C}/\text{min}$ was considered to be the most appropriate heating ramp rate.

4.2.2.3 The effect Nitric Acid proportion the gelation process

There are two roles that Nitric Acid plays in this Sol-Gel process, one is to dissolve Se powder, which is insoluble in water, following equation 4-1.



Equation 4-1

In addition, sufficient Nitric Acid in the solution provides a suitable environment for gelation. An excess of Nitric Acid provides a large amount of H^+ and maintains the pH of the solution, the acidic environment itself could promote the hydrolysis of citric acid and keeps the reaction moving forward, thus facilitating the formation of the gel. It is worth mention that the SeO_3^{2-} anion would combine with the Bi^{3+} cation in the solution to form an insoluble white precipitate $\text{Bi}_2(\text{SeO}_3)_3$. And it was observed that the appearance of this precipitation could be suppressed when the Nitric Acid content in the solution exceeded a certain level. Since the solution was kept heating during the gelation process, some of the HNO_3 molecules in the solution would be consumed due to volatilization or decomposition. Hence, sufficient amount of Nitric Acid is necessary for the preparation of BiCuSeO by the sol-gel method.

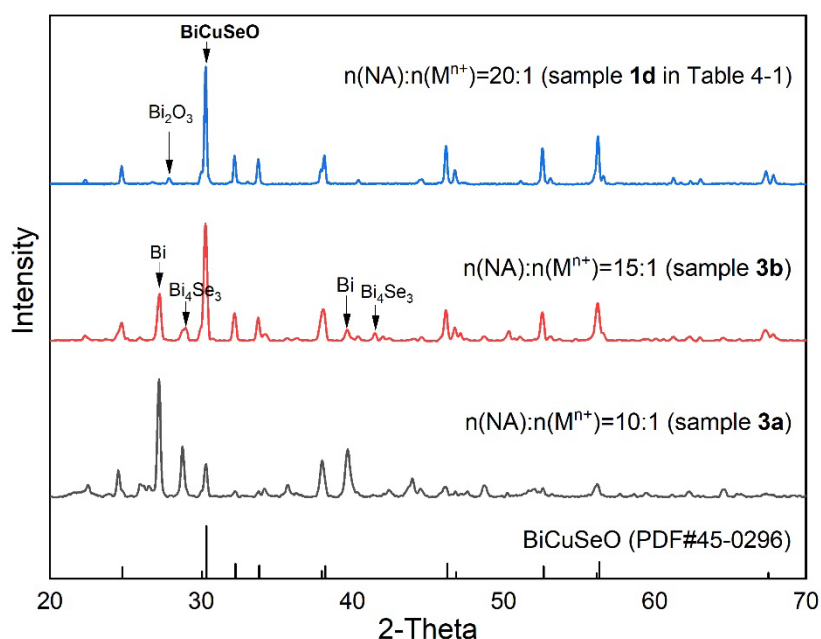


Figure 4-5 XRD patterns of calcined gel samples, with different molar ratio of $n(\text{NA}):n(\text{M}^{n+})=10:1$, $15:1$ and $20:1$ in their gel formula, the highest proportion of BiCuSeO phase was observed on sample with $n(\text{NA}):n(\text{M}^{n+})=20:1$

Figure 4-5 shows the XRD patterns of the calcined samples with different molar ratio of Nitric Acid to metal cations M^{n+} , corresponding to samples 3a, 3b and

1d in Table 4-1. The characteristic peak of BiCuSeO can be clearly observed on all of the spectrums, and the intensity of the peaks at $2\theta=30.2$ become larger with the increase of $n(\text{NA}):n(\text{M}^{n+})$. In the meantime, the intensity of the peaks $2\theta=27.1$ and $2\theta=28.7$ (corresponding to secondary phases Bi and Bi_4Se_3 , respectively) has dramatically decreased. When $n(\text{NA}):n(\text{M}^{n+})=20:1$, the intensity of secondary phases in sample 3a were less than 3% of the intensity of BiCuSeO phase. In contrast, the intensity of Bi and Bi_4Se_3 phases was even higher than that of the target phase BiCuSeO for the sample with $n(\text{NA}):n(\text{M}^{n+})=10:1$. As discussed above, this may be due to the fact that the concentration of Nitric Acid in the solution during gel formation is not high enough, so the generation of $\text{Bi}_2(\text{SeO}_3)_3$ hasn't been completely inhibited, which result in the decomposition of $\text{Bi}_2(\text{SeO}_3)_3$ during the calcination procedure and the formation of secondary phases Bi and Bi_4Se_3 . Besides, it is suggested that a molar ratio of $n(\text{NA}):n(\text{M}^{n+})$ higher 30:1 should be avoided, which would result in the presence of a large amount of NO_3^- anions in the dried gel and have a huge negative impact on the formation of target phase BiCuSeO during calcination. Hence, In order to obtain high purity sample with BiCuSeO phase, a molar ratio of $n(\text{NA}):n(\text{M}^{n+})$ between 15:1 and 20:1 was recommended.

4.2.2.4 The effect of Citric Acid proportion on the gelation process

It is well known that Citric Acid usually works as a chelating agent in the sol-gel method. Citric Acid traps the free metal cations in the solution and immobilizes them within the gel. It seems reasonable to speculate that high concentration of Citric Acid in the solution strengthen its ability in trapping metal cations. On the contrary, a large number of Citric Acid molecules will eventually leads to a greater volume of the gel, and therefore loosen the structure of the calcination product. In order to investigate the appropriate proportion of Citric Acid in the recipe, molar ratios of Citric Acid to total metal cations $n(\text{CA}):n(\text{M}^{n+})=0.5:1$, $1:1$, $2:1$ and $3:1$ were chosen for the gel preparation, corresponding to samples 4a, 1d, 4b and 4c, respectively.

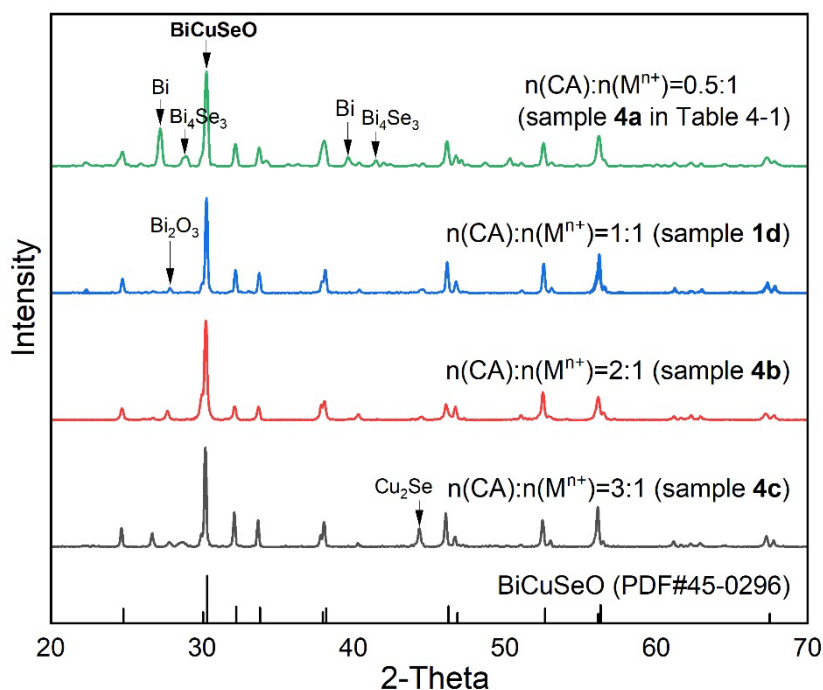


Figure 4-6 XRD patterns of the calcined samples with molar ratio of $n(\text{CA}):n(\text{M}^{n+})=0.5:1$, $1:1$, $2:1$ and $3:1$, the optimal ratio among these results is $n(\text{CA}):n(\text{M}^{n+})=1:1$

During the preparation procedure, it could be clearly observed that the gel formation efficiency increased significantly with the increase of Citric Acid content. For example, the solution was first heated to 100°C to achieve the gel, the gelation took as long as 4h for the sample with molar ratio $n(\text{CA}):n(\text{M}^{n+})=0.5:1$ and the sample is mainly in the form of powder after calcination; For sample with $n(\text{CA}):n(\text{M}^{n+})=3:1$, however, the gelation took only 1h and the morphology of its calcination products are honeycomb and lamellar structure, which also consist with the discussion above. The XRD patterns in Figure 4-6 show the difference of the calcination products of gel with different molar ratios. Four secondary phases were identified at $2\theta=27.1$, 28 , 28.7 and 44.4 except for the target phase BiCuSeO, which is believed to be Bi, Bi_2O_3 , Bi_4Se_3 and Cu_2Se , respectively.

Therefore, it can be concluded that single-phase sample with both high purity and porosity could be obtained within a molar ratio of $n(\text{CA}):n(\text{M}^{n+})$ between $1:1$ and $2:1$. Increasing or decreasing the proportion of Citric Acid will leading to an

increase in the intensity of Bi peak. It is considered that due to the increase of Citric Acid proportion, the network structure of the gel was enlarged and the metal cations were dispersed inside the gel, makes it more difficult to form a regularly arranged BiCuSeO crystalline structure.

The secondary phases Bi and Bi₄Se₃ in sample with n(CA):n(Mⁿ⁺)=0.5:1 might come from the absence of Citric Acid during the gelation process, while some free Bi³⁺ or Cu²⁺ cations interact with SeO₃²⁻ and produced Bi-Se or/and Cu-Se compound as secondary phase during the calcination. Among all the patterns in Figure 4-6, the smallest peak intensity of secondary phases are observed from sample 1d (n(CA):n(Mⁿ⁺)=1:1).

4.2.2.5 The study on proportion of Ethylene Glycol to Citric Acid

Ethylene Glycol usually plays the role of solvent in Sol-Gel method for those reagents that are difficult to dissolve in water, in this Sol-Gel process, a condensation polymerization also happens between Ethylene Glycol and Citric Acid to strengthen the connection of gel network. In addition, Zhang *et al.* has found that Ethylene Glycol functioned as a spacer to modulate the distance between metal ions, preventing metal oxides from aggregation during earlier stage of organic removal (Zhang *et al.*, 1999). In order to investigate the influence of Ethylene Glycol on the composition of calcination products, three gel samples with n(EG):n(CA) = 0, 1:1 and 2:1 (corresponding to samples 5a, 1d, 5b, respectively) was prepared and the XRD patterns of calcined samples are shown in Figure 4-7. The characteristic peaks of the target phase BiCuSeO can be observed in the Figure, as well as several small peaks of Bi, Bi₂O₃ and Bi₄Se₃ at 2 θ =27.1, 28 and 28.7.

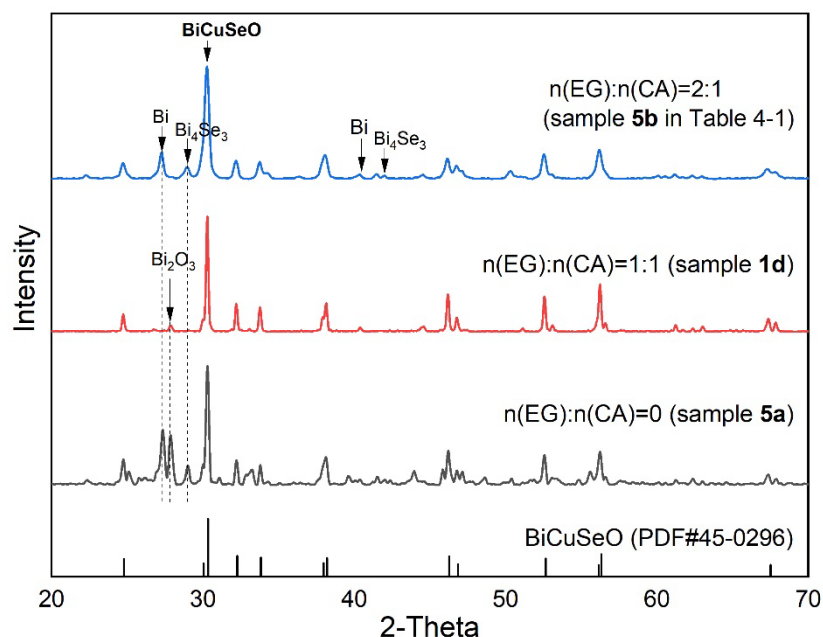


Figure 4-7 XRD patterns of the calcined samples with molar ratio of $n(\text{EG}):n(\text{CA})=0, 1:1$ and $2:1$

The generation of secondary phases Bi and Bi_4Se_3 in sample 5a may be due to the non-uniform distribution of metal cations in the solution during the gelation process. When $n(\text{EG}):n(\text{CA})=2:1$, more Citric Acid was believed to participate in the condensation polymerization and its ability of trapping metal cations was weakened, therefore led to the occurrence of secondary phases upon calcination.

The XRD pattern of sample 5b exhibits a significant difference with the other patterns. A possible explanation is that the metal cations were not well-dispersed in the solvent without the help of Ethylene Glycol, the ions trend to aggregate upon gelation hence different kinds of metal compounds would be generated, which consistent with the fact that the peak intensity of Bi, Bi_2O_3 and Bi_4Se_3 is markedly increased. In contrast, a molar ratio of $n(\text{EG}):n(\text{CA})=1:1$ is to be preferred.

4.2.2.6 Different coating method onto the bulk sample surface

Based on the results of the previous sections, the gel formula that corresponding to sample 1d was selected as the fixed parameter for the subsequent sol-gel preparation of BiCuSeO . The gel was applied to the surface

of the sample using dip coating or drop coating methods, they are named as BCSO @Dip coating and BCSO @Drop coating, respectively. Moreover, sample BCSO @50wt% Gel was added for comparison, it was obtained by mixing BiCuSeO powder that made of Flux Method and Sol-Gel Method with a weight ratio of 1:1. These samples were characterized by XRD, as shown in Figure 4-8.

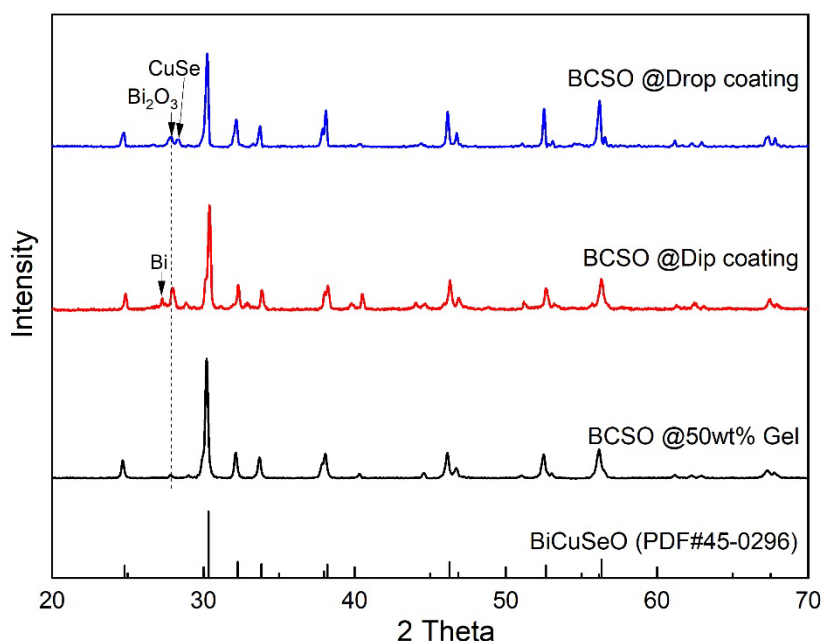
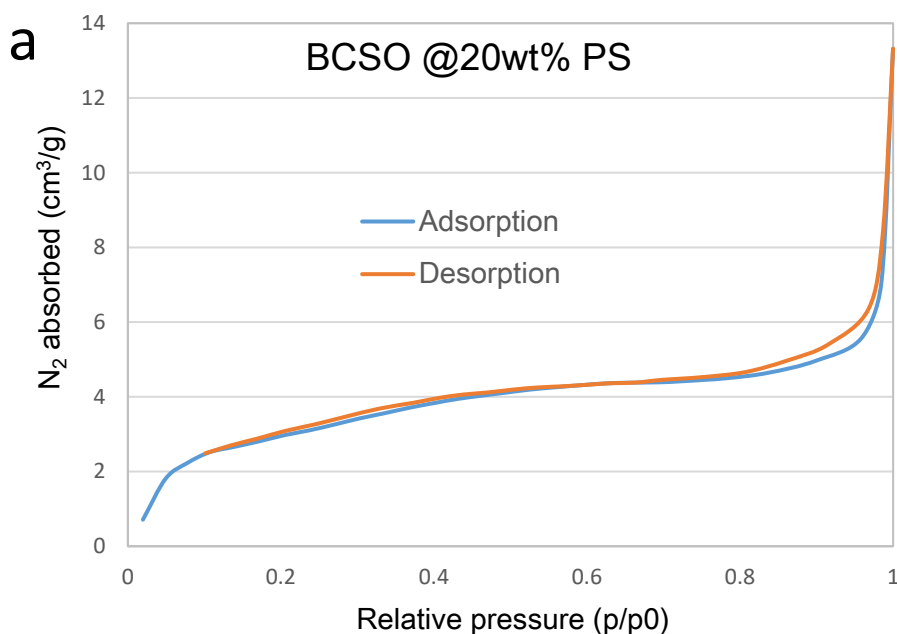


Figure 4-8 More secondary phases appear on the XRD patterns of dip-coated or drop-coated BiCuSeO samples rather than sample BCSO @50wt% Gel

Distinct BiCuSeO peaks were found on all three XRD spectrums shown in Figure 4-8, along with some low intensity peaks of secondary phases such as Bi₂O₃. Besides, Bi and CuSe peaks were observed on the XRD spectrums of dip coating and drop coating samples. The peak intensity of the secondary phases was much lower than that of the target phase BiCuSeO, suggesting that different coating methods can be used to produce porous BiCuSeO samples. However, the hybrid of two kinds of BiCuSeO that derive from Flux Method and Sol-Gel Method (sample BCSO @50wt% Gel) lead to lesser impurity. In the following chapters, the porosity and surface morphology of these three samples will be compared and a modified preparation procedure is adopted.

4.2.3 BET surface area measurement results

The BET surface area was measured using a 3P instrument. The isotherms of porous BiCuSeO samples prepared by different methods are depicted in Figure 4-9. It can be concluded that the feature of isotherms of porous BiCuSeO samples prepared by introducing pores (mixing with PS and then removing it by sintering) or by sol-gel method are nearly the same, which can be classified as type II isotherm, indicating that there are mainly macropores (pores >50 nm in diameter) in these samples. Mesoporosity (pores with diameters between 2 and 50 nm) were unlikely to have been obtained. Numerous hierarchical macropores can still be observed from SEM images (Figure 4-10). This increases the surface area of the porous BiCuSeO samples. Table 4-1 lists the BET surface area of different samples. It can be seen that the surface area of porous samples are significantly higher than that of non-porous one. For example, the surface area of sample BCSO @50wt% Gel is 13.9 times larger than that of non-porous one, while the surface area increased by 11.7, 14.1 and 17.1 times through introducing 10wt%, 15wt%, and 20wt% PS to non-porous BiCuSeO, respectively. The samples BCSO @Dip coating and BCSO @Drop coating had limited improvement on surface area and was therefore abandoned.



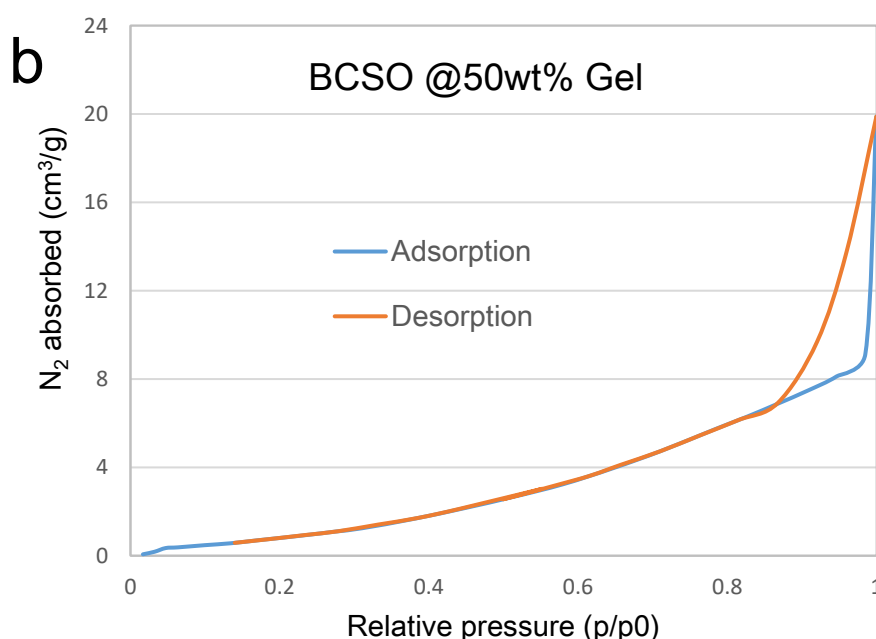


Figure 4-9 The isotherm of samples (a) BCSO @20wt% PS and (b) BCSO @50wt% Gel

Table 4-2 The BET surface area of non-porous sample BCSO @Flux and they other porous samples

Sample	BCSO @Flux	BCSO @10wt% PS	BCSO @15wt% PS	BCSO @20wt% PS
BET surface area (m^2/g)	0.515	6.536	7.778	9.348

Sample	BCSO @50wt% Gel	BCSO @Dip coating	BCSO @Drop coating
BET surface area (m^2/g)	7.602	1.602	1.549

4.2.4 The surface morphology of BiCuSeO samples

In the previous sections, the BET surface area of different porous materials was discussed. Although the results indicating that only a small amount of meso- or micro-porosity (<2 nm in diameters) was detected in the porous BiCuSeO samples, but the SEM images revealed a significant number of pores on the surface. Therefore, the distribution of the pores on the surface of porous

samples were counted and trend of the change of porosity was summarized.

4.2.4.1 Pores distribution of porous BiCuSeO under low magnification

In Figure 4-10, the surface morphology of all samples is shown with the magnification of 200 times. Among them, different sizes of pores can be clearly observed in Figure 4-10a to 4-10i, X wt% PS (X=10, 15, 20) and Y MPa (Y=0.53, 1.07, 1.60) under each image represent the amount of PS addition and cold pressing pressure, respectively. It should be noted that the additive PS and BCSO powder were sufficiently mixed during the preparation process, so we assumed that the pores on the surface of the product samples are uniformly distributed throughout the sample. Therefore in the following discussion, the pore distribution data obtained from Figure 4-10 is used to characterize the overall situation of the sample.

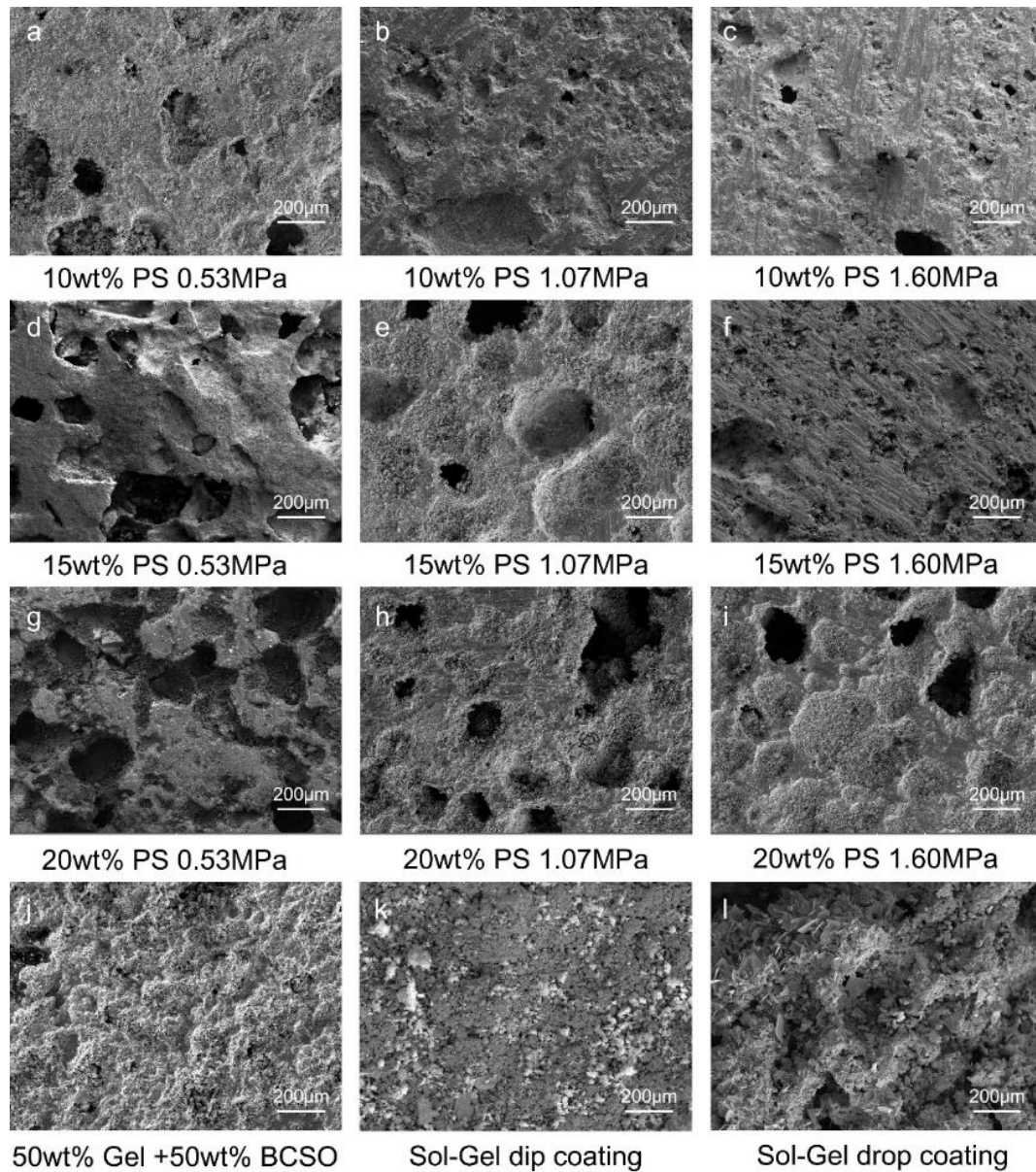


Figure 4-10 The surface morphology of porous BiCuSeO samples at 200X

The number of pores is generally increasing with the increase of PS addition and the decrease of cold pressing pressure. For example, the pores are independently and uniformly distributed on the surface of sample BCSO @10wt% PS 0.53MPa (Figure 4-10a); in Figure 4-10d, some pores started to interconnect with each other at the bottom of the image; when the PS addition is 20wt%, there are more connection between the pores, resulting in the groove-like patterns that across the entire image. In addition, with the increasing of cold pressing pressure, the pores on the sample surface is more dispersed, and the number of interconnected pores is reduced, as can be seen

from Figure 4-10g, 4-10h and 4-10i. Figures 4-10j, 4-10k, and 4-10l present porous samples prepared through different sol-gel methods. In these three images, no apparent pores can be observed, indicating that the pore size introduced by the sol-gel method is much smaller than that of adding PS, thus the pore distribution needs to be statistically analyzed using software.

The statistical analysis of pore diameter distribution was performed using Nano Measurer software. Taking Figure 4-10g as an example, the image was enlarged (Figure 4-11a) and the dimension of about 40 visible pores were marked and measured, as shown in Figure 4-11b. Statistical results showed that the pore diameters in the Figure are range from tens to hundreds of micrometers, which are close to the size of the added PS particles ($<155\mu\text{m}$).

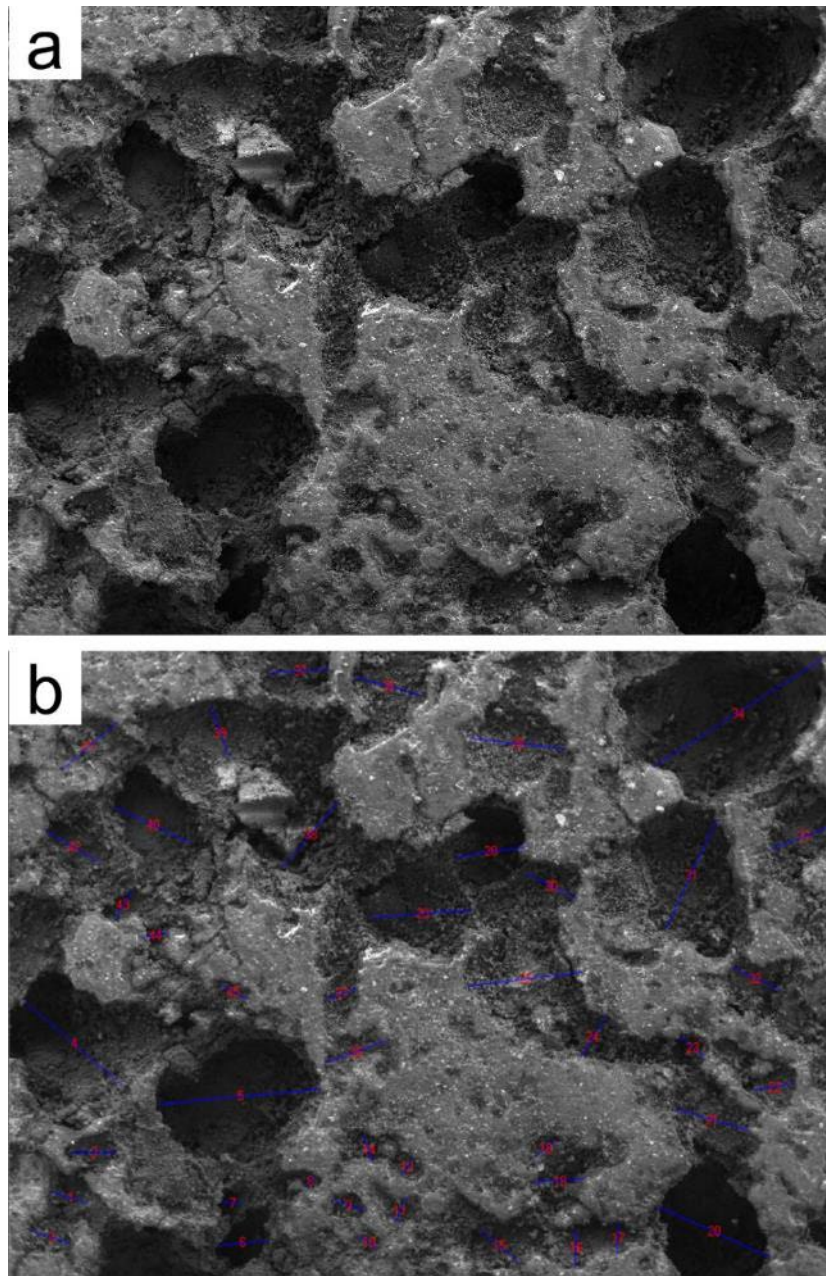
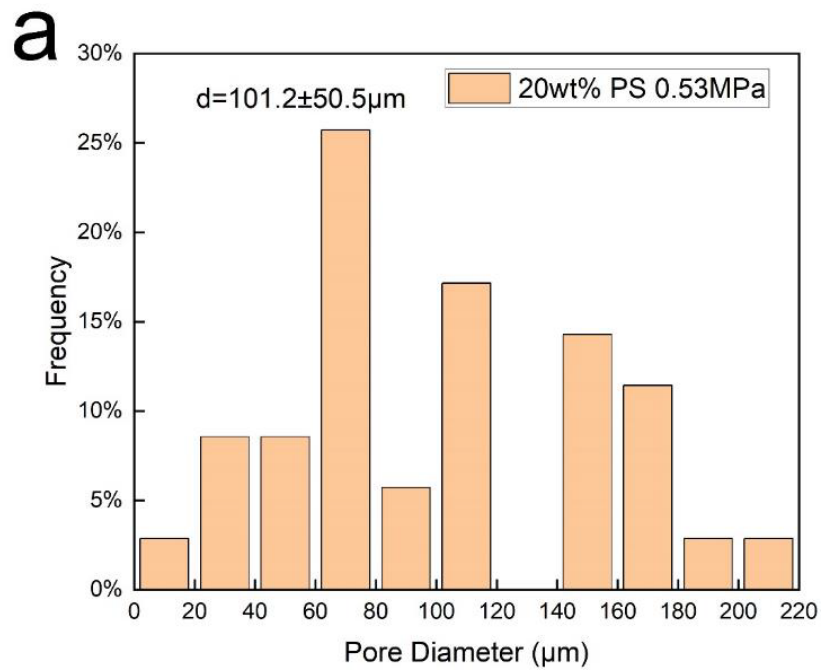
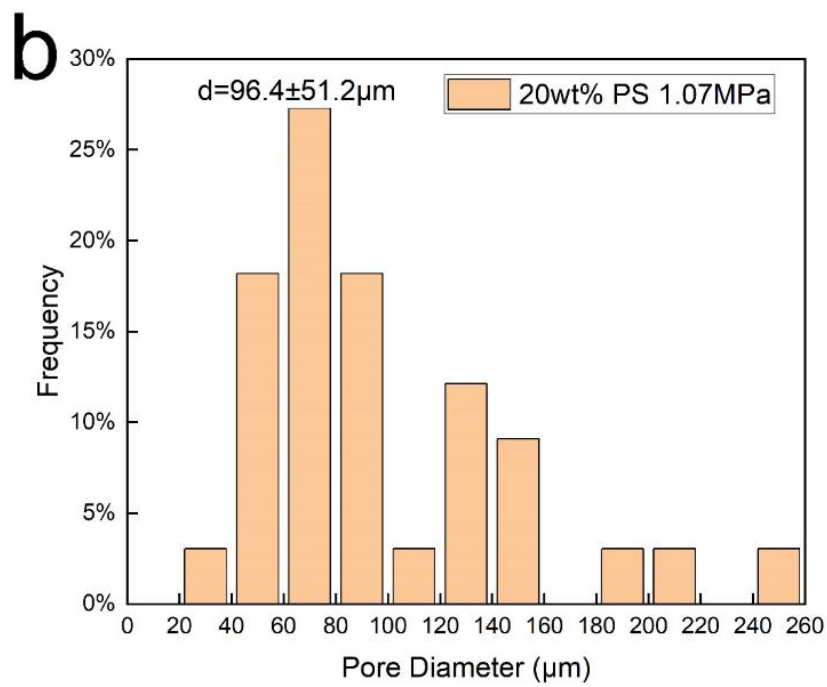


Figure 4-11 Statistic of pore diameter distribution

Three samples from Figure 4-10 were subsequently selected for pore diameter distribution statistics analysis, and the results are plotted in Figure 4-12 by Origin. Figure 4-12a, b, and c present the pore diameter distributions of Figure 4-10g, h, and i, respectively. The average pore diameters of BCSO @20wt% PS 0.53MPa, BCSO @20wt% PS 1.07MPa, and BCSO @20wt% PS 1.60MPa were 101.2 μ m, 96.4 μ m, and 95.6 μ m, respectively, indicating that the average pore diameter slightly decreased with increasing cold pressing pressure. However, the standard deviation of their surface pore diameters was not

significantly changed, which were 50.5, 51.2, and 53.1 μm , respectively.



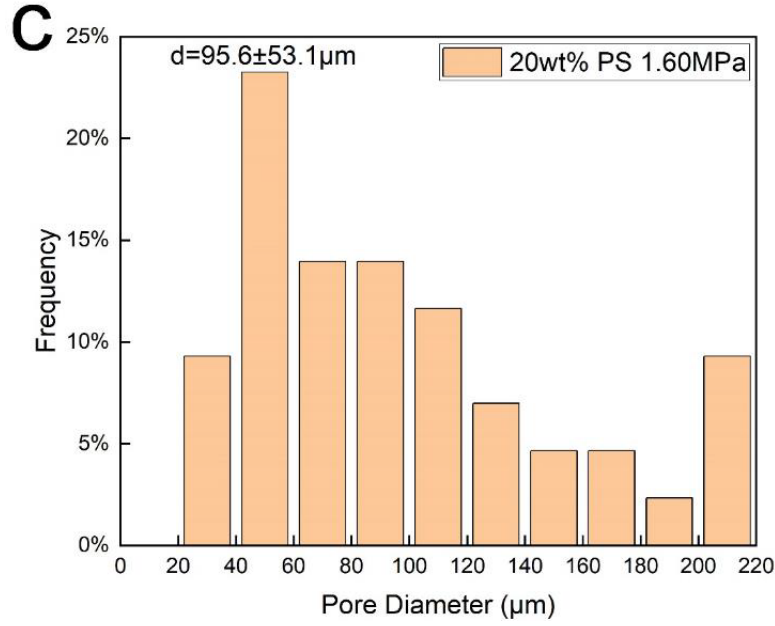


Figure 4-12 Pore diameter distributions of (a) BCSO @20wt% PS 0.53MPa, (b) BCSO @20wt% PS 1.07MPa, and (c) BCSO @20wt% PS 1.60MPa

The comparison of Figure 4-12a, b, and c shows that the proportion of pores with diameters <60μm on the surface of the sample increased from 20% (@0.53MPa) to 33% (@1.60MPa) on sample prepared under higher pressing pressure, while the proportion of pores with diameters >140μm decreased from 31% to 21%. This means that the sample is more compact and unlikely to form larger pores under high pressure.

4.2.4.2 Statistic analysis of surface porosity of porous/nano-porous BiCuSeO

In this section, the surface porosity of all samples were estimated in order to investigating the effects of different preparation conditions on surface morphology of porous BiCuSeO samples. ImageJ was used to measure the pore area in the images of Figure 4-10. It recognizes and distinguishes areas with different contrast on the SEM image to get the pore area S_{pores} , as shown in Figure 4-13b. The total area of the image S_{all} can also be obtained from the software. The surface porosity $\phi\%$ can be calculated using the following Equation 4-2.

$$\phi\% = S_{\text{pores}} / S_{\text{all}} * 100$$

Equation 4-2

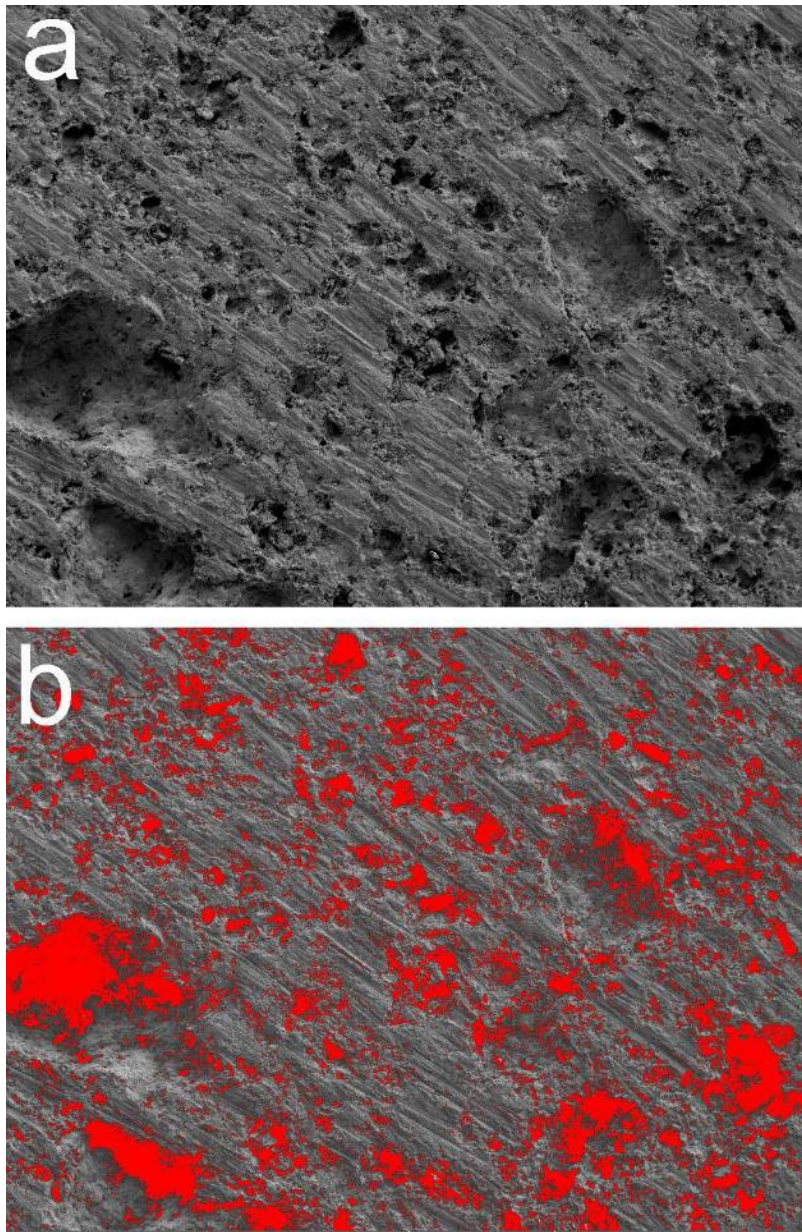


Figure 4-13 Pore area measurement using imageJ

In addition, the porosity of the samples prepared under different conditions were listed in Table 4-2. Although these statistical results are not exactly the same as the actual porosity, these measured data can be used as a reference at least for porosity.

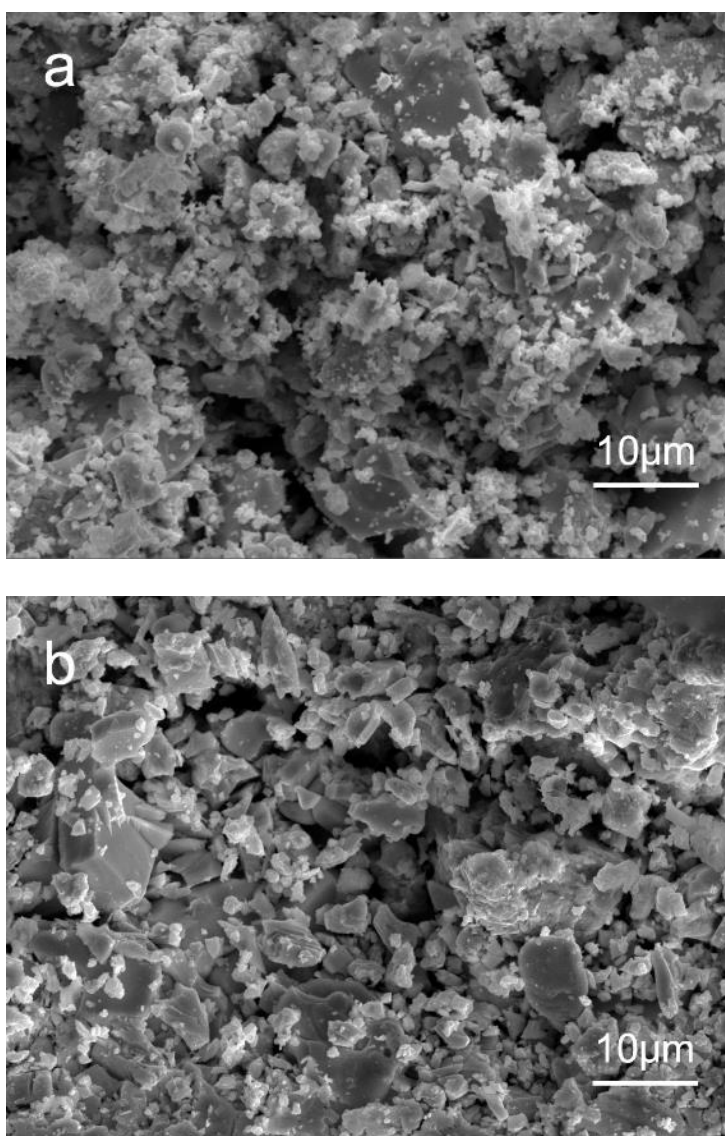
Table 4-3 Surface porosity measurement results

Substrate	Additive	Cold-pressing Pressure(MPa)	$\phi\%$
BiCuSeO	10wt% PS	0.53	20.3
BiCuSeO	10wt% PS	1.07	15.5
BiCuSeO	10wt% PS	1.60	12.1
BiCuSeO	15wt% PS	0.53	27.5
BiCuSeO	15wt% PS	1.07	22.8
BiCuSeO	15wt% PS	1.60	18.4
BiCuSeO	20wt% PS	0.53	37.3
BiCuSeO	20wt% PS	1.07	23.4
BiCuSeO	20wt% PS	1.60	20.7
BiCuSeO	50wt% BCSO Gel	1.07	18.0
BiCuSeO (Dip coating)	BCSO Gel	-	19.6
BiCuSeO (Drop coating)	BCSO Gel	-	22.5

It can be concluded from the above table that the surface porosity of the samples increases with the increase of PS addition and the decrease of cold pressing pressure. This is reasonable because PS can easily decompose into gas molecules during the sintering process and pores are remained inside the sample, therefore a larger PS content in the sample will lead to a higher porosity. Besides, lower cold pressing pressure results in a looser compact structure. This means that the gas generated by PS decomposition may dilate the pores, which also affect the overall porosity. The porosity of the dip-coated (19.6%) and drop-coated (22.5%) samples are higher than that of sample BCSO @50wt% Gel (18%), but the BET surface area measurement shows the opposite result in chapter 4.2.3. This is understandable, as the powders obtained for the BET

measurement from these two samples most likely contained non-porous bulk BiCuSeO powders. Also, the pore size in the sol-gel samples are much smaller than those of PS-added samples, lots of them was unresolvable in the SEM image but can be measured by the BET method. This can explain why the sol-gel sample has the highest BET surface area, but displayed lower porosity from the ImageJ analysis of the SEM images than the PS added samples.

4.2.4.3 SEM and EDS analysis on surface morphology



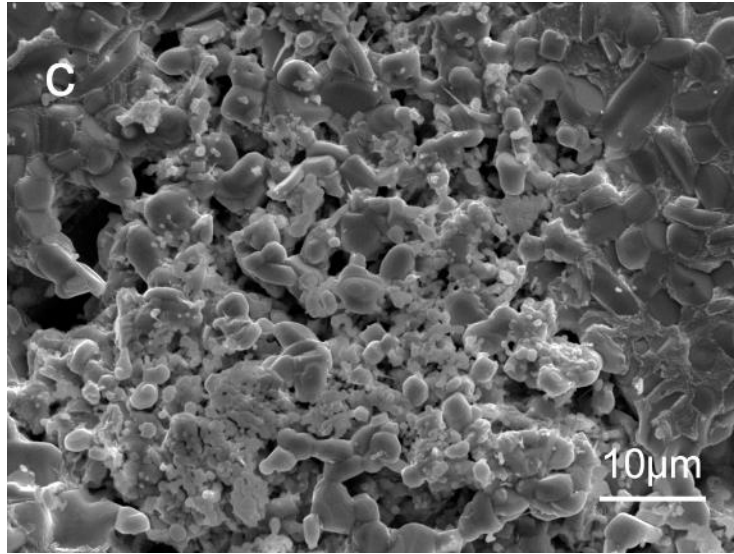
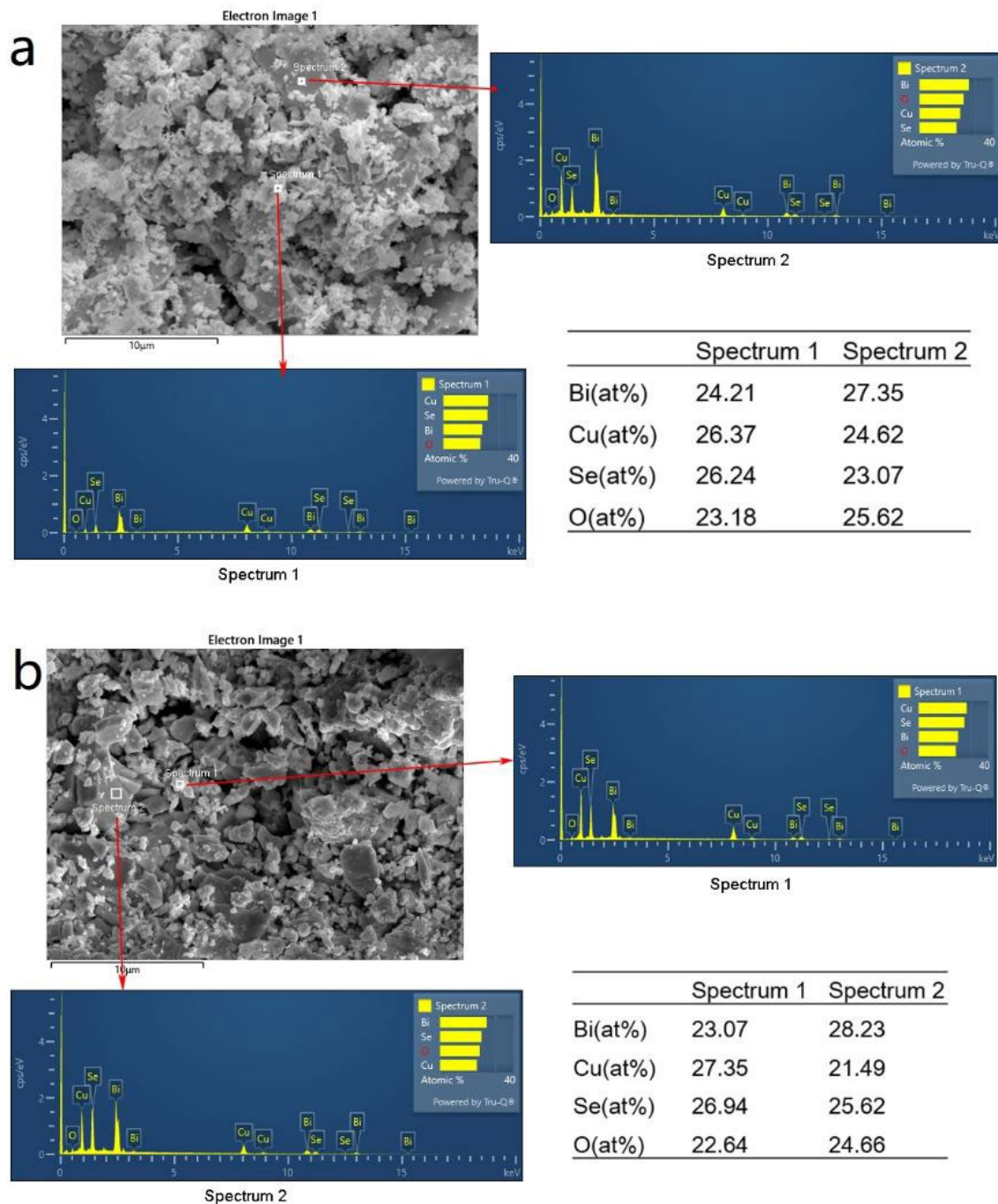


Figure 4-14 5000X SEM images for porous BiCuSeO samples pressed under pressures (a) 0.53MPa; (b) 1.07MPa; (c) 1.60MPa

In order to further investigate the surface structure of the porous samples, the sample surfaces were magnified up to 5000 times and EDS was used for component analysis. Figure 4-14 shows the SEM morphology of the surface of samples BCSO @20wt% 0.53MPa, BCSO @20wt% 1.07MPa, and BCSO @20wt% 1.60MPa, while the corresponding EDS analysis results are plotted in Figure 4-15. In Figure 4-14a, bulk phases with diameter greater than 10 μ m and small white particle phases attached to them can be observed. The EDS analysis result (Figure 4-15a) indicates that the white particles consist of four elements: Bi, Cu, Se, and O. The atom percentage of the four elements is similar, but that of Cu and Se are slightly higher than the other two elements, suggesting that the composition of those white particles are mainly BiCuSeO with a small amount of CuSe. On the contrary, higher Bi and O percentage in the bulk phase indicate the presence of Bi₂O₃ or Bi. In Figure 4-14b, a large number of irregular particles with diameter of several micron can be seen. Fewer white particles are observed compared to Figure 4-14a, but their volume has increased slightly. EDS analysis was performed on two regions with obvious contrast and the results reveal the additional CuSe except for BiCuSeO in white particle phases, while the significantly higher Bi content at the dark

zone suggests secondary phase Bi. The particle edges in Figure 4-14c are smoother and their shape are more spherical. Those particles integrated and formed a mesh-like structure, leaving behind many pores. The EDS mapping scan result confirms that the composition is primarily BiCuSeO. Thus it can be concluded that higher cold pressing pressure contribute to the fusion of the grain and slightly improve the evenly distribution of the elements.



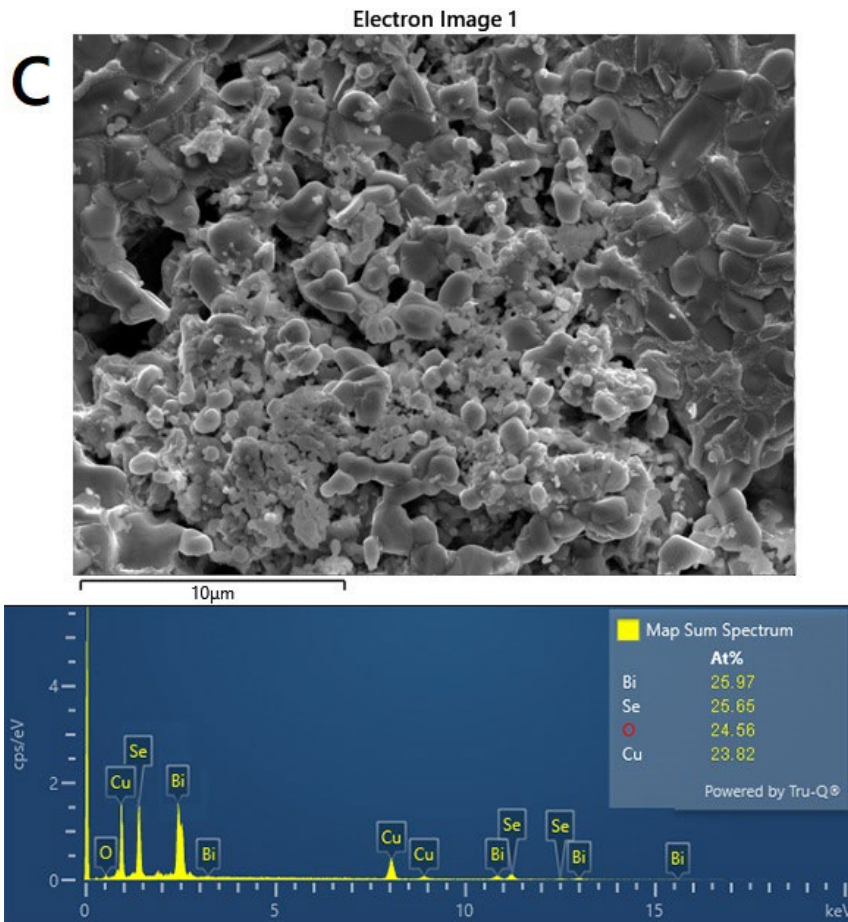


Figure 4-15 Compositional analysis of porous BiCuSeO samples surface

Figure 4-16 shows the surface structures of the samples with PS addition of (a) 10wt%, (b) 15wt%, and (c) 20wt% with the sample cold pressing pressure of 0.53MPa. As shown in Figure 4-16a, most of the microstructures are layer with different growth directions, and the thickness of each layer is about 1 μm. They stack together to form particles with a diameter of tens of microns and leave many gaps in between them. When the amount of PS addition increases to 15wt%, part of the layer structures are replaced by particle. These particles with diameter of several microns have smooth edges, they clustered together and stick to the top of the layer structures, big gaps can be observed in the image as well.

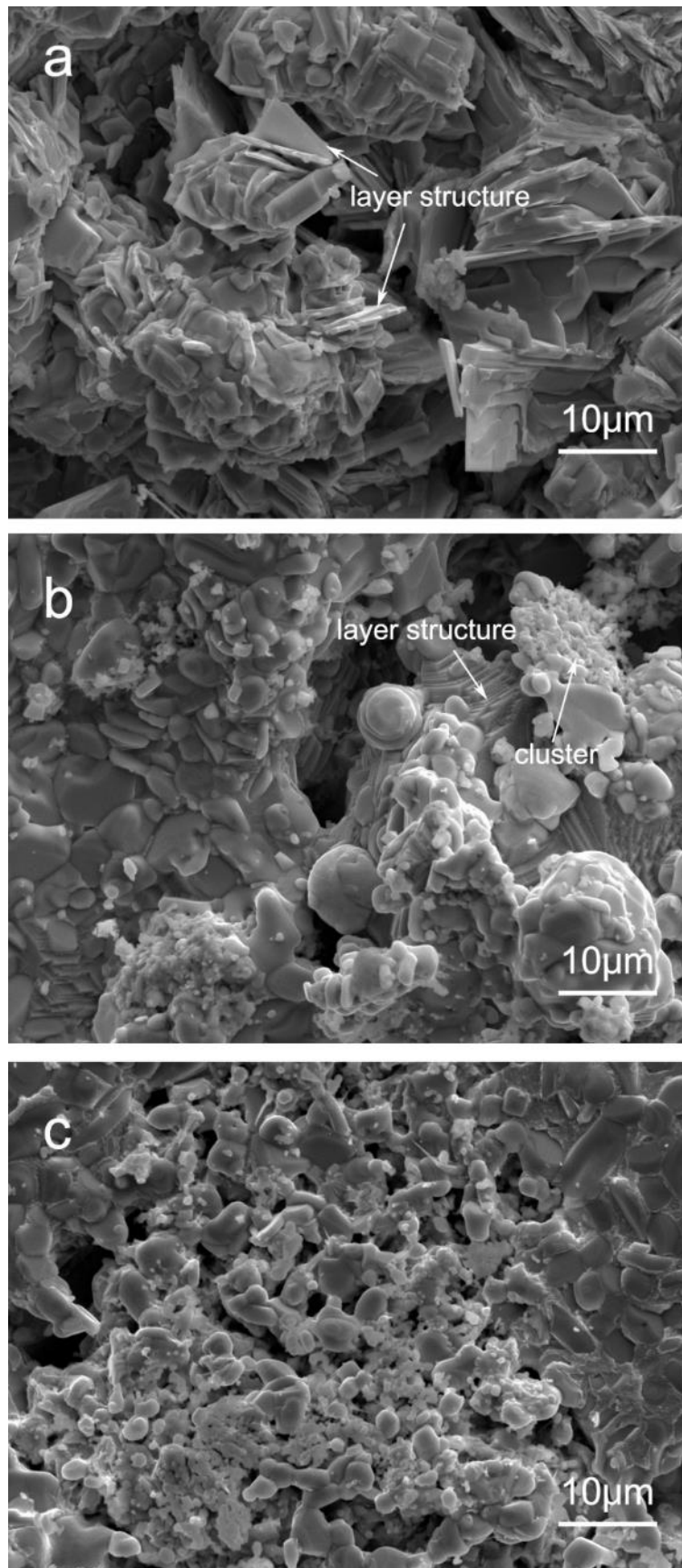


Figure 4-16 5000X SEM images for porous BiCuSeO samples with PS additions (a) 10wt%; (b) 15wt%; (c) 20wt%

For the sample with 20wt% PS addition, its surface is covered with interconnected particles, some particle even have diameters of less than 1 μ m. Most of the particles are connected by sintered necks, and lots of pores could be observed. By comparing the three images, it can be found that with the increasing amount of PS addition, the number of layer structures in the sample decreases significantly. However, a great number of particle phase generated instead of those layer structure. This indicates that the addition of PS block the connection of BiCuSeO grain and makes it difficult for them to aggregate during the sintering process, thereby hindering grain growth and resulting in the presence of many small particles in the images.

4.2.5 Band gap

To characterize the influence of sintering conditions on the width of the band gap, the Ultraviolet–visible (UV-Vis) spectroscopy was applied on BiCuSeO samples sintered at different temperatures and SPSed sample, as shown in Figure 4-17, and the band gap width could be estimated subsequently. It can be seen from the Figure that the band gaps of the four samples are close to 0.8 eV, which is consistent with the reported value of BiCuSeO (Zhao *et al.*, 2011; Zhao *et al.*, 2014). The band gap of SPSed sample is the highest among them, at approximately 0.82 eV. Moreover, it gradually decrease with the sintering temperature, the band gap widths are 0.81, 0.8, and 0.79 eV for BiCuSeO sintered at 650°C, 600°C, and 550°C, respectively. The band gap represents a minimum energy that is required to activate an electron so that it can participate in conduction, which significantly affects the electrical transport performance of the material. A lower band gap width means that electrons will be activated more easily and generate holes in the valence band, led to an increase in electrical conductivity.

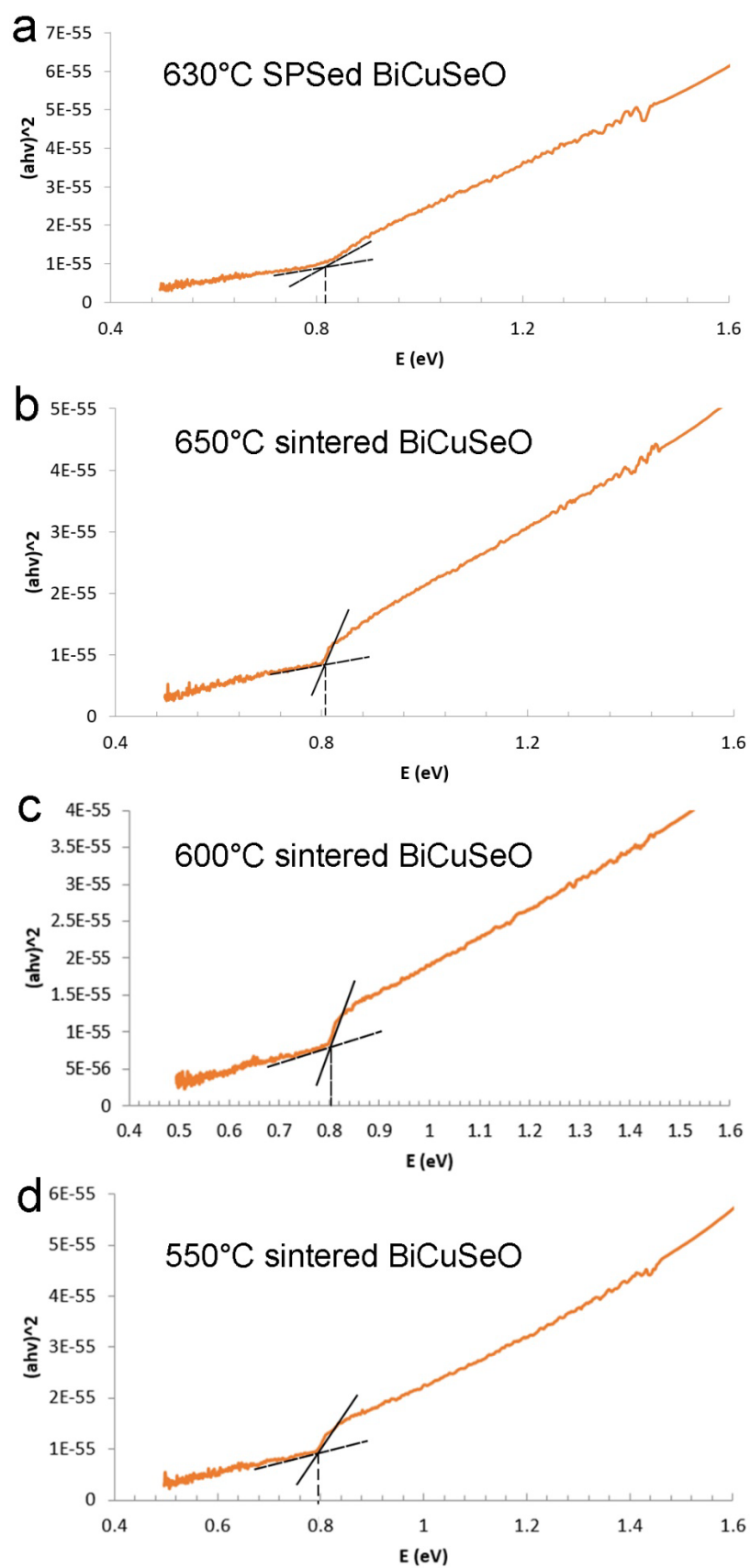


Figure 4-17 Band gap measurement result of BiCuSeO under different sintering conditions

4.3 Conclusion

Porous BiCuSeO sample is successfully prepared by using Sol-Gel method and the adding of PS fine powders. High purity of the target phase of BiCuSeO was confirmed by XRD analysis. The Sol-Gel method provides a possibility to introduce nano-porous coating to the surface of a non-porous sample, while the addition of PS generate pores within the entire sample. Porous samples with relatively high surface porosity and BET surface area can be prepared through coating methods.

5 Simulation and experimental verification of temperature distribution of thermoelectric samples under reaction conditions

5.1 Introduction

The temperature difference between the hot side and cold side of the TE sample in the reaction chamber has a direct impact on its catalytic activity. In addition, the hot surface of TE sample could get closer to the heat source by increasing the sample thickness, thereby effectively increases the temperature difference across the sample. In order to explore the temperature distribution of thermoelectric samples with different thickness, a series of computational simulation on the temperature distribution of TE samples in the reaction chamber are carried out in this chapter using finite element simulation software Ansys. On the one hand, the simulated temperature distribution data is compared with the experimental data to verify the simulation. On the other hand, the simulation was then used to predict the temperature distribution of TE samples with different thicknesses. The overall research process of this chapter is divided into three steps, as shown in Figure 5-1.

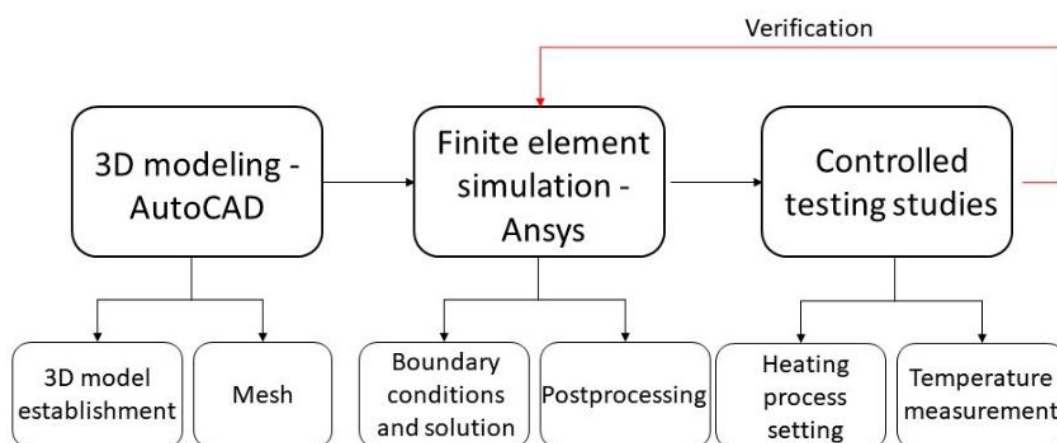


Figure 5-1 Diagram of the analysis process

5.2 Result and discussion

5.2.1 3D modelling and heating process

5.2.1.1 3D modeling of the reaction chamber and the hot plate

The reaction chamber used in this project is self-designed and its structure is shown in Figure 3-2b. The reaction chamber consists of base, cap, heat insulation O-ring and sample holder. A water tank with a cooling water circulation system is located inside the cap. A hot plate is placed underneath the reaction chamber, which could reach to temperatures as high as 800°C. The 3D model of the reaction chamber is established by AutoCAD and imported into the Ansys workbench, as shown in Figure 5-2. The main body of the reaction chamber is consisted of 316 stainless steel, while the sample holder is made of Macor and the o-ring is made of a polymer materials that can withstand temperatures of 400°C.

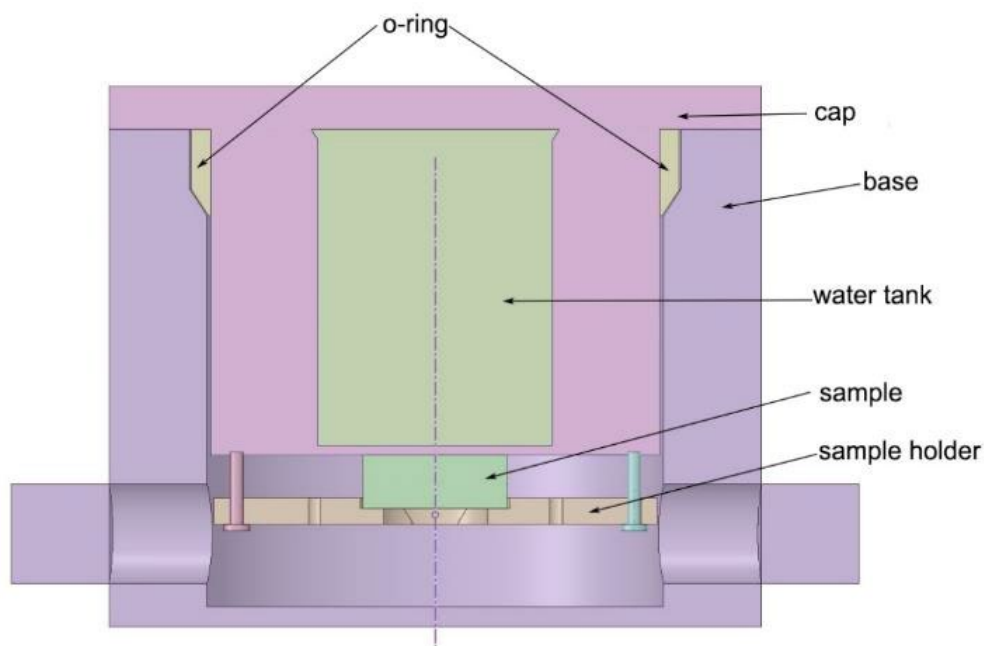


Figure 5-2 3D model of reaction chamber

5.2.1.2 Heating process

During the experiment, the maximum heating temperature was fixed at 760°C to maintain the stability and durability of the hot plate. A same heating process as the chemical reaction experiment was used in the simulation to ensure the

simulation results are closer to the reality. The heating process start at room temperature, the temperature will raise to a preset temperature at a rate of 5°C/min and maintained for 30 minutes before being raised to the next setting temperature until it reaches the highest temperature of 760°C. The heating ramp rate is fixed at 5°C/min and the dwelling time for each temperature is 30 minutes (as illustrated in Figure 5-3). The correlation between the simulation time and related temperature could be seen in Table 5-1.

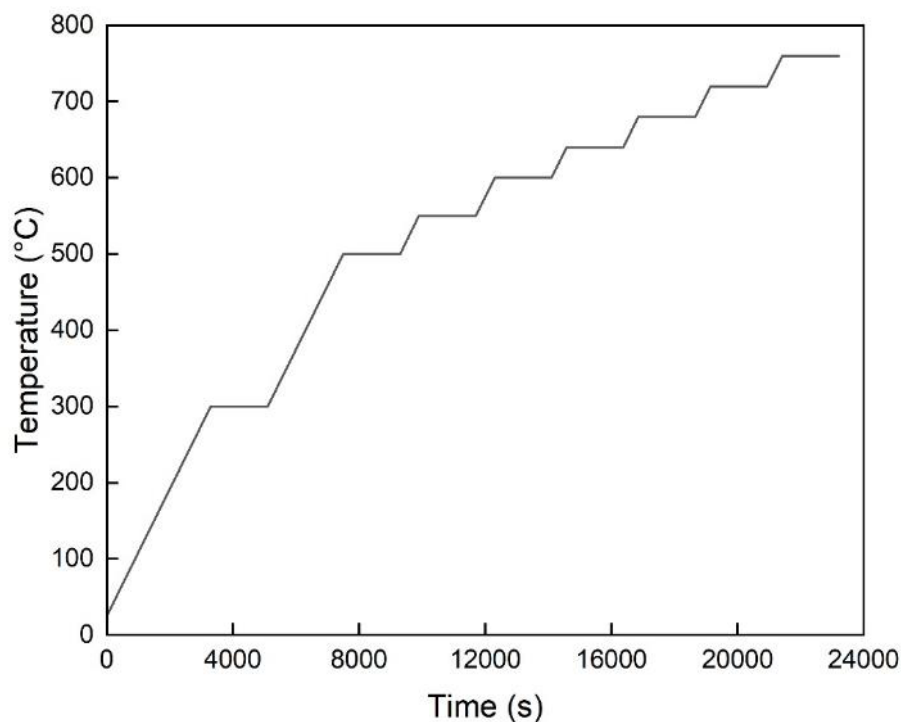


Figure 5-3 The Time-Temperature curve during the heating process for finite element simulation

Table 5-1 The simulation time nodes and their correlation temperature

time/s	0	3300	5100	7500	9300	9900	11700	12300	14100
temperature/°C	25	300	300	500	500	550	550	600	600
time/s		14580	16380	16860	18660	19140	20940	21420	23220
temperature/°C		640	640	680	680	720	720	760	760

5.2.2 The establishment of a simplified 3D model and implement of finite element simulation

5.2.2.1 The simplification of the 3D model

The geometric model serves as the foundation of the finite element simulation for the thermal field. In order to obtain reasonable simulation results, the model itself must not only match the structural properties of the item, but also needs to be easy realizable to have the computation efficiency.

Transient temperature simulations are employed in this chapter to indicate the change of temperatures of the reaction chamber and the TE sample inside of it during the heating process. The establishment of the model is based on the following presumptions and simplifications, with the core structure remaining unchanged:

- (1) The whole reaction chamber is considered to be a regular cylinder, as well as the water tank inside the cap of reaction chamber; the inlet and outlet channels on the side of the reaction chamber are neglected;
- (2) Small components such as the sample holder and the screws that fix the sample holder are removed from the model because they have little influence on the thermal field;
- (3) The interior space of the reaction chamber apart from the TE sample is modeled as the gas. As more than 95% of the reactant or product gas mixture is He, the mixed gas in the reaction chamber is regarded as pure He. The properties such as heat transfer coefficient of pure He are applied to the simulation when required. Moreover, the mixed gas that slowly flows through the reaction chamber is considered to be static.
- (4) The convection was also simplified during the transient temperature simulations, the convection heat transfer coefficient of the mixture gas was considered to be similar to air, which was set as $5 \text{ W}/(\text{m}^2 \cdot \text{K})$ at 25°C and linearly increased to $25 \text{ W}/(\text{m}^2 \cdot \text{K})$ at 760°C .

5.2.2.2 The establishment of the 3D model

The geometric features are generally regular and simple once the reaction

chamber model has been simplified. The simplified model of the reaction chamber and TE sample could be established using the modeling function of Ansys Workbench. The dimensions of the main part of the model are listed in Table 5-2. The simplified model of the reaction chamber and TE sample are shown in Figure 5-4.

Table 5-2 The dimensions of the main part of the model

component	Diameter/mm	Height/mm	Thickness/mm
Base (exterior)	80	60	-
Base (interior)	50	35	-
Cap (exterior)	80	80	-
Water tank	50	77	-
Sample	20	-	2,4,6,10,20

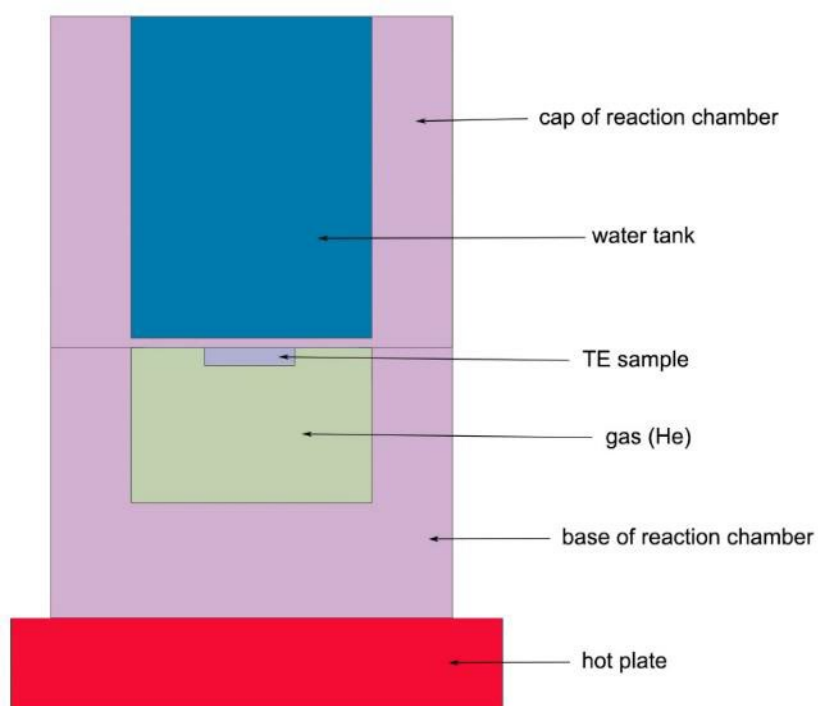


Figure 5-4 Sectional view of the simplified model of the reaction chamber with TE sample

5.2.3 Meshing

5.2.3.1 Meshing parameters

The meshing methods provided by Ansys Workbench for 3D models include: Automatic, Hex Dominant, Tetrahedrons, Sweep and Multi-Zone. Among them, Hex Dominant method generate meshes with higher quality, which improves the accuracy of simulation results. However, it also significantly increase the computing time for the simulation. The majority of the simplified model is consist of cylindrical components. Therefore, the main objects with a small volume were meshed by Hex Dominant method, while the unimportant components with a huge volume were meshed by Sweep method. The meshing parameters are shown in Table 5-3.

Table 5-3 The meshing parameters for the simplified model

components	meshing method	element size/ 10^{-6}m
TE sample	Hex Dominant	7.5
Base of reaction chamber	Sweep	100
Cap of reaction chamber	Sweep	100
Water tank	Sweep	50
hot plate	Sweep	100

A quality check for all the obtained meshes is usually carried out after meshing. The element quality is based on the ratio of the volume to the sum of the square of the edge lengths for 2D quad/tri elements, or the square root of the cube of the sum of the square of the edge lengths for 3D elements. It is a composite quality metric that ranges between 0 and 1, where 1 represents a perfectly shaped element. For example, the TE sample was meshed according to the method in Table 5-3, the obtained number for elements and nodes are 6551 and 32088, respectively. The average grid quality is 0.906. The model of TE sample after meshing is shown in Figure 5-5.

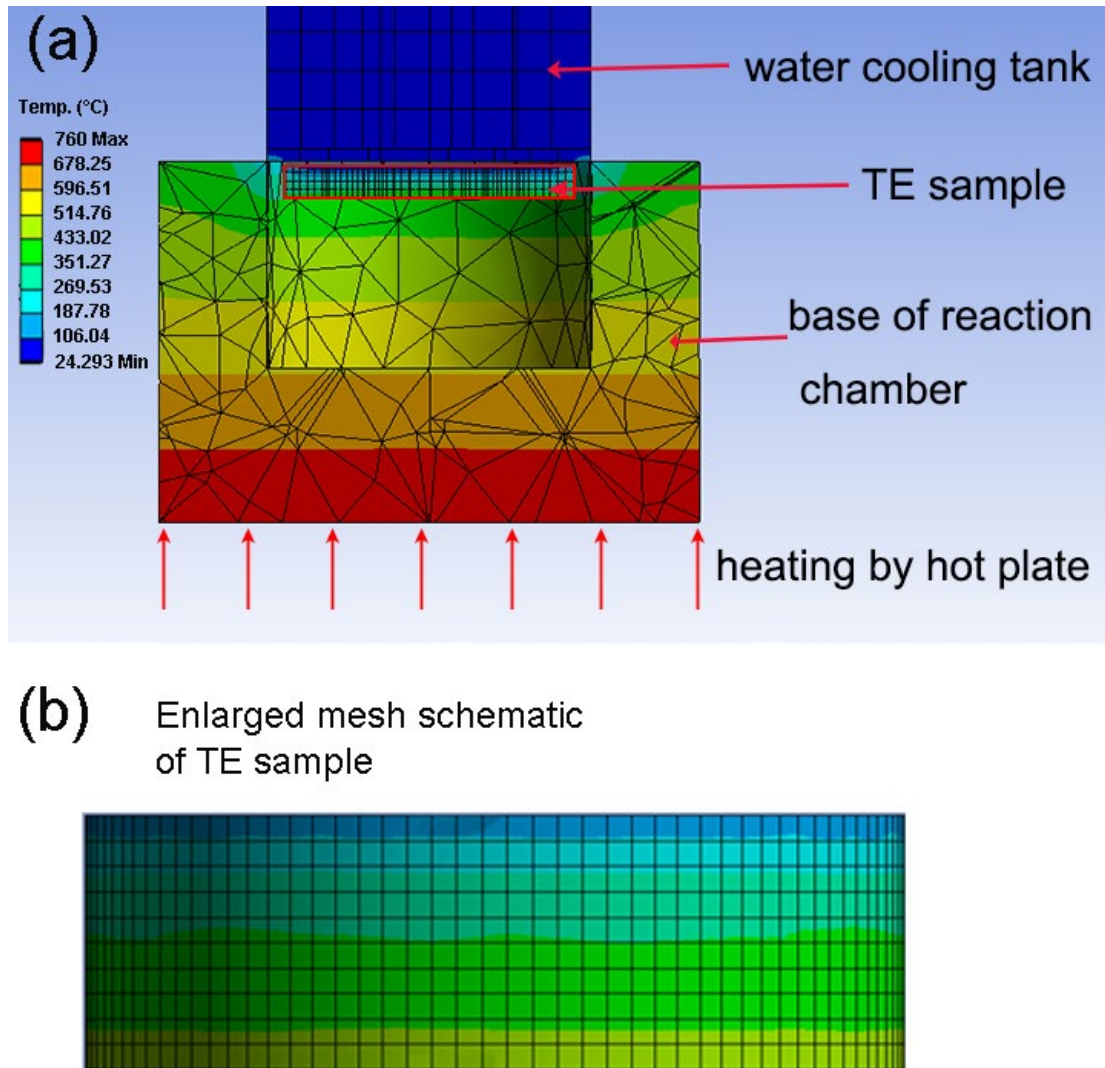


Figure 5-5 Meshing diagram of (a) The reaction rig with TE sample inside and (b) the enlarged TE sample

5.2.3.2 Mesh Independence Test

The accuracy and convergence of the simulation results in finite element analysis are directly influenced by the mesh fineness. Therefore a mesh independence test was conducted to verify the rationality of the current meshing parameters. Firstly, a 2mm TE sample was modeled, while a total amount of 4 probes were inserted at the center and edge of the hot side and cold side surfaces of the TE sample. Then the effect of mesh fineness on the simulation results is evaluated by comparing the difference between the measured temperatures of these four probes. The final temperature after dwelling at

760°C for 30 minutes was taken as the reference. The numbers of the elements in this chapter are obtained as 5032, 6068, 6551, 9407 and 10362 after meshing. Their quality check results are listed in Table 5-4. Element quality=1 corresponds to a perfectly regular element while a high value of average element quality indicates an ideal meshing method (Staten *et al.*, 2010).

Table 5-4 the quality check results under different meshing conditions, better average element quality were obtained from model 3, 4 and 5

Model number		1	2	3	4	5
element size/10 ⁻⁶ m		5	7.5	10	20	30
Element quality	min	0.423	0.228	0.309	0.150	0.152
	max	0.999	0.999	0.999	0.999	0.999
	average	0.867	0.860	0.906	0.907	0.907
	standard deviation	0.123	0.134	0.096	0.093	0.094
Node numbers		49511	38826	32088	29560	27418
Element numbers		10362	9407	6551	6068	5032

Figure 5-6 shows a schematic diagram of the location of four probes and the final temperatures of the probes under five meshing conditions. According to the simulation results, there is a relatively high temperature difference of up to 2°C between model 5 (with elements number of 5032) and the other models so model 5 is excluded. For the rest of the models, the temperature differences measured at the four probes are all smaller than 1°C. After all, Model 3 with elements number of 6551 was chosen as the meshing method for TE samples when combined with the quality check results in Table 5-4, because it has a high average quality and a moderate elements number.

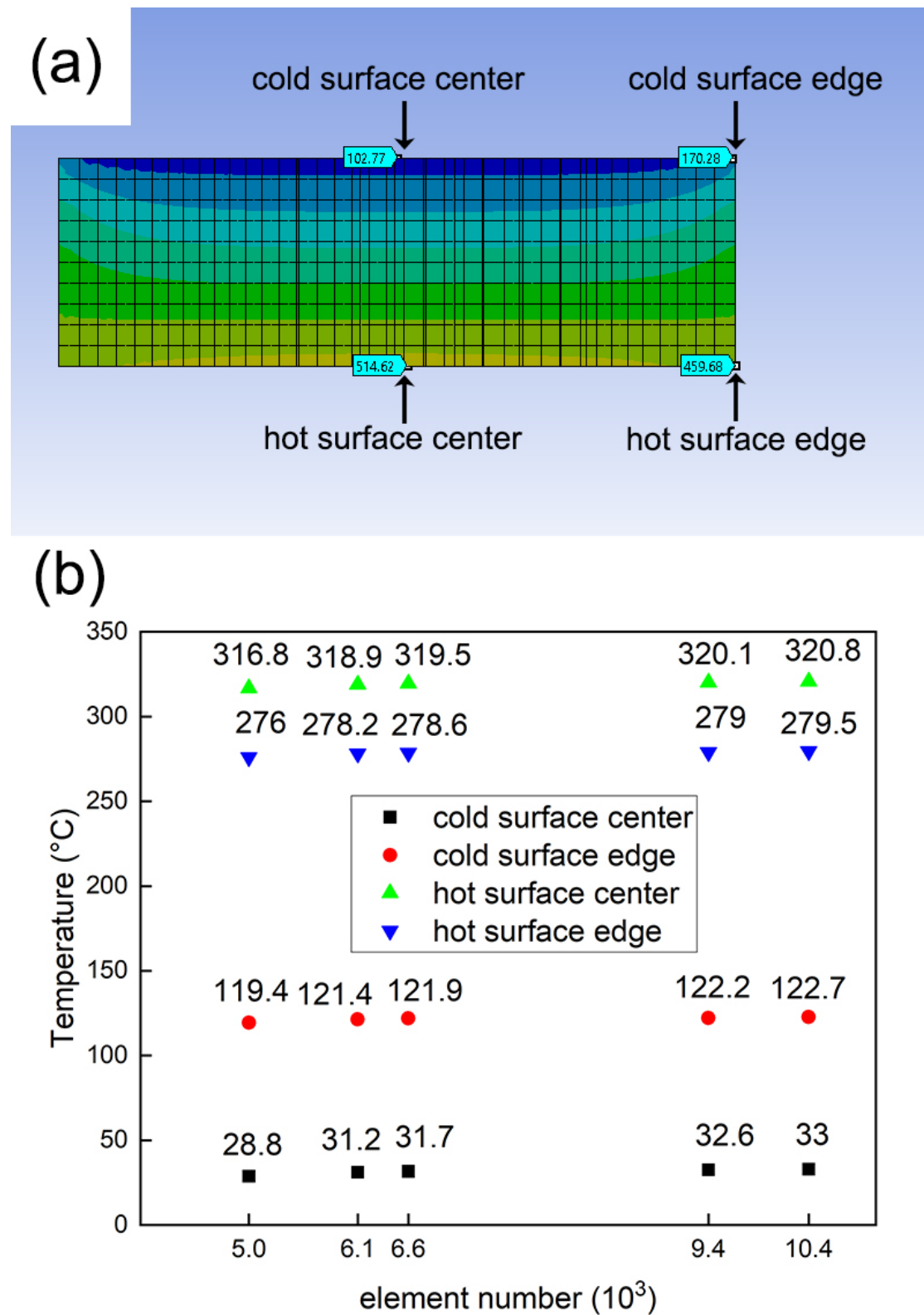


Figure 5-6 (a) Schematic diagram of the location of four probes (b) the final temperatures at these four probes changed slightly with the meshing condition

Table 5-5 Thermo-physical properties of the materials that used for the simulation

Material	Density (g·cm ⁻³)	Temperature/K	300	400	500	600	700	800	900	1000	1100
BiCuSeO	8.903	κ (W·m ⁻¹ ·K ⁻¹)	0.84	0.6	0.49	0.44	0.43	0.42	-	-	-
		Cp (J·kg ⁻¹ ·K ⁻¹)	34.03	34.73	34.98	35.21	35.43	35.65	35.83	36.01	-
Helium (Gas)	1.78*10 ⁻⁴	κ (W·m ⁻¹ ·K ⁻¹)	0.156	0.190	0.222	0.252	0.281	0.309	0.336	0.363	-
		Cp (J·kg ⁻¹ ·K ⁻¹)	5238.3								
316 Stainless Steel	7.98	κ (W·m ⁻¹ ·K ⁻¹)	13.96	15.53	17.1	18.68	20.25	21.82	23.39	24.96	26.53
		Cp (J·kg ⁻¹ ·K ⁻¹)	500.64	514.08	527.52	540.54	553.98	567.42	580.86	593.88	607.32
		Temperature/K	295	305	315	325	335	345	355	365	
Water (pure)	1	κ (W·m ⁻¹ ·K ⁻¹)	0.6009	0.6176	0.6322	0.6445	0.6546	0.6624	0.668	0.6714	
		Cp (J·kg ⁻¹ ·K ⁻¹)	4184		4078	4011	3910		3842	3787	

5.2.3.3 Thermophysical parameter setting

The temperature distribution of the TE sample is nonlinear, it is influenced by the changes in the thermophysical properties of the TE material. At the same time, the TE sample itself is also continuously conducting heat with the nearby water cooling tank and heated reaction chamber. Therefore, the constituent materials of each component in the simulation model should be consistent with the reality. The thermophysical properties of these materials, such as thermal conductivity, specific heat capacity and density are provided in Table 5-5.

5.2.4 The setting of loading conditions and solution

Finite element simulations show how a structure or component will respond to certain loading conditions. In thermal analysis, the loading conditions include temperature, heat flow rate, radiation, convection, and internal heat generation, etc.

5.2.4.1 The initial conditions and boundary condition settings

As for thermal simulation, the initial condition is the temperature distribution of each component of the model at the beginning of the simulation process, while the boundary conditions normally refer to heat radiation, heat convection, etc. In this chapter, the initial conditions and boundary conditions of the reaction chamber model are set as follows:

- (1) The initial temperature of the overall model is set to 25°C;
- (2) The temperature of the water cooling tank is kept constant at 25°C;
- (3) The surfaces of the water tank are considered to be adiabatic except for the surface in contact with TE sample, so the water cooling system does not exchange heat with the environment;
- (4) The heating process of the hot plate is set with reference to Figure 5-3;
- (5) Since the gas in the reaction chamber is considered to be static, a smaller thermal convection coefficient of $10\text{W}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ is selected;
- (6) The influence of thermal radiation on the temperature distribution is neglected.

5.2.4.2 The setting of heating program

In this chapter, the preset heating temperature of the hot plate is equivalent to its surface temperature, and the heating process is simulated by placing the bottom surface of the reaction chamber model close to the surface of the hot plate model. Since the surface temperature of the hot plate varies regularly following the preset program, the reaction chamber will be heated in accordance with the hot plate. At the heating stage, the thermal field inside the reaction chamber changes with time, but the temperature inside the reaction chamber will gradually stabilize during the heat preservation stage. If the dwelling time is long enough, there is only tiny temperature change at the end. Then the thermal field within the reaction chamber can be regarded as steady-state, the simulated temperature distribution of TE sample is considered to be valid.

For the purpose of investigating the impact of dwelling time on the stabilization of thermal field within the reaction chamber, several simulations were conducted with dwelling times of 20, 30, 40, 50 and 60 minutes. Figure 5-7 present the temperature of four probes (referring Figure 5-6a) on the TE sample as a function of dwelling time at a fixed heating temperature. The results indicate that when the dwelling time increases from 20 minutes to 30 minutes, the temperatures at the cold surface center, cold surface edge, hot surface edge and hot surface center of the TE sample increase by 4.6°C, 5.4°C, 8.5°C and 7.2°C, respectively; however, the temperature differences at the four probes are all less than 0.5°C as the dwelling time increase from 30 minutes to 60 minutes. Considering that a longer dwelling time would prolong the duration of the simulation, the dwelling time was then set at 30 minutes.

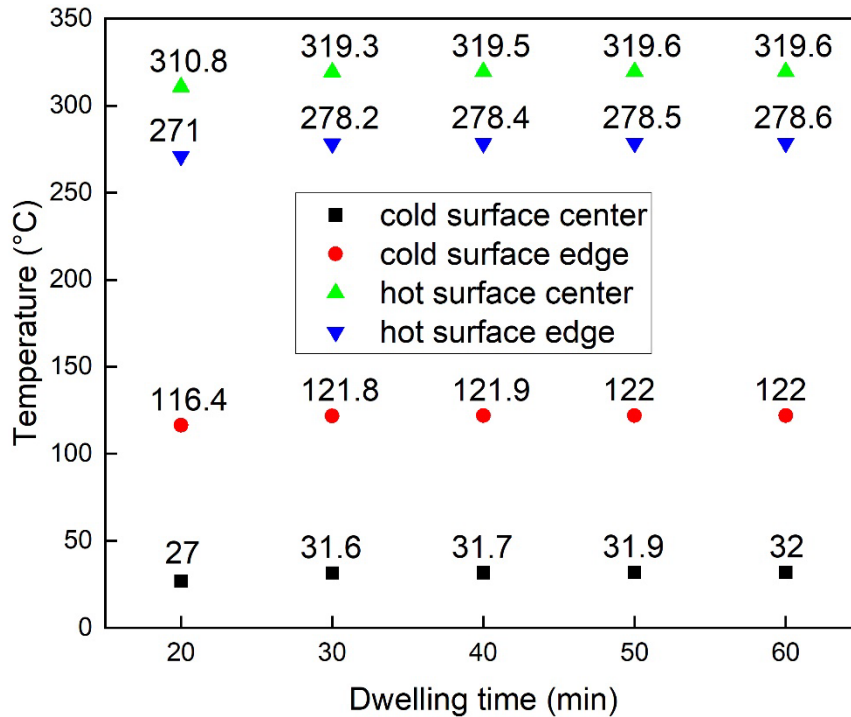


Figure 5-7 The temperatures at four specific positions on the TE sample was lower under a dwelling time of 20 mins, but kept stable when dwelling time range from 30 mins to 60 mins

5.2.4.3 Step-size independence test

During the calculation process of transient thermal simulation, one or more load steps can be set for any load history. Therefore, a more precise solution can be obtained by adjusting the number of step (i.e. step size). To make sure that the step size setting in this chapter meet the requirement of simulation without significantly changing the simulation duration, it is necessary to conduct an experimental test on the step size independence (in the previous section 5.2.4.2, the model has gone through the mesh independence test). Then a simplified heating program (as shown in Figure 5-8) was designed: firstly, the heating temperature of hot plate raises from 25°C to 325°C at a rate of 5°C/min; after dwelling for 30 minutes, the hot plate is kept heating to 525°C with a subsequent heat preservation process of another 30min; finally the temperature of hot plate decrease to 25°C at a rate of 10°C/min. During the heating process, 7 specific points are chosen and the corresponding hot surface center temperatures of TE sample are recorded at step sizes of 0.5, 1, 2, 3 and 4 minutes. The results

are listed in Table 5-6.

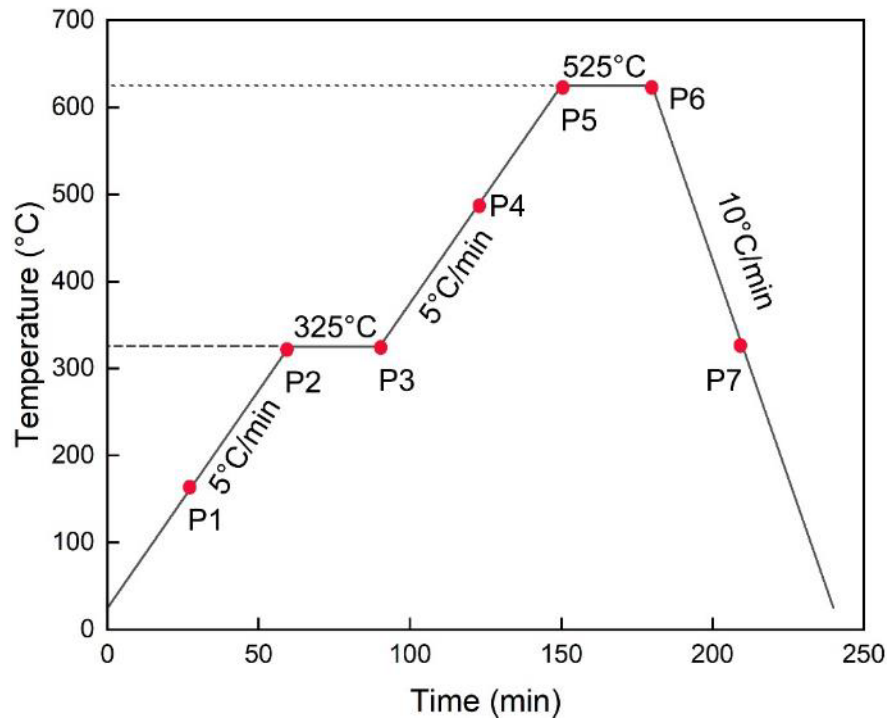


Figure 5-8 The simplified heating process

Table 5-6 The recorded hot surface temperatures of TE sample at step sizes of 0.5, 1, 2, 3 and 4 minutes, P1-P7 represent seven stages during the heating process and were pointed out in Figure 5-8

step size/min		0.5	1	2	3	4
Temperature/°C	P1	71.4	71.3	71.4	71.2	71.3
	P2	113.6	113.5	113.3	113.7	113.4
	P3	135.4	135.2	135.2	135.4	135.2
	P4	196.9	196.8	196.5	196.8	196.7
	P5	265.1	265.3	265.5	265.4	265.7
	P6	317.5	317.5	317.4	317.5	317.4
	P7	234.6	234.7	234.5	234.9	234.4

It can be concluded from Table 5-6 that the step size barely affect the thermal field. When the step size varied from 0.5 to 4 minutes, the temperature differences at all 7 specific points (P1-P7) are smaller than 0.4°C. This is due

to the perfect meshing method of the model. Generally speaking, the simulation was realized by solving a series of interrelated calculation. The step size theoretically affects the number of calculations that can be performed within a certain time, the more calculations are performed and the better reliability the results will be (Boz *et al.*, 2014). However, the size and shape of the mesh elements can have a significant effect on the accuracy and computational cost of the simulation. A finer mesh (i.e., smaller elements) typically leads to a more accurate simulation but with higher computational costs, because they help capture the details and complexities of the geometry being simulated, which may affect the behavior of materials, structures, or fluids. When a simulation is run using larger mesh elements, the details and nuances of the simulation may not be captured, which can cause errors and the results may not be as accurate. Additionally, using smaller elements in the mesh allows for the simulation to more accurately approximate the real-world physics since it can better follow and represent the contours and changes in the geometry of the modeled objects (Stolarski *et al.*, 2018). On the other hand, since the temperature rises steadily at a relatively low heating ramp rate (5°C/min) during the simulation process. Hence the influence of the step size on the thermal field is negligible considering that there are some systematic errors exist throughout the simulation.

5.2.5 The temperature distribution of the TE sample under simulated and experimental heating conditions

5.2.5.1 The temperature distribution of TE sample during simulation

After the modeling and setting of the above-mentioned parameters, the temperature distribution of 2mm, 4mm, 6mm, 8mm and 10mm BiCuSeO samples were simulated under a heating temperature range of 25°C -760°C. In the meantime, four probes were inserted at the edge and center of the hot/cold surface of each sample to record the temperature change at these positions. The schematic of the positions of the probes were shown in Figure 5-9.

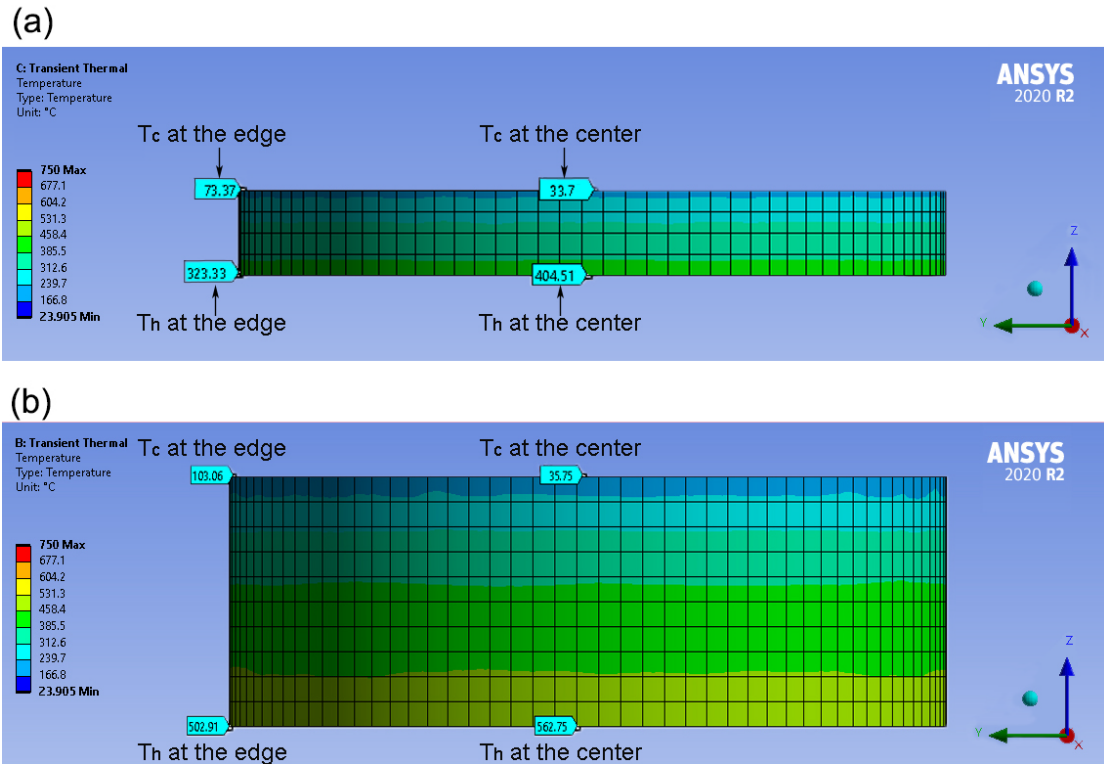


Figure 5-9 The temperature distribution of (a) 4mm and (b) 10mm TE sample at heating temperature of 750°C

Figure 5-9 show the temperature distribution of 4mm and 10mm BiCuSeO samples at heating temperature of 750°C. T_c and T_h represent the temperature at the cold and hot surfaces, respectively. It should be noted that Figure 5-9a and 5-9b were side views of the sample. Therefore, the center of cold and hot surface are unobservable but the temperatures at these positions could be read from their probes. Referring the values at the four blue labels in the figure, the temperatures were not evenly distributed on the surface of heated TE samples. The temperatures was found to be higher at the edge than the center of cold surface in Figure 5-9, whereas the hot surface center is hotter than its edge. In addition, the color of the meshes change rapidly along the Z axis direction rather than in Y axis direction Figure 5-9a and 5-9b. By comparing to the colored legend at the left side of the figure, a much higher temperature difference along Z axis direction was suggested. Similar result could be obtained from both figures.

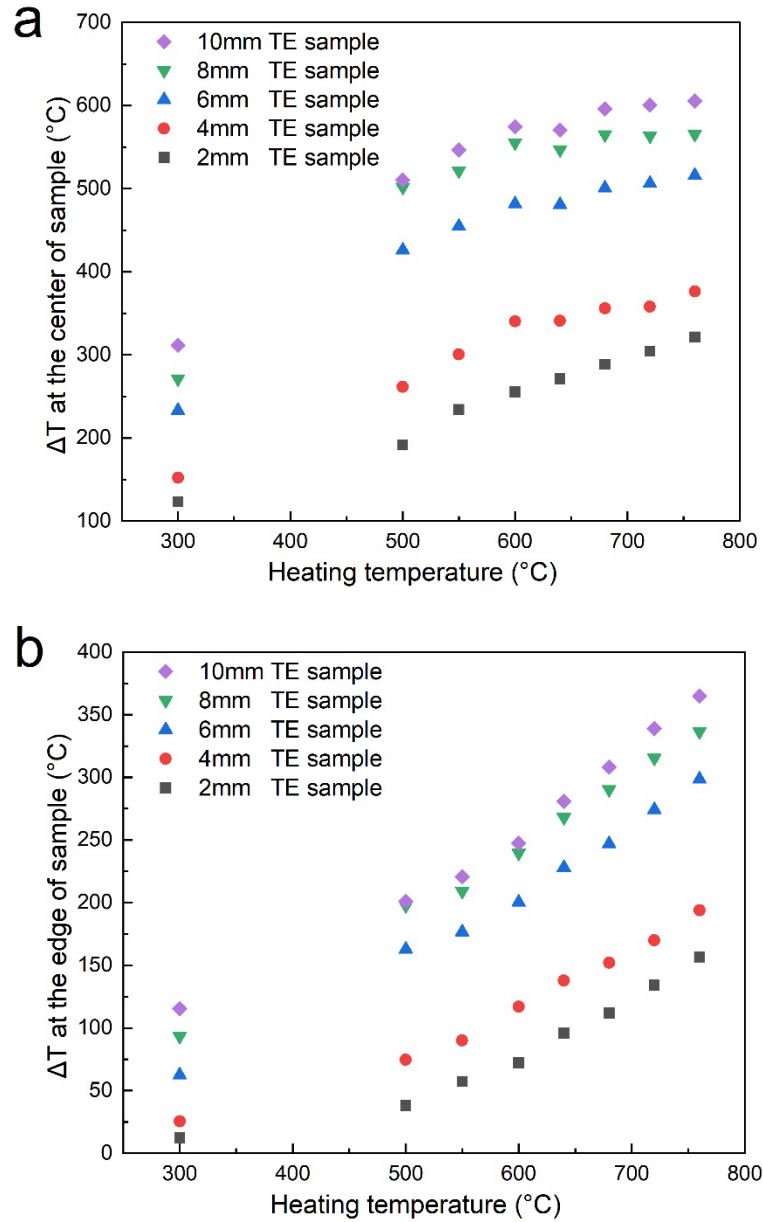


Figure 5-10 The temperature difference ΔT at (a) the center and (b) the edge of 2mm, 4mm, 6mm, 8mm and 10mm TE samples

From Figure 5-9 we know that the T_c at the center are various from that at the edge, so does the T_h . Since the generated Seebeck voltage is proportional to the temperature difference ΔT ($\Delta T = T_h - T_c$) across the sample, the values of ΔT at the center and the edge were calculated separately for 2mm, 4mm, 6mm, 8mm and 10mm samples, the results are plotted in Figure 5-10. The ΔT at both the center and the edge increase gradually with the heating temperature in Figure 5-10a and 5-10b, while thicker sample perform a larger ΔT on the other

hand. It should be noted that the ΔT at the edge is smaller than that at the center, which indicate that the Seebeck voltage generated at the edge of the sample is also smaller, and therefore, may exhibit lower catalytic activity during the catalytic chemical reaction.

5.2.5.2 The temperature measurement for the designed experiments

In order to verify the temperature distribution of BiCuSeO sample obtained by simulation, a series of experiments were designed to measure the temperature of BiCuSeO sample under heating condition. The thermocouple and the thermometer linked to it were used for the measurement. The configuration of thermocouples inside the reaction chamber is plotted in Figure 5-11. Two hollow ceramic tubes (black dashed box) penetrate the cap of the reaction chamber, which enable the thermocouples (red line) to pass through, the tip of the two thermocouples are placed close to the bottom surface edge and the top surface center of the TE sample. Then the instant temperature could be read and recorded from the screen of thermometer. Insulating glue is used to seal the end of ceramic tubes to isolating the interior of the reaction chamber from the atmosphere outside.

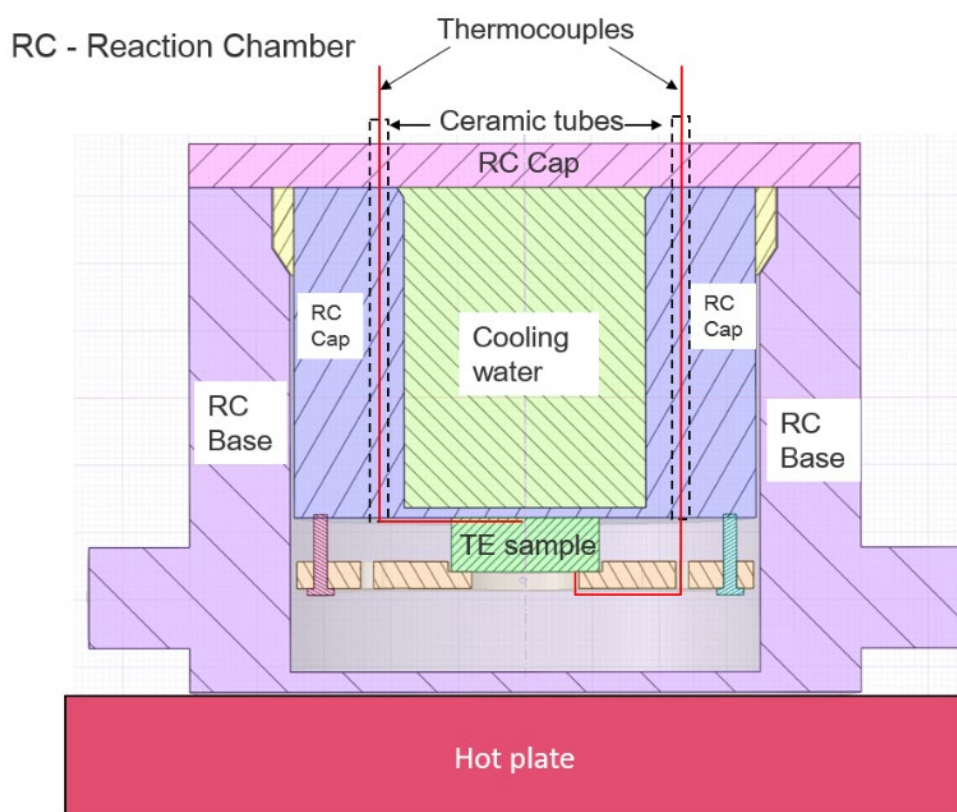


Figure 5-11 The schematic of the thermocouples within the reaction chamber

During the experiment, the sample was put into the reaction chamber and the whole chamber was heated by the hot plate below, 300°C, 500°C, 550°C, 600°C, 640°C, 680°C, 720°C, 760°C were chosen as the preset temperatures. The experimental procedures are:

Step 1: the hot plate is heated to 300°C at a moderate ramp rate from room temperature;

Step 2: maintain the temperature at 300°C for at least 30 minutes, record the temperature of the hot and cold side of TE sample every 2 minutes for 5 times;

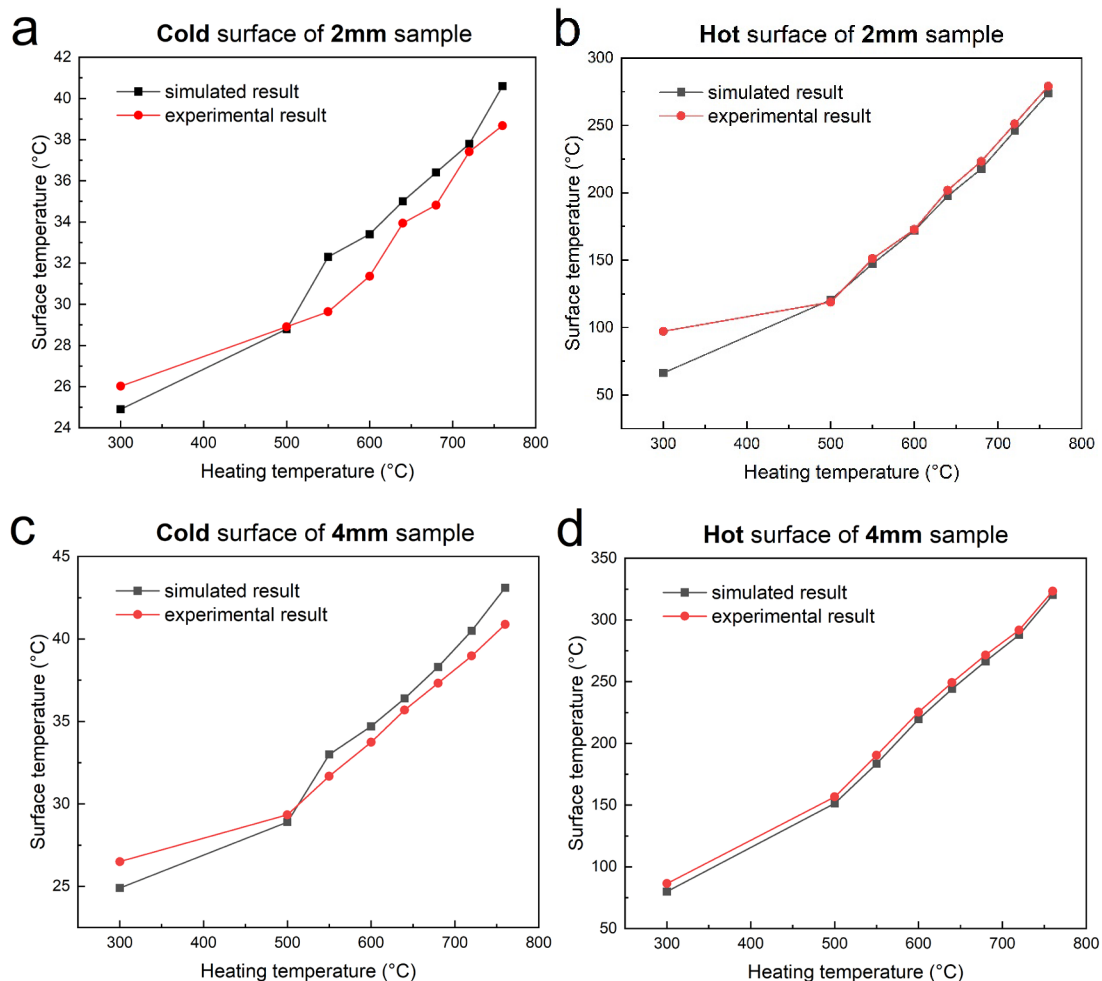
Step 3: keep heating the hot plate to the next preset temperature (here is 500°C);

Step 4: record the temperatures for 5 times every 2minutes after heat preservation stage;

Step 5: repeating Step 3 and Step 4 until the temperature reaches 760°C;

Step 6: take the average value of 5 measurements as the result.

The comparison of simulated temperature and experimental data of 2mm, 4mm and 6mm BiCuSeO sample is presented in Figure 5-12. The results show that the simulated temperatures are very close to the experimental data of all three samples. The difference between them at the cold surface is smaller than 3°C, that is, a relative error of 8%. In terms of the hot surface, their temperature difference is 5°C-7°C, indicating an error of 3%-5%. These results are predictable because the temperature of hot plate fluctuated within a certain temperature range (normally that is $\pm 8^{\circ}\text{C}$) during the heat preservation stage of experiment. Whereas the hot plate temperature increased steadily throughout the simulation process, therefore the temperature of the TE sample surface is able to keep at a constant value. In addition, the ambient temperature has a significant impact on the temperature of the cooling water under experimental condition, which may led to the relatively high temperature difference between simulated and experimental data at cold surface.



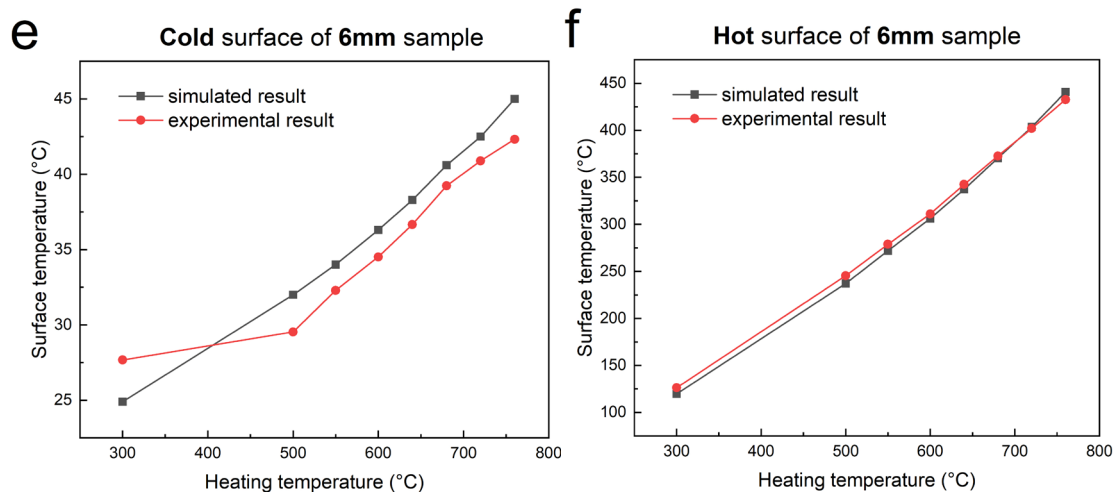


Figure 5-12 The values of simulated and experimental measured temperatures of 2mm (a), (b); 4mm (c), (d) and 6mm (e), (f) BiCuSeO samples are very close

5.3 Conclusion

A simplified 3D model for the TE sample and the reaction chamber was established and a series of transient thermal simulation under different conditions were carried out using Ansys 2021R software. The appropriate parameters for meshing and loading conditions were investigated and verified independently, a high quality meshing method was successfully applied onto the 3D model of simplified reaction chamber and TE sample. The transient simulation results indicate that the temperature are unevenly distributed on the surface of TE samples under heating conditions. It also reveal the fact that the temperature difference between the cold and hot surface of TE sample increase significantly with the thickening of sample. In addition, the finite element simulation provide reasonable and valid data for predicting the temperature distribution of a TE sample under real experimental conditions.

6 Effect of sample thickness and porosity on the catalytic activity of BiCuSeO

6.1 Introduction

BiCuSeO, as a thermoelectric material, was proved to be effective as a support and promoter of catalysis for CO₂ hydrogenation reaction for Thermoelectric Promotion of Catalysis (TEPOC). In this chapter, different methods have been employed to modify the BiCuSeO sample and maximize its catalytic activity for CO₂ hydrogenation, such as increasing the thickness of the sample or introducing porous structure onto the sample surface to increase the surface area. A significant enhancement was observed on samples with high thickness and/or surface area, which provide the possibility to achieve greater CO₂ conversion rate at lower temperature by the combined effect of surface area and Seebeck voltage. It should be noted that although several BiCuSeO samples with different porosity and BET surface areas were prepared, we only carried out CO₂ hydrogenation reactions using the porous BCSO @50wt% Gel sample due to the limitation of PhD project duration.

6.2 Result and discussion

6.2.1 The characterization of porous and non-porous BiCuSeO samples

Figure 6-1 shows the (a) thermal conductivity, (b) electrical conductivity, (c) Seebeck coefficient and (d) ZT value as a function of temperature for the porous BiCuSeO sample prepared by adding 50wt% Gel and 20wt% PS, respectively. Due to the adoption of the same preparation process, the TE properties of non-porous BiCuSeO prepared by Flux method (Achour *et al.*, 2018) was referred as well. Meanwhile the introduction of Bhaskar's data was to compare the TE properties of BiCuSeO samples prepared by another Sol-Gel method.

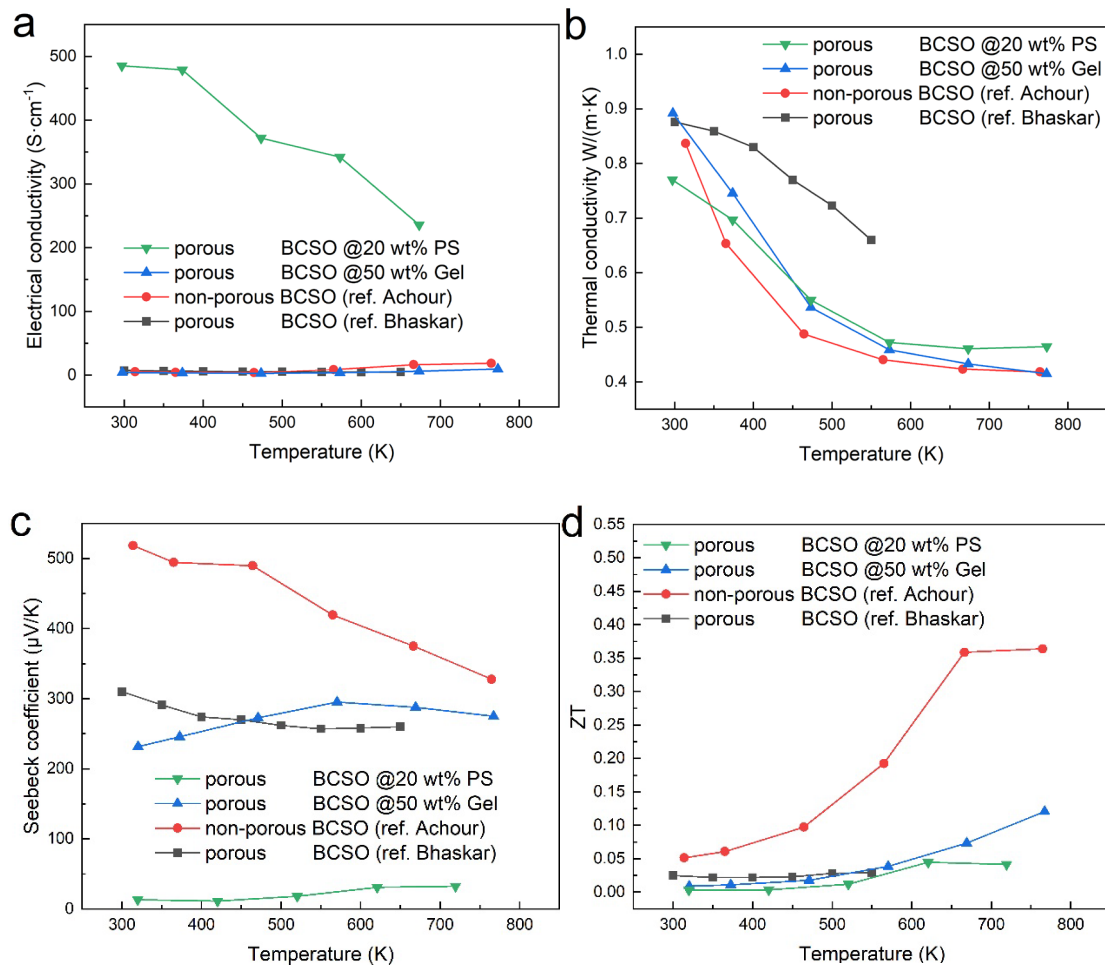


Figure 6-1 (a) thermal conductivity, (b) electrical conductivity, (c) Seebeck coefficient and (d) ZT value as a function of temperature for porous/non-porous BiCuSeO samples

It was found that sample BCSO @20wt% PS exhibits a relatively low thermal conductivity, Seebeck coefficient, and ZT value, but an abnormally high electrical conductivity. By comparing the properties of porous samples BCSO @20 wt% PS and BCSO @50 wt% Gel to that from the reference data, it can be seen that our BCSO has a lower thermal conductivity and a relatively higher Seebeck coefficient above 450K, while the electrical conductivity and ZT value are basically the same. In addition, non-porous BCSO (Achour *et al.*, 2018) shows the lowest thermal conductivity, highest Seebeck coefficient and ZT value than the porous samples, which was predictable because porous materials have more defects and pores inside, which can easily lead to the deterioration of their thermoelectric performance. Given the overall

thermoelectric performance and porosity, although the porous BCSO @20wt% PS sample exhibited better pore size and higher BET surface area, its thermoelectric properties, especially the Seebeck coefficient which is critical for the TEPOC application, is extremely small (1/10 of that of sample BCSO @50wt% Gel). Therefore in this chapter, only the catalytic activity of the porous BCSO @50wt% Gel sample is discussed.

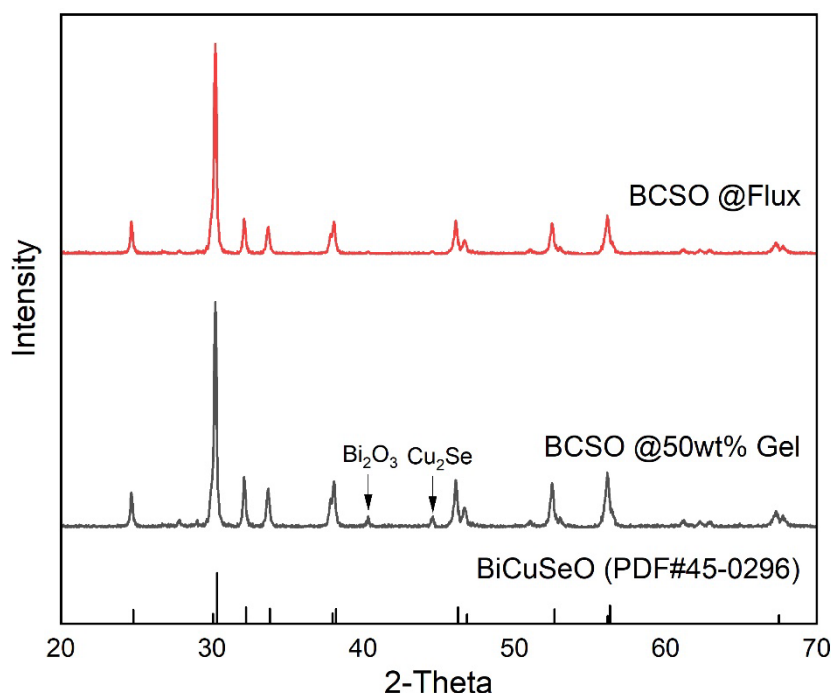


Figure 6-2 XRD patterns of the newly prepared non-porous sample BCSO @Flux and porous sample BCSO @50wt% Gel before being used for chemical reaction

Figure 6-2 displays the XRD patterns of the porous BiCuSeO sample prepared by the Sol-Gel method and the bulk BiCuSeO sample prepared by Solid-State Reaction. We have tested on both sides of the porous samples because these two surfaces were varied in terms of porosity. The peaks of secondary phases Bi₂O₃ and Cu₂Se could be seen clearly on patterns of BCSO @50wt% Gel. The existence of impurities such as Bi₂O₃ and Cu₂Se is not surprised for samples prepared by Sol-Gel method. From the technical point of view, it is very challenging to keep Bi, Cu and Se uniformly distributed within the solution. Besides, the diffusion of the ions is restricted owing to the obstruction of the

organic gel which formed during the gelation process, therefore these secondary phases would be easily appeared in the calcined Sol-Gel samples. In order to investigate the stability of BiCuSeO samples at temperatures higher than 450°C, we performed XRD tests on the hot sides of the samples which were involved in multiple catalytic chemical reactions (the highest temperature during the reaction was about 723 K, i.e. 450°C, and the dwell time under this temperature was over 20 hours). The results are shown in Figure 6-3.

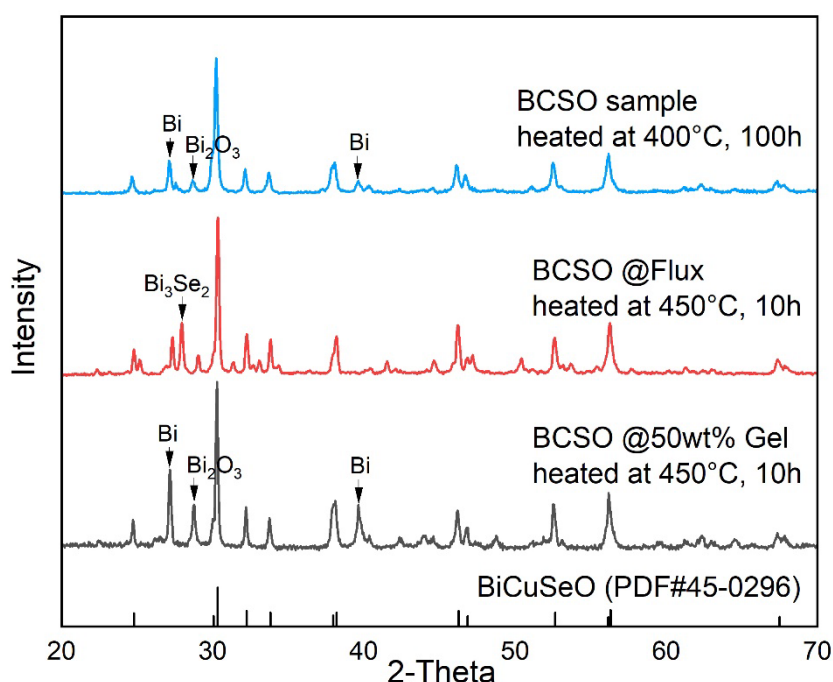


Figure 6-3 The BiCuSeO samples BCSO @Flux and BCSO @50wt% Gel decomposed severely after applied in catalytic chemical reactions at 450°C for 10 hours, but it was more stable at 400°C after over 100 hours

It is obvious that the composition of hot side surface has changed dramatically after dwelling at 450°C for nearly 10 hours (red and black patterns in Figure 6-3). There are secondary phases other than BiCuSeO appear on the XRD pattern of both porous and bulk BiCuSeO samples that indicate the occurrence of second phases. The second phases in the bulk sample are mainly Bi and Bi₂O₃, while an additional Bi₃Se₂ peaks appear at $2\theta=28.7$ on the pattern of porous sample. This indicates that our BiCuSeO sample is not stable at 450°C, and the spontaneous decomposition of BiCuSeO into the second phases such

as Bi, Bi₂O₃ and Bi₃Se₂ happens. These second phases would inevitably affect the thermoelectric properties of the BiCuSeO sample and thus its catalytic activity. A long duration stability test was subsequently conducted onto the BiCuSeO samples and it revealed that a limited numbers of secondary phase generated at the sample surface after heated under 400°C for over 100 hours (blue pattern in Figure 6-3). Therefore, we tried to avoid exposing BiCuSeO to temperatures above 400°C in subsequent experiments to ensure the stability of the thermoelectric properties of the samples in different tests.

6.2.2 Initial test on 4mm bulk BiCuSeO sample under TE and RTE conditions

It was reported that a significant change in the rate of catalytic chemical reactions requires a large Seebeck voltage for TEPOC, which corresponds to a large temperature difference for thermoelectric materials (Achour *et al.*, 2018). For thermoelectric (TE) conditions, it can be seen that the surface of the TE sample is in close contact with a water cooling system(referring Figure 3-2a) to ensure that the temperature of this surface didn't exceed 373K, so the temperature difference across the sample could be optimized. However under reduced thermoelectric (RTE) conditions, the cold surface of the sample is detached with the water cooling system. Thus the temperature at cold surface under RTE conditions should be much higher compared to that of TE conditions, leading to a lower temperature difference across the sample which generate a much smaller Seebeck voltage, therefore a different catalytic performance of BiCuSeO sample under RTE conditions is expected. The main purpose of comparing the catalytic behavior of BiCuSeO under TE and RTE conditions is to explore the influence of the Seebeck voltage on its catalytic activity. Referring to the literature of Achour *et al.*, it was found that the 2mm BiCuSeO sample could hardly catalyze the CO₂ hydrogenation reaction under RTE conditions. In this section, two test on 4mm bulk BiCuSeO sample were performed at inlet gas ratio H₂:CO₂=4:1 (hereinafter BCSO 4B @4:1) to characterize its catalytic

activity in CO₂ hydrogenation reaction under TE and RTE condition.

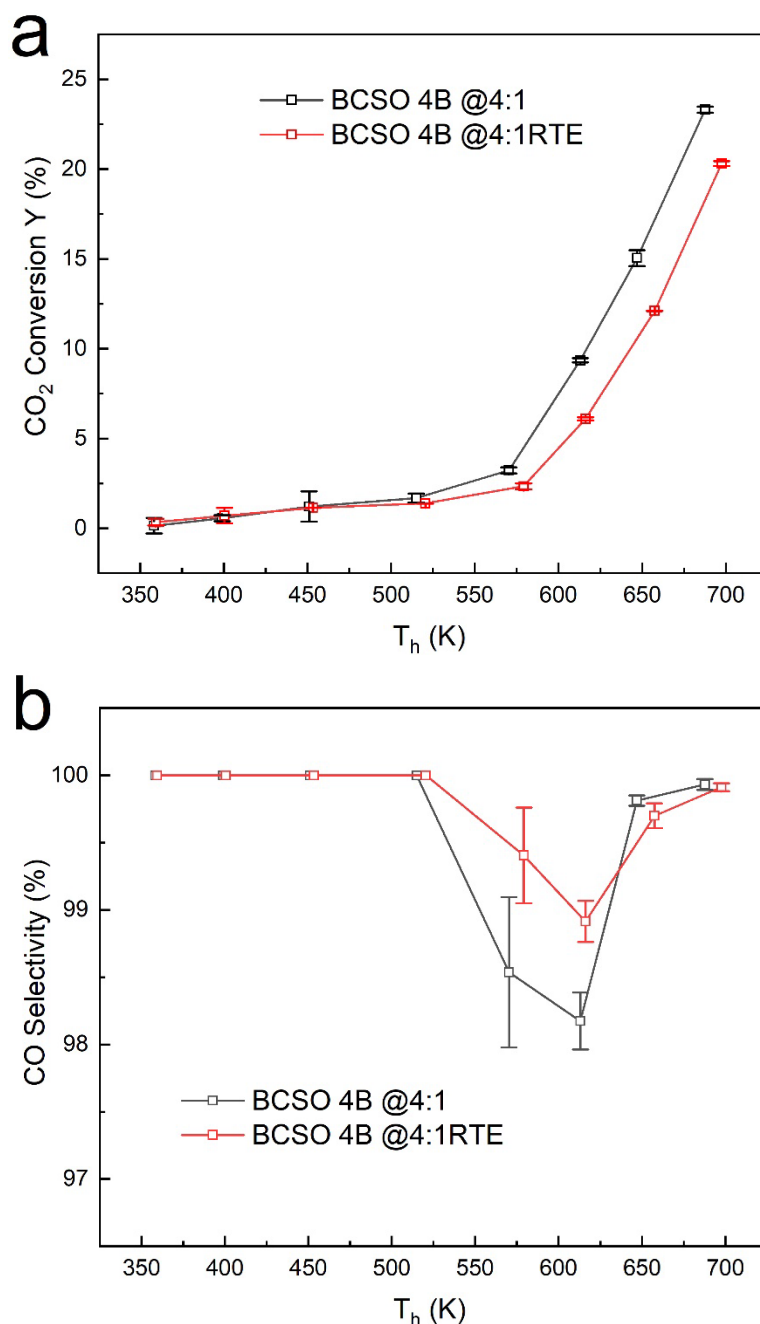


Figure 6-4 The (a) CO₂ conversion and (b) CO selectivity as a function of T_h for samples hereinafter

Figure 6-4 shows the relationship of (a) T_h -CO₂ conversion and (b) T_h -CO selectivity for the 4 mm bulk BiCuSeO sample under both TE and RTE conditions, the inlet gas ratio was H₂:CO₂ = 4:1. It can be seen from Figure 6-4a that the CO₂ conversion under TE condition was significantly higher than that under RTE condition at temperatures ranged from 550K to 700K. The CO

selectivity as a function of hot side temperature T_h are shown in Figure 6-4b, it can be seen that the vast majority of the products here for CO_2 hydrogenation reaction is CO. The product CO was observed for the first time at 359K for both TE and RTE conditions, whilst the CO selectivity is always higher than 98% at the temperature range of 350-700 K. For both curves in Figure 6-4b, the CO selectivity starts to decrease from 100% after 520K and reaches the lowest value at 613K, where the CO selectivity is 98.2% and 98.9% for TE and RTE condition, respectively, then it gradually increases to more than 99.5% at around 650K.

6.2.3 The effect of sample thickness on the catalytic activity of BiCuSeO samples

For the purpose of studying the effect of sample thickness on the catalytic activity of BiCuSeO samples, we firstly performed catalytic chemical reactions with 6mm, 4mm, and 2mm bulk BiCuSeO samples under inlet gas ratio of $\text{H}_2:\text{CO}_2 = 1:1$ and $4:1$, respectively (which are written as BCSO 2B, BCSO 4B, BCSO 6B with the suffix @1:1 or @4:1 in the context). Figure 6-5 shows three T_h -V curves for BiCuSeO samples with thicknesses of 6mm, 4mm, and 2mm. The curves indicate a direct correlation between the voltage and the sample thickness, with the voltage increasing as the thickness of the sample increases, demonstrating a linear relationship between thickness and voltage. The highest voltage achieved for the three samples at around 600K are 56mV, 81mV and 103mV, respectively. For thicker samples, it can be observed that the voltage is higher at a certain T_h . This indicates that with the thickening of the BiCuSeO sample, it is more difficult to conduct heat from the sample hot side to its cold side due to the intrinsic low thermal conductivity of BiCuSeO. Hence the cold side temperature T_c of the sample is lower. Hence, this is actually the effect of different T_c on the catalytic activity at the same T_h .

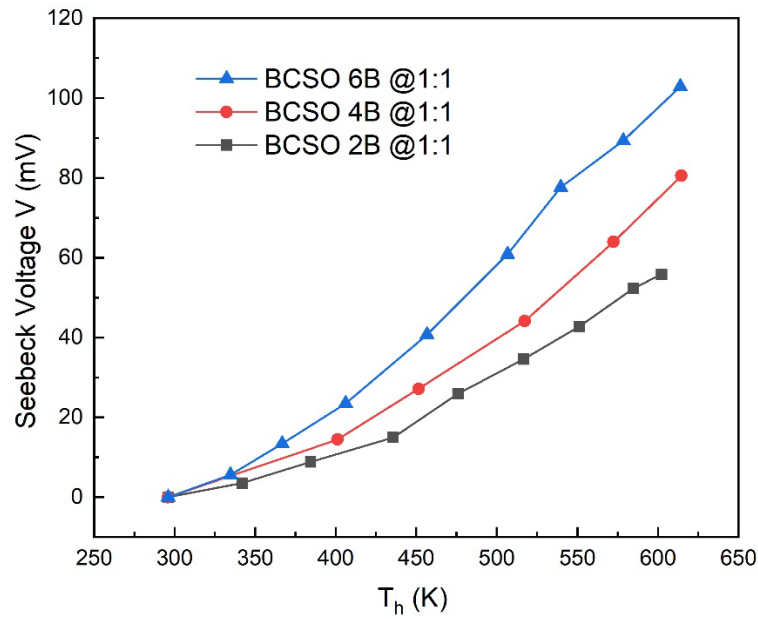
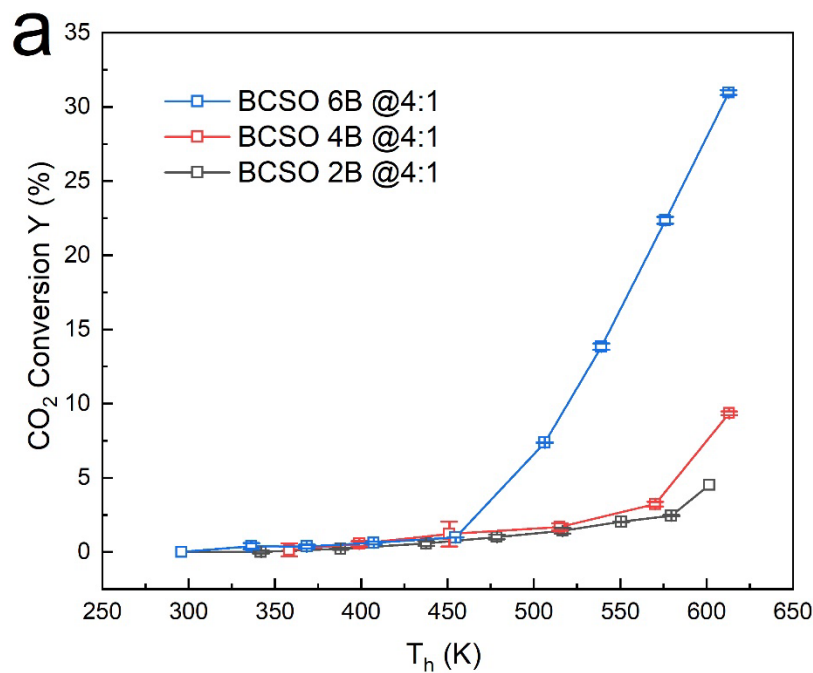


Figure 6-5 the Seebeck voltage as a function of T_h for samples BCSO 6B @1:1, BCSO 4B @1:1 and BCSO 2B @1:1

According to the definition of Seebeck voltage (i.e. Equation 2-1), the Seebeck coefficient S is calculated as,

$$S = V / (T_h - T_c) \quad \text{Equation 6-1}$$

When T_h and S are identical for BiCuSeO, the Seebeck voltage of 6mm sample should be larger because it has a smaller T_c . This behavior can be useful in predicting the electrical behavior of BiCuSeO samples in different applications and can be applied to optimize the design of electronic devices.



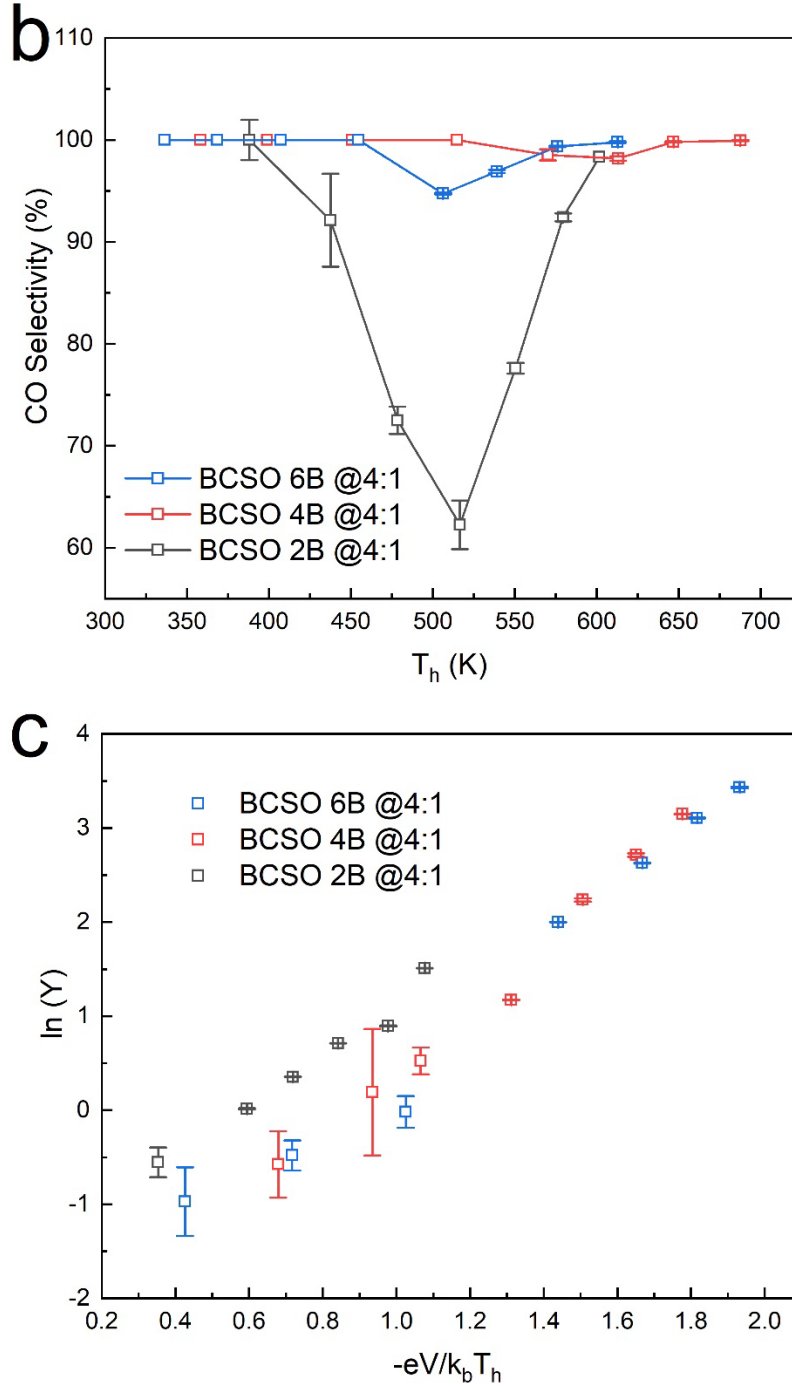


Figure 6-6 The relationship between (a) T_h - CO_2 Conversion, (b) T_h - CO Selectivity and (c) $-eV/k_b T_h$ - $\ln(Y)$ for samples BCSO 6B @4:1, BCSO 4B @4:1 and BCSO 2B @4:1

It can be seen that the CO_2 Conversion rate kept at a very low level at a temperature range of 300K-450K in Figure 6-6a. However, sample BCSO 6B @4:1 shows a remarkably higher CO_2 conversion than samples BCSO 4B @4:1 and BCSO 2B @4:1 under the same temperature when $T_h > 450\text{K}$. For

example, the CO₂ conversion of BCSO 6B @4:1 is about 29% at 600K, 8% for BCSO 4B @4:1 and 4% for BCSO 2B @4:1. Combined with the discussion above, it is clear that a thicker sample generates higher Seebeck voltage at a specific temperature $T_h > 450K$, Thus a higher chemical reaction rate could be achieved at the hot surface of thicker sample, which contribute to the increase of its CO₂ conversion. In other words, the same CO₂ conversion could be achieved at a much lower temperature by using a thicker sample. Similar results could be obtained from the experiments with inlet gas ratio $H_2/CO_2=1:1$, For sample BCSO 6B @1:1, BCSO 4B @1:1 and BCSO 2B @1:1, their CO₂ conversion rates at 600K are 21%, 4% and 3%, respectively.

Figure 6-6c plotted the $\ln(Y)$ as a function of $-eV/k_b T_h$, a mostly linear relationship was observed for the three samples. According to Equation 2-31, which could be rewritten as:

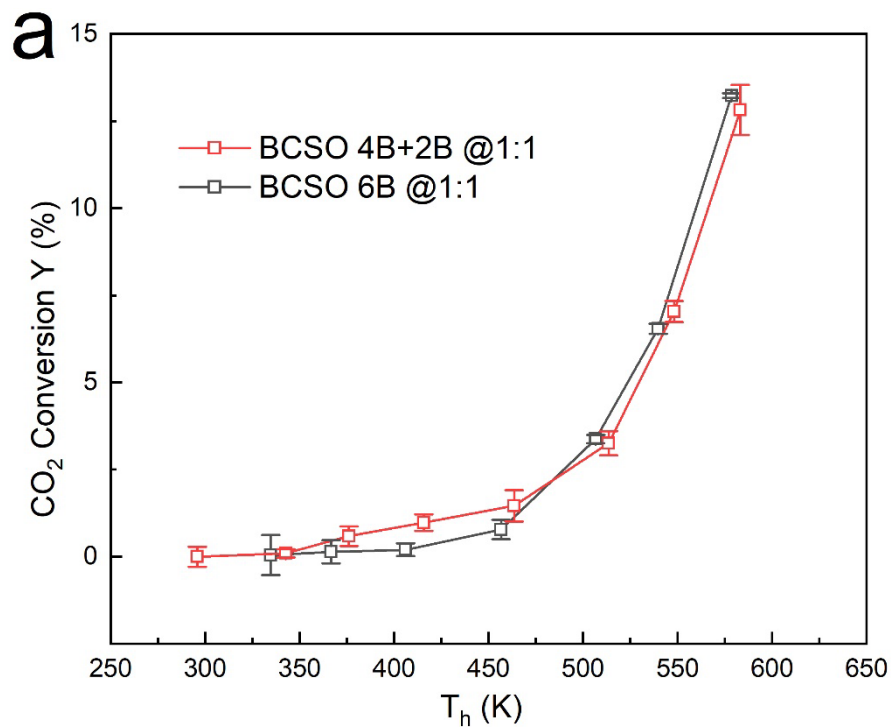
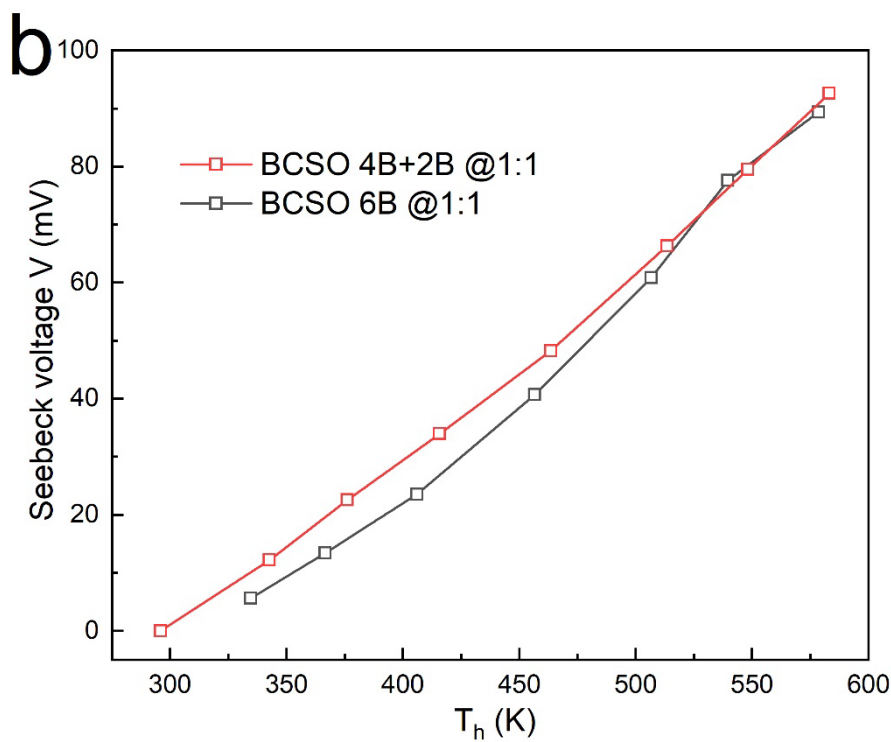
$$\ln(Y) = \gamma \cdot (-eV/k_b T_h) + \ln(Y_0) \quad \text{Equation 6-2}$$

From the $-eV/k_b T_h - \ln(Y)$ curve and the equation above, the values of γ and $\ln(Y_0)$ for each sample could be obtained, thus the ratio Y/Y_0 were also calculated as 6974, 5642 and 4818 for sample BCSO 6B @1:1, BCSO 4B @1:1 and BCSO 2B @1:1 at 600K, indicating that the CO₂ conversion was enhanced by thousands of times for all the samples by TEPOC (Achour *et al.*, AEnM, 2018).

6.2.4 The use of stacked sample in CO₂ hydrogenation reactions

In order to investigate the effect of thickness and porosity on the catalytic activity of BCSO samples, initially we planned to prepare samples with thicknesses of 2 mm, 4 mm and 6 mm and of porous non-porous, respectively. However, it is not possible for us to control and to know the exact porosity and other thermoelectric properties of all these samples, so instead, the thinner samples were polished carefully and stacked together to form thicker samples. For example, we stacked two samples of 2mm (2mm + 2mm) to form a 4mm thickness, and 4mm + 2 mm to form a 6mm thickness. And for all these samples, the top 2mm sample was the same one. In this way, we kept the surface area

and the thermoelectric properties at the reaction surface to be the same, as chemical reactions are considered to take place at the surface with the highest temperature only. In another word, this minimize the variation in the result generated by samples with different surface area and composition.



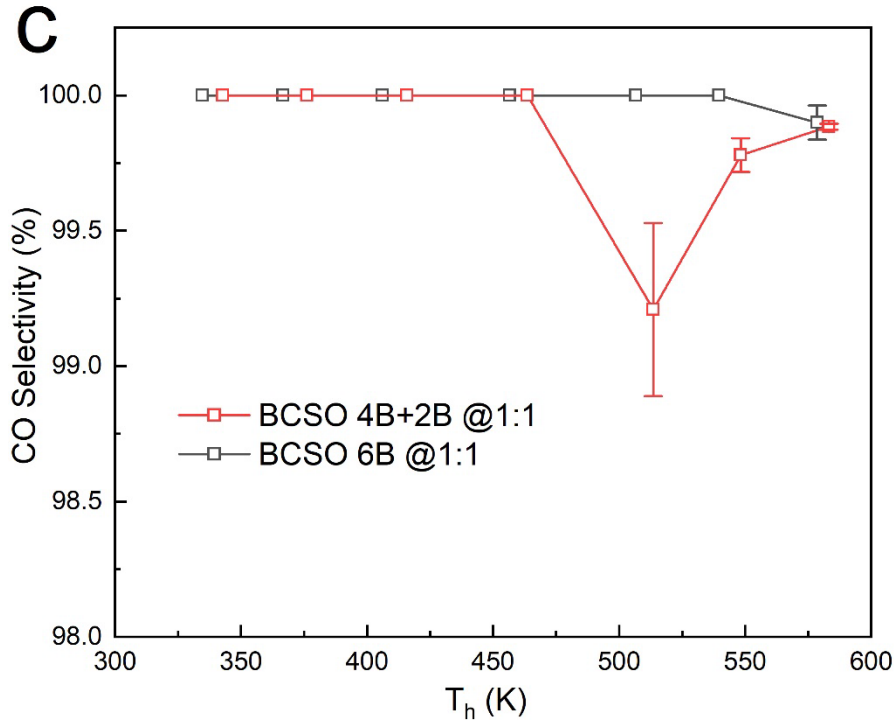


Figure 6-7 The (a) CO₂ conversion, (b) Seebeck voltage V , and (c) CO selectivity as a function of T_h for samples BCSO 4B + 2B @1:1 and BCSO 6B@1:1

One open question is that whether the stacked sample has the same catalytic activity as that of a single sample. So we performed catalytic chemical reactions using a 6mm bulk BiCuSeO sample and a stacked sample consisted of a 4mm and a 2mm bulk BiCuSeO samples. The diameter of the samples is 20mm, the inlet gas ratio for catalytic chemical reaction is $H_2:CO_2=1:1$. The (a) CO₂ conversion, (b) Seebeck voltage V , and (c) CO selectivity as a function of T_h are plotted in Figure 6-7. It is shown in Figure 6-7a that the CO₂ conversion of single sample was similar to that of stacked sample in the range of 350 K-450 K. For example, the CO₂ conversion for sample BCSO 6B @1:1 was 0.97% at 415 K while that of the sample BCSO 4B + 2B @1:1 was 0.25%. The difference between them was maintained at a small value with increasing temperature, e.g. the CO₂ conversions were 13.2% and 12.7% for sample BCSO 6B @1:1 and BCSO 4B + 2B @1:1 at 580K, respectively.

From Figure 6-7b it can be seen that the Seebeck voltage of sample BCSO 4B + 2B @1:1 is slightly higher than that of sample BCSO 6B @1:1 at temperatures

below 500 K. This might be because of the slight difference in Seebeck coefficient between different samples prepared under the same conditions. In addition, the CO₂ conversion is very small (<3%) at this stage, so it can be assumed that the CO₂ conversion is not significantly affected by the Seebeck voltage. As the temperature increases, the Seebeck voltage of these two samples increase similarly. This indicates that there is no loss of the Seebeck voltage of the stacked sample as compared to the single sample. It is noteworthy that the contact surfaces were finely polished before stacking the two samples together. The CO selectivity for both samples are higher than 99% over the entire temperature range, so it can be concluded that the vast majority of the product was CO. The difference was found at 513K, the CO selectivity for sample BCSO 4B + 2B @1:1 decreased to 99%, but it kept at 100% for sample BCSO 6B @1:1. This sudden drop of CO selectivity at about 513K, which also occurred on the curves in Figure 6-6b, can be explained by the thermodynamic equilibrium conversion (TEC) for RWGS reaction referring Figure 7-5 and its context, herein it will be briefly discussed. Firstly, the TEC of CO₂ at a certain temperature was strongly affected by the product of RWGS reaction (i.e. CH₄ generated or not). According to Figure 7-5a, the TEC decreases at around 510K for all the curves, indicating that the production of CH₄ is constricted. Therefore in the cases where CH₄ generated in Figure 6-6b and 6-7c, lesser CH₄ was produced at $T_h > 510K$, leading to the increase in CO selectivity. In summary, the catalytic activity of the single sample and the stacked sample are essentially the same.

6.2.5 The effect of porosity on the thermoelectric properties of stacked BiCuSeO samples

In order to maintain the uniformity of the surface structure and composition of the samples, we produced several stacked samples for the subsequent experiments. Bulk samples with thickness of 2 mm 4 mm were stacked with porous non-porous samples and subjected to the catalytic chemical reactions, a schematic diagram for the stacked sample is present in Figure 6-8, with their

name listed in Table 6-1.

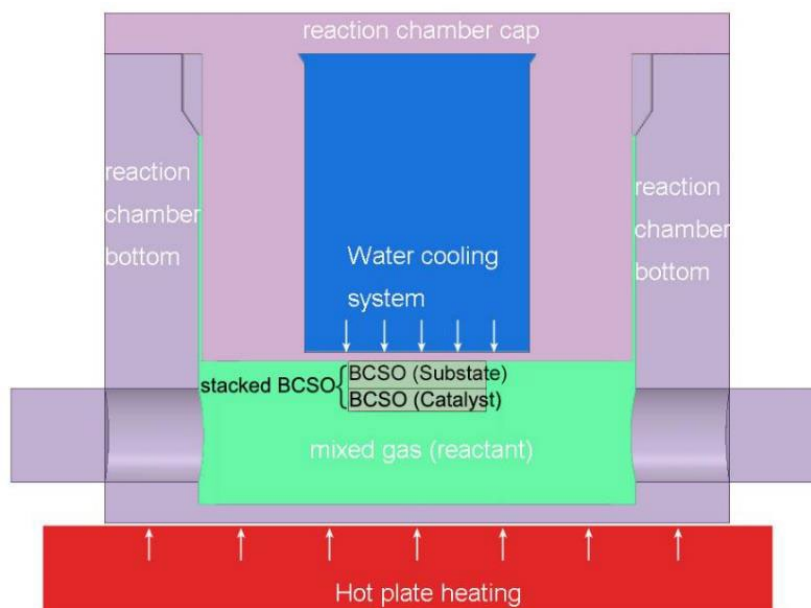


Figure 6-8 Schematic diagram for the stacked BCSO sample

Table 6-1 The combination of stacked BCSO sample refer to Figure 6-8

BCSO(Substrate) BCSO(Catalyst)	2mm bulk BiCuSeO (non-porous)	4mm bulk BiCuSeO (non-porous)
	2B + 2B BCSO	4B + 2B BCSO
2mm bulk BiCuSeO (non-porous)	2B + 2B BCSO	4B + 2B BCSO
2mm porous BiCuSeO	2B + 2P BCSO	4B + 2P BCSO

The (a) Seebeck voltage and (b) Seebeck coefficient as a function of T_h for four stacked samples are shown in Figure 6-9, each sample was tested under TE conditions with $H_2:CO_2 = 4:1$. Note that the slope of the curve here in Figure 6-9a is not equal to the Seebeck coefficient because the X axis stand for T_h but not ΔT . It can be seen that the bulk samples produce higher Seebeck voltage than the porous samples at the same T_h , this is because the porous sample has a poorer Seebeck coefficient due to the porous structure and the existence of second phases. The maximum Seebeck coefficient for the bulk sample in Figure 6-9b is 349 $\mu V/K$ for BCSO 2B + 2B at 528 K. Whilst the Seebeck

coefficient for sample BCSO 4B + 2B also reaches 347 $\mu\text{V/K}$ at 585 K. In terms of porous samples, a Seebeck coefficient of 275 $\mu\text{V/K}$ could be achieved for sample BCSO 2B + 2P under 625K. The above data also indicate that it is still possible to obtain a relatively high and stable Seebeck coefficient within the temperature range of the catalytic reaction by using stacked samples.

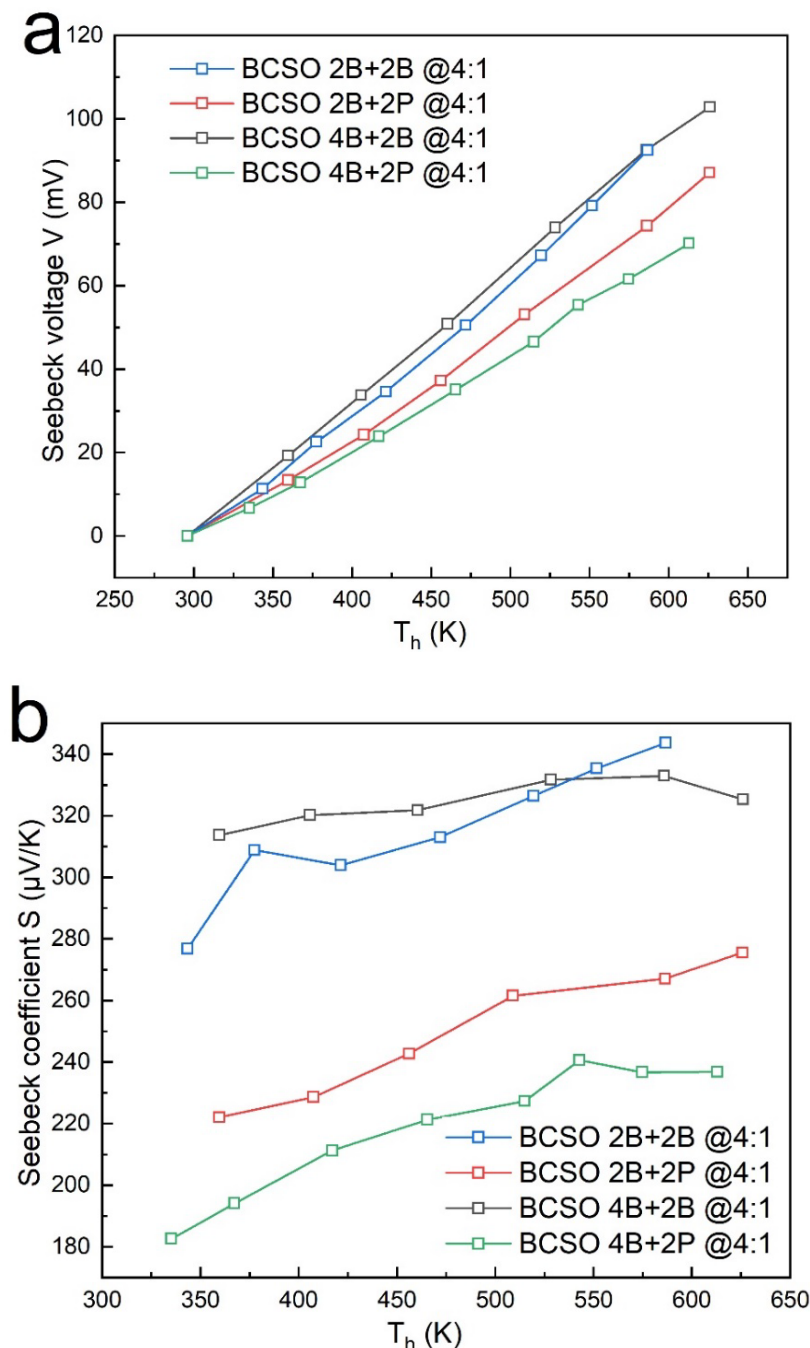


Figure 6-9 The (a) Seebeck voltage and (b) Seebeck coefficient as a function of T_h for samples BCSO 4B+2P, BCSO 4B+2B, BCSO 2B+2P and BCSO 2B+2B

6.2.6 The effect of porosity on the CO₂ conversion and CO selectivity

A series of CO₂ hydrogenation reactions has been performed by using samples BCSO 2B + 2B, BCSO 4B + 2B, BCSO 2B + 2P and BCSO 4B + 2P as catalyst.

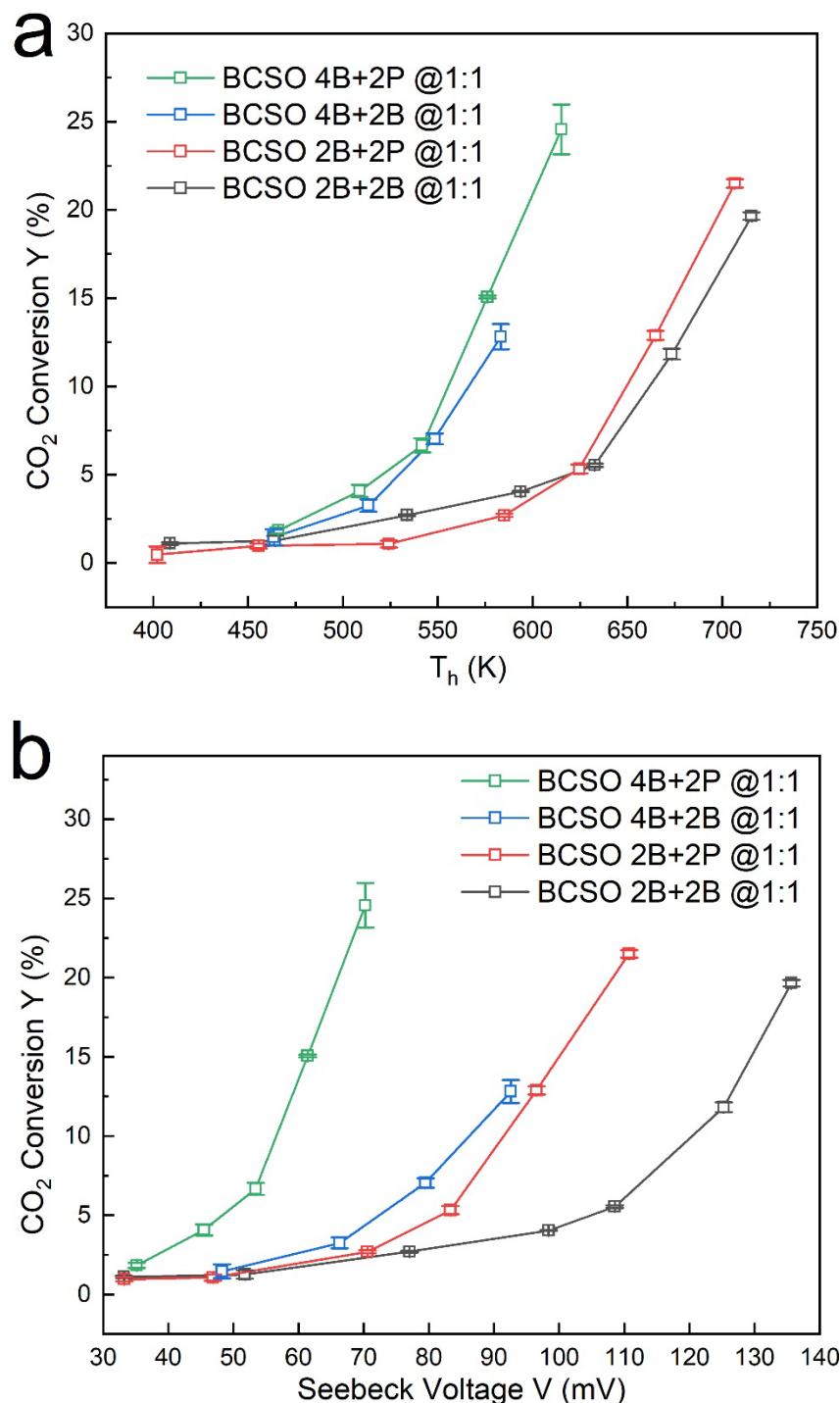


Figure 6-10 CO₂ conversion as a function of (a) temperature T_h and (B) Seebeck voltage V for samples BCSO 4B + 2P @1:1, BCSO 4B + 2B @1:1, BCSO 2B + 2P @1:1 and BCSO 2B + 2B @1:1

Figure 6-10 plotted the CO₂ conversion as a function of (a) temperature T_h and (b) Seebeck voltage, the inlet gas ratio is H₂:CO₂=1:1 for all the cases. It can be seen from Figure 6-10a that the CO₂ conversion of porous and non-porous samples are close to each other at the initial stage, then it increasing slightly while the conversion is larger for porous samples than that of non-porous ones. This complex relationship between T_h and CO₂ conversion is affected by multiple factors, Seebeck voltage and the porosity are considered to be the key factors among them. It was reported that the CO₂ conversion could be increased significantly by Seebeck voltage (Achour *et al.*, AEnM, 2018). Therefore, we are focusing on the effect of porosity to CO₂ conversion.

The introduction of porosity onto the sample surface brings two notable changes for BiCuSeO sample. First of all, it increases the surface area on which the catalytic chemical reaction occurs. However, it should be noted that the thermoelectric property of the porous sample are much inferior to the non-porous samples. This is also consistent with our observation from Figure 6-9b that the calculated Seebeck coefficient for the porous samples are lower than that of bulk samples. As the Seebeck voltage measured in our experiments is the potential difference across the whole sample, therefore the Seebeck coefficient calculated from it is only an average value.

The difference in CO₂ conversion of porous and non-porous samples can be explained by comparing the cases in Figure 6-10b. All cases show a similar trend, that is, the conversion increases with increasing temperature. The porous sample display a much higher CO₂ conversion than non-porous sample at the same Seebeck voltage. For example, the corresponding CO₂ conversion for samples BCSO 4B + 2P @1:1 and BCSO 4B + 2B @1:1 with Seebeck voltage of 60mV are 23% and 12%, respectively. Based on Equation 2-32:

$$Y = B \times A_s \times \exp(-(E_a + \gamma eV)/k_b T_h)$$

The conversion is decided by several variables, among them e and k_b are identical for all the reactions, while the independent constants B and γ is similar in given conditions, therefore we assumed that the CO₂ conversion Y is mainly

controlled by the Seebeck voltage V , working temperature T_h and the surface area A_s . Here V remain the same, but T_h for non-porous BCSO 4B + 2B is much smaller than that of porous BCSO 4B + 2P according to Figure 6-9a. As a result, porous BCSO 4B + 2P sample shows a smaller value of $\exp(-\gamma eV/k_b T_h)$ but a double overall CO_2 conversion, indicating that surface area A_s plays an important role. This might due to the enlargement of surface area helps to improve the physisorption of CO_2 on the catalytic surface and therefore led to the higher CO_2 conversion. Similar results can be obtained by comparing cases BCSO 2B + 2P @1:1 and BCSO 2B + 2B @1:1 as well.

We have seen that for the porous samples investigated so far, the higher surface area A_s is accompanied by a smaller Seebeck voltage, leading to a modest promotional effect. So both the boosting effect of high surface area and offset effect of low Seebeck voltage should be taken in to consideration when comparing the CO_2 conversion at a particular temperature. This also explains the small difference in CO_2 conversion between porous and non-porous samples at same T_h in Figure 6-10a. When the enhancement due to high surface area is offset by the weakening due to low Seebeck voltage, the CO_2 conversion was not significantly improved after all. We have to say that it also has a lot to do with the porous sample we have used in the tests. According to the BET test, the measured surface area of the porous sample is $5 \text{ m}^2/\text{g}$, which is only 3 times larger than the $1.6 \text{ m}^2/\text{g}$ of the non-porous sample.

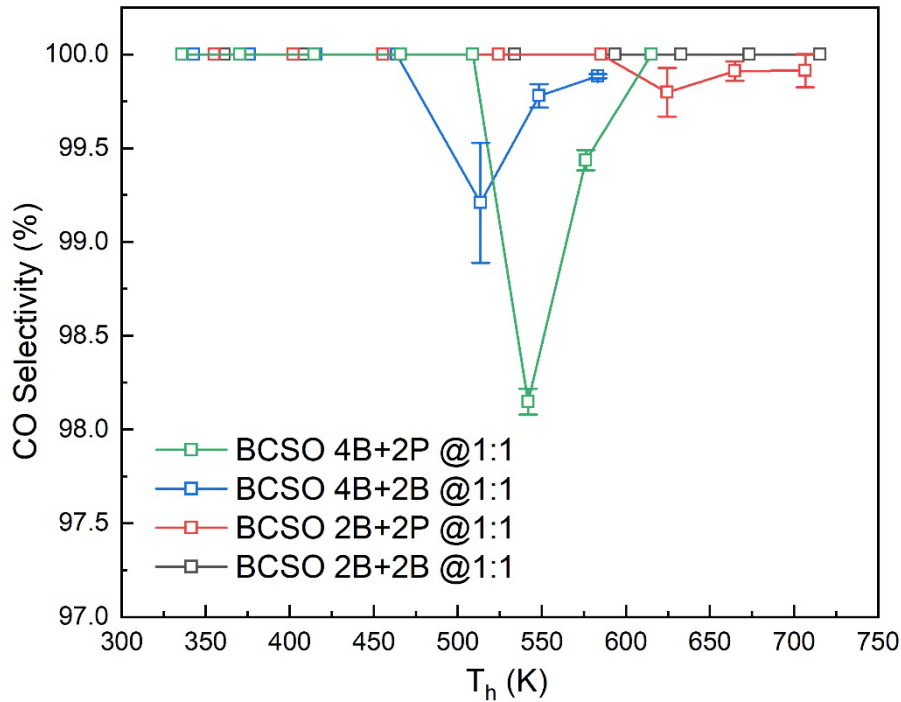


Figure 6-11 CO selectivity as a function of T_h for BCSO 4B + 2P @1:1, BCSO 4B + 2B @1:1, BCSO 2B + 2P @1:1 and BCSO 2B + 2B @1:1

The reaction products were found to be CO and CH_4 , Figure 6-11 shows the CO selectivity as a function of T_h . It can be seen that the CO selectivity is always greater than 98% for all these cases. This indicates that the low H_2 concentration in the inlet gas lead to a high CO selectivity. For samples BCSO 2B + 2B @1:1 and BCSO 2B + 2P @1:1, their CO selectivity is >99% within the whole temperature range. In terms of BCSO 4B + 2B @1:1 and BCSO 4B + 2P @1:1, the minimum value of their CO selectivity were achieved at 513K for BCSO 4B + 2B @1:1 (99.2%) and 541K for BCSO 4B + 2P @1:1 (98.1%). Then their CO selectivity increase to 100% at 624K.

6.3 Conclusion

By increasing the thickness of BiCuSeO samples, we successfully obtained large temperature difference ΔT and Seebeck voltage at a relatively low temperature T_h . And therefore greater CO_2 conversion was achieved by increasing sample thickness at a certain reaction temperature. In order to produce a sufficient Seebeck voltage at low reaction temperatures, it is suggested to use thicker BiCuSeO samples considering its low stability at

temperatures above 400°C.

The Sol-Gel method was applied to introduce porous structure onto the surface of BiCuSeO, which increased the surface area, but in contrast, worsening its Seebeck coefficient. The enhancement of higher surface area on its CO₂ conversion was partly offset by the poor Seebeck voltage compared with non-porous samples. But importantly, we have confirmed that the TEPOC dynamic equation $\ln(Y/Y_0) = -\gamma eV/k_b T_h$ is still valid for porous thermoelectric materials.

7 Thermoelectric $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ for the CO_2 mitigation reactions

7.1 Introduction

Chapters 4, 5 and 6 presented porous BiCuSeO for the application of TEPOC. The sol-gel prepared porous BiCuSeO have a surface area more than 10 times larger than their non-porous ones, but also possess much lower Seebeck coefficient. These lead to an improved catalytic promotional effect over the non-porous counterparts. However, those porous BiCuSeO displays much more severe high temperature instability problem than their non-porous counterparts. This makes it necessary to search for other oxide thermoelectric materials which can be used for TEPOC at high temperatures ($> 450^\circ\text{C}$). After a comprehensive survey of oxide thermoelectric materials, the $\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO) based materials attracted our attention.

$\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO) is a material that has gained much research interest in recent years due to its excellent thermoelectric properties. This oxide material exhibits a unique combination of high electrical conductivity and low thermal conductivity. The high electrical conductivity is attributed to the presence of Co^{3+} ions, while the low thermal conductivity is due to the structural complexity of the material. The combination of high temperature stability and outstanding thermoelectric properties makes $\text{Ca}_3\text{Co}_4\text{O}_9$ potentially one of the best candidates for TEPOC application at high temperatures. Moreover, the $\text{Ca}_3\text{Co}_4\text{O}_9$ phase maintained high stability in air at high temperatures (Lin *et al.*, 2007), which is a significant advantage compared with BiCuSeO. However, the Seebeck coefficient of $\text{Ca}_3\text{Co}_4\text{O}_9$ itself is not high enough for TEPOC investigation. The survey of doping elements indicated that the doping of Terbium into $\text{Ca}_3\text{Co}_4\text{O}_9$ could enhance its thermoelectric properties such as Seebeck coefficient (from $160\mu\text{V/K}$ to $320\mu\text{V/K}$ at 800K, Shrikant *et al.*, 2017), which meet our requirement. Thus the $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ (CTCO) with the best properties was chosen and its catalytic activities was further investigated in this chapter.

7.2 Result and discussion

7.2.1 Microstructural characterization of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples

7.2.1.1 XRD analysis of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples

The XRD pattern of the SPSed $\text{Ca}_3\text{Co}_4\text{O}_9$ sample shows a good match with the PDF#23-0110, and a few impurity peaks at around $2\theta=37$, which can be referred to Co_3O_4 , indicating that the sample has a well-ordered crystal structure. However, the XRD patterns of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ were apparently different from that of $\text{Ca}_3\text{Co}_4\text{O}_9$. First, the peak intensity at $2\theta=16$ and $2\theta=33$ varies significantly, suggesting that some transformation have occurred after Tb doping. Further analysis reveal the existence of phase Tb at $2\theta=28$ on XRD patterns of both SPS and SSR $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples. The intensity of impurity peaks for SSR $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ is slightly higher than that of SPSed sample, alongside this, there is barely any difference between XRD results of SPS and SSR $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples.

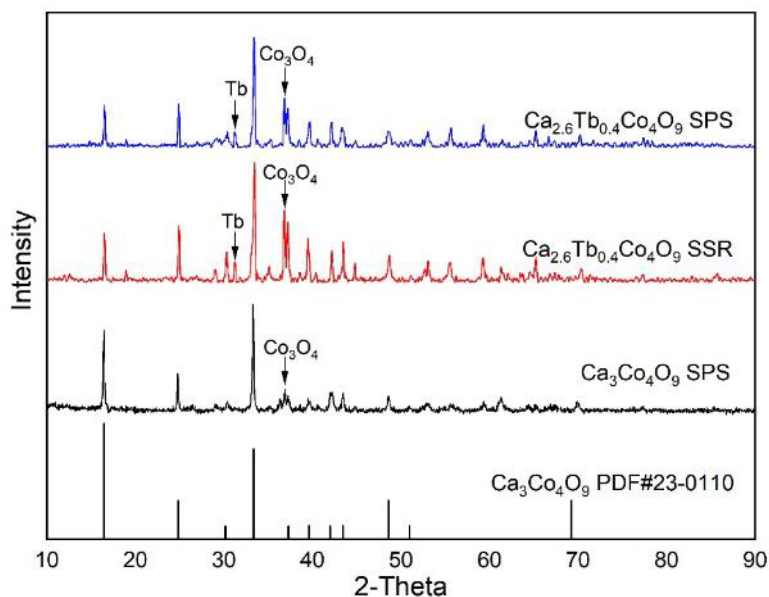


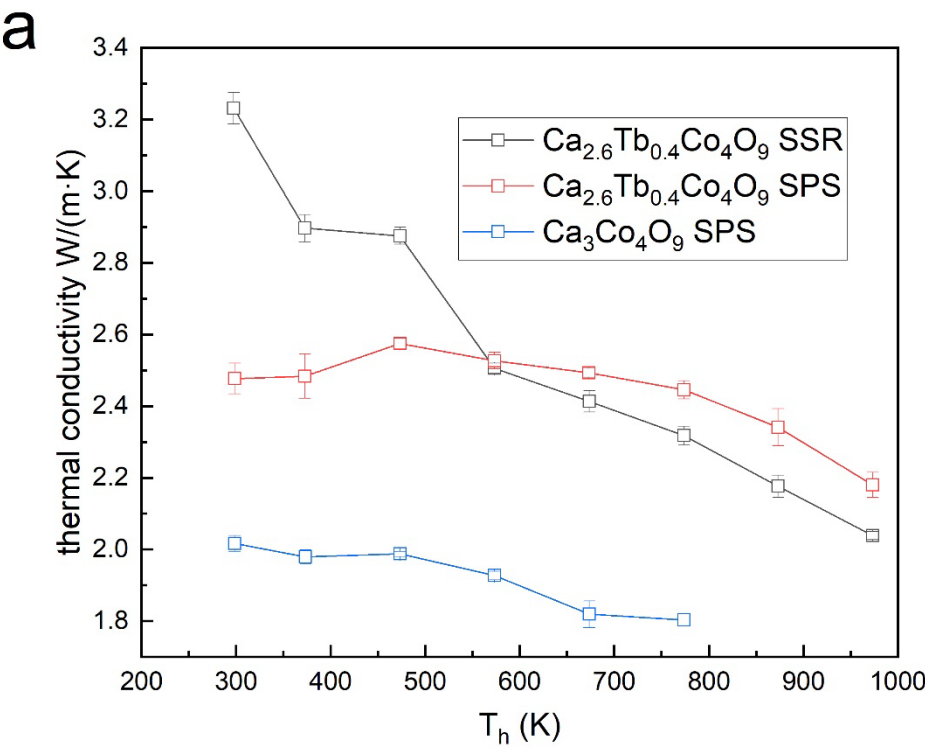
Figure 7-1 XRD pattern of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples

Figure 7-2 shows the thermal conductivity and Seebeck coefficient of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ prepared using spark plasma sintering and solid-state reaction methods. All the samples showed very small thermal conductivity, a comparison of these results reveals that Tb-doping increases the thermal

conductivity of CCO. At the same time, the Seebeck coefficient of CTCO significantly improved, the Seebeck coefficient of samples CTCO SPS and CTCO SSR reach 1.7 and 1.3 times of sample CCO at 723K, respectively. The room temperature electrical conductivity was measured and listed in Table 7-1. It can be clearly observed that the doping of Tb can improve the thermoelectric properties of CCO. Nonetheless, further studies and optimization are needed to fully characterize and understand the influence of Tb-doping on the thermoelectric performance of these samples.

Table 7-1 Room temperature electrical conductivity for $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ prepared using SPS and SSR

sample name	$\text{Ca}_3\text{Co}_4\text{O}_9$ SPS	$\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ SPS	$\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ SSR
Electrical			
conductivity (S/cm)	39.2	13.8	7.73



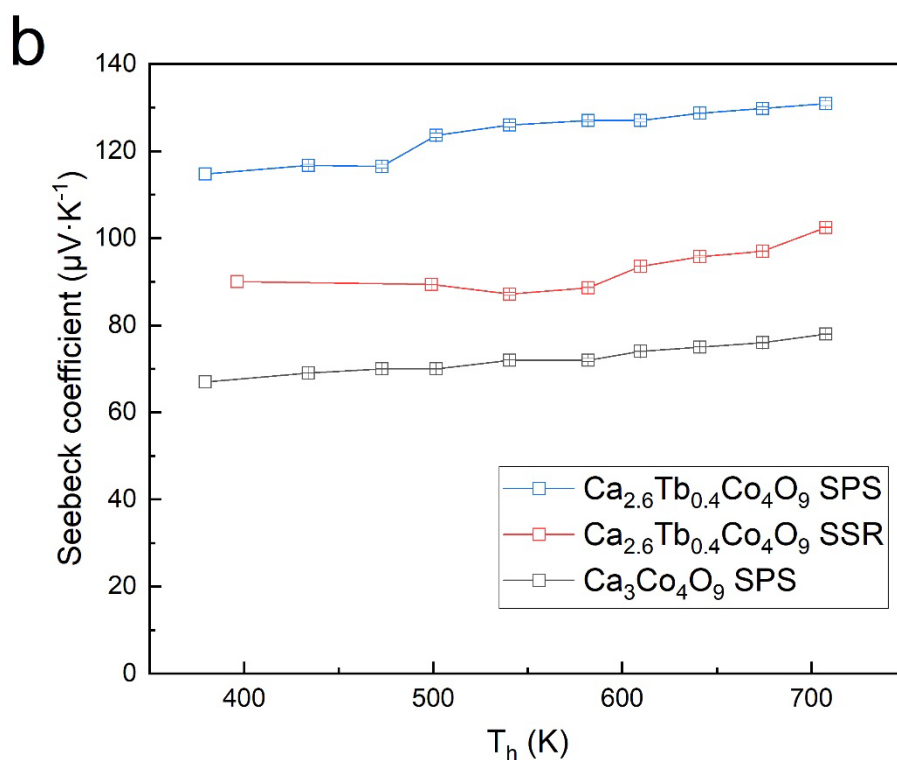


Figure 7-2 (a) thermal conductivity and (b) Seebeck coefficient of $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples

7.2.1.2 High temperature stability of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$

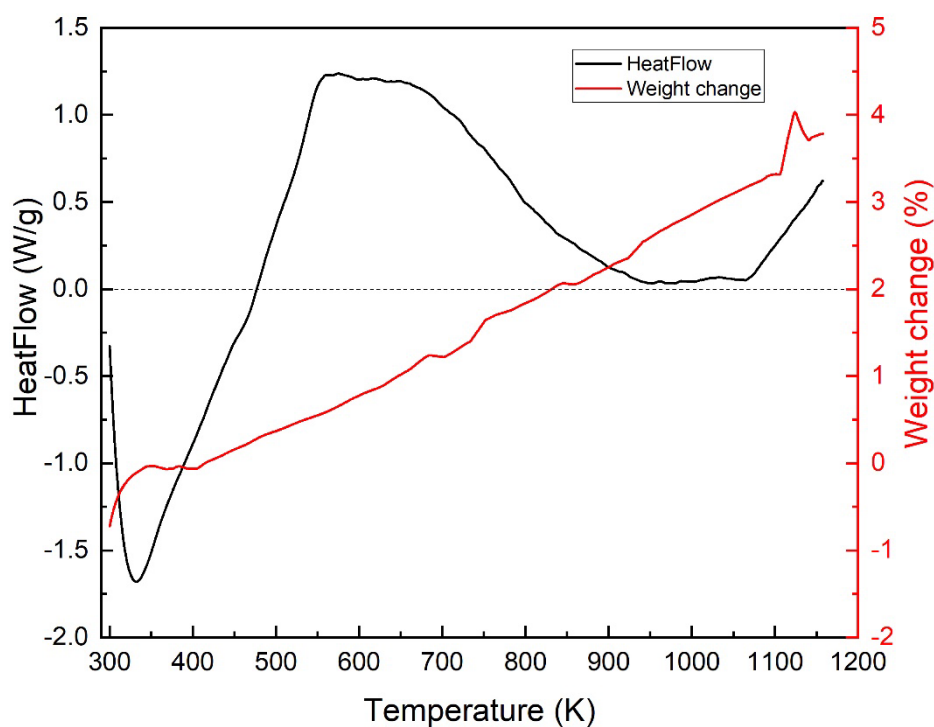


Figure 7-3 DSC and TG analysis of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ sample

High temperature thermal stability of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ sample was

characterized by DSC and TG, the test was conducted under a temperature range from 300K to 1173K in air. As shown in Figure 7-3, the exothermic peak between 300K and 473K on the heat flow curve was considered as a first-order phase transition (Yin *et al.*, 2017), at the same time the sample weight fluctuated around 0%. Subsequently, an upward trend on the heat flow curve have shown and a significant exothermic peak appeared between 473K and 1073K, which was believed to be caused by the absorption of oxygen from the air at high temperatures, resulting in a small amount of sample oxidation. The sample weight increased continued after 400K, with a maximum weight gain of 4%. Considering the fact that a second phase of Tb existed in the sample, this weight gain could be due to the oxidation of the second phase Tb. The test was terminated when the temperature reached 1173K, which was close to the melting point of Co_3O_4 . In summary, the $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ sample underwent a first-order phase transition at first and then slightly oxidized during the DSC test, which result in a weight gain of around 4%, indicating that the $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ sample behaved a relatively good stability under temperatures as high as 1173K.

7.2.2 The effect of sample thickness on the catalytic activity of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$

After the $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ sample was successfully prepared and characterized by XRD, the 2mm CTCO sample was applied in a catalytic chemical reaction to verify its catalytic ability. Then a series of CTCO samples with different thickness were prepared to investigate the effect of sample thickness on the catalytic activity of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$. Figure 7-4 present the relationship between (a) hot side temperature T_h and CO_2 conversion; (b) Seebeck voltage V and CO_2 conversion; (c) T_h and CO selectivity. The inlet gas ratio is $\text{H}_2:\text{CO}_2=3:1$ for all the cases.

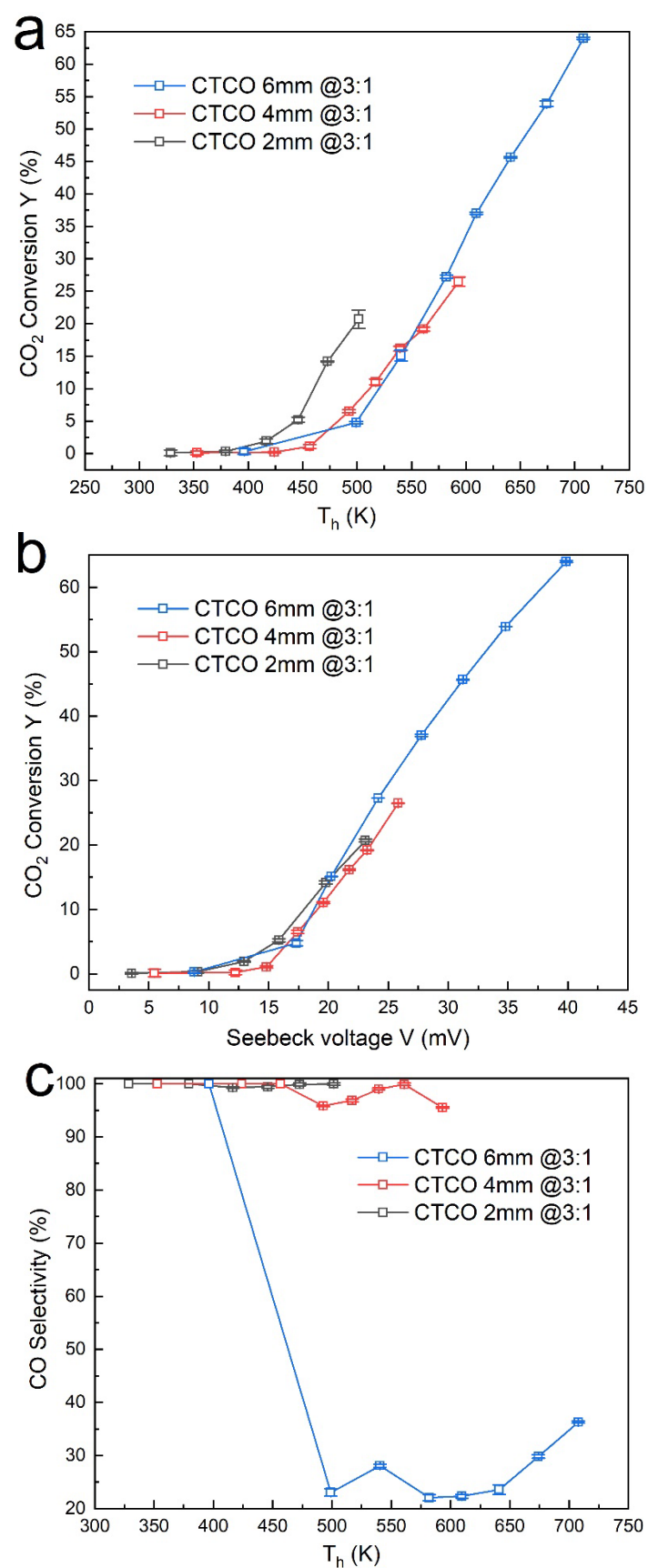


Figure 7-4 The relationship between (a) T_h and CO_2 conversion; (b) Seebeck voltage V and CO_2 conversion; (c) T_h and CO selectivity.

The CO₂ conversions were obtained as: 0.11% at 329K for CTCO 2mm @ 3:1, 0.11% at 353K for CTCO 4mm @ 3:1 and 0.31% at 396K for CTCO 6mm @ 3:1. The CO₂ conversions keep at a very small level (<1%) at temperatures below 400K, then they rise rapidly with temperature for all the cases and reach to 21% at 501K for CTCO 2mm @ 3:1, 27% at 582K for CTCO 4mm @ 3:1 and 64% at 707K for CTCO 6mm @ 3:1. Within the temperature range from 400K to 501K, the CO₂ conversion of CTCO 2mm @ 3:1 is significantly higher than that of CTCO 4mm @ 3:1 and CTCO 6mm @ 3:1 at the same temperature, while it is slightly different for 4mm and 6mm. For example, the CO₂ conversions at 480K are 16%, 5% and 4% for CTCO 2mm @ 3:1, CTCO 4mm @ 3:1 and CTCO 6mm @ 3:1, respectively. And they rise to 21%, 8% and 5% at 500K. The CO₂ conversion shows a linear relationship with temperature when it is higher than 1% for all the cases.

The Seebeck voltage - CO₂ conversion curves for three cases are much close to each other, as shown in Figure 7-4b. The CO₂ conversion is no more than 2% when the Seebeck voltage is smaller than 15mV, but it increases linearly with the Seebeck voltage. In the end, a CO₂ conversion of 64% was obtained with the Seebeck voltage of 40mV for the 6mm Ca_{2.6}Tb_{0.4}Co₄O₉ sample. Based on the discussion of the previous chapter, the surface area and Seebeck voltage should be considered as the main factors that affect the CO₂ conversion. The three samples here do not have any introduced porosity, all three cylindrical samples have the same diameter. The T_h and corresponding ΔT, V and S for these cases are listed in Table 7-2.

**Table 7-2 The preset temperatures of hot plate during heating process
and the corresponding T_h , ΔT , V and S**

	Hot plate temperature/K	573	773	823	873	913	953	993	1033
CTCO 2mm @ 3:1	Th/K	330	380	415	450	475	500		
	$\Delta T/K$	32	77	111	136	160	186		
	V/mV	4	9	13	16	20	23		
	$S/\mu V \cdot K^{-1}$	113	118	117	116	123	124		
CTCO 4mm @ 3:1	Th/K	350	425	455	485	515	540	570	600
	$\Delta T/K$	55	122	150	183	205	226	243	274
	V/mV	5	12	15	17	20	22	23	26
	$S/\mu V \cdot K^{-1}$	99	100	99	95	95	96	96	94
CTCO 6mm @ 3:1	Th/K	400	500	540	580	610	640	670	700
	$\Delta T/K$	98	194	232	273	297	326	359	389
	V/mV	9	17	20	24	28	31	35	40
	$S/\mu V \cdot K^{-1}$	90	89	87	89	94	96	97	102

It can be seen that for CTCO 2mm @ 3:1, the Seebeck coefficient S is about $120\mu V/K$, slightly higher than that of CTCO 4mm @ 3:1 ($98\mu V/K$) and CTCO 6mm @ 3:1 ($98\mu V/K$). Therefore in Figure 7-3a, a larger Seebeck voltage and a greater CO_2 conversion was obtained for sample CTCO 2mm @ 3:1 at the same T_h .

The main products of the chemical reaction are identified as CO and CH_4 . The CO selectivity also changes with sample thickness (Figure 7-3c). For CTCO 2mm @ 3:1, the CO selectivity sustained above 99% within the whole temperature range from 353K to 501K. But the CO selectivity decrease from 100% to 96% and 23% for CTCO 4mm @ 3:1 and CTCO 6mm @ 3:1 at 501K, respectively. Then their CO selectivity fluctuate and reach 95% at 593K for CTCO 4mm @ 3:1 and 36% at 707K for CTCO 6mm @ 3:1. It is noteworthy that CH_4 is more likely to be generated for samples with higher thickness under

the same temperature T_h . As shown in Figure 7-3c, the CO selectivity varies between 99% and 100% for CTCO 2mm @ 3:1, which indicate that only 1% of CH_4 is produced during the reaction. However, the lowest CO selectivity for CTCO 4mm @ 3:1 and CTCO 6mm @ 3:1 are 95% and 23%, respectively. That means the percentage of CH_4 in the product could be as high as 77% for 6mm CTCO sample.

To understand the complex behaviors of the CO and CH_4 formation at TE and RTE conditions, we need to know the thermodynamic equilibrium conversion (TEC) of CO_2 for the so called RWGS reaction with methanization (the CO_2 hydrogenation reaction would be carried out according to Equation 2-13, 2-14 and 2-15) or without methanization (the RWGS reaction would be carried out only according to Equation 2-13).



Figure 7-5 below shows the calculated TEC for the both cases (U. R. Bajirao, 2012). It can be seen that the CO formation (from RWGS reaction) increases monotonically with temperature. This feature allows us to ignore the reaction on the T_c surface as well as on the side wall, all the reaction can be considered taken place on the T_h surface. However, for CH_4 formation (from the methanization), the above simplification can no longer be allowed. Firstly, the TEC to CH_4 at low temperatures are very high. Secondly, under certain temperatures the TEC to CH_4 decreases with the increasing temperature. Because the methanization reactions occurs not only on the T_h surface but on all the surfaces, which including the T_c , T_h and the side wall. Therefore T_h alone cannot define the reaction rate for the CH_4 formation. The high selectivity for CH_4 formation under certain conditions and the TEC's complex temperature behavior make the quantitative analysis of the chemical reactions involved very difficult if not impossible.

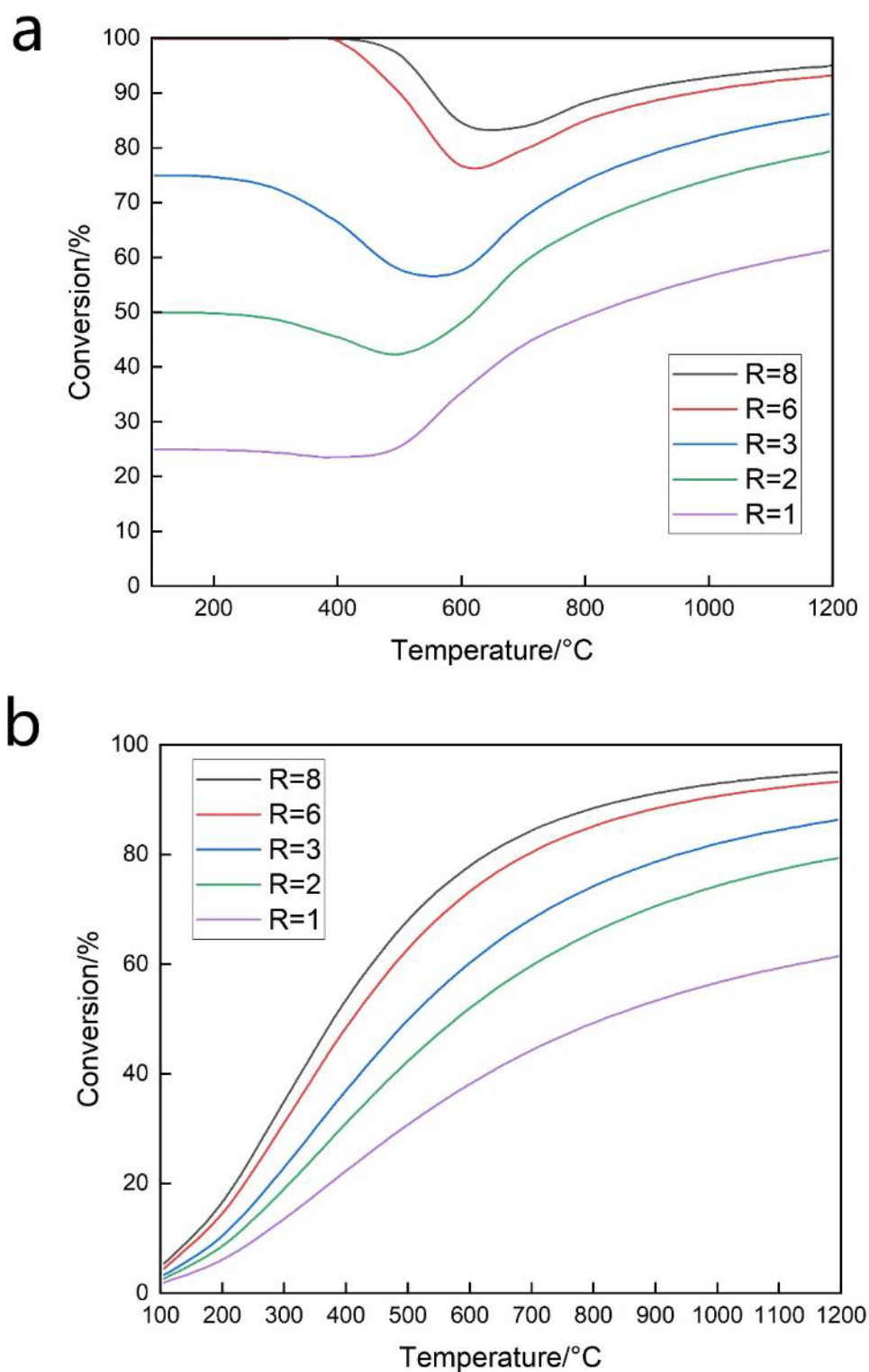
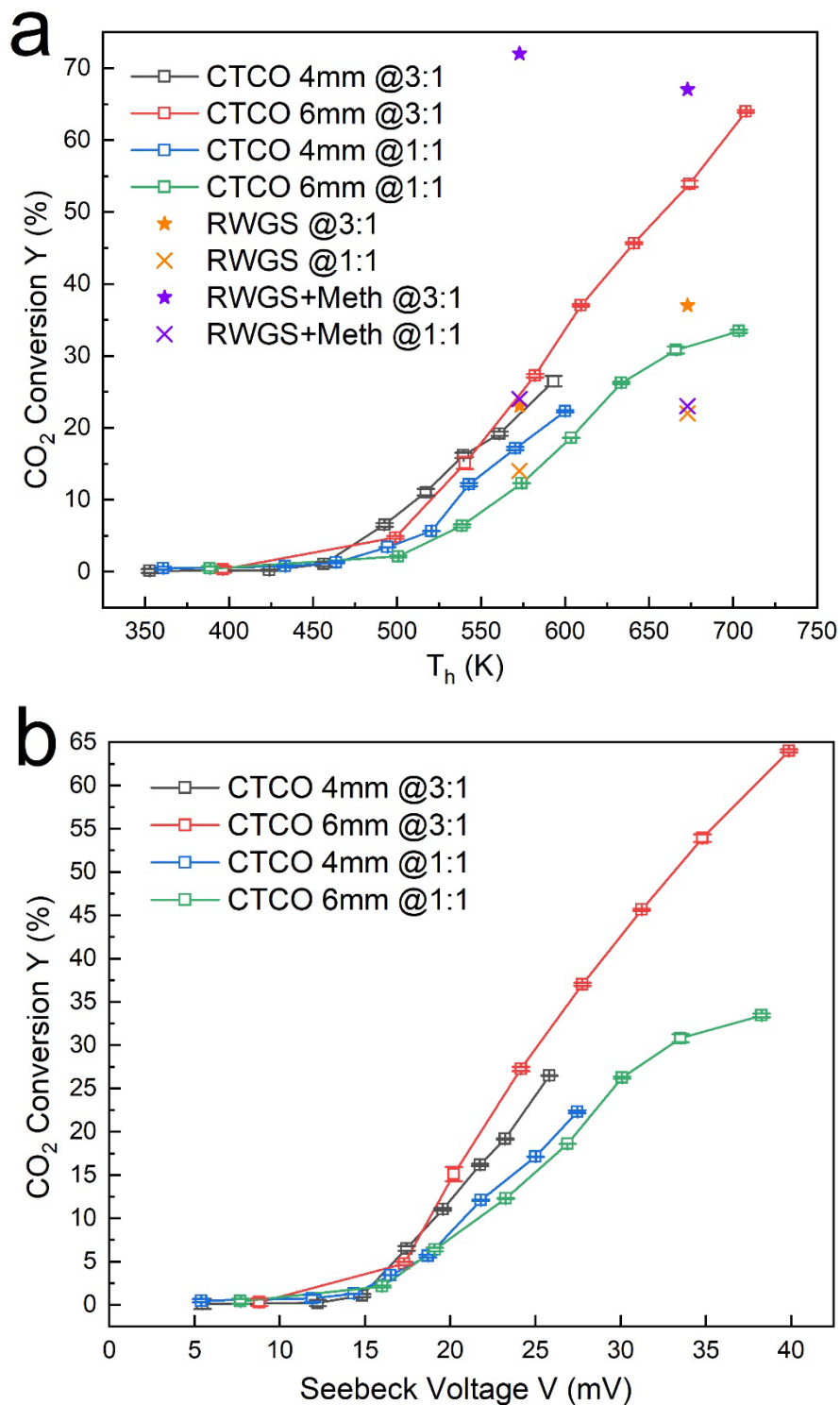


Figure 7-5 The calculated TEC for RWGS (a) with methanization and (b) without methanization (U. R. Bajirao, 2012)

In general, the significance of increasing the sample thickness is to increase the temperature difference ΔT between the cold side and the hot side of CTCO sample, which result in higher Seebeck voltage and CO_2 conversion. Besides,

thicker samples provide the possibility to achieve higher T_h at the same hot plate temperature (Table 7-2) under the current experimental condition. The reactions under inlet gas ratio $H_2:CO_2=1:1$ by using 4mm and 6mm CTCO samples are also investigated, the CO_2 conversion as a function of (a) T_h and (b) V are plotted in Figure 7-6.



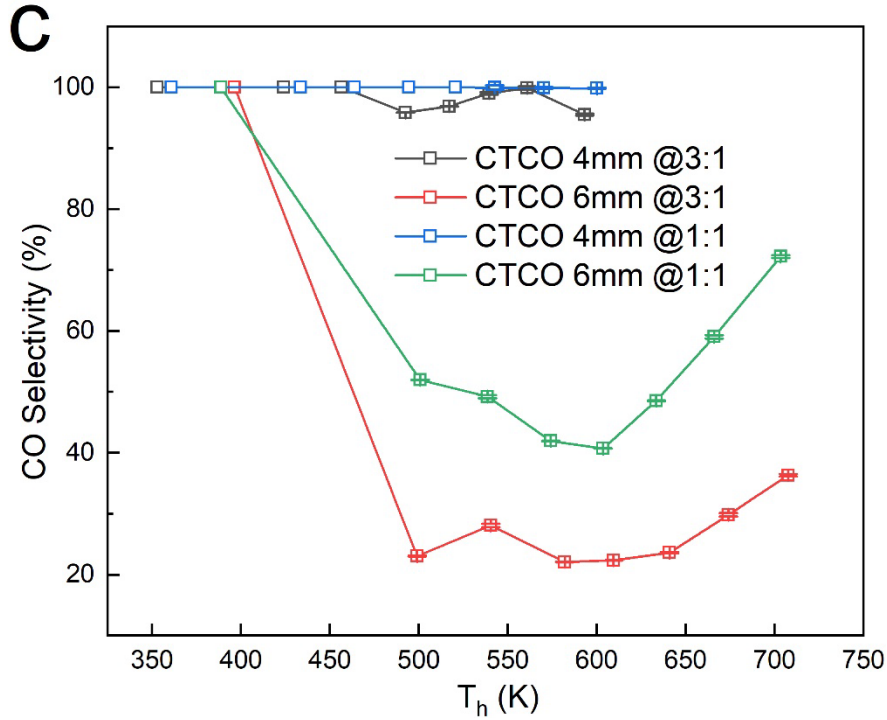


Figure 7-6 The CO₂ conversion as a function of (a) T_h and (b) V ; and the CO selectivity as a function of (c) T_h for 4mm and 6mm CTCO samples at H₂:CO₂=1:1 and 3:1

The CO₂ conversion increase gradually with the temperature T_h and Seebeck voltage V for CTCO 4mm @ 1:1 and CTCO 6mm @ 1:1. A small difference in CO₂ conversion could be observed between two curves in Figure 7-6a. For example the CO₂ conversion for CTCO 4mm @ 1:1 at 500K is 3% and it is 2% for CTCO 6mm @ 1:1. Then at 600K, they become 22% and 19% for 4mm and 6mm CTCO samples, respectively. For the purpose of comparison, the TEC values for RWGS reactions with methanization (namely RWGS+Meth @1:1 and @3:1, violet color) and without methanization (RWGS @1:1 and @3:1, orange color) at 573 K and 673K are also presented in Figure 7-6a. The main products of the four cases are identified as: CO (>99.8%) for CTCO 4mm @ 1:1; CO and CH₄ (>5%) for CTCO 4mm @ 3:1, CTCO 6mm @ 1:1 and CTCO 6mm @ 3:1, so the methanization need to be taken into consideration for the last three cases. The relationship between CO₂ conversion for each case and the TEC are discussed below: For CTCO 4mm @ 1:1 the CO₂ conversion is 17% at 573K, that is slightly higher than the TEC (14% for RWGS reaction

without methanization at $\text{H}_2:\text{CO}_2=1:1$); For CTCO 4mm @ 3:1, the CO_2 conversion is 22% at 573K, much lower than that of TEC for RWGS reaction with methanization at $\text{H}_2:\text{CO}_2=3:1$ (72%); The CO_2 conversion for CTCO 6mm @ 1:1 and CTCO 6mm @ 3:1 are 12% and 24% at 573K, the TEC with methanization here at $\text{H}_2:\text{CO}_2=1:1$ and 3:1 are 24% and 72%, respectively; However, the CO_2 conversion for CTCO 6mm @ 1:1 (32%) exceeded TEC (23%) at 673K, but for CTCO 6mm @ 1:1 (53%), it is still less than TEC (67%). It is clear that the CO_2 conversion of some cases have been above TEC. This is not surprising because similar results have been observed before (Oshima *et al.*, 2014). This agrees with the observation that an electric field (via the NEMCA mechanism) shifted the chemical equilibrium, increased the RWGS reaction, and decreased the (backward) water-gas shift reaction (Oshima *et al.*, 2014).

In Figure 7-6c, the CO selectivity of CTCO 4mm @ 1:1 is initially obtained as 100% at 360K and it decrease to 99.8% at 600K. For the CTCO 6mm @ 1:1, the CO selectivity starts decreasing at 396K and reaches its lowest value (40%) at 603K, then it goes up to 72% at 703K. It can be seen that the CO selectivity keeps at a low level within the temperature range 500K-600K for CTCO 6mm @ 1:1, in other words, CH_4 is more likely to be generated at these temperatures. Similar result was obtained from CTCO 6mm @ 3:1 in Figure 7-3c.

7.2.3 High CH_4 selectivity under Reduced Thermoelectric condition

In reduced thermoelectric (RTE) condition, the cold side of the sample was detached from the water cooling surface, thus a relatively small temperature difference across the sample is obtained which result in a small Seebeck voltage. In order to investigate the catalytic activity of $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples under RTE condition, we performed catalytic chemical reactions by using 2mm and 4mm CTCO samples under TE and RTE conditions, respectively. The CO_2 conversion as a function of (a) hot side temperature and (b) Seebeck voltage were plotted in Figure 7-7.

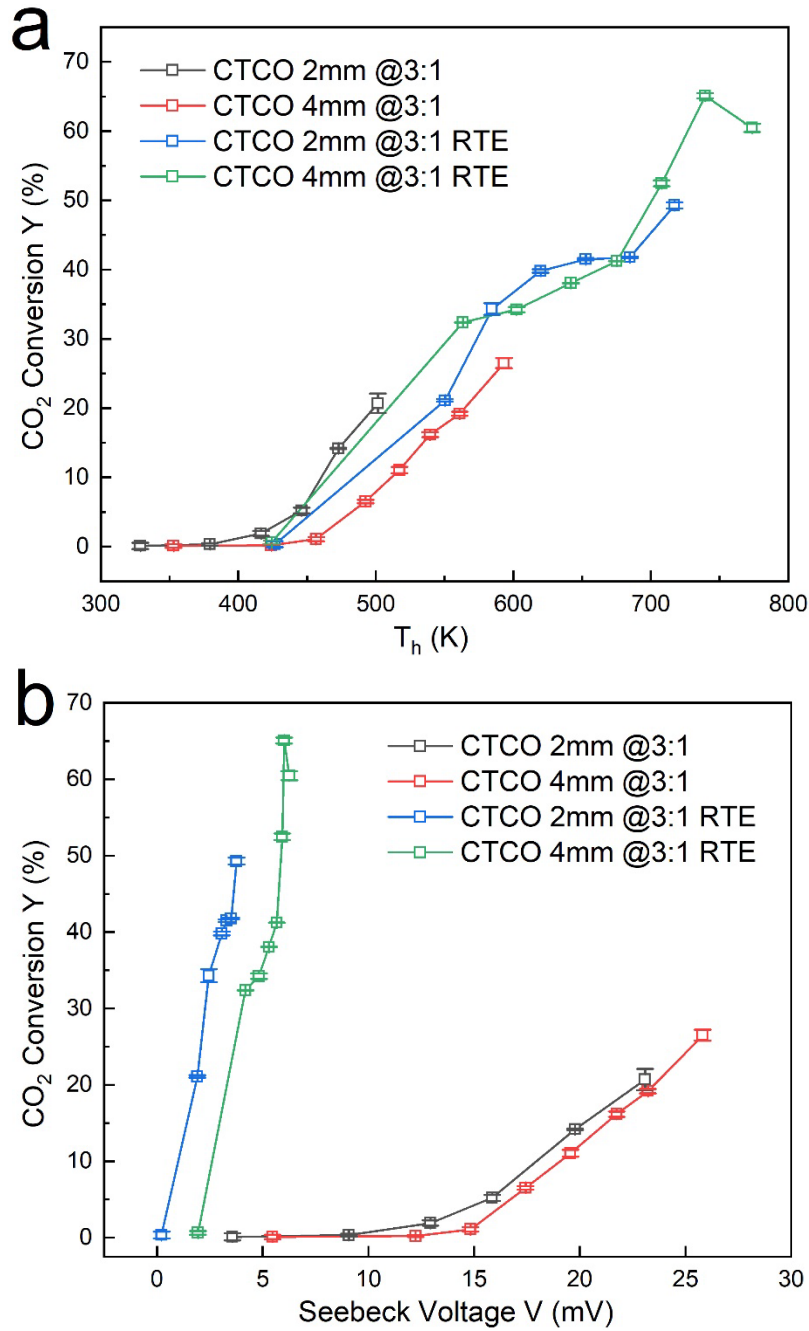
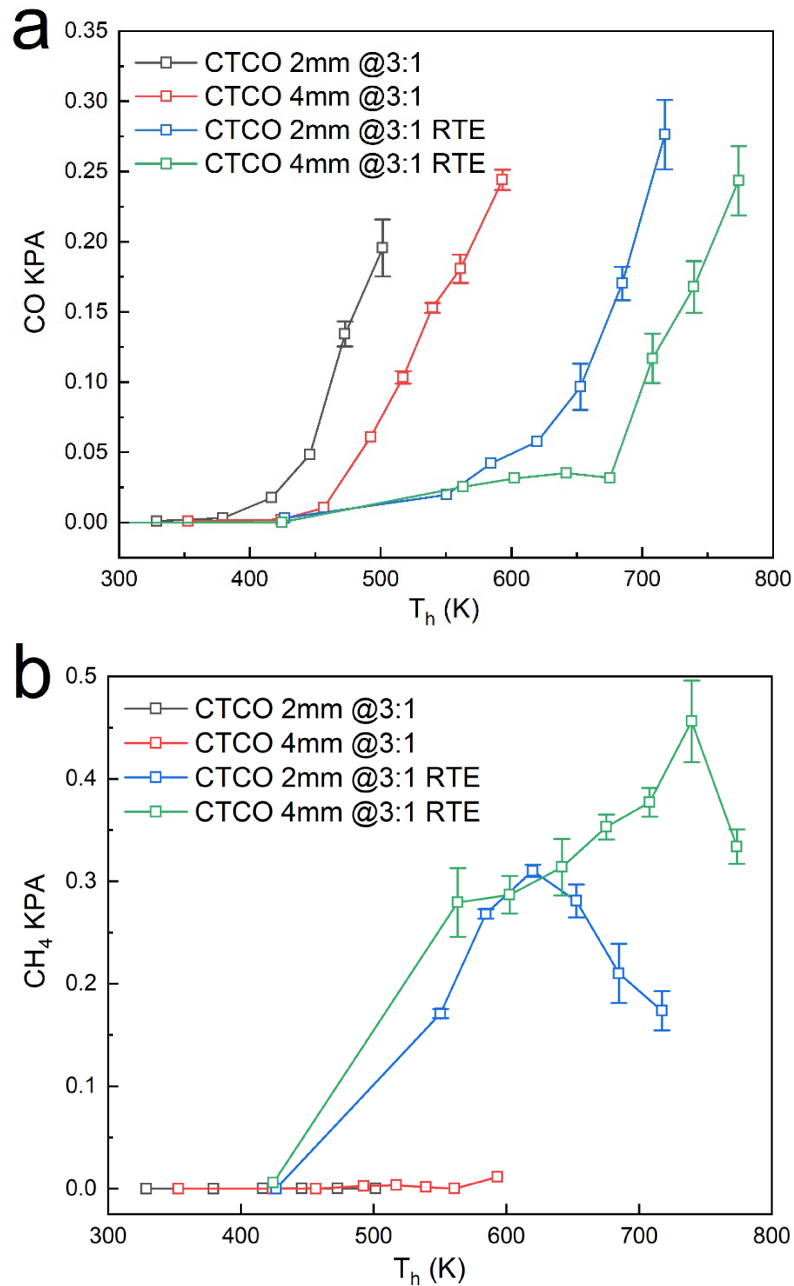


Figure 7-7 The CO₂ conversion as a function of (a) T_h and (b) V for 2mm and 4mm CTCO samples under TE and RTE conditions

The cases CTCO 2mm @ 3:1 TE and CTCO 4mm @ 3:1 TE were discussed in section 7.2.2, here we focus on cases CTCO 2mm @ 3:1 RTE and CTCO 4mm @ 3:1 RTE. The CO₂ conversion was firstly observed at T_h of 424K and 426K for CTCO 2mm @ 3:1 RTE (0.3%) and CTCO 4mm @ 3:1 RTE (0.6%), respectively. They become larger with the increasing temperature and reach 52.4% at 708K for CTCO 4mm @ 3:1 RTE and 49.3% at 717K for CTCO 2mm

@ 3:1 RTE. The TEC for RWGS reaction with methanization is above 80% at 750K at gas ratio $H_2:CO_2=3:1$, so the CO_2 conversion for two RTE cases doesn't exceed the TEC. Figure 7-7b shows that the CO_2 conversion increases rapidly with a small Seebeck voltage for these two RTE cases, this is quite different from those cases under TE conditions. The products for two RTE cases are CO and CH_4 as measured by GC. Thus we plot the relationship between CO/ CH_4 KPA (the amount of the CO/ CH_4) and T_h/V separately, as shown in Figure 7-8.



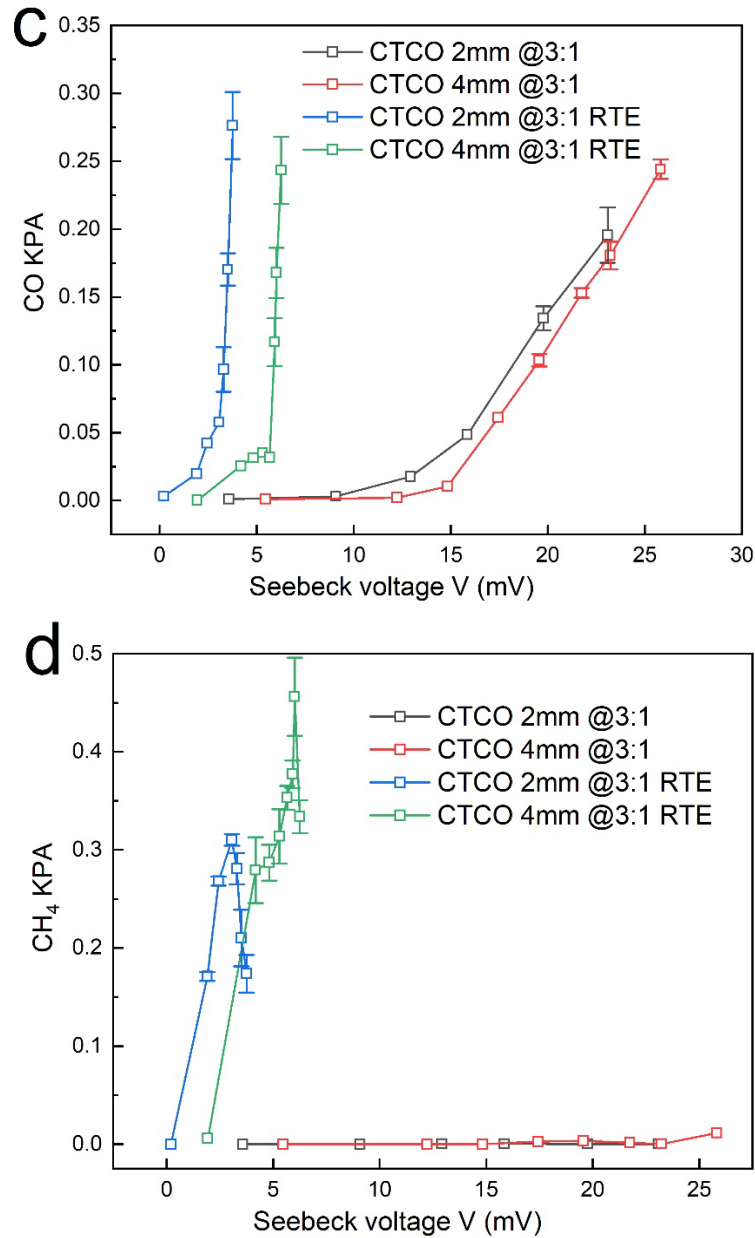


Figure 7-8 The relationship between (a) T_h – CO KPA; (b) T_h – CH₄ KPA; (c) V – CO KPA; and (d) V – CH₄ KPA for 2mm and 4mm CTCO samples under TE and RTE conditions

It can be seen that the CO KPA and CH₄ KPA appear simultaneously at 424K for CTCO 2mm @ 3:1 RTE and at 426K for CTCO 4mm @ 3:1 RTE. However, the CH₄ KPA increase significantly at temperatures from 425K to 600K for the two RTE cases, while their CO KPA just change slightly. For example, the CH₄ KPA for CTCO 2mm @ 3:1 RTE is 0.3 at 600K, 5 times larger than its CO KPA (0.05); the CH₄ KPA for CTCO 4mm @ 3:1 RTE is 0.28 at 600K, which is more than 9 times of CO KPA (0.03). Then the CH₄ KPA of CTCO 2mm @ 3:1 RTE

starts to fall at 620K whereas the CO KPA starts to rise rapidly. For CTCO 4mm @ 3:1 RTE, the CH₄ KPA reaches the highest value of 0.46 at 720K, while its CO KPA is increasing significantly from 675K. The main difference between these two RTE cases are considered to be caused by different Seebeck voltage. As discussed before, a sample with higher thickness is able to generate higher Seebeck voltage at the same temperature T_h . Thus the catalytic activity for 4mm CTCO sample should be greater than that of 2mm CTCO sample due to the high Seebeck voltage. As shown in Figure 7-8c and 7-7d, the maximum CO KPA are similar for CTCO 2mm @ 3:1 RTE (0.27) and CTCO 4mm @ 3:1 RTE (0.24). But the CH₄ KPA for CTCO 4mm @ 3:1 RTE is 0.45 at the Seebeck voltage of 6mV, which is about 1.5 times of that of CTCO 2mm @ 3:1 RTE (0.31 at the Seebeck voltage of 3mV). The product CO is present at both $V < 6.2\text{mV}$ and $V > 10\text{mV}$ under RTE and TE conditions (Figure 7-8c). Comparatively, CH₄ was produced at $V < 6.2\text{mV}$ under RTE condition but keep at an extremely low level (< 0.003) at $V < 23.2\text{mV}$ under TE condition (Figure 7-8d).

Table 7-3 The temperature T_h and the corresponding ΔT and V of 2mm and 4mm samples CTCO samples under TE and RTE conditions

2mm	Th/K	329	379	417	446	473	502				
CTCO	ΔT/K	32	77	111	136	160	186				
@ 3:1 TE	V/mV	3.6	9.1	12.9	15.9	19.8	23.1				
2mm	Th/K			427	550	585	620	653	685	717	
CTCO	ΔT/K			20	36	41	47	55	62	68	
@ 3:1 RTE	V/mV			0.2	1.9	2.4	3.1	3.3	3.5	3.8	
4mm	Th/K	353		424	457	493	517	540	561	593	
CTCO	ΔT/K	55		122	150	183	205	226	243	274	
@ 3:1 TE	V/mV	5.5		12.2	14.8	17.4	19.6	21.7	23.2	25.8	
4mm	Th/K			424	563	602	642	675	708	740	774
CTCO	ΔT/K			22	48	54	52	54	60	65	67
@ 3:1 RTE	V/mV			1.9	4.2	4.8	5.3	5.7	5.9	6.0	6.3

The boldface data in Table 7-3 can be used to support the discussion above. For RTE cases, the T_h can be as high as 740K while their Seebeck voltage still remains below 6.2mV. However for TE cases, their T_h should be lower than 380K at $V=6.2\text{mV}$, so it is reasonable to say that no CH_4 is generated at such a low temperature.

Based on the observation from Figure 7-8b, the CH_4 KPA started to increase significantly at $T_h > 423\text{K}$ for RTE cases, the correlating Seebeck voltage is 0.2mV for case CTCO 2mm @ 3:1 RTE (at 427K); 1.9mV for CTCO 4mm @ 3:1 RTE (at 424K) ; 12.9mV for CTCO 2mm @ 3:1 TE (at 417K) and 12.2mV for CTCO 4mm @ 3:1 TE (at 424K). At $T_h > 423\text{K}$, the RTE cases show a relatively low Seebeck voltage but a higher CH_4 KPA than that of TE cases under a similar T_h , which indicate that the CH_4 production is inhibited when the Seebeck voltage reaches a certain level. Comparatively, there is no sign of inhibition on the generation of CO. The CO KPA start to increase at about 423K for the two RTE cases and CTCO 4mm @ 3:1 TE. For CTCO 2mm @ 3:1 TE, CO is able to be generated at temperatures as low as 379K.

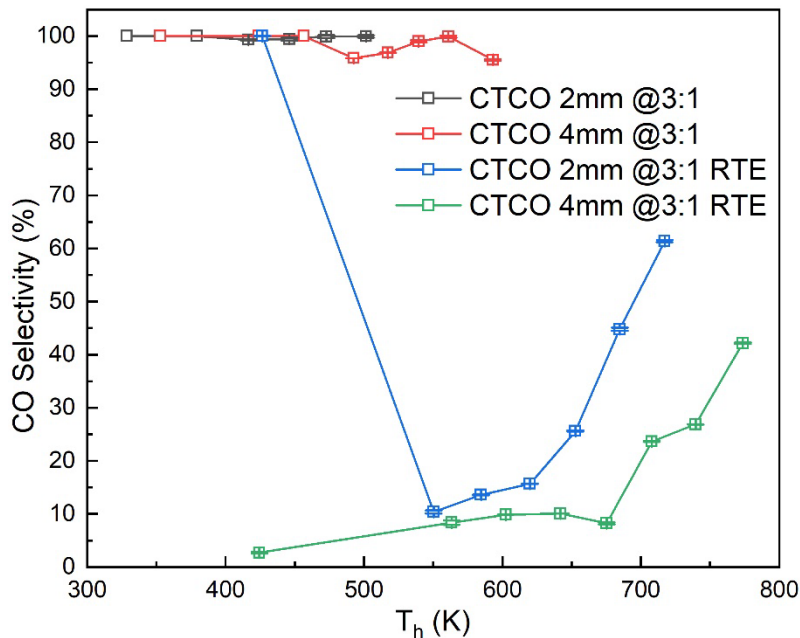


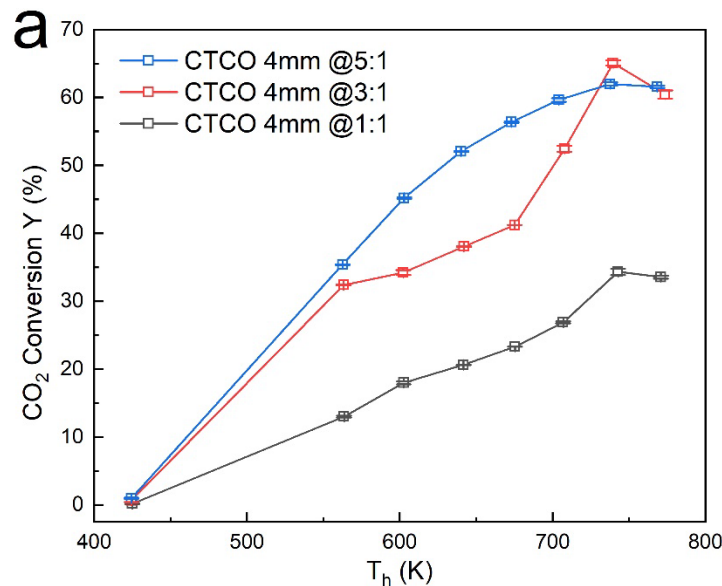
Figure 7-9 The CO selectivity as a function of T_h for 2mm and 4mm CTCO samples under TE and RTE conditions

The relationship between temperature T_h and CO selectivity is plotted in Figure

7-9. The products were initially detected as CO (100%) for CTCO 2mm @ 3:1 RTE at 427K and CO(3%) + CH₄(97%) for CTCO 4mm @ 3:1 RTE at 424K. It revealed that the CH₄ selectivity could be at least 90% within a wide temperature range of 424K-675K for 4mm CTCO sample under RTE condition, while CH₄ selectivity for 2mm CTCO sample is kept above 85% at 550K-620K as well. One possible reason for the high CH₄ selectivity performed under RTE conditions is the cobalt itself catalyze the CO₂ hydrogenation reaction without the enhancement of TEPOC. Generally speaking, TEPOC doesn't work under RTE conditions because the generated Seebeck voltage is limited, but the dispersed cobalt on the surface of CTCO sample might have a promoting onto the CO₂ reforming of CH₄ (Zhang *et al.*, 2014) under a certain condition. As a consequence, this provide a possibility to adjust the CO/CH₄ selectivity by change the cold side temperature of the sample in CO₂ hydrogenation reactions.

7.2.4 The effect of inlet gas ratio H₂:CO₂ on the catalytic activities of Ca_{2.6}Tb_{0.4}Co₄O₉ under Reduced Thermoelectric condition

In order to investigate the catalytic activity of Ca_{2.6}Tb_{0.4}Co₄O₉ sample at different inlet gas ratio under RTE condition. A series of CO₂ hydrogenation reactions were performed with H₂:CO₂=1:1, 3:1 and 5:1 using 4mm CTCO sample. The (a) CO₂ conversion; (b) CO selectivity; (c) CO KPA and (d) CH₄ KPA as a function of T_h were present in Figure 7-10.



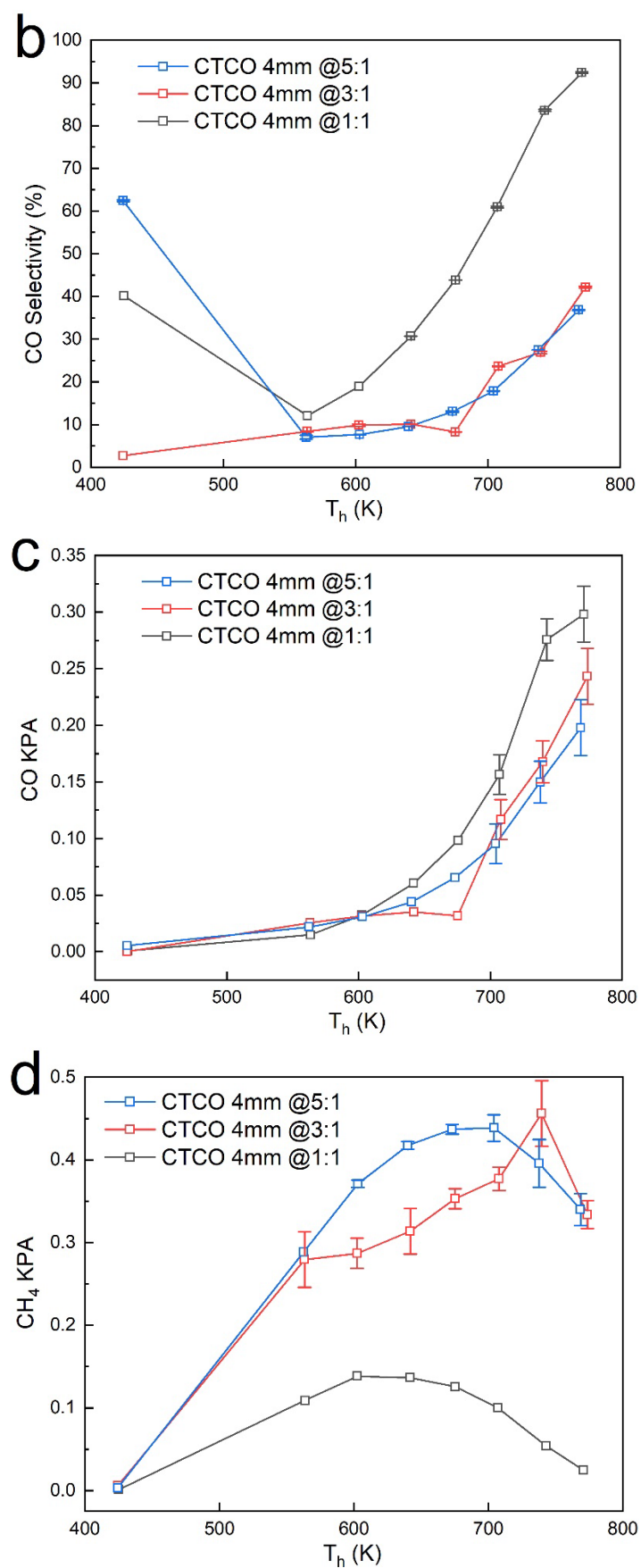


Figure 7-10 The (a) CO₂ conversion; (b) CO selectivity; (c) CO KPA and (d) CH₄ KPA as a function of T_h

The reaction products CO and CH₄ are detected at 424K for all three cases and their CO₂ conversion increase gradually with increasing temperature, as shown in Figure 7-10a. The CO₂ conversion reach the maximum values of 34% for CTCO 4mm @ 1:1 RTE at 743K; 65% for CTCO 4mm @ 3:1 RTE at 740K and 62% for CTCO 4mm @ 5:1 RTE at 739K, and then show a downward trend until the end of the reaction. An obvious difference in CO selectivity could be observed at 424K in Figure 7-10b, the lowest CO selectivity of 3% is obtained at H₂:CO₂=3:1 while they are 40% and 62% at H₂:CO₂=1:1 and 5:1, respectively. The CO selectivity for CTCO 4mm @ 1:1 RTE and CTCO 4mm @ 5:1 RTE reach the minimum values of 12% and 7% at 563K, then rise to 92% and 37% at 770K. Generally speaking, the CTCO 4mm @ 5:1 RTE shows the lowest CO selectivity of <10% at 424K-563K among these three cases. At T_h>563K, the CO selectivity of CTCO 4mm @ 1:1 RTE increase significantly from 12% to 92%, in the meantime a clear upward trend in CO selectivity is showed for the other two cases. The dramatic change in CO selectivity with inlet ratio could possibly be explained by the observation of Bredy *et al.*, they found that the selectivity to CH₄ appears to increase monotonously with decreasing surface coverage of CO (Bredy *et al.*, 2022). Whereas the increasing proportion of CO₂ within the inlet gas will mainly lead to the decrease of CO coverage. Therefore the CO selectivity varied with different inlet ratio.

The CO KPA of three cases exhibited a similar tendency, they increase steadily with temperature from 300K to 600K and all reach 0.03 at 600K. At T_h>600K, the CO KPA for CTCO 4mm @ 1:1 RTE and CTCO 4mm @ 5:1 RTE rise rapidly with temperature but the curve of CTCO 4mm @ 3:1 RTE fluctuated at 600K-675K, the maximum values are obtained as: 0.3 for CTCO 4mm @ 1:1 RTE at 771K; 0.24 for CTCO 4mm @ 3:1 RTE at 773K and 0.2 for CTCO 4mm @ 5:1 RTE at 769K. In addition, it can be concluded from Figure 7-10c that the CO KPA decrease with the increasing inlet gas ratio H₂:CO₂ from 1:1 to 5:1 at T_h>700K. As for CH₄ KPA in Figure 7-10d, the reaction product CH₄ were initially obtained at 424K for all the cases, their CH₄ KPA increase at first and

then decrease with increasing temperature. The CH₄ KPA for CTCO 4mm @ 1:1 RTE reaches its maximum value of 0.14 at 603K and drop to 0.02 at 770K. The maximum values of CH₄ KPA for CTCO 4mm @ 3:1 RTE and CTCO 4mm @ 5:1 RTE are 0.44 (at 704K) and 0.46 (at 740K). Although those values drop a bit afterwards, they are still as high as 0.34 at about 770K. In summary, 4mm Ca_{2.6}Tb_{0.4}Co₄O₉ sample displays greater CO₂ conversion at inlet gas ratio H₂:CO₂>1:1, especially at temperatures over 600K. The CO selectivity for cases with different inlet gas ratio varies with temperature while a relatively low CO selectivity of 20% can be obtained at 550K-600K for all of them. In the end, the CO selectivity for CTCO 4mm @ 1:1 RTE goes up to 92% while they remain at 40%±2% for CTCO 4mm @ 1:1 RTE and CTCO 4mm @ 1:1 RTE at 770K. In terms of the reaction products, the CO KPA for three cases rise gradually with temperature but their CH₄ KPA decrease significantly at the highest T_h compared with the maximum values. It can be seen in Figure 7-10d, that the CH₄ KPA for CTCO 4mm @ 1:1 RTE is only 0.02 at 770K, which indicate the generation of CH₄ is strongly inhibited at this temperature.

7.3 Conclusion

A series of Ca_{2.6}Tb_{0.4}Co₄O₉ samples with different thickness were successfully prepared by doping Tb into Ca₃Co₄O₉ and its feasibility for TEPOC application was verified by conducting CO₂ hydrogenation reactions using CTCO as a catalyst. The high catalytic efficiency of CTCO suggests that it can be a new choice for high-temperature TEPOC applications. When catalyzed by CTCO, the product of CO₂ hydrogenation reactions can be switched between CO and CH₄ just by changing the cold side temperature. Besides, the CO₂ conversion rate could be significantly improved by increasing the sample thickness for our reaction chamber set-up. The maximum CO₂ conversion rate can reach to 64% using 6mm CTCO as a catalyst at 700K and an inlet gas ratio H₂:CO₂=3:1, while the CO selectivity is 72%. In addition, it should be noted that under RTE conditions, a relatively high CH₄ selectivity is obtained. The CH₄ selectivity is

kept above 70% in the range of 550-650K at $\text{H}_2:\text{CO}_2=1:1$, 3:1 and 5:1, while the maximum CH_4 selectivity can be as high as 92%. The results above suggest an enormous potential of applying CTCO into catalytic chemical reactions at high temperatures.

8 Conclusions

In summary, the following objectives have been fulfilled:

- By utilizing the Sol-Gel method as well as the addition of fine PS powder, porous BiCuSeO thermoelectric materials have been produced successfully. The sol-gel method enables a porous coating to the surface of non-porous TE samples. Both techniques produced porous samples with significant porosity and BET surface area more than 10 times larger than the non-porous counterparts. In fact, the porosity as high as 37% and 22% was attained by adding 20wt% PS and applying the sol-gel method, respectively. The BET surface area of the two samples were 17.1 and 13.9 times higher than that of the non-porous sample, respectively. On the other hand, the porous BiCuSeO showed more severe instability problems at temperatures higher than 400°C than their non-porous counterparts.
- A 3D model of reaction chamber with thermoelectric sample inside was created using the AutoCAD software, it was then introduced into Ansys 2021R to carry out a transient thermal simulation in order to understand the temperature evolution of the thermoelectric materials during a practical chemical reaction run. The parameters and boundary conditions of the simulation was obtained through a series of controlled tests. In addition, the accuracy of the simulation was validated by comparing the simulated temperatures with the actual temperature measured during experiments.
- The temperature distributions of thermoelectric BiCuSeO samples with thickness of 2mm, 4mm, 6mm, 8mm and 10mm were simulated through Ansys 2021R. The results indicating that the temperature difference between the cold side and hot side of the BiCuSeO sample increase significantly with the increasing thickness of the sample. This result is then used to guide the design of the actual catalytic chemical reactions. By

increasing the thickness of BiCuSeO samples, a larger temperature difference and Seebeck voltage across the sample was obtained at a fixed reaction surface temperature T_h , therefore led to a greater CO₂ conversion. For example at $T_h=600$ K, the CO₂ conversion of the 6mm BiCuSeO sample is 29% with an inlet gas ratio H₂:CO₂=4:1, but much lower 8% and 4% for 4mm and 2mm BiCuSeO samples.

- Although porous TE materials BiCuSeO have higher surface area, they also have much lower Seebeck coefficient. The combined effects of these two factors lead to a modest increase of the catalytic activity of the porous TE as compared to the non-porous counterparts at the same reaction temperature T_h . For example, the CO₂ conversion rate of porous BiCuSeO sample prepared through Sol-Gel method is similar to that of non-porous BiCuSeO sample under the same T_h . However, they are very different under the same Seebeck voltage V . The CO₂ conversion for porous sample BCSO 4B + 2P @1:1 is 24.55% at a Seebeck voltage of 70mV, which is more than 5 times higher than 4.2% of the non-porous sample BCSO 4B + 2B @1:1. Moreover, the CO selectivity is not much affected by the porous surface structure.
- The stacked samples was utilized in TEPOC. It has been demonstrated that TEPOC can also be realized by connecting two (or more) thermoelectric materials in series. The Seebeck voltages and CO₂ conversion rates of a single sample and stacked samples with an equivalent thickness were compared, and the difference was confirmed to be very small, less than 5%. This enables the fabrication of the bulk and surface thermoelectric materials used in TEPOC to be separated.
- For porous thermoelectric materials the previously observed TEPOC dynamic equation $\ln(Y/Y_0) = -\gamma eV/k_b T_h$ is still valid if all the chemical reactions are carried out at the T_h surface.

- Thermoelectric $\text{Ca}_3\text{Co}_4\text{O}_9$ and $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples were successfully prepared using spark plasma sintering and solid-state reaction methods. Tb-doping increases the Seebeck coefficient and thermal conductivity of the samples. The Seebeck coefficient of samples CTCO SPS and CTCO SSR reached 1.7 and 1.3 times of that of the CCO at 723K, respectively.
- A series of CTCO samples with different thickness were successfully prepared and its feasibility for TEPOC application was verified by applying it into CO_2 hydrogenation reactions. A maximum CO_2 conversion rate of 64% is obtained from 6mm CTCO sample at 700K and an inlet gas ratio $\text{H}_2:\text{CO}_2=3:1$, the CO selectivity is 72%. CCO and CTCO showed better stability than BiCuSeO at temperatures higher than 400°C
- Under RTE conditions, a relatively high CH_4 selectivity was obtained from the CO_2 hydrogenation reactions catalyzed by CTCO. The CH_4 selectivity is kept above 70% in the range of 550-650K at $\text{H}_2:\text{CO}_2=1:1$, 3:1 and 5:1, while the maximum CH_4 selectivity can be as high as 92%.

In summary, all the objectives of the project have been fulfilled and the aim of the project, i.e., to develop high surface area thermoelectric materials to work at highest possible temperature difference in a particular reaction chamber, has been achieved.

9 Recommendations for Future Work

- Our current heat source, the hot plate, has a maximum working temperature of 1023K, which led to a maximum temperature T_h of 823K for a 6mm TE samples fixed within it. With a thicker sample of 10mm, its ideal T_h will increase to 873K-923K. Alternatively, a newly designed reaction chamber with higher heating efficiency would be suggested to increase the temperature difference between the hot and cold surfaces of the sample, which leading to higher Seebeck voltage and reaction rates according to the theoretical equation of TEPOC.
- Further investigation on BiCuSeO samples with different porosity. A finer particle size of PS or a modified Sol-Gel parameter would be suggested to achieve greater meso-porosity or micro-porosity. Therefore a systematic study on the variation of catalytic activity at different BET surface area could be performed. Additionally, the current partial pressure of CO_2 in the reactant gas is only 1%. If we can obtain a BET surface area large enough, such samples with extremely high BET surface area could be applied to catalyze reactant gas which containing higher partial pressures of H_2 and CO_2 .
- In this study, catalytic behaviors of thermoelectric $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples with thicknesses ranging from 2mm to 6mm were investigated. It would be very interesting to investigate the impact of sample thickness and porosity on CO_2 conversion and product selectivity by prepare and further test 8-12mm $\text{Ca}_{2.6}\text{Tb}_{0.4}\text{Co}_4\text{O}_9$ samples with relatively high porosity. This would also contribute to a better understanding of the complex behaviors of CO and CH_4 formation under TE and RTE conditions.
- Based on the research mentioned above, samples with high catalytic activity can also be applied to catalytic chemical other than the CO_2 hydrogenation reactions, such as the reduction of NO_x , the oxygen

evolution reaction (OER) and the hydrogen evolution reaction (HER) in water splitting, to demonstrate the universal applicability of TEPOC.

10 REFERENCES

- Achour, A., Chen, K., Reece, M. J., Huang, Z. (2017). Tuning of Catalytic Activity by Thermoelectric Materials for Carbon Dioxide Hydrogenation. *Advanced Energy Materials*, 8(5), 1701430.
- Achour, A., Liu, J., Peng, P., Shaw, C., Huang, zhaorong. (2018). In-Situ Tuning of Catalytic Activity by Thermoelectric Effect for Ethylene Oxidation. *ACS Catalysis*, 8, 10164-10172.
- Achour, A., Chen, K., Reece, M. J., Huang, Z. (2018). Enhanced thermoelectric performance of Cs doped Bi₂Se₃ prepared through eco-friendly flux synthesis, *Journal of Alloys Compounds*, 735, 861-869.
- Ahmad, S., Singh, A., Bohra, A., Basu, R., Bhattacharya, S., Bhatt, R., Gupta, S. K. (2016). Boosting thermoelectric performance of p-type SiGe alloys through in-situ metallic YSi₂ nano-inclusions. *Nano Energy*, 27, 282–297.
- Amadeo, N. (1995). Hydrogen production from the low-temperature water-gas shift reaction: Kinetics and simulation of the industrial reactor. *International Journal of Hydrogen Energy*, 20(12), 949–956.
- Aitbekova, A., Wu, L., Wrasman, C. J., Boubnov, A., Hoffman, A. S., Goodman, E. D., ... Cargnello, M. (2018). Low-temperature restructuring of CeO₂-supported Ru nanoparticles determines selectivity in CO₂ catalytic reduction. *Journal of the American Chemical Society*.
- Banik, A., Shenoy, U. S., Anand, S., Waghmare, U. V., Biswas, K. (2015). Mg Alloying in SnTe Facilitates Valence Band Convergence and Optimizes Thermoelectric Properties. *Chemistry of Materials*, 27(2), 581–587.
- Barreteau, C., Pan, L., Amzallag, E., Zhao, L. D., Bérardan, D., Dragoe, N. (2014). Layered oxychalcogenide in the Bi–Cu–O–Se system as good thermoelectric materials. *Semiconductor Science and Technology*, 29(6),

064001.

Basu, R., Bhattacharya, S., Bhatt, R., Roy, M., Ahmad, S., Singh, A., Gupta, S. K. (2014). Improved thermoelectric performance of hot pressed nanostructured n-type SiGe bulk alloys. *Journal of Materials Chemistry A*, 2(19), 6922.

Bathula, S., Jayasimhadri, M., Gahtori, B., Singh, N. K., Tyagi, K., Srivastava, A. K., Dhar, A. (2015). The role of nanoscale defect features in enhancing the thermoelectric performance of p-type nanostructured SiGe alloys. *Nanoscale*, 7(29), 12474–12483.

Bathula, S., Jayasimhadri, M., Gahtori, B., Kumar, A., Srivastava, A. K., Dhar, A. (2017). Enhancement in thermoelectric performance of SiGe nanoalloys dispersed with SiC nanoparticles. *Physical Chemistry Chemical Physics*, 19(36), 25180–25185.

Beck, G., Fischer, H., Mutoro, E., Srot, V., Petrikowski, K., Tchernychova, E. Janek, J. (2007). Epitaxial Pt(111) thin film electrodes on YSZ(111) and YSZ(100) — Preparation and characterisation. *Solid State Ionics*, 178(5-6), 327–337.

Bhardwaj, A., Rajput, A., Shukla, A. K., Pulikkotil, J. J., Srivastava, A. K., Dhar, A., Budhani, R. C. (2013). Mg₃Sb₂-based Zintl compound: a non-toxic, inexpensive and abundant thermoelectric material for power generation. *RSC Advances*, 3(22), 8504.

Bhaskar, A., Lai, R.-T., Chang, K.-C., Liu, C.-J. (2017). High thermoelectric performance of BiCuSeO prepared by solid state reaction and sol-gel process. *Scripta Materialia*, 134, 100–104.

Biswas, K., He, J., Zhang, Q., Wang, G., Uher, C., Dravid, V. P., Kanatzidis, M. G. (2011). Strained endotaxial nanostructures with high thermoelectric Figure of merit. *Nature Chemistry*, 3(2), 160–166.

Biswas, K., He, J., Blum, I. D., Wu, C.-I., Hogan, T. P., Seidman, D. N., Kanatzidis, M. G. (2012). High-performance bulk thermoelectrics with all-scale hierarchical architectures. *Nature*, 489(7416), 414–418.

Bittner, M., Kanas, N., Hinterding, R., Steinbach, F., Groeneveld, D., Wemhoff, P., Feldhoff, A. (2018). Triple-phase ceramic 2D nanocomposite with enhanced thermoelectric properties. *Journal of the European Ceramic Society*.

Bittner, M., Kanas, N., Hinterding, R., Steinbach, F., Räthel, J., Schrade, M., Feldhoff, A. (2019). A comprehensive study on improved power materials for high-temperature thermoelectric generators. *Journal of Power Sources*, 410-411, 143–151.

Bobadilla, L. F., Svetlana, I., Luis, S. J., Odriozola José Antonio, Atsushi, U. (2018). Unravelling the role of oxygen vacancies in the mechanism of the reverse water-gas-shift reaction by operando drifts and uv-vis spectroscopy. *ACS Catalysis*, acscatal.8b02121-.

Boz, Z., Erdogan, F., Tutar, M. (2014). Effects of mesh refinement, time step size and numerical scheme on the computational modeling of temperature evolution during natural-convection heating. *Journal of Food Engineering*, 123, 8-16.

Bredy, P., Farrusseng, D., Schuurman, Y., Meunier, F. C. (2022). On the link between CO surface coverage and selectivity to CH₄ during CO₂ hydrogenation over supported cobalt catalysts. *Journal of Catalysis*, 411, 93-96.

Brown, S. R., Kauzlarich, S. M., Gascoin, F., Snyder, G. J. (2006). Yb₁₄MnSb₁₁: New High Efficiency Thermoelectric Material for Power Generation. *Chemistry of Materials*, 18(7), 1873–1877.

Brunauer L. S. Deming, W. E. Deming, and E. Teller (1940). *Journal of the*

American Chemical Society, 62, 1723

Bux, S. K., Zevalink, A., Janka, O., Uhl, D., Fleurial, J. P. (2013). Glass-like lattice thermal conductivity and high thermoelectric efficiency in Yb₉Mn₄2Sb₉. *Journal of Materials Chemistry A*, 2(1).

Butt, S., Xu, W., He, W. Q., Tan, Q., Ren, G. K., Lin, Y., Nan, C.-W. (2014). Enhancement of thermoelectric performance in Cd-doped Ca₃Co₄O₉ via spin entropy, defect chemistry and phonon scattering. *J. Mater. Chem. A*, 2(45), 19479–19487.

Butt, S., Liu, Y.-C., Lan, J.-L., Shehzad, K., Zhan, B., Lin, Y., Nan, C.-W. (2014). High-temperature thermoelectric properties of La and Fe co-doped Ca–Co–O misfit-layered cobaltites consolidated by spark plasma sintering. *Journal of Alloys and Compounds*, 588, 277–283.

Cao, Q., Zheng, J., Zhang, K., Ma, G. (2016). Thermoelectric properties of YbCd₂Sb₂ doped by Mg. *Journal of Alloys and Compounds*, 680, 278–282.

Cao, Z., Guo, L., Liu, N., Zheng, X., Li, W., Shi, Y., Xi, Y. (2016). Theoretical study on the reaction mechanism of reverse water–gas shift reaction using a Rh–Mo₆S₈ cluster. *RSC Advances*, 6(110), 108270–108279.

Çetin Karakaya, G., Özçelik, B., Nane, O., Sotelo, A., Rasekh, S., Torres, M. A., Madre, M. A. (2017). Improvement of Bi₂Sr₂Co₂O_y thermoelectric performances by Na doping. *Journal of Electroceramics*, 40(1), 11–15.

Cha, J. S., Choi, S.-M., Kim, G. H., Kim, S.-J., Park, K. (2018). High-temperature thermoelectric properties of Sm³⁺-doped Ca₃Co₄O_{9+δ} fabricated by spark plasma sintering. *Ceramics International*, 44(6), 6376–6383.

Chang, C., Wu, M., He, D., Pei, Y., Wu, C. F., Wu, X., et al. (2018). 3d charge and 2d phonon transports leading to high out-of-plane zt in n-type SnSe crystals. *Science*, 360(6390), 778–783.

Chen, C.-S., Cheng, W.-H., Lin, S.-S. (2003). Study of reverse water gas shift reaction by TPD, TPR and CO₂ hydrogenation over potassium-promoted Cu/SiO₂ catalyst. *Applied Catalysis A: General*, 238(1), 55–67.

Chen, C. (2004). Study of iron-promoted Cu/SiO₂ catalyst on high temperature reverse water gas shift reaction. *Applied Catalysis A: General*, 257(1), 97–106.

Chen, L., Gao, S., Zeng, X., Mehdizadeh Dehkordi, A., Tritt, T. M., Poon, S. J. (2015). Uncovering high thermoelectric Figure of merit in (Hf,Zr)NiSn half-Heusler alloys. *Applied Physics Letters*, 107(4), 041902.

Chen, X., Wu, H., Cui, J., Xiao, Y., Zhang, Y., He, J., Sui, J. (2018). Extraordinary thermoelectric performance in n-type manganese doped Mg₃Sb₂Zintl: High band degeneracy, tuned carrier scattering mechanism and hierarchical microstructure. *Nano Energy*, 52, 246–255.

Chen, Y., Liu, J., Li, X., Li, Y., Lu, M. (2018). Enhancement of thermoelectric performance of Sr_{0.9-x}Nd_{0.1}Ti_{0.9}Nb_{0.1}O₃ ceramics by introducing Sr vacancies. *Physica Status Solidi (a)*, 215(21).

Chen, J., McGraw, M., Chen, E. Y. X. (2019). Diverse catalytic systems and mechanistic pathways for hydrosilylative reduction of CO₂. *ChemSusChem*, 12(20), 4543-4569.

Chere, E. K., Zhang, Q., Dahal, K., Cao, F., Mao, J., Ren, Z. (2016). Studies on thermoelectric Figure of merit of Na-doped p-type polycrystalline SnSe. *Journal of Materials Chemistry A*, 4.

Chu, F., Zhang, Q., Zhou, Z., Hou, D., Jiang, W. (2018). Enhanced thermoelectric and mechanical properties of Na-doped polycrystalline SnSe thermoelectric materials via CNTs dispersion. *Journal of Alloys and Compounds*, 741.

Colder, H., Guilmeau, E., Harnois, C., Marinel, S., Retoux, R., Savary, E.

(2011). Preparation of Ni-doped ZnO ceramics for thermoelectric applications. *Journal of the European Ceramic Society*, 31(15), 2957–2963.

Consuelo Ivarez Galván, Schumann, J., Behrens, M., José Luis García Fierro, Frei, E. (2016). Reverse water-gas shift reaction at the cu/zno interface: influence of the cu/zn ratio on structure-activity correlations. *Applied Catalysis B Environmental*, 195, 104-111.

Cutler, M., Mott, N. F. (1969). Observation of Anderson Localization in an Electron Gas. *Physical Review*, 181(3), 1336–1340.

D., Chung. (2000). Csbi4te6: a high-performance thermoelectric material for low-temperature applications. *Science*.

Daza, Y. A., Kent, R. A., Yung, M. M., Kuhn, J. N. (2014). Carbon Dioxide Conversion by Reverse Water–Gas Shift Chemical Looping on Perovskite-Type Oxides. *Industrial Engineering Chemistry Research*, 53(14), 5828–5837.

Delorme, F., Diaz-Chao, P., Giovannelli, F. (2018). Effect of Ca substitution by Fe on the thermoelectric properties of Ca₃Co₄O₉ ceramics. *Journal of Electroceramics*, 40(2), 107–114.

DiSalvo, F. J. (1999). Thermoelectric cooling and power generation. *Science*, 285(5428), 703-706.

Dresselhaus, M. S., Chen, G., Tang, M. Y., Yang, R., Lee, H., Wang, D., Gogna, P. (2007). New Directions for Low-Dimensional Thermoelectric Materials. *ChemInform*, 38(26).

Feng, X., Jiang, K., Fan, S., Kanan, M. W. (2015). Grain-boundary-dependent CO₂ electroreduction activity. *Journal of the American Chemical Society*, 137(14), 4606-4609.

Feng, B., Li, G., Pan, Z., Hou, Y., Zhang, C., Jiang, C., Fan, X. (2018). Effect

of Ba and Pb dual doping on the thermoelectric properties of BiCuSeO ceramics. *Materials Letters*, 217, 189–193.

Fu, C., Bai, S., Liu, Y., Tang, Y., Chen, L., Zhao, X., Zhu, T. (2015). Realizing high Figure of merit in heavy-band p-type half-Heusler thermoelectric materials. *Nature Communications*, 6(1).

Gao, F., He, Q., Cao, R., Wu, F., Hu, X., Song, H. (2015). Enhanced thermoelectric properties of the hole-doped Bi_{2-x}K_xSr₂Co₂O_y ceramics. *International Journal of Modern Physics B*, 29(28), 1550192.

Gao, J., Wu, Y., Jia, C., Zhong, Z., Gao, F., Yang, Y., Liu, B. (2016). Controllable synthesis of α -MoC_{1-x} and β -Mo₂C nanowires for highly selective CO₂ reduction to CO. *Catalysis Communications*, 84, 147–150.

Gascoin, F., Ottensmann, S., Stark, D., Haïle, S. M., Snyder, G. J. (2005). Zintl phases as thermoelectric materials: tuned transport properties of the compounds CaxYb_{1-x}Zn₂Sb₂. *Advanced Functional Materials*, 15(11), 1860-1864.

Girard, S. N., He, J., Li, C., Moses, S., Wang, G., Uher, C., Kanatzidis, M. G. (2010). In situ nanostructure generation and evolution within a bulk thermoelectric material to reduce lattice thermal conductivity. *Nano letters*, 10(8), 2825-2831.

Goddard, J. D. (2011). On the thermoelectricity of W. Thomson: Towards a theory of thermoelastic conductors, *Journal of Elasticity*, 104(1–2), pp. 267–280.

Goguet, A., Meunier, F. C., Tibiletti, D., Breen, J. P., Burch, R. (2004). Spectrokinetic Investigation of Reverse Water-Gas-Shift Reaction Intermediates over a Pt/CeO₂Catalyst. *The Journal of Physical Chemistry B*, 108(52), 20240–20246.

Grebenkemper, J. H., Klemenz, S., Albert, B., Bux, S. K., Kauzlarich, S. M.

(2016). Effects of Sc and Y substitution on the structure and thermoelectric properties of Yb₁₄MnSb₁₁. *Journal of Solid State Chemistry*, 242, 55–61.

Guo, K., Cao, Q.-G., Feng, X.-J., Tang, M.-B., Chen, H.-H., Guo, X., Zhao, J.-T. (2011). Enhanced Thermoelectric Figure of Merit of Zintl Phase YbCd_{2-x}MnxSb₂ by Chemical Substitution. *European Journal of Inorganic Chemistry*, 2011(26), 4043–4048.

Guo, J., Duchesne, P. N., Wang, L., Song, R., Xia, M., Ulmer, U., Ozin, G. A. (2020). High-Performance, Scalable, and Low-Cost Copper Hydroxyapatite for Photothermal CO₂ Reduction. *ACS Catalysis*, 10(22), 13668–13681.

Hasanova, G. S., Aghazade, A. I., Babanly, D. M., Imamaliyeva, S. Z., Yusibov, Y. A., Babanly, M. B. (2021). Experimental study of the phase relations and thermodynamic properties of Bi-Se system. *Journal of Thermal Analysis and Calorimetry*.

Hao, H., Ye, J., Liu, Y., Hu, X. (2010). High-Temperature Thermoelectric Properties of Pb-and La-Substituted Bi₂Sr₂Co₂O_y Misfit Compounds. *China international conference on high-performance ceramics*.

He, J., Blum, I. D., Wang, H. Q., Girard, S. N., Doak, J., Zhao, L. D., Dravid, V. P. (2012). Morphology control of nanostructures: Na-doped PbTe–PbS system. *Nano letters*, 12(11), 5979-5984.

He, R., Kim, H. S., Lan, Y., Wang, D., Chen, S., Ren, Z. (2014). Investigating the thermoelectric properties of p-type half-heusler $\text{Hf}_{1-x}\text{Zr}_x\text{Ti}_{1-x}\text{CoSb}_{0.8}\text{Sn}_{0.2}$ by reducing Hf concentration for power generation. *Rsc Advances*, 4.

He, R., Kraemer, D., Mao, J., Zeng, L., Jie, Q., Lan, Y., et al. (2016). Achieving high power factor and output power density in p-type half-heuslers $\text{Nb}_{1-x}\text{Ta}_x\text{FeSb}$. *Proceedings of the National Academy of Sciences of the United States of America*.

Heremans, J. P., Jovovic, V., Toberer, E. S., Saramat, A., Kurosaki, K.,

- Charoenphakdee, A., et al. (2008). Enhancement of thermoelectric efficiency in pbte by distortion of the electronic density of states. *Science* (5888), 321.
- Hira, U., Han, L., Norrman, K., Christensen, D. V., Pryds, N., Sher, F. (2018). High-temperature thermoelectric properties of Na- and W-Doped $\text{Ca}_3\text{Co}_4\text{O}_9$ system. *RSC Advances*, 8(22), 12211–12221.
- Hou, C.-C., Wang, H.-F., Li, C., Xu, Q. (2020). From Metal-Organic Frameworks to Single/Dual-Atom and Cluster Metal Catalysts for Energy Applications. *Energy Environmental Science*.
- Hsu, K. F., Loo, S., Guo, F., Chen, W., Dyck, J. S., Uher, C., et al. (2004). Cubic $\text{AgPbmSbTe}_2 + m$: Bulk Thermoelectric Materials with High Figure of Merit.(reports).
- Hsueh, T.-J., Shieh, J.-M., Yeh, Y.-M. (2014). Hybrid Cd-free CIGS solar cell/TEG device with ZnO nanowires. *Progress in Photovoltaics: Research and Applications*, 23(4), 507–512.
- Hu, Y., Wang, J., Kawamura, A., Kovnir, K., Kauzlarich, S. M. (2014). $\text{Yb}_{14}\text{MgSb}_{11}$ and $\text{Ca}_{14}\text{MgSb}_{11}$ —New Mg-Containing Zintl Compounds and Their Structures, Bonding, and Thermoelectric Properties. *Chemistry of Materials*, 27(1), 343–351.
- Huang, L., Zhang, Q., Wang, Y., He, R., Shuai, J., Zhang, J., Ren, Z. (2017). The effect of Sn doping on thermoelectric performance of n-type half-Heusler NbCoSb . *Physical Chemistry Chemical Physics*, 19(37), 25683–25690.
- Ioffe, A. F., Stil'bans, L. S., Iordanishvili, E. K., Stavitskaya, T. S., Gelbtuch, A., Vineyard, G. (1959). Semiconductor Thermoelements and Thermoelectric Cooling, *Physics Today*, 12(5), 42–42.
- Iordanova, R., Dimitrov, V., Dimitriev, Y., Klissurski, D. (1994). Glass formation and structure of glasses in the V_2O_5 MoO_3 Bi_2O_3 system. *Journal of non-crystalline solids*, 180(1), 58-65.

- Ito, M., Furumoto, D. (2008). Effects of noble metal addition on microstructure and thermoelectric properties of $\text{Na}_x\text{Co}_2\text{O}_4$. *Journal of Alloys and Compounds*, 450(1-2), 494–498.
- Iversen, B. B., Palmqvist, A. E. C., Cox, D. E., Nolas, G. S., Stucky, G. D., Blake, N. P., Metiu, H. (2000). Why are Clathrates Good Candidates for Thermoelectric Materials? *Journal of Solid State Chemistry*, 149(2), 455–458.
- Japheth F. Rauscher, Susan M. Kauzlarich, Teruyuki Ikeda, G. Jeffrey Snyder. (2007). Synthesis, structure, and high temperature thermoelectric properties of $\text{yb}_{11}\text{sb}_9.3\text{ge}_{0.5}$. *Zeitschrift für anorganische und allgemeine Chemie*.
- Joshi, G., Lee, H., Lan, Y., Wang, X., Zhu, G., Wang, D., Ren, Z. (2008). Enhanced Thermoelectric Figure -of-Merit in Nanostructured p-type Silicon Germanium Bulk Alloys. *Nano Letters*, 8(12), 4670–4674.
- Jovovic, V., Heremans, J. P. (2008). Measurements of the energy band gap and valence band structure of AgSbTe_2 . *Physical Review B*, 77(24), 245204.
- Jung, K.-H., Hyoungh Lee, K., Seo, W.-S., Choi, S.-M. (2012). An enhancement of a thermoelectric power factor in a Ga-doped ZnO system: A chemical compression by enlarged Ga solubility. *Applied Physics Letters*, 100(25), 253902.
- Kaloyannis, A., Vayenas, C. G. (1997). Non-Faradaic Electrochemical Modification of Catalytic Activity. *Journal of Catalysis*, 171(1), 148–159.
- Kattel, S., Yan, B., Yang, Y., Chen, J. G., Liu, P. (2016). Optimizing Binding Energies of Key Intermediates for CO_2 Hydrogenation to Methanol over Oxide-Supported Copper. *Journal of the American Chemical Society*, 138(38), 12440–12450.
- Kim, S. S., Lee, H. H., Hong, S. C. (2012). A study on the effect of support's reducibility on the reverse water-gas shift reaction over Pt catalysts. *Applied*

Catalysis A: General, 423-424, 100–107.

Kimura, Y., Ueno, H., Mishima, Y. (2009). Thermoelectric Properties of Directionally Solidified half-Heusler ($M_{0.5}^a M_{0.5}^b$)NiSn ($M^a, M^b = \text{Hf, Zr, Ti}$) Alloys. *JOURNAL OF ELECTRONIC MATERIALS*.

Korkosz, R. J., Chasapis, T. C., Lo, S., Doak, J. W., Kim, Y. J., Wu, C.-I., Kanatzidis, M. G. (2014). High ZT in p-Type $(\text{PbTe})_{1-2x}(\text{PbSe})_x(\text{PbS})_x$ Thermoelectric Materials. *Journal of the American Chemical Society*, 136(8), 3225–3237.

Kroon, R., Mengistie, D. A., Kiefer, D., Hynynen, J., Ryan, J. D., Yu, L., Müller, C. (2016). Thermoelectric plastics: from design to synthesis, processing and structure–property relationships. *Chemical Society Reviews*, 45(22), 6147–6164.

Kurosaki, K., Muta, H., Uno, M., Yamanaka, S. (2005). Thermoelectric properties of NaCo_2O_4 . *Cheminform*, 315(1-2), 234-236.

Lan, J.-L., Liu, Y.-C., Zhan, B., Lin, Y.-H., Zhang, B., Yuan, X., Nan, C.-W. (2013). Enhanced Thermoelectric Properties of Pb-doped BiCuSeO Ceramics. *Advanced Materials*, 25(36), 5086–5090.

Lan, J.-L., Deng, C., Ma, W., Ren, G.-K., Lin, Y.-H., Yang, X. (2017). Ultra-fast synthesis and high thermoelectric properties of heavy sodium doped BiCuSeO. *Journal of Alloys and Compounds*, 708, 955–960.

Lee, Y., Lo, S.-H., Chen, C., Sun, H., Chung, D.-Y., Chasapis, T. C., Kanatzidis, M. G. (2014). Contrasting role of antimony and bismuth dopants on the thermoelectric performance of lead selenide. *Nature Communications*, 5(1).

Li, Z. J., Liu, R. Q., Xie, Y. H., Feng, S., Wang, J. D. (2005). A novel method for preparation of doped $\text{Ba}_3(\text{Ca}_{1.18}\text{Nb}_{1.82})\text{O}_{9\delta}$: application to ammonia synthesis at atmospheric pressure. *Solid State Ionics*, 176(11-12), 1063-

1066.

Li, F., Li, J. F., Zhao, L. D., Xiang, K., Liu, Y., Zhang, B. P., Zhu, H. M. (2012). Polycrystalline BiCuSeO oxide as a potential thermoelectric material. *Energy Environmental Science*, 5(5), 7188-7195.

Li, J.; Sui, J.; Pei, Y.; Barreateau, C.; Berardan, D.; Dragoe, N.; Cai, W.; He, J.; Zhao, L.D. (2012). A High Thermoelectric Figure of Merit $zT > 1$ in Ba Heavily Doped BiCuSeO Oxyselenides. *Energy Environ. Sci.*, 5, 8543–8547.

Li, Z.-Y., Li, J.-F. (2013). Fine-Grained and Nanostructured AgPbmSbTem + 2Alloys with High Thermoelectric Figure of Merit at Medium Temperature. *Advanced Energy Materials*, 4(2), 1300937.

Li, J., Sui, J., Pei, Y., Meng, X., Berardan, D., Dragoe, N., Zhao, L.-D. (2014). The roles of Na doping in BiCuSeO oxyselenides as a thermoelectric material. *Journal of Materials Chemistry A*, 2(14), 4903.

Li, L., Liu, Y., Qin, X., Li, D., Zhang, J., Song, C., Wang, L. (2014). Enhanced thermoelectric performance of highly dense and fine-grained (Sr_{1-x}Gdx)TiO_{3-δ} ceramics synthesized by sol-gel process and spark plasma sintering. *Journal of Alloys and Compounds*, 588, 562–567.

Li, Z., Xiao, C., Fan, S., Deng, Y., Zhang, W., Ye, B., Xie, Y. (2015). Dual Vacancies: An Effective Strategy Realizing Synergistic Optimization of Thermoelectric Property in BiCuSeO. *Journal of the American Chemical Society*, 137(20), 6587–6593.

Li, Y.-N., Wu, P., Zhang, S.-P., Chen, S., Yan, D., Yang, J.-G., Huai, X.-L. (2018). Thermoelectric properties of lower concentration K-doped Ca₃Co₄O₉ ceramics. *Chinese Physics B*, 27(5), 057201.

Li, C., Chen, Q., Yan, Y. (2018). Effects of Pr and Yb Dual Doping on the Thermoelectric Properties of CaMnO₃. *Materials*, 11(10), 1807.

- Li, K., Chen, J. G. (2019). CO₂ hydrogenation to methanol over ZrO₂-containing catalysts: Insights into ZrO₂ induced synergy. *ACS Catalysis*.
- Lin, H., Bozin, E. S., Billinge, S. J. L., Quarez, E., Kanatzidis, M. G. (2005). Nanoscale clusters in the high performance thermoelectric AgPbmSbTem + 2. *10.1103/PhysRevB.72.174113*.
- Lin, S., Wang, C., Chen, H., Huo, D., Savvides, N., Chen, X. (2014). Microstructure and thermoelectric properties of Ga-DOPED SiGe alloys prepared by mechanical alloying and induction hot pressing. *Functional Materials Letters*, 07(02), 1450008.
- Lin, Y., Sun, S., Zhang, Q., Shen, H., Shao, Q., Wang, L., Jiang, W. (2016). Preparation of AgNPs/Ca₃Co₄O₉ nanocomposites with enhanced thermoelectric performance. *Materials Today Communications*, 6, 44–49.
- Lin, Y. H., Nan, C. W., Liu, Y., Li, J., Mizokawa, T., Shen, Z. (2007). High - temperature electrical transport and thermoelectric power of partially substituted Ca₃Co₄O₉ - based ceramics. *Journal of the American Ceramic Society*, 90(1), 132-136.
- Lin, Y.-J., Khan, I., Saha, S., Wu, C.-C., Barman, S. R., Kao, F.-C., Lin, Z.-H. (2021). Thermocatalytic hydrogen peroxide generation and environmental disinfection by Bi₂Te₃ nanoplates. *Nature Communications*, 12(1).
- Liu, H., Shi, X., Xu, F., Zhang, L., Zhang, W., Chen, L., Snyder, G. J. (2012). Copper ion liquid-like thermoelectrics. *Nature materials*, 11(5), 422-425.
- Liu, W. S., Zhang, Q., Lan, Y., Chen, S., Ren, Z. (2011). Thermoelectric property studies on Cu-doped n-type CuxBi₂Te_{2.7}Se_{0.3} nanocomposites. *Advanced Energy Materials*, 1(4), 577-587.
- Liu, W., Tan, X., Yin, K., Liu, H., Uher, C. (2012). Convergence of Conduction Bands as a Means of Enhancing Thermoelectric Performance of N-Type Mg₂Si_{1-x}Sn_x Solid Solutions. *Physical Review Letters*, 108(16), 166601.

- Liu, J., Wang, C. L., Li, Y., Su, W. B., Zhu, Y. H., Li, J. C., Mei, L. M. (2013). Influence of rare earth doping on thermoelectric properties of SrTiO₃ ceramics. *Journal of Applied Physics*, 114(22), 223714.
- Liu, Y., Zhao, L.-D., Zhu, Y., Liu, Y., Li, F., Yu, M., Nan, C.-W. (2016). Synergistically Optimizing Electrical and Thermal Transport Properties of BiCuSeO via a Dual-Doping Approach. *Advanced Energy Materials*, 6(9), 1502423.
- Liu, Y., Fu, C., Xia, K., Yu, J., Zhao, X., Pan, H., Zhu, T. (2018). Lanthanide Contraction as a Design Factor for High-Performance Half-Heusler Thermoelectric Materials. *Advanced Materials*, 30(32), 1800881.
- Mackey, J., Dynys, F., Sehirlioglu, A. (2015). Si/Ge–WSi₂ composites: Processing and thermoelectric properties. *Acta Materialia*, 98, 263–274.
- Mahan, G. D. (Academic, 1998). *Solid State Physics* (eds Ehrenreich, H. Spaepen, F.) Vol. 51, 81–157.
- Martin, J., Tritt, T. and Uher, C. (2010). High temperature Seebeck coefficient metrology, *Journal of Applied Physics*, 108(12).
- Meng, Y., Wang, T., Chen, S., Zhao, Y., Ma, X., Gong, J. (2014). Selective oxidation of methanol to dimethoxymethane on V₂O₅–MoO₃/γ-Al₂O₃ catalysts. *Applied Catalysis B: Environmental*, 160, 161-172.
- Morelli, D. T., Jovovic, V., Heremans, J. P. (2008). Intrinsically minimal thermal conductivity in cubic I–V–VI₂ semiconductors. *Physical review letters*, 101(3), 035901.
- Muta, H., Kanemitsu, T., Kurosaki, K., Yamanaka, S. (2009). High-temperature thermoelectric properties of Nb-doped MNiSn (M=Ti, Zr) half-Heusler compound. *Journal of Alloys and Compounds*, 469(1-2), 50–55.
- Nagira, T., Ito, M., Katsuyama, S., Majima, K., Nagai, H. (2003).

Thermoelectric properties of $(\text{Na}_{1-y}\text{M}_y)\text{Co}_2\text{O}_4$ ($\text{M}=\text{K}, \text{Sr}, \text{Y}, \text{Nd}, \text{Sm}$ and Yb ; $y=0.010.35$). *Cheminform*, 348(14), 263-269.

Nam, W. H., Lim, Y. S., Choi, S.-M., Seo, W.-S., Lee, J. Y. (2012). High-temperature charge transport and thermoelectric properties of a degenerately Al-doped ZnO nanocomposite. *Journal of Materials Chemistry*, 22(29), 14633.

Nolas, G. S., Kendziora, C. A. (1999). Raman spectroscopy investigation of lanthanide-filled and unfilled skutterudites. *Physical Review B*, 59(9), 6189–6192.

Nozariasbmarz, A., Roy, P., Zamanipour, Z., Dycus, J. H., Cabral, M. J., LeBeau, J. M., Vashaee, D. (2016). Comparison of thermoelectric properties of nanostructured Mg_2Si , FeSi_2 , SiGe , and nanocomposites of $\text{SiGe-Mg}_2\text{Si}$, SiGe-FeSi_2 . *APL Materials*, 4(10), 104814.

Nozariasbmarz, A., Zamanipour, Z., Norouzzadeh, P., Krasinski, J. S., Vashaee, D. (2016). Enhanced thermoelectric performance in a metal/semiconductor nanocomposite of iron silicide/silicon germanium. *RSC Advances*, 6(55), 49643–49650.

Okamoto, H. (1994). The bi-se (bismuth-selenium) system. *Journal of Phase Equilibria*, 15(2), 195-201.

Onsager, L. (1931). Reciprocal Relations in Irreversible Processes. II., *Phys. Rev. American Physical Society*, 38(12), pp. 2265–2279.

Oshima, K., Shinagawa, T., Nogami, Y., Manabe, R., Ogo, S., Sekine, Y. (2014). Low temperature catalytic reverse water gas shift reaction assisted by an electric field. *Catalysis Today*, 232, 27–32.

Owens, G. J., Singh, R. K., Foroutan, F., Alqaysi, M., Han, C. M., Mahapatra, C., et al. (2016). Sol-gel based materials for biomedical applications. *Progress in Materials Science*, 77, 1-79.

Papadakis, V. G., Pliangos, C. A., Yentekakis, I. V., Verykios, X. E., Vayenas, C. G. (1996). Development of high performance, Pd-based, three way catalysts. *Catalysis Today*, 29(1-4), 71–75.

Park, S.-W., Joo, O.-S., Jung, K.-D., Kim, H., Han, S.-H. (2000). ZnO/Cr₂O₃ catalyst for reverse-water-gas-shift reaction of CAMERE process. *Korean Journal of Chemical Engineering*, 17(6), 719–722.

Park, S.-W., Joo, O.-S., Jung, K.-D., Kim, H., Han, S.-H. (2001). Development of ZnO/Al₂O₃ catalyst for reverse-water-gas-shift reaction of CAMERE (carbon dioxide hydrogenation to form methanol via a reverse-water-gas-shift reaction) process. *Applied Catalysis A: General*, 211(1), 81–90.

Park, K., Jang, K. U., Kwon, H.-C., Kim, J.-G., Cho, W.-S. (2006). Influence of partial substitution of Cu for Co on the thermoelectric properties of NaCo₂O₄. *Journal of Alloys and Compounds*, 419(1-2), 213–219.

Park, K., Choi, J. W. (2012). High-temperature thermoelectric properties of na(co_{0.91}, ni_{0.09})₂o₄ fabricated by solution combustion method for power generation. *Journal of Nanoscience Nanotechnology*.

Park, K., Son, J. S., Woo, S. I., Shin, K., Oh, M.-W., Park, S.-D., Hyeon, T. (2014). Colloidal synthesis and thermoelectric properties of La-doped SrTiO₃ nanoparticles. *Journal of Materials Chemistry A*, 2(12), 4217.

Pei, Y., Shi, X., LaLonde, A., Wang, H., Chen, L., Snyder, G. J. (2011). Convergence of electronic bands for high performance bulk thermoelectrics. *Nature*, 473(7345), 66–69.

Pei, Y.-L., Wu, H., Wu, D., Zheng, F., He, J. (2014). High Thermoelectric Performance Realized in a BiCuSeO System by Improving Carrier Mobility through 3D Modulation Doping. *Journal of the American Chemical Society*, 136(39), 13902–13908.

Porosoff, M. D., Chen, J. G. (2013). Trends in the catalytic reduction of CO₂ by hydrogen over supported monometallic and bimetallic catalysts. *Journal of Catalysis*, 301, 30–37.

Poudel, B., Hao, Q., Ma, Y., Lan, Y., Minnich, A., Yu, B., Ren, Z. (2008). High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys. *Science*, 320(5876), 634–638.

Prasoetsopha, N., Pinitsoontorn, S., Bootchanont, A., Kidkhunthod, P., Srepusharawoot, P., Kamwanna, T., Yamanaka, S. (2013). Local structure of Fe in Fe-doped misfit-layered calcium cobaltite: An X-ray absorption spectroscopy study. *Journal of Solid State Chemistry*, 204, 257–265.

Prasoetsopha, N., Pinitsoontorn, S., Kamwanna, T., Amornkitbamrung, V., Kurosaki, K., Ohishi, Y., Yamanaka, S. (2014). The effect of Cr substitution on the structure and properties of misfit-layered $\text{Ca}_3\text{Co}_{4-x}\text{Cr}_x\text{O}_9 + \delta$ thermoelectric oxides. *Journal of Alloys and Compounds*, 588, 199–205.

Qiu, P., Shi, X., Chen, X., Huang, X., Liu, R., Chen, L. (2011). Effects of Sn-doping on the electrical and thermal transport properties of p-type Cerium filled skutterudites. *Journal of Alloys and Compounds*, 509(4), 1101–1105.

Roduner, E. (2014). Understanding catalysis. *Chemical Society Reviews*, 43(24), 8226–8239.

Rothenberg, G. (2017). *Catalysis: concepts and green applications*. John Wiley Sons.

Rubin, K., Pohar, A., Dasireddy, V. D. B. C., Likozar, B. (2018). Synthesis, characterization and activity of CuZnGaO_x catalysts for the water–gas shift (WGS) reaction for H₂ production and CO removal after reforming. *Fuel Processing Technology*, 169, 217–225.

Saini, S., Yaddanapudi, H. S., Tian, K., Yin, Y., Magginetti, D., Tiwari, A. (2017).

Terbium Ion Doping in $\text{Ca}_3\text{Co}_4\text{O}_9$: A Step towards High-Performance Thermoelectric Materials. *Scientific Reports*, 7(1).

Sapountzi, F. M., Tsampas, M. N., Vayenas, C. G. (2009). Electrochemical promotion of CO conversion to CO_2 in PEM fuel cell PROX reactor. *Catalysis Today*, 146(3-4), 319–325.

Seo, J. W., Cha, J., Won, S. O., Park, K. (2017). Electrical transport and thermoelectric properties of $\text{Ca}_{0.8}\text{Y}_{0.2-x}\text{Dy}_x\text{MnO}_{3-\delta}$ ($0 \leq x \leq 0.2$). *Journal of the American Ceramic Society*, 100(8).

Serrano-Sánchez, F., Gharsallah, M., Nemes, N. M., Mompean, F. J., Martínez, J. L., Alonso, J. A. (2015). Record Seebeck coefficient and extremely low thermal conductivity in nanostructured SnSe. *Applied Physics Letters*, 106(8), 083902.

Shi, X., Yang, J., Salvador, J. R., Chi, M., Cho, J. Y., Wang, H., Chen, L. (2011). Multiple-Filled Skutterudites: High Thermoelectric Figure of Merit through Separately Optimizing Electrical and Thermal Transports. *Journal of the American Chemical Society*, 133(20), 7837–7846.

Shi, X., Wu, A., Liu, W., Moshwan, R., Wang, Y., Chen, Z. G., et al. (2018). Polycrystalline snse with extraordinary thermoelectric property via nanoporous design. *ACS nano*. (11), 12.

Shimonishi, R., Hagiwara, M., Fujihara, S. (2019). Fabrication of highly textured $\text{Ca}_3\text{Co}_4\text{O}_9$ ceramics with controlled density and high thermoelectric power factors. *Journal of the European Ceramic Society*.

Shuai, J.; Kim, H.S.; Liu, Z.; He, R.; Sui, J.; Ren, Z. (2016). Thermoelectric Properties of Zintl Compound $\text{Ca}_{1-x}\text{Na}_x\text{Mg}_2\text{Bi}_{1.98}$. *Applied Physics Letters*, 108(18), 703.

Shuai, J., Geng, H., Lan, Y., Zhu, Z., Wang, C., Liu, Z., et al. (2016). Higher Thermoelectric Performance of Zintl Phases $(\text{Eu}_{0.5}\text{Yb}_{0.5})_{1-x}\text{Ca}_x\text{Mg}_2\text{Bi}_2$ by

Band Engineering and Strain Fluctuation. *Proceedings of the National Academy of Sciences* (29).

Shuai, J., Mao, J., Song, S., Zhu, Q., Sun, J., Wang, Y., Ren, Z. (2017). Tuning the carrier scattering mechanism to effectively improve the thermoelectric properties. *Energy Environmental Science*, 10(3), 799–807.

Shuai, J., Ge, B., Mao, J., Song, S., Wang, Y., Ren, Z. (2018). Significant Role of Mg Stoichiometry in Designing High Thermoelectric Performance for $\text{Mg}_3(\text{Sb,Bi})_2$ -Based n-Type Zintl. *Journal of the American Chemical Society*, 140(5), 1910–1915.

Shutoh, N., Sakurada, S. (2003). Thermoelectric properties of the $\text{Tix}(\text{Zr}_{0.5}\text{Hf}_{0.5})_{1-x}\text{NiSn}$ half-Heusler compounds. *Thermoelectrics, 2003 Twenty-Second International Conference on - ICT. IEEE*.

Skoug, E. J., Morelli, D. T. (2011). Role of lone-pair electrons in producing minimum thermal conductivity in nitrogen-group chalcogenide compounds. *Physical review letters*, 107(23), 235901.

Souentie, S., Hammad, A., Vayenas, C. G. (2009). Steady-state multiplicity phenomena during the electrochemical promotion of no reduction by C_2H_4 in presence of O_2 on thin rh and pt catalyst-electrodes in a monolithic electropromoted reactor. *Catalysis Today*, 146(3-4), 285-292.

Staten, M. L., Shimada, K. (2010). A close look at valences in hexahedral element meshes. *International journal for numerical methods in engineering*, 83(7), 899-914.

Stolarski, T., Nakasone, Y., Yoshimoto, S. (2018). *Engineering analysis with ANSYS software*. Butterworth-Heinemann.

Stoukides, M. (1981). The effect of electrochemical oxygen pumping on the rate and selectivity of ethylene oxidation on polycrystalline silver. *Journal of*

Catalysis, 70(1), 137–146.

Su, J., Zhou, H., Liu, S., Wang, C., Jiao, W., Wang, Y., He, M. (2019). Syngas to light olefins conversion with high olefin/paraffin ratio using ZnCrOx/AlPO-18 bifunctional catalysts. *Nature Communications*, 10(1).

Sun, Y., Zhang, C., Cao, C., Fu, J., Peng, L. (2017). Co-doping for significantly improved thermoelectric Figure of merit in p -type $\text{Bi}_{1-2} \times \text{mg} \times \text{pb} \times \text{cuseo}$ oxy-selenides. *Ceramics International*, S0272884217320679.

Tan, G., Shi, F., Hao, S., Chi, H., Zhao, L.-D., Uher, C., Kanatzidis, M. G. (2015). Codoping in SnTe: Enhancement of Thermoelectric Performance through Synergy of Resonance Levels and Band Convergence. *Journal of the American Chemical Society*, 137(15), 5100–5112.

Tan, G., Zhao, L.-D., Kanatzidis, M. G. (2016). Rationally Designing High-Performance Bulk Thermoelectric Materials. *Chemical Reviews*, 116(19), 12123–12149.

Tan, W., Wu, Z., Zhu, M., Shen, J., Zhu, T., Zhao, X., Xia, S. (2017). $\text{A}_{14}\text{MgBi}_{11}$ (A=Ca, Sr, Eu): Magnesium Bismuth Based Zintl Phases as Potential Thermoelectric Materials. *Inorganic Chemistry*, 56(17), 10576–10583.

Tan, G., Hao, S., Cai, S., Bailey, T. P., Luo, Z., Hadar, I., Kanatzidis, M. G. (2019). All-scale hierarchically Structured p-type PbSe Alloys with High Thermoelectric Performance Enabled by Improved Band Degeneracy. *Journal of the American Chemical Society*.

Tanimu, A., Jaenicke, S., Alhooshani, K. (2017). Heterogeneous catalysis in continuous flow microreactors: A review of methods and applications. *Chemical Engineering Journal*, 327, 792-821.

Thiel, P., Eilertsen, J., Populoh, S., Saucke, G., Döbeli, M., Shkabko, A., Weidenkaff, A. (2013). Influence of tungsten substitution and oxygen deficiency

on the thermoelectric properties of $\text{CaMnO}_{3-\delta}$. *Journal of Applied Physics*, 114(24), 243707.

Titlbach, S., Hoffbauer, W., Glaum, R. (2012). Equilibrium relations in the system $\text{TiO}_2/\text{V}_2\text{O}_5/\text{P}_2\text{O}_5$ and crystal structure of a NASICON-related vanadyl (V) titanium (IV) phosphate. *Journal of Solid State Chemistry*, 196, 565-573.

Toberer, E. S., Cox, C. A., Brown, S. R., Ikeda, T., May, A. F., Kauzlarich, S. M., Snyder, G. J. (2008). Traversing the Metal-Insulator Transition in a Zintl Phase: Rational Enhancement of Thermoelectric Efficiency in $\text{Yb}_{14}\text{Mn}_{1-x}\text{Al}_x\text{Sb}_{11}$. *Advanced Functional Materials*, 18(18), 2795–2800.

Toberer, E. S., Zevalkink, A., Crisosto, N., Snyder, G. J. (2010). The Zintl Compound $\text{Ca}_5\text{Al}_2\text{Sb}_6$ for Low-Cost Thermoelectric Power Generation. *Advanced Functional Materials*, 20(24), 4375–4380.

Vayenas, C. G., Bebelis, S., Pliengos, C., Brosda, S., Tsiplakides, D. (2001). *Electrochemical activation of catalysis: promotion, electrochemical promotion and metal support interactions*. New York: Kluwer Academic/Plenum Publishers.

Vayenas, C. G. (2011). Bridging electrochemistry and heterogeneous catalysis. *Journal of Solid State Electrochemistry*, 15(7-8), 1425–1435.

Vining, C. B. (2009). An inconvenient truth about thermoelectrics. *Nature Materials*, 8(2), 83–85.

Wang, Y., Sui, Y., Su, W. H. (2008). High temperature thermoelectric characteristics of $\text{Ca}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ ($r=\text{La, Pr, Yb}$). *Journal of Applied Physics*, 104(9), 1325.

Wang, X.-J., Tang, M.-B., Chen, H.-H., Yang, X.-X., Zhao, J.-T., Burkhardt, U., Grin, Y. (2009). Synthesis and high thermoelectric efficiency of Zintl phase $\text{YbCd}_{2-x}\text{Zn}_x\text{Sb}_2$. *Applied Physics Letters*, 94(9), 092106.

Wang, S., Li, H., Lu, R., Zheng, G., Tang, X. (2013). Metal nanoparticle

decorated n-type Bi_2Te_3 -based materials with enhanced thermoelectric performances. *Nanotechnology*, 24(28), 285702.

Wang, C., Lin, S., Chen, H., Zhao, Y., Zhao, L., Wang, H., Chen, X. (2015). Thermoelectric performance of $\text{Si}_{80}\text{Ge}_{20-x}\text{Sb}_x$ based multiphase alloys with inhomogeneous dopant distribution. *Energy Conversion and Management*, 94, 331–336.

Wang, X., Shi, H., Kwak, J. H., Szanyi, J. (2015). Mechanism of CO_2 Hydrogenation on $\text{Pd}/\text{Al}_2\text{O}_3$ Catalysts: Kinetics and Transient DRIFTS-MS Studies. *ACS Catalysis*, 5(11), 6337–6349.

Wang, W., Zhang, Y., Wang, Z., Yan, J., Ge, Q., Liu, C. (2016). Reverse water gas shift over $\text{In}_2\text{O}_3-\text{CeO}_2$ catalysts. *Catalysis Today*, 259, 402–408.

Wang, Y., Zhang, X., Wang, Y., Liu, H., Zhang, J. (2019). Enhanced Thermoelectric Properties of n-type Mg_3Sb_2 by Excess Magnesium and Tellurium Doping. *Physica Status Solidi (a)*, 1800811.

Wongprakarn, S., Pinitsoontorn, S., Tanusilp, S., Kurosaki, K. (2017). The effect of YSi_2 nanoinclusion on the thermoelectric properties of p-type SiGe alloy. *Physica Status Solidi (a)*, 214(10), 1700235.

Wood, M., Aydemir, U., Ohno, S., Snyder, G. J. (2018). Observation of valence band crossing: the thermoelectric properties of $\text{CaZn}_2\text{Sb}_2-\text{CaMg}_2\text{Sb}_2$ solid solution. *Journal of Materials Chemistry A*, 6(20), 9437–9444.

Wu, D., Zhao, L.-D., Hao, S., Jiang, Q., Zheng, F., Doak, J. W., He, J. (2014). Origin of the High Performance in GeTe -Based Thermoelectric Materials upon Bi_2Te_3 Doping. *Journal of the American Chemical Society*, 136(32), 11412–11419.

Wu, J., Li, F., Wei, T.-R., Ge, Z., Kang, F., He, J., Li, J.-F. (2015). Mechanical Alloying and Spark Plasma Sintering of BiCuSeO Oxyselenide: Synthesis

Process and Thermoelectric Properties. *Journal of the American Ceramic Society*, 99(2), 507–514.

Wu, D., Zhao, L.-D., Tong, X., Li, W., Wu, L., Tan, Q., He, J. (2015). Superior thermoelectric performance in PbTe–PbS pseudo-binary: extremely low thermal conductivity and modulated carrier concentration. *Energy Environmental Science*, 8(7), 2056–2068.

Yang, X., Su, X., Chen, X., Duan, H., Liang, B., Liu, Q., Zhang, T. (2017). Promotion effects of potassium on the activity and selectivity of Pt/zeolite catalysts for reverse water gas shift reaction. *Applied Catalysis B: Environmental*, 216, 95–105.

Yin, Y., Saini, S., Maggini, D., Tian, K., Tiwari, A. (2017). Thermoelectric response of porous $\text{Ca}_3\text{Co}_4\text{O}_9$ prepared by an eco-friendly technique. *Ceramics International*, 43(12), 9505–9511.

Yiokari, C. G., Pitselis, G. E., Polydoros, D. G., Katsaounis, A. D., Vayenas, C. G. (2000). High-Pressure Electrochemical Promotion of Ammonia Synthesis over an Industrial Iron Catalyst. *The Journal of Physical Chemistry A*, 104(46), 10600–10602.

Yoon, J., Jang, H., Oh, M.W., Hilberath, T., Hollmann, F., Jung, Y.S., Park, C.B. Heat-fueled enzymatic cascade for selective oxyfunctionalization of hydrocarbons. *Nature Communications*, 13, 3741 (2022).

Yuan, H., Zhu, X., Han, J., Wang, H., Ge, Q. (2018). Rhenium-promoted selective CO_2 methanation on Ni-based catalyst. *Journal of CO_2 Utilization*, 26, 8–18.

Zamanipour, Z., Vashaee, D. (2012). Comparison of Thermoelectric Properties of p-Type Nanostructured Bulk $\text{Si}_{0.8}\text{Ge}_{0.2}$ Alloy with $\text{Si}_{0.8}\text{Ge}_{0.2}$ Composites Embedded with CrSi_2 Nano-Inclusions. *Journal of Applied Physics*, 112(9), p.1-9.

Zhai, X., Shamoto, J., Xie H., Tan, Y., Han, Y., Tsubaki, N. (2008). Study on the deactivation phenomena of Cu-based catalyst for methanol synthesis in slurry phase. *Fuel*, 87(4-5), 430–434.

Zhang, G., Liu, M. (1999). Preparation of nanostructured tin oxide using a sol-gel process based on tin tetrachloride and ethylene glycol. *Journal of Materials Science*, 34(13), 3213-3219.

Zhang, H., Baitinger, M., Tang, M. B., Man, Z. Y., Chen, H. H., Yang, X. X., et al. (2010). Thermoelectric Properties of $\text{Eu}(\text{Zn}_{1-x}\text{Cd}_x)_2\text{Sb}_2$. *Dalton Transactions*, 39.

Zhang, Q., Zhang, Q., Chen, S., Liu, W., Lukas, K., Yan, X., Ren, Z. (2012). Suppression of grain growth by additive in nanostructured p-type bismuth antimony tellurides. *Nano Energy*, 1(1), 183–189.

Zhang, G., Su, A., Du, Y., Qu, J., Xu, Y. (2014). Catalytic performance of activated carbon supported cobalt catalyst for CO_2 reforming of CH_4 . *Journal of colloid and interface science*, 433, 149-155.

Zhang, B., Wang, J., Zou, T., Zhang, S., Yaer, X., Ding, N., Wu, Y. (2015). High thermoelectric performance of Nb-doped SrTiO_3 bulk materials with different doping levels. *Journal of Materials Chemistry C*, 3(43), 11406–11411.

Zhang, D.-B., Zhang, B.-P., Ye, D.-S., Liu, Y.-C., Li, S. (2016). Enhanced Al/Ni co-doping and power factor in textured ZnO thermoelectric ceramics prepared by hydrothermal synthesis and spark plasma sintering. *Journal of Alloys and Compounds*, 656, 784–792.

Zhang, J., Song, L., Pedersen, S. H., Yin, H., Hung, L. T., Iversen, B. B. (2017). Discovery of high-performance low-cost n-type Mg_3Sb_2 -based thermoelectric materials with multi-valley conduction bands. *Nature Communications*, 8, 13901.

Zhang, X., Feng, D., He, J., Zhao, L. D. (2018). Attempting to realize n-type BiCuSeO. *Journal of Solid State Chemistry*, 510-516.

Zhang, X., Liu, C., Tao, Y., Li, Y., Guo, Y., Chen, Y., Wang, J. (2020). High ZT 2D Thermoelectrics by Design: Strong Interlayer Vibration and Complete Band-Extrema Alignment, *Advanced Functional Materials*, 2001200.

Zhao, L. D., Berardan, D., Pei, Y. L., Byl, C., Pinsard-Gaudart, L., Dragoe, N. (2010). Bi_{1-x}Sr_xCuSeO oxyselenides as promising thermoelectric materials. *Applied Physics Letters*, 97(9), 092118.

Zhao, L.-D., He, J., Hao, S., Wu, C.-I., Hogan, T. P., Wolverton, C., Kanatzidis, M. G. (2012). Raising the Thermoelectric Performance of p-Type PbS with Endotaxial Nanostructuring and Valence-Band Offset Engineering Using CdS and ZnS. *Journal of the American Chemical Society*, 134(39), 16327–16336.

Zhao, H., Sui, J., Tang, Z., Lan, Y., Jie, Q., Kraemer, D., Ren, Z. (2014). High thermoelectric performance of MgAgSb-based materials. *Nano Energy*, 7, 97–103.

Zhao, L. D., Dravid, V. P., Kanatzidis, M. G. (2014). The panoscopic approach to high performance thermoelectrics. *Energy Environ. Sci.*, 7(1), 251–268.

Zhao, L. D., Lo, S. H., Zhang, Y., Sun, H., Tan, G., Uher, C., Kanatzidis, M. G. (2014). Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. *Nature*, 508(7496), 373-377.

Zhao, L. L., Wang, X. L., Wang, J. Y., Cheng, Z. X., Dou, S. X., Wang, J., et al. (2015). Superior intrinsic thermoelectric performance with zt of 1.8 in single-crystal and melt-quenched highly dense Cu_{2-x}Se bulks. *Scientific Reports*, 5, 7671.

Zhou, G., Dai, B., Xie, H., Zhang, G., Xiong, K., Zheng, X. (2017). CeCu

composite catalyst for CO synthesis by reverse water–gas shift reaction: Effect of Ce/Cu mole ratio. *Journal of CO2 Utilization*, 21, 292–301.

Zhou, C., Lee, Y. K., Yu, Y., Byun, S., Luo, Z.-Z., Lee, H., Chung, I. (2021). Polycrystalline SnSe with a thermoelectric Figure of merit greater than the single crystal. *Nature Materials*.

Zhu, H., He, R., Mao, J., Zhu, Q., Li, C., Sun, J., Ren, Z. (2018). Discovery of ZrCoBi based half Heuslers with high thermoelectric conversion efficiency. *Nature Communications*, 9(1).

Zhu, M., Tian, P., Ford, M. E., Chen, J., Xu, J., Han, Y.-F., Wachs, I. E. (2020). Nature of Reactive Oxygen Intermediates on Copper-Promoted Iron-Chromium Oxide Catalysts during CO₂ Activation. *ACS Catalysis*.