

Porous Thermoelectric Materials for Energy Conversion by Thermoelectrocatalysis

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Novel uses of thermoelectric (TE) materials as catalyst and catalyst promoters have been reported recently for a variety of applications such as environmental gas mitigation, battery, and photoreduction of nuclear wastewater. TE Seebeck voltage is found to increase the catalytic activities by tens to hundreds of times, and this effect is termed thermoelectrocatalysis. In these uses, the TE materials are in an open-circuit configuration, which is different from the usual closed-circuit configuration in the TE energy generation and cooling devices. A new figure of merit defined as the Seebeck voltage per unit heat loss is proposed for the application of thermoelectrocatalysis. Techniques such as dense bulk porous surface and increased thickness of the TE materials are used for the optimization of the thermoelectrocatalysis of the oxyselenide BiCuSeO for the carbon dioxide hydrogenation reactions.

1. Introduction

Thermoelectric (TE) materials can convert a temperature difference into a voltage and are considered promising for energy harvesting from waste heat. Conversely, they can also convert electricity into a temperature gradient and are being used for noiseless refrigeration and for precision temperature control for scientific instruments.^[1] In these applications, TE devices are configured as modules: the P- and N-type legs are connected thermally in parallel and electrically in series in closed-circuit conditions. The energy transformation efficiency of these processes can be evaluated by a dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature. The thermal conductivity consists of lattice conductivity κ_l and electron conductivity κ_e , that is, $\kappa = \kappa_l + \kappa_e$, and the electrical conductivity σ is proportional to the thermal conductivity κ_e

through the Wiedemann–Franz relation $\kappa_e = L\sigma T = Lne\mu T$, where L is the Lorenz number, n the carrier density, and μ the carrier mobility. The optimization of ZT is often a complex matter because its contributing parameters are interrelated; improving one parameter usually leads to an adverse effect on another.^[2] For example, usually a higher charge carrier density leads to higher electrical conductivity σ , but a smaller Seebeck coefficient S .

Recently, a novel use of TE material has been reported in open-circuit configuration, as a catalyst, catalyst support, and promoter, and it has been demonstrated that a Seebeck voltage $V = -S\Delta T$ from TE material with a temperature gradient ΔT can increase the catalytic activity by tens to hundreds of times.^[3,4] This thermoelectrocatalysis effect or TE promotion of catalysis has since been used for the promotion of other catalytic chemical reactions by many researchers in the world.^[5–12] Yoon et al. reported using a temperature gradient over TE Bi₂Te₃ particles to drive oxygen reduction reaction to generate hydrogen peroxide H₂O₂, which in turn catalyzes a range of highly stereoselective hydroxylation and epoxidation reactions under mild reaction conditions.^[5] They also investigated and confirmed the validity of the dynamic equation proposed in ref. [3], expressed as $\ln(r/r_0) = -\gamma S\Delta T/k_b T_h$, where r is the reaction rate and r_0 is the reaction rate when temperature gradient ΔT is zero, k_b is the Boltzmann constant, T_h is the temperature of the reaction surface (at hot side), and γ is an empirically determined dimensionless constant.^[3–5] Lin et al. demonstrated that a temperature difference across the TE Bi₂Te₃ nanoplates can increase the generation of hydrogen peroxide and that can be used for antibacterial environmental disinfection.^[6] Xu et al. reported that a temperature gradient across an Er-doped BiCuSeO TE support can greatly enhance the transformation of carbon dioxide (CO₂) into carbon monoxide (CO) by solar energy.^[7] Zheng et al. designed a breathing air electrode using P-type and N-type TE materials as charge and discharging thermoelectrocatalysts and obtained much-improved energy efficiency of the Zn–air battery.^[8] Their observed reduction in the overpotential is much larger than the Seebeck voltage itself, further demonstrating the catalytic promotional effect of a Seebeck voltage.^[8] Fan et al. demonstrated TE SnSe can serve as thermoelectrocatalysts for the degradation of methylene blue.^[9] Of particular interest is the observed coupling of thermoelectrocatalytic and photochemical effects as reported by He et al. that is, a significant increase in the lifetime of the photogenerated electrons by the TE effect.^[10] All these demonstrate the wide range of potentials of

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the TE materials to separate electrons and holes at a material interface to promote chemical reactions. Furthermore, thermoelectrically initiated and enhanced electrocatalysis in hydrogen evolution reaction has also been reported by Sharifi et al.^[11] Hence, the thermoelectrocatalysis effect by TE materials has been well established. It is noteworthy that both thermoelectrocatalytic and thermocatalytic effects have been used for the description of the previous phenomena,^[3,6,11] but we consider thermoelectrocatalytic/thermoelectrocatalysis is more appropriate as this is not a direct thermal to chemical process, but a thermal to electrical (i.e., a temperature gradient across the material) then to chemical effect. In other words, a temperature gradient, rather than a uniform temperature, is the precondition for this phenomenon.

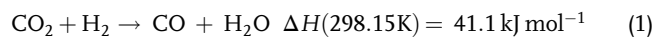
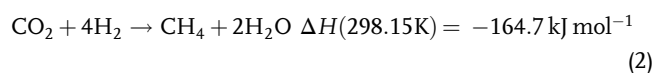
The underlying mechanisms for the aforementioned phenomena have also been proposed. Abdenour et al. argued that this is due to the change in the work function of the catalyst supported on the TE materials or the TE material itself when it was also used as a catalyst.^[3,4] It has been established that the catalyst activity is linearly proportional to the change of work function of the catalyst.^[13] Mechanisms based on a better alignment of energy levels between the surface electrons of the TE material and the reactant due to the TE effect and a TE P–N heterojunction-induced electric field model have also been presented.^[9,12,14] These mechanisms based on the change of the energy level of the surface electrons due to the TE effect are generic, suggesting that the thermoelectrocatalysis effect is a universal phenomenon and research on this effect and its applications is only in its infancy; further studies on the basic properties of this technology are urgently needed.

For the application of thermoelectrocatalysis, only one piece of TE material is used, and a closed circuit of P-type legs connected to N-type legs is not necessary; hence the best figure of merit (FOM) for TE may no longer be the ZT. First, as TE is in an open-circuit configuration, no electrical current is involved, hence no energy loss from electrical resistance. The electrical conductivity, at least its magnitude, may no longer be as important as in the closed-circuit configuration. Second, the change of activation energy for the chemical reaction^[3,4] and the change of the surface energy are all linearly proportional to the Seebeck voltage. Third, the value of thermal conductivity determines how much temperature gradient can be built up and how much thermal energy (heat) is lost. In order to provide some guidance on the search for the best TE materials for thermoelectrocatalysis, we propose a new parameter β , the amount of the Seebeck voltage per unit of heat loss as the FOM for the TE for the thermoelectrocatalysis application: $\beta = V/Q = S\Delta T/\kappa\Delta T = S/\kappa$. This definition gives positive values for the P-type TEs and negative values for the N-type TEs, and the higher the magnitude of the $|\beta|$, the higher the capability of the TE material for thermoelectrocatalysis according to the observed rate equation $\ln(r/r_0) = -\gamma \cdot S \cdot \Delta T/k_b T_h$. Higher $|\beta|$ will lead to higher energy conversion efficiency as will be discussed in the Discussion section. Generally speaking, heat loss is inversely proportional to the thermal conductivity of the TE, and for many practical application scenarios, the temperature gradient ΔT is dependent on the thermal conductivity of the TE materials, not an independent variable. As this FOM involves Seebeck coefficient S and thermal conductivity κ only, its optimization should be different and easier than for the energy conversion dimensionless figure of merit

ZT. We have surveyed a large number of TE materials and calculated their β and summarized them in Table 1.^[15–47] Some values in this table are calculated from the values of other parameters of the respective publications. From this, it can be observed that the highest β is achieved by the specially purified SnSe without any tin oxide and generally SnSe compounds.^[45–47] Other high β TE materials are the BiCuSeO-based oxyselenides, and up to $1328 \mu\text{V m W}^{-1}$ was achieved for the undoped compound.^[15] It is apparent that β is different from the other FOMs such as the ZT and the power factor $S^2\sigma$; the high values of the latter two do not necessarily lead to a high value for β . As BiCuSeO is easy to prepare, inexpensive, and can work at moderately high temperatures (up to 723 K), it is suited for the applications in thermoelectrocatalysis.

In practice, catalysts and catalyst supports are often porous to increase the surface area. It is of critical importance to demonstrate the promotional effect of thermoelectrocatalysis on porous TE materials before they are used widely as catalysts. Furthermore, TE properties such as the Seebeck coefficient and thermal and electrical conductivity are also affected by porosity.^[48] The optimization of porosity for high surface area and for TE properties should be an interesting subject for the application of thermoelectrocatalysis. As thermoelectrocatalysis itself is a new subject, few report has been published on how porous TE materials perform in thermoelectrocatalysis applications.^[12] Sol-gel processing offers a number of advantages such as low-temperature processing, ease of fabrication, and precise microstructural and chemical control and has been widely used for producing porous structures.^[49] This work reports on the application of sol-gel prepared porous TE materials for thermoelectrocatalysis and methods to maximize temperature gradient in a given reaction chamber.

The level of CO₂ concentration in the air has increased greatly since the industrial revolution.^[50] The catalytic conversion of CO₂ to CO (an important intermediate in many chemical processes) is a key step in the economical utilization of CO₂ and carbon recycling.^[51] Thus, the reverse water gas shift (RWGS) reaction (Equation (1)) that involves the conversion of CO₂ and hydrogen (H₂) into industrial chemicals carbon CO and methanization (CH₄) is increasingly being valued.^[52,53] The basic equations concerning the CO₂ hydrogenation are



The RWGS reaction (Equation (1)) is endothermic; hence high temperatures are more favorable. The CO₂ methanization (Equation (2)) is exothermic at low temperatures, so it could become increasingly dominant at low temperatures.

2. Results and Discussion

2.1. Porous Thermoelectric BiCuSeO

Sol-gel preparation conditions to produce oxyselenides BiCuSeO (PDF#45-0296) with a minimum amount of second phases were obtained first (Table S1 and Figure S1–S6, Supporting

Table 1. Summary of thermoelectric properties including their thermal conductivity κ , Seebeck coefficient S , electrical conductivity σ , the energy conversion dimensionless figure of merit ZT , the power factor, and the newly defined figure of merit (FOM) $\beta = S/\kappa$ for thermoelectrocatalysis applications for a number of thermoelectric materials.

Materials	Dopant	Thermal conductivity κ [W m ⁻¹ K ⁻¹]	Seebeck Coefficient S [μ V K ⁻¹]	Electric conductivity σ [S cm ⁻¹]	Energy conversion FOM ZT	Power factor [μ W cm ⁻¹ K ⁻²]	Thermoelectrocatalysis FOM $\beta = S/\kappa$ [μ V m W ⁻¹]	References
BiCuSeO		0.32	425	13.5	0.45	2.5	1328	[15]
BiCu _{1-x} SeO	Cu	0.5	275	50	0.81	3.8	550	[16]
Bi _{0.975} Cu _{0.975} SeO		0.36	300	4700	0.6	2.88	833	[17]
Ca ₃ Co ₄ O ₉	Tb	1.57	320	112	0.73	11.5	204	[18]
Na _x CoO ₂	K, Sr, Y, Nd, Sm, Yb	1.6	160	285	0.5	7.3	100	[19]
ZnO	Al	2	-145	262	0.34	5.5	-72	[20]
SrTiO ₃	Gd	3	-275	144	0.37	10.9	-92	[21]
CaMnO ₃	Dy, Ho, Er, Yb	1.7	-155	146	0.2	3.5	-91	[22]
In ₂ O ₃	Ge, Mn, Zn	10	-180	111	0.08	3.6	-18	[23]
Yb ₁₄ MnSb ₁₁	Al	0.5	240	153	1.28	8.82	480	[24]
Ca ₅ Al ₂ Sb ₆	Na	0.7	200	111	0.605	4.44	286	[25]
Yb ₃ Mn _{4.2} Sb ₉		0.56	190	126	0.74	4.54	339	[26]
CaZn ₂ Sb ₂	Na, Mg	0.8	240	160	0.85	9.24	300	[27]
YbCd ₂ Sb ₂	Mn	0.7	235	181	1.13	10	336	[28]
CaMg ₂ Bi ₂	Na	1.25	200	308	0.88	12.3	160	[29]
Mg ₃ Sb ₂	Na	0.59	400	26	0.58	4.2	678	[30]
Mg ₃ Sb ₂	Bi, Te	0.56	-260	186	1.59	12.6	-464	[31]
FeNb _{0.88} Hf _{0.12} Sb		4.2	240	885	1.45	51	57	[32]
ZrCoBi _{0.65} Sb _{0.15} Sn _{0.20}		2.62	225	751	1.42	38	86	[33]
TiNiSn		4	-250	384	0.4	24	-62	[34]
Si _{0.8} Ge _{0.2}	P	0.93	-284	196	1.84	15.8	-305	[35]
Si _{0.8} Ge _{0.2}	B, Y ₂ O ₃	1.9	310	406	1.81	39	163	[36]
PbSe _{0.85} PbTe _{0.15}	Na, Cd	0.89	250	248	1.65	15.5	281	[37]
AgPb ₁₈ SbTe ₂₀		1.1	-370	200	2.1	27.4	-336	[38]
PbTe	Tl	1	340	168	1.5	19.4	340	[39]
PbS	Na	1	300	150	0.9	10.9	300	[40]
PbSe	Sb	1.05	-240	257	1.3	14.8	-229	[41]
GeTe	Pb, Bi	1.4	270	480	1.8	35	193	[42]
PbTePbS	Na	0.85	250	339	2.3	21.2	294	[43]
SnTe	In, Cd	1.4	200	418	1.1	16.7	143	[44]
SnSe	Single cryst	0.35	350	80	2.6	9.8	1000	[45]
SnSe	Na, purified	0.25	300	110	3.1	9	1200	[46]
SnSe	Br	0.25	-480	40	2.8	9	-1920	[47]

Information). The gels obtained under these conditions were used for the preparation of different porous samples. **Figure 1a** shows X-ray diffraction patterns of samples prepared by different methods including solid-state reaction (called BCSO dense), sol-gel method, a mixture of 50% wt. of solid-state reaction and 50 wt%. of the sol-gel powders (called 50% sol-gel), dip coating of the gel on a dense BCSO pellet, and drop coating of the gel on a dense BCSO pellet. It can be observed that the dense

BCSO had a small amount of the second phase Bi₂O₃, but the amount of second phases was larger for other samples, in the order dense < 50% sol-gel < sol-gel < drop coating < dip coating. This suggests the sol-gel prepared BCSO is not as pure or stable as the solid-state prepared materials (which were sintered at the higher temperature of 923 K instead of 823 K for the sol-gel method), particularly at the sample surface. Scanning electron microscopy (SEM) images of the sol-gel

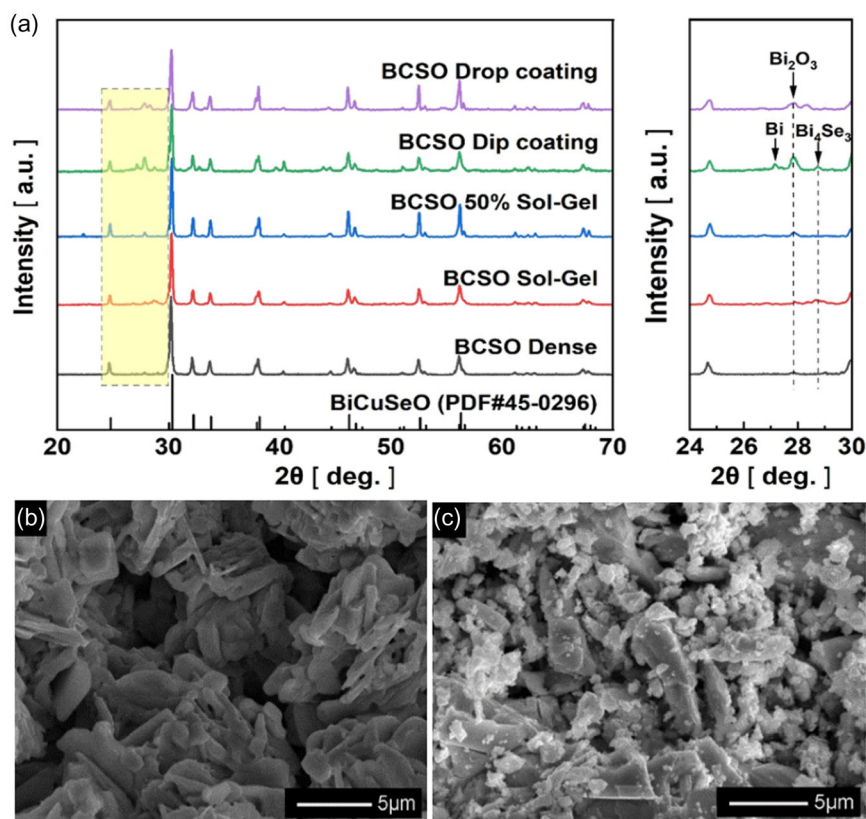


Figure 1. a) X-ray diffraction patterns of samples BCSO (dense), BCSO sol-gel, BCSO 50% sol-gel, BCSO dip coating, BCSO drop coating, and the BiCuSeO #45-0296 with area $24 < 2\theta < 30$ enlarged to show the peaks of secondary phases and the SEM microstructural images for b) BCSO sol-gel and c) BCSO 50% sol-gel samples.

and the 50% sol-gel pellets are shown in Figure 1b,c, respectively. Porosity can be observed on the surfaces of both samples. The measured Brunauer–Emmett–Teller (BET) surface areas were 0.5, 7.6, 1.6, and $1.5 \text{ m}^2 \text{ g}^{-1}$ for the dense, 50% sol-gel, dip-coated, and drop-coated samples, respectively. As the 50% sol-gel sample had the minimum amount of second phases among the porous samples and a much higher surface area, only this sample was used as our porous TE samples for catalytic chemical reaction investigations in the following.

2.2. Thermoelectrical Properties of the Porous BiCuSeO

Figure 2 shows (a) electrical conductivity and thermal conductivity, (b) Seebeck coefficient, and (c) ZT and $\beta = S/\kappa$ as functions of temperature for the 50% sol-gel pellets. As a comparison, the properties of the dense and another sol-gel prepared BCSO are also displayed.^[3,54] The electrical conductivity was low, ranging from 2.8 S cm^{-1} at 473 K to 9.7 S cm^{-1} at 773 K. Similar to the other sol-gel prepared and then spark plasma sintered (SPSed) BCSO samples,^[54] and the solid-state reaction prepared and then SPSed BCSO,^[3] the electrical conductivity decreased with increasing temperature when $T < 450 \text{ K}$; however, at higher temperatures, it increased with temperature. The thermal conductivity was $0.89 \text{ W m}^{-1} \text{ K}^{-1}$ at 298 K, then decreased with increasing temperature, to $0.42 \text{ W m}^{-1} \text{ K}^{-1}$ at 773 K. Generally

speaking, its thermal conductivity is much lower than the other sol-gel sample but higher than that of the dense and SPSed BCSO. Its Seebeck coefficient was $232 \mu\text{V K}^{-1}$ at 320 K, increased to $295 \mu\text{V K}^{-1}$ at 570 K, then decreased slightly with temperature, and reached $275 \mu\text{V K}^{-1}$ at 767 K. The calculated dimensionless figure of merit ZT was 0.12 at 767 K. The β value was $301 \mu\text{V m W}^{-1}$ at 320 K and $592 \mu\text{V m W}^{-1}$ at 767 K. So generally speaking, our 50% sol-gel pellets had similar TE properties as the other reported sol-gel prepared then SPSed BCSO samples but inferior to those of the solid-state reaction and SPSed ones.

2.3. Thickness Effect for Thermoelectrocatalysis

It is apparent from the reaction rate equation $\ln(r/r_0) = -\gamma S \Delta T / k_b T_h$ that in order to maximize the thermoelectrocatalysis effect, the temperature gradient across the TE sample needs to be maximized.^[3,4] For this purpose, a numerical modeling of the heating process of the chemical reaction chamber during a typical measurement was carried out (Figure S7 and S8, Supporting Information). The simulation results (Figure S9, Supporting Information) indicate that the most effective way to obtain a large temperature gradient ΔT is to increase the sample thickness.

Figure 3 shows the (a) Seebeck voltage, (b) CO_2 conversion, and (c) CO selectivity as functions of the temperature T_h at the hot surface of the dense BCSO pellets with thicknesses of

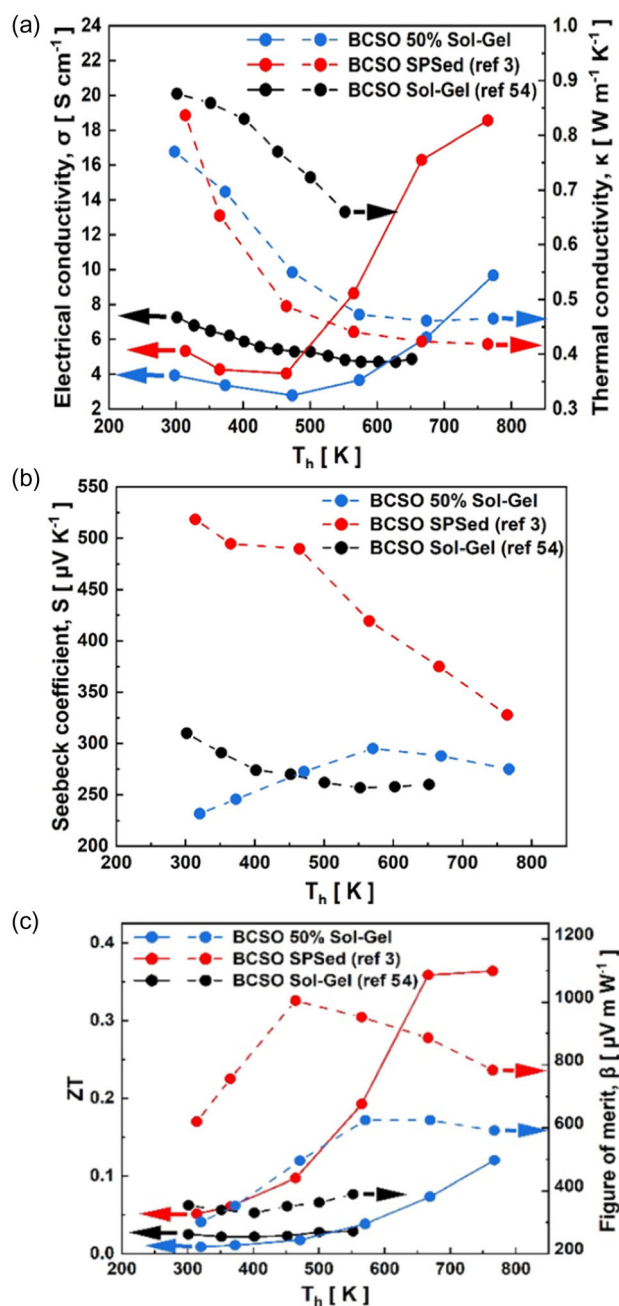


Figure 2. Temperature dependence of the thermoelectric properties: a) electrical conductivity σ (left axis) and thermal conductivity κ (right); b) Seebeck coefficient S ; c) $ZT = S^2\sigma/\kappa$ (left) and $\beta = S/\kappa$ (right) for the 50% sol-gel pellets. As a comparison, the data for a solid-state reaction prepared then spark plasma sintered (ref. [3]) and another sol-gel prepared then SPSeD (ref. [54]) BCSO are also displayed.

2, 4, and 6 mm. It can be seen for the same T_h , thicker samples had higher Seebeck voltage (Figure 3a). The highest Seebeck voltage achieved for the three samples were 55.8 mV for the 2 mm at 602 K, 80.5 mV for the 4 mm at 614 K, and 102.9 mV for the 6 mm at 614 K. Assuming the three samples had similar Seebeck coefficient as they are all dense BCSO prepared by

solid-state reaction, this means thicker samples had a larger temperature difference over their respective thickness and lower temperatures T_c at the cold side. Corresponding to the higher Seebeck voltage, a thicker sample also had higher CO_2 conversion (Figure 3b), achieving 4.5%, 9.3%, and 31% for the 2, 4, and 6 mm samples at their respective highest temperatures, when the inlet gas ratio was $\text{H}_2/\text{CO}_2 = 4:1$ (stoichiometric for the CO_2 methanization). The CO selectivity for these three samples was also different. The 4 mm sample had CO selectivity at or very close to 100% for the whole temperature range; however, for the 2 and 6 mm samples, the CO selectivity was lower in the middle-temperature range, reaching their lowest values of 94.7% at 506 K for the 2 mm and 62.3% at 516.6 K for the 6 mm samples. Nevertheless, a good linear relationship between the logarithm of the conversion ($\ln(Y)$) and $-eV/k_b T_h$ was still observed (Figure 3d).

We can simply stack two samples together to increase the thickness of the TE materials to increase the thermoelectrocatalysis effect. **Figure 4** shows (a) Seebeck voltage, (b) CO_2 conversion, and (c) CO selectivity as functions of the hot side temperature T_h for a single pellet of 6 mm thick sample and a 2 mm + 4 mm stacked pellets (called BCSO 4D + 2D) when the inlet gas was $\text{H}_2/\text{CO}_2 = 1:1$. The single and stacked samples had similar Seebeck voltage, CO_2 conversion, and CO selectivity for the whole temperature range.

2.4. Thermoelectrocatalytic Effect of the Porous BiCuSeO

To obtain a higher reaction surface (from the porous samples) and higher Seebeck voltage (the dense BCSO has a higher Seebeck coefficient), we prepared stacked samples (to increase the sample total thickness) of the dense and porous samples to demonstrate the effect of porosity on thermoelectrocatalysis. The dense samples were one 4 and one 2 mm thick pellets called 4D and 2D, respectively, and the porous sample was the 50% sol-gel with a thickness of 2 mm called 2P. **Figure 5** shows (a) Seebeck voltage, (b) CO_2 conversion, and (c) CO selectivity as functions of the hot surface temperature T_h for the two stacked samples 4D + 2D and 4D + 2P when the inlet gas was $\text{H}_2/\text{CO}_2 = 1:1$ (stoichiometric for the RWGS reaction). It can be observed that at the same hot side temperature T_h , the Seebeck voltage for 4D + 2D was higher than 4D + 2P; for example, the Seebeck voltage was 70.2 mV at 613 K for the 4D + 2P but much higher 92.5 mV at a lower T_h (586.8 K) for the 4D + 2D. This is understandable because the dense 2D had a higher Seebeck coefficient than the porous 2P. However, the CO_2 conversion for the 4D + 2P was higher across the whole temperature range. For example, the conversion was 12.8% at 583.3 K for the 4D + 2D, but it was higher at 15.1% at an even lower T_h of 576.2 K and reached 24.6% at 615.2 K for the 4D + 2P. This is a very high CO_2 to CO conversion reported at this temperature when the inlet gas ratio is $\text{H}_2/\text{CO}_2 = 1:1$ because it is higher than the calculated thermal equilibrium conversion of the RWGS in Equation (1).^[53] For comparison, the calculated thermal equilibrium conversion for the RWGS and the combined RWGS + methanization are plotted in Figure 5b as well. This gives a CO production rate of $662.4 \mu\text{mol h}^{-1}$ and $41.9 \mu\text{mol g}^{-1} \text{h}^{-1}$. Apparently, a higher surface area of the 2P

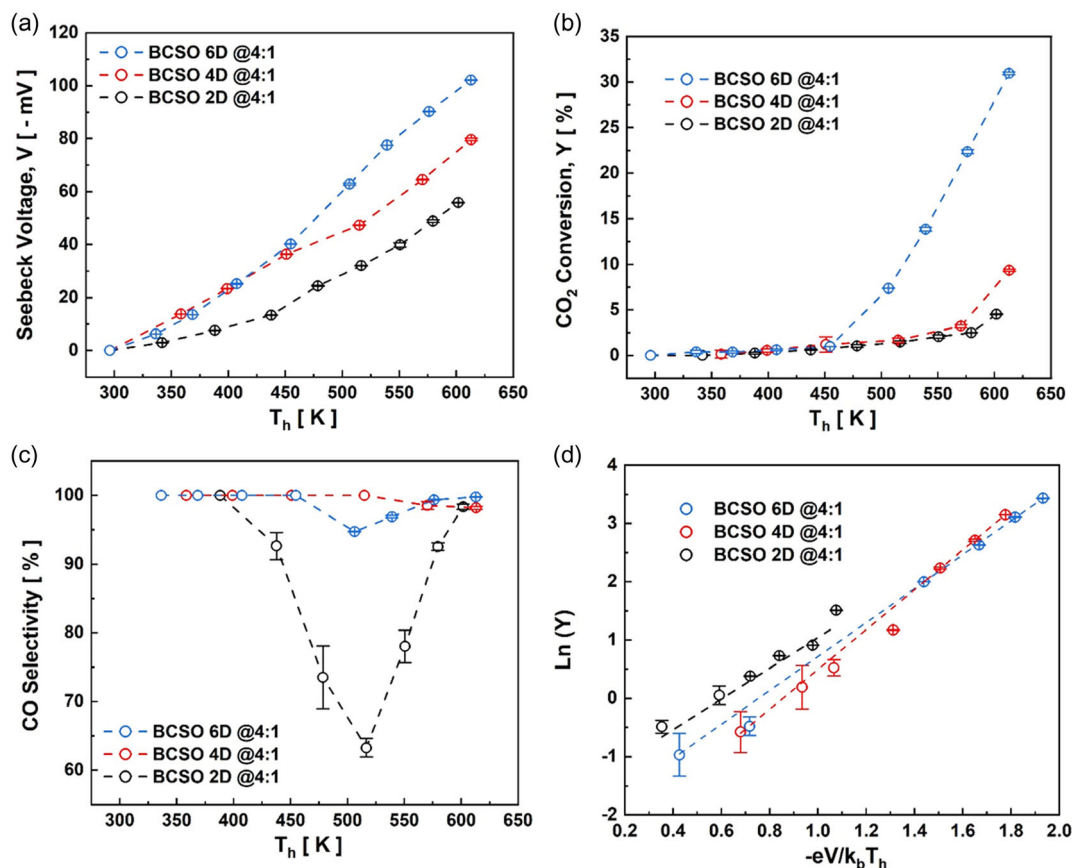


Figure 3. a) Seebeck voltage, b) CO_2 conversion, and c) CO selectivity as functions of the hot side temperature for BCSO pellets with different thickness 2, 4, and 6 mm when the inlet gas was $\text{H}_2/\text{CO}_2 = 4:1$. d) The $\text{Ln}(Y/Y_0)$ is a function of $-eV/k_b T_h$, where the relationship between them can be approximated by a linear function for each sample.

pellet enabled this higher catalytic activity despite its lower Seebeck voltage. The CO selectivity was close to 100% for both samples for all the temperatures (Figure 5c), and a linear relationship between the logarithm of the conversion and $-eV/k_b T_h$ was observed as well (Figure 5d). Further experiments using more stacked samples at different inlet gas ratios obtained similar results which confirmed the same conclusion.

2.5. Discussion

As shown in Figure 2, our porous oxy-selenide BCSO prepared by the sol-gel method had a lower Seebeck coefficient and higher thermal conductivity than its dense counterpart prepared by solid-state reaction^[3] and similar Seebeck coefficient but lower electrical and thermal conductivities than the other sol-gel prepared then SPSed BCSO.^[54] The lower Seebeck coefficient and electrical conductivity of our sample may be related to its lower crystallinity and therefore higher defect density, because the other two were both SPS sintered but ours were not. The lower electrical but higher thermal conductivities as compared to its dense counterpart^[3] indicate our samples had higher lattice (or phonon) thermal conductivity. The existence of a small amount of second phases could be partly responsible

for this (assuming they have higher thermal conductivity than the TE material) but should not be the main reason because our sample still had much lower thermal conductivity than the other sol-gel prepared BCSO (ref. [54]), which had little second phase.^[54] So the porosity in our sol-gel prepared BCSO did not result in any significant reduction in thermal conductivity (or increased phonon scattering) as compared to the dense and well-crystallized BCSO (ref. [3]). This is not entirely surprising because the mesoscale porosity that leads to higher BET surface area as measured by N_2 adsorption techniques in our sol-gel sample may not be the “right” porosity which can significantly increase the phonon scattering at its boundaries. This is because only those well-defined atomic or nanoscale porosity that can increase phonon scattering but maintain electron conduction and Seebeck coefficient can improve the ZT for TE materials.^[48e,f]

The existence of some second phases did not appear to have much effect on the selectivity of the reactions either, as the CO selectivity kept close to 100% under most conditions. The minute amount of the second phases could be a reason, but it is noteworthy that Cu-based catalysts are one of the best catalysts for the RWGS reaction,^[51c,55] and either the redox or formate intermediate route takes place on the Cu^0 surface. Therefore, from the viewpoint of catalysis in the RWGS reaction, the exact compound

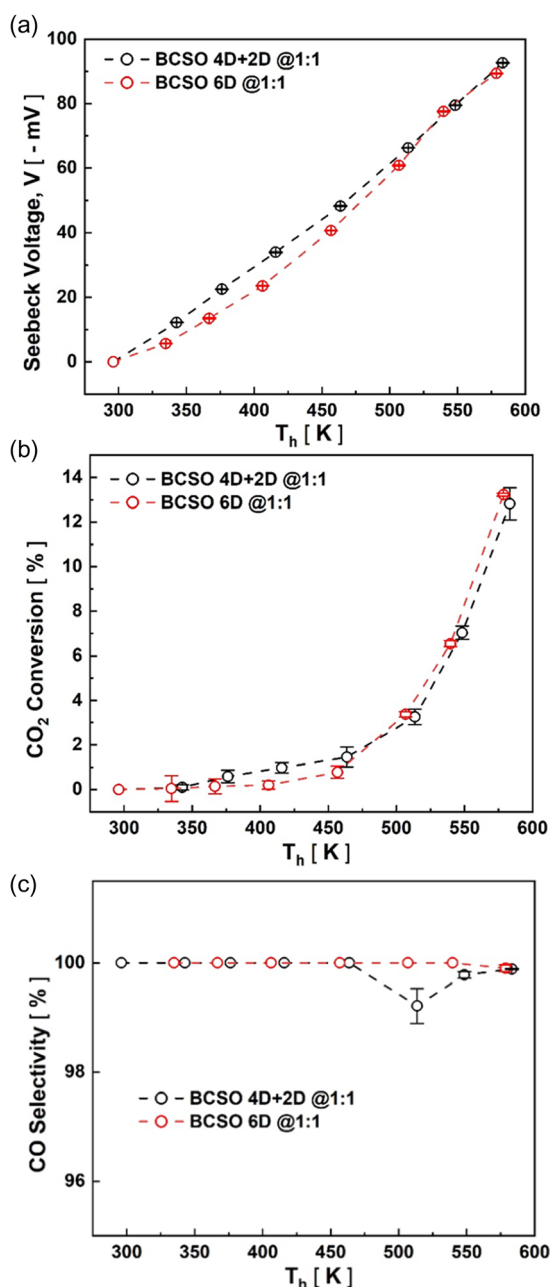


Figure 4. a) Seebeck voltage V , b) CO_2 conversion, and c) CO selectivity as functions of thickness for samples of single pellet and stacked pellets.

form of Cu is not important as long as there are Cu atoms present on the surface.

A number of methods have been reported for converting CO_2 into CO using renewable energy, including piezocatalytic,^[56] pyroelectrocatalytic,^[57] synergetic thermoelectric-photocatalytic,^[7] thermoelectrocatalytic,^[3] and others. Each technique has its pros and cons in terms such as applicability, scale-up, energy conversion efficiency, etc. Table S2, Supporting Information, lists some of the highest CO production rates reported for the methods mentioned earlier. Our CO production rate of $41.9 \mu\text{mol g}^{-1} \text{h}^{-1}$

is higher than pyroelectrocatalytic and synergetic photo-thermoelectrocatalytic methods but lower than the piezocatalysis method. Piezocatalysis can have a very high rate because ultrasonic waves can flip the polarization direction of the piezo materials at high frequencies, for example, 50 kHz, but this is difficult to obtain from a renewable source and the frequency of a harvestable mechanical vibration is usually much lower.

The energy conversion efficiency of the thermoelectrocatalysis process can be defined as the total product produced/total heat loss per time unit, so the obtained energy conversion efficiency corresponding to the $41.9 \mu\text{mol g}^{-1} \text{h}^{-1}$ was 24.5 nmol J^{-1} (Table S2, Supporting Information). As heat loss is an intrinsic process associated with the TE effect, this is the intrinsic energy conversion efficiency for the thermoelectrocatalytic process and will be higher to a higher β . For comparison, the energy conversion efficiency for the other techniques is also listed in Table S2, Supporting Information. It is noteworthy for other three techniques (S2, S3 & S4 in Table S2) they are not the intrinsic conversion efficiency. Considering the same thermoelectrocatalytic process (this work and ref. [3]), a thicker sample (this work) has a much higher energy conversion efficiency because the heat loss is inversely proportional to the sample thickness. Furthermore, as TE materials usually have very low thermal conductivity, when a section of the wall of a reactor is replaced by the TE material, the only extra cost is the TE material itself, and the heat loss can be maintained similar to the usual walls.

The effect of the sample thickness on its thermoelectrocatalysis can also be regarded as a tuning effect of the cold side temperature T_c to the catalytic activity at the T_h side. According to the Seebeck voltage definition, $V = -S(T_h - T_c)$, for the same T_h , a larger Seebeck voltage V means lower T_c . This means that for the same reaction temperature T_h , its catalytic activity can be tuned by changing the temperature T_c at the other side. This could find application in practice.

Figure 5d shows there exists a linear relationship between the $\ln(Y)$ and $-eV/k_b T_h$, as for the dense samples shown in Figure 3 and in previous publications.^[3–5] This demonstrates the applicability of the dynamic rate equation for the thermoelectrocatalysis for porous materials as well. It is noteworthy that this indicates almost all the chemical reactions take place on the hot surface with the temperature T_h , chemical reactions on the cold surface T_c as well as the side wall of the pellet can be ignored, and also the conversion Y is proportional to the reaction rate r .^[3] This is also the reason why the stacked samples had the same CO_2 conversion as the single sample of the same thickness because the extra surfaces at the connection between the two stacked pellets had a temperature much lower than the hot surface temperature T_h ; hence chemical reactions on these extra surfaces were much less than at the T_h surface and can be ignored. This is easy to understand when the CO selectivity is close to 100% as the RWGS to form CO is endothermic; therefore, high temperature is favored. If however the CO selectivity is much lower than 100% and the formation of CH_4 is substantial, then the linear relationship between $\ln(Y)$ and $-eV/k_b T_h$ may no longer exist. This is because the CO_2 methanization reaction to form CH_4 is exothermic at low temperatures (e.g., $<773 \text{ K}$ when $\text{H}_2/\text{CO}_2 = 3$);^[53] hence CO_2 methanization at the cold surface and side walls may no longer be ignored, and the conversion at the hot surface T_h cannot represent all the reactions.

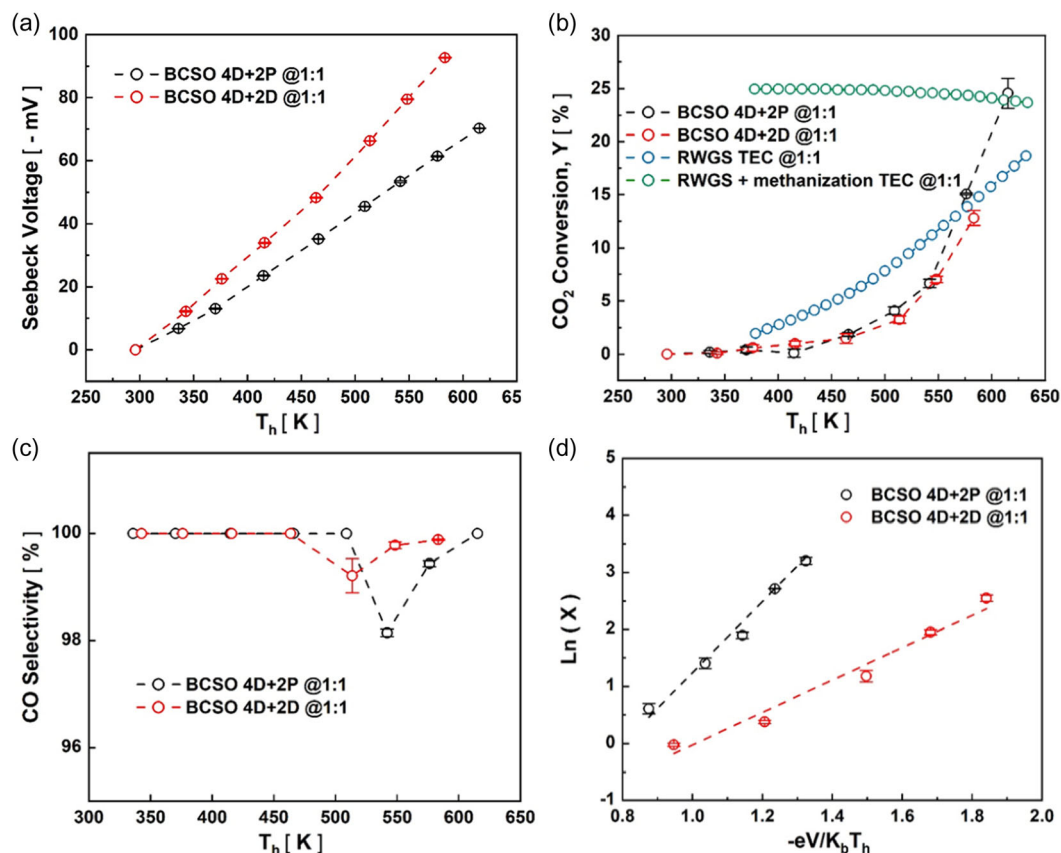


Figure 5. a) Seebeck voltage V , b) CO_2 conversion Y , and c) CO selectivity as a function of T_h for stacked dense and porous BCSO samples, and d) the relationship between $\text{Ln}(Y)$ and $-eV/k_b T_h$ can be approximated by a linear line. The calculated thermal equilibrium conversions (ref. [53]) of the RWGS in Equation 1 and the combined conversions for RWGS + methanization (Equation (1) and (2)) are plotted in the figure for comparison.

Figure 5b shows the CO_2 conversion for the 4D + 2P sample is higher than the thermal equilibrium conversion of the RWGS but still lower than (or similar to) that of the combined RWGS + methanization. This agrees with the previous report that TE energy $-eV$ could shift the chemical equilibrium and promote the forward RWGS reaction over the backward WGS reaction.^[3] It has also been reported that an electrical field (via the non-faradaic electrochemical promotion mechanism) enabled achieving 40.6% CO_2 conversion at 648 K when the thermal equilibrium conversion was about 20% with an inlet gas ratio of $\text{H}_2/\text{CO}_2 = 1:1$.^[58] These results suggest that the Seebeck voltage or the electrochemical energy $-eV$ affected the RWGS and the CO_2 methanization differently and promoted the forward RWGS reaction greatly but much less promotion to or even inhibited the CO_2 methanization, that is, promoting the CO selectivity.

3. Conclusion

A new figure of merit $\beta = S/\kappa$ for TE materials for thermoelectrocatalysis applications has been proposed. Unlike the dimensionless figure of merit ZT which indicates the energy conversion efficiency, this new FOM indicates the capability for promoting the catalytic activity of the TE materials.

The optimization of the β is different and should be easier than the optimization of ZT , for the selection of the most appreciate TE materials for thermoelectrocatalysis applications.

Porous oxyseLENIDE BiCuSeO has been prepared by a sol-gel method. These TE materials were found to have inferior TE properties as compared to their dense counterpart prepared by solid-state reactions and SPS sintering. However, its surface area is increased by at least one order of magnitude. This enhanced surface area was more than enough to compensate for the smaller effect from a smaller Seebeck voltage for catalysis promotion, achieving CO_2 conversion higher than the thermal equilibrium conversion of the RWGS across a large temperature range. The CO selectivity was also enhanced by a Seebeck voltage. Furthermore, we have confirmed that the dynamic equation $\text{Ln}(Y/Y_0) = -\gamma eV/k_b T_h$ is still valid for porous TE BiCuSeO.

4. Experimental Section

TE Materials Preparation: The TE oxyseLENIDE BiCuSeO (BCSO) samples were prepared by solid-state reaction and sol-gel methods. Details of the solid-state reaction with a B_2O_3 flux agent can be found in a previous publication.^[59] The obtained BCSO powders were cold-pressed into pellets of 20 mm in diameter, followed by sintering at 923 K for 10 h with a heating and cooling ramp rate of 1 K min^{-1} under an argon atmosphere. This sample is called the dense BCSO.

For the sol-gel method, the $\text{Bi}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, and Se powders of stoichiometric amount were used. 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, and a light yellow clarified solution was obtained after several minutes, indicating that the Se powder had been completely dissolved. In contrast, $\text{Bi}(\text{NO}_3)_3$, $\text{Cu}(\text{NO}_3)_2$, and citric acid (CA) powders were dissolved into 30 mL distilled water to obtain a blue transparent solution, and then a certain amount of ethylene glycol (EG) was added. The aforementioned two solutions were mixed and heated to 90 °C with a stir. A light blue gel was formed within 3 h; it was then dehydrated in an oven at 80 °C for 8 h to form a dry blue gel. A systematic investigation was conducted in order to obtain the best CA and EG concentrations as well as calcination conditions for obtaining the target BCSO phase. It was found calcination at 823 K in the air at atmospheric pressure for 10 h would obtain a blackish BiCuSeO powder containing a minimum amount of the second phase (Figure 1a).

To obtain porous TE samples, three methods were used: dip coating (dip a dense BCSO pellet into the sol-gel prepared gel), drop coating (drop the gel onto the surface of a dense BCSO pellet), and mixed powder (the dried gel was mixed with the flux-method-prepared BCSO powder in a weight ratio of 1:1, and then the mixed powder was ball milled for 12 h and then cold-pressed into a pellet of 20 mm in diameter under a pressure of 1.07 MPa). The dip-coated and drop-coated samples were calcined at 823 K for 10 h in an argon atmosphere. The mixed powders were cold-pressed into the 20 mm diameter pellet and then sintered at 823 K for 10 h in an argon atmosphere.

TE Property Measurements: Seebeck coefficient and electrical resistivity were measured simultaneously by using an LSR-3 Linseis at a range of 300–723 K. The thermal diffusivity (D) is determined by using an LFA-457 Netzsch laser flash method under a continuous argon flow. The thermal conductivity (κ) could be calculated by the equation $\kappa = D \cdot \rho \cdot C_p$, where ρ is the sample density and C_p is the specific heat capacity determined using a differential scanning calorimeter instrument. The sample density was determined using the Archimedes method.

Reaction Chamber: Chemical reactions were performed in a single-chamber reactor. The schematic of the reaction chamber is shown in Figure S7, Supporting Information, and more details can be found in ref. [3]. 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 ($\varnothing$ 0.25 mm, 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-hole alumina tubes (Omegatite 350). A high-temperature hot plate 1500F model (HP99YX, Wenesco, Inc.) with a temperature controller was used to heat the reaction chamber.

The reaction chamber was placed on the top of the hotplate with a connection to the water cooling system by two pipes. A sample pellet was placed into a predesigned ceramic (MACOR) holder and attached (with a thin mica sheet for electrical insulation) to the cooling surface of the cover plate. The bottom side of the TE sample faces toward the hot bottom of the reaction chamber and is surrounded by the mixed reactant gases.

Catalytic Activity Experiment: The catalytic activity measurements for different catalysts were carried out in the reaction chamber described previously. A set of three mass flow controllers were used to control the gas composition and flow rate. The 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 and two columns, molecular sieve 5 A and a Porapak Q. Data acquisition and manipulation were performed using the TotalChrom Workstation (version 6.2.1 for Windows) data system. Each experiment was repeated for five cycles to test the stability and reproducibility. At each temperature, the catalyst was allowed to reach a steady state for at least 30 min, and then five injections were performed for GC measurements. The average of the three closest data out of the five GC measurements at each temperature is calculated. Carbon mass balance was monitored for all the chemical reaction data and was found to be within 6%.

For the CO_2 hydrogenation reaction, the reactants were BOC standards of H_2 supplied as a 30% mixture in He and 3% CO_2 mixture in He, and the gases were mixed with helium gas (BOC, 99.996%) to obtain the desired concentrations. The inlet gas ratio was set as H_2 : CO_2 = 1:1 or 4:1. All samples were tested at an overall flow rate of 100 mL min^{-1} . The conversion of CO_2 and the selectivity of CO and CH_4 were evaluated from the outlet carbon percentage values obtained by the gas analysis. Because the reaction product water vapor could not be detected by GC, the CO_2 conversion and the selectivity of product X ($X = \text{CO}, \text{CH}_4$) can be calculated as follows:

$$\text{CO}_2 \text{ Conversion (\%)} = \frac{(\text{CO}(\text{KPa}) + \text{CH}_4(\text{KPa}))}{(\text{CO}(\text{KPa}) + \text{CH}_4(\text{KPa}) + \text{CO}_2(\text{KPa}))} \times 100 \quad (3)$$

$$X \text{ Selectivity (\%)} = \frac{X(\text{KPa})}{(\text{CO}(\text{KPa}) + \text{CH}_4(\text{KPa}))} \times 100 \quad (4)$$

Here, CO_2 (KPa), CO (KPa), and CH_4 (KPa) stand for the partial pressure of CO_2 , CO, and CH_4 within the outlet gas, which could be identified and calculated from GC data.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

carbon dioxide hydrogenation, porous materials, promotion of catalysis, thermoelectric materials, thermoelectrocatalysis

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Porous thermoelectric materials for energy conversion by thermoelectrocatalysis

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