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Electrocatalysts for Electro-Oxidation of Direct Alcohol Fuel Cell: Chemistry and Applications

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Abstract:

In the present scenario, civilization wholly depends on energy generation and storage for better technological progress and extension in several scientific applications. Due to limited conventional energy sources and high energy requirement; absolute, cost-effective, and eco-friendly substitute roots of energy are of the principal interest. In this direction, direct alcohol fuel cell (DAFC) is becoming more familiar and promising due to its straightforward configuration system, weight and elevated power generation efficiency. Indeed, recent years have seen extensive research on the preparation and properties of the fuel cell system. The literature review presented in this article provides comprehensive information on electro-oxidation of alcohol developed on different type of electro-catalyst. The integration of a range of nanomaterials is depicted, in order to comprehend the effect of different properties such as a well-ordered porous structure, exemplary high specific surface areas, electronic conductivity, tremendous convenience to active sites, and improved mass

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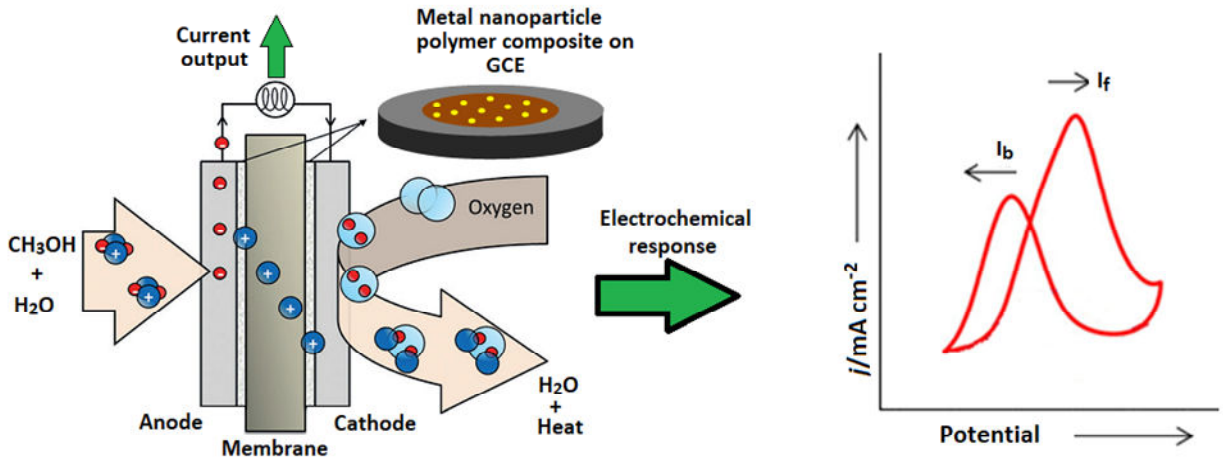
transport for electro-oxidation of fuel cell. In this article, we have presented a detailed review of fuel cells and defined the main perspective, rationale and motivation, research tasks and objectives of study as well as the delimitation of the study.

Keywords: Direct alcohol fuel cell; electro-oxidation; nanomaterials, anode catalyst.



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Abbreviations:

DAFC:	*Direct alcohol fuel cell*
PEMFCs:	*Proton exchange membrane fuel cells*
DMFCs:	*Direct methanol fuel cells*
Pt/C:	*Platinum nanoparticles sustains carbon*
SOFC:	*Solid oxide fuel cell*
AFC:	*Alkaline fuel cell*
MCFC:	*Molten-carbonate fuel cell*
PAFC:	*Phosphoric-acid fuel cell*
DEFCs:	*Direct ethanol fuel cells*
FTIR:	*Fourier transform infrared spectroscopy*
CV:	*Cyclic voltammetry*
PEDOT:	*Poly (3, 4-ethylenedioxy thiophene)*
ORR:	*Oxygen reduction reaction*
DFT:	*Density functional theory*
MWCNTs:	*Multiwall carbon nanotubes*
THH PtNCs:	*Tetrahexahedral platinum nanocrystals*
CrN:	*Chromium nitride*
MOR:	*Methanol oxidation reaction*
EOR:	*Ethanol oxidation reaction*
TEM:	*Transmission electron microscopy*
SEM:	*Scanning electron microscopy*
XRD:	*X-ray diffraction*
EDS:	*Energy-dispersive X-ray spectroscopy*
GO:	*Graphene oxide*
GNS:	*Graphene nanosheets*
RGO-CF:	*Reduced graphene- decorated carbon fiber*

LSV:	*Linear sweep voltammetry*
XPS:	*X-ray photoelectron spectroscopy*
PdNPs:	*Palladium nanoparticles*
CP:	*Conductive polymer*
MN:	*Metal nanoparticle*
PANI:	*Polyaniline*
IPCF:	*In-situ polymerization and composite formation*
CSA-PPyCC:	*Camphor sulfonic acid- based polypyrrole carbon catalyst*
ECSA:	*Electrochemical surface area*
CNT:	*Carbon nanotube*
Pt/MC:	*Platinum mesoporous carbon*
PDDA:	*poly (diallyl dimethyl ammonium chloride)*
pDAN:	*Poly 1, 8-diamino naphthalene*
PPCA HN:	*Poly (pyrrole-co-aniline) hollow nanospheres*
PDPB-nf:	*poly (diphenyl butadyine) polymer nanofiber*
gC_3N_4:	*Graphitic carbon nitride*
NG:	*Nitrogen doped graphene*
PT3A:	*Poly 4-(thiophen-3-yl) aniline*

1. Introduction

Recently, fuel cells as a neat energy tool for example proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) have taken strong consideration. In certain tools, Pt/carbon-based catalysts are employed as electrode substances for the potential chemical reformation of combustible to electricity through electrocatalytic reactions, such as methanol oxidation effect at the positive electrode of DMFCs and oxygen reduction reaction (ORR) on the negative electrode of PEMFCs [1]. Liquid fuel cells covering methanol and formic acid fuel cells are recognized to be the encouraging clean energy origins with high energy efficiency and low environmental contamination. Current reports point out that the electro-catalytic performances of

these Pd-based bimetallic nanocrystals are better to those of absolute Pd counterparts [2]. The Au-Pd NPs have been found to exhibit better catalytic activity in comparison to the similar monometallic equivalents, viz., AuNPs and PdNPs developed below similar circumstances. The activation energy specifications of the Au-Pd NP modified graphite electrodes were below, presenting them possible anode catalysts in an alkaline electrolyte based methanol fuel cells at room temperature [3]. Fuel cells are engaging PEMs as well as PEMFCs, and DMFCs have been recognized to be a potential energy origin of substitute energy as of their purity, high performance, the recyclability of fatigue heat and their conformity for portable, transportation, and stable purposes. Recent research attempts in PEMFCs and DMFCs are concentrated on the construction of inexpensive, stable, high-performance fuel cell ingredients to comprehend their latent for full commercialization. Platinum nanoparticles sustained on porous carbon (Pt/C) are usually one of the best anode material of major interest [4]. The methanol oxidation investigations have confirmed that the appearance of Au and Sn in Pt-based catalysts completely specified their potential to overcome the high Pt content needed for this purpose, explaining the function of Au in enhancing current/potential response and implying the effect of supporting matrices [5]. So far, bi-metallic catalysts have turned out to have a remarkable electrocatalytic performance for the methanol oxidation when used as DMFC anode system. Though, the expense, sluggish oxidation kinetics, durability of the bimetallic catalyst, methanol crossover and deteriorating catalyst performance are some factors which have restricted the commercialization of DMFC tools. The summation of metal oxides to Pt-modified with both Ru and IrPt-Ru and Pt-Ir gives better catalytic activity for methanol electro-oxidation in comparison to the bi-metallic Pt-Ru system [6].

So keeping in mind the different perspectives, this article focuses on different electro-catalysts for fuel cells and defines the main perspective, rationale and motivation of research tasks and objectives of the study as well as the delimitation of the study. The outline of this review article can be summarized as follows:

1.1. The potential of fuel cells

Fuels cells do not accumulate electricity but deliver it straight from fuel. Additionally, they require being stocked with combustible and oxygen to working. They have some benefits over conventional batteries such as extended running time, compact load and efficiency of recharging. Further, the world's power arrives from combusting fossil fuels in low-efficiency method [7]. The

extent of utilization of fuel cells may further offer an option to these methods both for motionless and moving purposes. Fossil fuels are not an effective long-term source of energy anymore due to exponential energy demands and growing environmental concerns. Efforts and research have been redirected to renewable power generation and/or power sources [8]. While a reliable and renewable power source, fuel cells have fascinated recognition for mobile accessories, electric transports and on-site energy production operations in which they have great energy productivity and low exhaust level. Due to the cost and endurance concerns, there is a hindrance for commercialization at larger scale [9]. The gaseous hydrogen as an oxidant has been recently replaced by liquid oxidants (fuels) having higher voltage, mass, warehouse, handling and processing [10-12]. There is a range of variables that can be adjusted within a fuel cell to ensure its sustainability and efficiency. Of these include, the pH of the electrolyte, nature of the oxidant and the respective materials of the anode along with its relative surface modifications. The nature of the design fuel cells was found to be depended on the proton exchange membranes (PEM). The PEM fuel cells are extremely capable among fuel cells and exhibit outstanding achievements with supplied hydrogen[13]. Throughout the generation, storehouse and worth of hydrogen remains un-explained while its production is strictly influenced by the contaminating varieties of hydrogen.

1.2. Brief review on the history of fuel cells

Firstly in 1839, Sir William Grove, pioneer of "Fuel Cell Technology" (generally referred to as the "Ancestor of the Fuel Cell") revealed that by inverting the electrolysis of water, it may be likely to produce electricity. Later in 1889, the two scientists, Mond and Langer [14], cast the expression of the fuel cell as they were seeking to design a primary realistic fuel cell adopting air and coal gas. Although additional efforts were initiated in the beginning 1900s to expand fuel cells that might alter carbon within electricity, the initiation of the internal ignition engine tentatively repealed the hope of additional growth in this fledgling technology.

In 1932, Francis expanded the primarily victorious fuel cell tool, with a hydrogen-oxygen cell using nickel electrodes and alkaline electrolytes as a low-cost substitutes to the catalysts handled by Mond and Langer. Later, the National Aeronautics and Space Administration (NASA) [15] started to construct a small current engine for space missions. NASA is releasing the research funds for those who are involved in fuel cell technology. After supplying electricity to numerous space missions, fuel cells now have an established role in the space program. During previous

years, some major automobile industries and agencies have kept supporting the enduring research in the field of fuel cell development for purpose in vehicles and other fields. Fuel cell Technology is demanded to substitute conventional energy roots in growing years from micro-level fuel cells to be utilised in mobile phones to high-potential fuel cells for stock car competition [16]. Pt-group metal nanoparticles such as palladium, ruthenium and platinum are particularly attractive due to their size-dependent electrical, optical and catalytic properties. Pt nanoparticles (Pt-NPs) had a progressing and promising role in the field electrocatalytic sensors for alcohol oxidation [17, 18]. Recently, platinum group metals based nanoparticles with different support materials are growing in fuel cell applications which exhibit excellent catalytic performance towards hydrogen evolution reaction [19]. The mixtures of elements to produce intermetallic compounds and alloys using the series of properties of metallic systems can significantly extend in material science. In several cases, there is an improvement in distinct properties against alloying it due to the synergistic influences and the wide range of configurations, structures and properties of metallic alloys has conducted to broad applications in microelectronics, engineering, and catalysis. The need to make materials with well-defined, controllable features and structures on the nanometer level coupled with the elasticity supported by intermetallic materials has formed concern in bimetallic and tri-metallic nanocluster [20]. To improve catalytic performance and reduce operational costs of platinum, advanced electrocatalysts designs relying on the bi-functional mechanism have been proposed. Platinum-group-metal-based nanostructures have great potential in the design of multifunctional catalysts for the electro-oxidation of fuel cells [21].

1.3. Typical models of fuel cells and their features

The fuel cells have several applications in the field of the gas turbine for energy manufacturing, gasoline in a motor car and laptop battery to name a few. Flaming engines is similar to the turbine and the gas generator flame fuels, where applied pressure is generated by the growth of the gases contents for the mechanical operations. Batteries alter the synthesized power back into electrical voltage when demanded fuel cells assigned powerfully [22]. Fuel cell affords a direct current (DC) voltage that may apply towards power engines, lights and electrical devices [23].

Fuel cells are typically distinguished with their consecutive temperature and the category of electrolyte. Several kinds of fuel cells (as given in table 1) serve as an application in fixed power

production. Another type of cells may be valuable for small transportable importance or horsepower cars. The primary examples regarding the fuel cells are described in table1.

Up to now, various class of electro-catalysts have been extensively investigated for versatile purposes varying from DMFCs, DEFCs, etc. Here, the main focus will be placed at the electro-catalysts towards electro-oxidation of DAFCs purposes. A brief overview will be provided in the most up-to-date progress in these areas. Active supplies DAFCs present tremendous potential as an innovative power system including more excellent energy production (greater than 1 kW). Though, there is a shortage of comprehensive reviews on particular individual methods of DAFCs to have comprehensive information about the research break about the system advancement. So, this article tries to perform a comprehensive review on DAFCs expansion focusing on the study toward the compact, issues, the effect of different types of catalysts and significant challenges. Several distinct kinds of alcohol-based fuels have been adopted as DAFCs; also, everyone has its merits and limitations. In this article reviews the most current alcohol fuels toward fuel cell applications.

2. Direct fuel cells

In current years, as we know that one of the optimistic prospect competitors for the substitute of the combustion-based power origins, direct fuel cells (DFCs) have been getting growing alertness because of their cleanness and high effectiveness.

2.1 Direct alcohol fuel cells

Many researchers are working in the field of direct alcohol fuel cell. First, let us hold attention where a direct alcohol fuel cell converted and this the main focus of the researchers in the present scenario. All along with the various kinds of DFCs, direct ethanol fuel cells (DEFCs), particularly DEFCs working in alkaline states, are particular fascinating consideration because of their numerous exclusive benefits [29]. In DMFCs, methanol fuel at the fuel cell anode instantly converted into electrical energy. Unlike in DMFCs, in other types of fuel cells such as the normal hydrogen-powered cells, there is a large dependence on an external hydrogen generation system, which at most times are unresponsive. Though, certain limitations hinder the commercialization of DMFCs, including its poor performance compared with hydrogen/air systems.

Table.1. Different types of fuel cells and their specifications.							
Types of fuel cell	**Operating temperature**	**Electrolyte**	**Efficiency**	**System output**	**Application**	**Advantages**	**Disadvantages**
Proton exchange membrane fuel cell (PEMFC) [24]	60 to 80 °C	Perfluoro sulfonic acid	60:35% for transportation and stationary	<1kW-100kW	• Handy power • Endorsement power • Spread age group • Transport • Motor vehicle	• Solid electrolyte decreases decay & electrolyte organization troubles • Low temperature • Swift start-up	• Costly catalyst • Receptive to fuel impurities • Low temperature heat squander
Solid oxide fuel cell (SOFC) [25]	700 to 1000 °C	Yttria stabilized zirconia	60 %	1kW- 2MW	• Supplementary power • Electric usefulness • Spread age group	• High competence • Fuel elasticity • Can employ a diversity of catalyst • Solid electrolyte reduces decay & electrolyte organization troubles	• High temperature rust & collapse of cell components • High temperature process needs long start-up time and restrictions
Alkaline fuel cell (AFC) [26]	90 to 100 °C	Aqueous solution of KOH soaked in a matrix	60 %	10- 100kW	• Armed forces • Space	• Negative electrode reaction is in alkaline media, show the way to higher-performance • Can use a variety of catalyst	• Sensitive to CO_2 in fuel and air • Electrolyte management
Molten-carbonate fuel cell (MCFC) [27]	600 to 700 °C	Liquid solution of lithium, sodium and/or sodium carbonates	50 %	300kW- 3MW (300 kW module)	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use a variety of catalyst	• High temperature corrosion & breakdown of cell components • Long start-up • Low power density

		soaked in a matrix					
Phosphoric-acid fuel cell (PAFC) [28]	150 to 200 °C	Liquid phosphoric acid soaked in a matrix	40 %	400kW (100kW module)	• Distributed generation	• Higher temperature enables CHP • Increased tolerance to fuel impurities	• Pt catalyst • Long start-up time • Low current and power

It has found that the primary cause of this poor performance is the requirement of a highly efficient methanol oxidation catalyst. Catalytic performance investigations on various methanol oxidation catalysts have undertaken and it has found that only platinum-based materials exhibit excellent activity and better stability [30, 31]. Recently, most of the scientists have been investigating the act of DEFCs as alternative energy resources. Although important outcomes are expected from DEFCs, there are still some improvements that need to be done to enhance their chances in future use [32]. Compared to methanol, ethanol is also environmentally favourable and simple production methods may be employed to produce its high amounts directly from agricultural products or biomass. That is one of the reasons why DEFCs have recently received considerable attention. Since this is a new technology, there are some drawbacks, which needs to be dealt with, before DEFCs can be commercialized. Many scientists have made several improvements on DEFCs to enhance their performance and it is believed that they could be of great potential for application as energy resources. DEFCs are classified into two types depending on the kind of electrolyte membrane used, i.e. acid- and alkaline-membrane DEFCs [33].

Lin *et al.*[34]explained the role of water in the electrocatalysis of methanol oxidation on Pt-modified electrodes straight onto a Nafion membrane and then instigating the methanol either by gas phase or straight through an electrolyte. Based on their study, they proposed that the system of the methanol oxidation effect depends on the environment of the enclosing and the introduction of the methanol on the electrode exterior. Gootzen *et al.,* [35] studied the irreversible adsorption of various C3 alcohols, ethane, and 1-butanol on platinized platinum with electrochemical mass spectrometry (MS) and Fourier transform infrared spectroscopy (FTIR) in the perchloric acid electrolyte. They have concluded in their study that with ethane and 2-propanol, there is a small volume of oxygen association that happens in the C_1 region, supported by decarbonylation to produce CO.

Hai and Gang [36] studied the electro-oxidation of C4 alcohol on Pt electrodes by employing cyclic voltammetry (CV) and *in situ* FTIR spectroscopy. They proposed a dual path mechanism for the electro-oxidation of 1-butanol in perchloric solution. Lamy and co-workers [11] discussed the reaction mechanism and catalytic activity of the anode material based on the electro-oxidation of several low molecular weight alcohols, including ethanol, n-propanol and ethylene glycol. They demonstrated their results with the different example of a particular cell, employing a proton exchange membrane (PEM) as an electrolyte, particularly for the direct electro-oxidation of ethanol. Patra and Munich [37] carried out their study on platinum nanoparticles based conductive polymer, poly(3,4-ethylene dioxythiophene) (PEDOT) and revealed a high catalytic motion for electro-oxidation of methanol. They examined the impacts of the concentration of the electrolyte, the weight of Pt, and the amount of PEDOT on mass-specific movement. To obtain a high catalytic performance of electrochemical oxidation of methanol on Pt-supported catalysts, catalyst shreds should have nanometric dimensions with a similar pattern in a shielding matrix. The shielding pattern for the scattering of Pt particles performs a significant role in the production of the electrocatalyst. Carbon materials are have been reported to be useful for carrying catalyst particles [38-40]. The carbon support gives electrical connectivity between the separated particles. Solla-Gullon *et al.* [41] analysed the surface structure of platinum nanoparticles, their reactivity towards methanol and formic acid electro-oxidation and compared the performance with single crystal electrodes having basal alignments. The results pointed out the importance of the facade formation/shape of well-defined Pt nanoparticles and their effects on methanol and formic acid electro-oxidation. The surface arrangement of the electrodes have a remarkable character in the reactivity of both oxidation methods, and therefore the electrocatalytic characteristics of nanoparticles are

controlled by their surface structure, especially the appearance of positions with (111) symmetry. Certain conclusions present the opportunity of inventing innovative and sound electrocatalytic materials having polished structure-controlled Pt nanoparticles as earlier explained with Pt individual crystal electrodes.

E. Antolini [42] reported that in low-temperature fuel cells, carbon strengthened platinum is usually applied as anode and cathode electro catalysts with hydrogen or low molecular weight alcohols as fuel. Furthermore, high cost of platinum and its poisoning via carbon monoxide(being in the reformate gas which is employed as an H_2 transmitter in the state of polymer electrolyte fuel cells, and a by-product of alcohol oxidation in the state of direct alcohol fuel cells) have hindered the application of platinum as anode catalyst. Moreover, when Platinum without any support is used as a cathode catalyst, does not give adequate performance for the oxygen reduction reaction. Some articles confer a survey on Pt and non-Pt-based catalysts towards electrode materials examined together as positive and negative electrode substances in favour of low-temperature fuel cells [43-45]. Palladium and platinum have many parallel effects as both relate to the same group within the periodic table. The act of Pd is, to some extent economical in comparison to Pt, for the ORR. By the addition of a suitable metal, the ORR performance of Pd can succeed that of Pt. Alternatively, the performance of Pd is significantly cheaper than the Pt for the hydrogen oxidation reaction (HOR). However, by attaching a small quantity of Pt, the HOR performance of Pd achieves that of absolute Pt[46]. Ferrin and Mavrikakis [47] have examined the formation responsiveness of methanol electro-oxidation on the surfaces of eight transition metals (Cu, Au, Ag, Pd, Pt, Ir, Ni, and Rh), with the help of density functional theory (DFT). They marked the dissimilarity in the reaction mechanisms among the (111) and (100) facets of these eight face cantered cubic transition metals employing the adsorption strengths of sixteen intermediates formed on two distinct phases of each metal, combined with a basic electrochemical model. They also examined two different reaction mechanisms for methanol electro-oxidation: one going through an intermediate product CO* and the second, oxidizes methanol directly to CO_2 without CO* as an intermedial. Guo *et al.* [48] proposed a chemical tactic for the production of 3-D Pt-on-Pd bimetallic nanodendrites based on graphene and as an exceptional nano electrocatalyst for methanol oxidation. Single-crystal Pt nano-branches supported on PdNCs have been found to exhibit a high electrochemical surface area with permeable structure and fine distribution of nanoparticles at the facade of graphene nanosheets. Besides, a group of chemical protocols recognized for obtaining biased control of NC patterns in a cube, [49, 50] tube, [51] wire, [52]

tetrahexahedral Pt, [53] mesoporous nanostructure, [54, 55] as well as dendrite, [56] between that Pt nanodentrites are of appropriate concern in catalysis due to their porous formation, large surface area, and significant catalytic activity. Kowal *et al.* [57] successfully synthesized nanoclusters of Pt, Pt-Rh, Pt-$SnO_2$and Pt-Rh-SnO_2via polyol process and dropped on large-area carbon for electrocatalytic oxidation of ethanol. Its inclusive oxidation to CO_2 capitulates twelve electrons per particle, but the reaction on Pt is quiet, and the main output is not CO_2 but acetic acid and acetaldehyde [58, 59]. Guo *et al.* [60] proposed one-pot, rapid synthesis of platinum nanoparticle supported-at-graphene hybrid nanosheets and worked as a novel electrode material as the electrochemical sensing. Umeda *et al.* [61] reported on development of a fresh electrode to facilitate manifests sensitized methanol electro-oxidation in an oxygen ambience. They developed a paired Pt-C electrode for application as the anode synergist for a DMFC employing a co-sputtering procedure. Pt and Pt-based alloy-stacking carbon catalysts employed as an anode catalyst for the methanol oxidation reaction [62-65]. In addition, the hydrogen-fuelling for PEMFCs have high potential density and power density with the DMFCs. The anode catalysts initiate hydrogen oxidation reaction effectively than methanol oxidation. So, to improve the power production features of DMFCs, at the anode catalyst is necessary to endorse the methanol oxidation reaction. Pt- and Pt-supported alloy priming have lately described improving the activation of methanol oxidation, of carbon materials on Pt- and Pt-supported alloy packing have newly published[38, 66-68].

Van Doorslaer and co-workers [69] performed Pd catalyzed alcohol oxidation in ionic liquids and introduced a methodology to extract reaction goods from ionic liquids devoid of the requirement of an organic solvent and also investigated the importance of Pd-catalyzed aliphatic alcohol oxidation. Ionic liquids (ILs) are getting growing attention as green substitutes for the traditional gaseous organic mechanisms due to their different solvent characteristics [70, 71]. In recent times, several transition metal catalyzed alcohol oxidation methods in ILs have been proposed [72-74]. In various examples, the IL still worked as solvent and catalyst, for example, including a catalytic metal class's member of the IL's anion [75, 76]. Although this type of catalytic methods implemented correctly for allylic or benzylic alcohols, they were not quite energetic for non-initiated aliphatic alcohols. Furthermore, the expected requirement for a removal move to distribute the reagent/outcome as of the IL appearance begins this come up to less engaging [77]. Maiyalagan *et al.* [78] synthesized extremely durable Pt-Ru nanoparticles carried on three-dimensional cubic patterned/structured mesoporous carbon (Pt-Ru/CMK-8) as electro oxidation of methanol. They have also discussed the cost of the

catalysts, and mostly the Pt-Ru bimetallic composite applied to the direct methanol fuel cell causes a significant hurdle to its extensive to utilize as a power resourceful and atmosphere-favourable fuel growth technology.

Singh and Awasthi [79] developed graphite oxide and used a base of palladium nanoparticles (PdNPs) catalyst towards the electro-oxidation of methanol and ethanol essentially. They recognized that homogeneously scattered Pd nanoparticles on graphene nanosheets (GNS) exhibit high performance as contrasted to those distributed at nanocarbons atoms (NC) or multiwall carbon nanotubes (MWCNTs) toward methanol and ethanol electro-oxidation below the same experimental circumstances. The GNS supported Pd nanoparticles improved the electrochemical movement of Pd/GNS through alcohol oxidation which can be attributed to the significant improvement in electrochemical active surface area. Yin *et al.* [80] studied CO poisoning with different surface compositions of PtAu alloys during methanol electro-oxidation. They concluded from the results that the CO generation could be decreased by slowly increasing with the surface of Au sections in PtAu compounds and CO poisoning can roughly be eliminated by adapting to a usual surface Au section.

Gao *et al.* [81] successfully synthesized Pd-graphene and Pt-graphene catalysts by a fabricated electroless plating technique electrodes for DAFCs, with a trace of SnO_2. Pd or Pt nanoparticles were dropped on the facade of graphene oxide modified by Sn^{2+} ions and $NaBH_4$ reduced further graphene. In the comparative study, they found that the issued graphene-Pd and Pt catalysts show improved electrocatalytic action and long-standing durability to alcohol electro-oxidation. Pt and Pt-supported paired combination (e.g., Pt-Ni) have been broadly applied as anodes in DMFCs owing to their significant catalytic exercise for the methanol oxidation [82-84]. Though, the realistic application of Pt anodes is inadequate as they are quite costly and quickly infected by CO. Pd and Pd-supported composites were considered being one of the most significant replacements for Pt composites due to their high and exceptional protection against CO polluting [85, 86].

Li *et al.* [87] investigated the oxidation of the mixture of methanol and ethylene glycol together with Pt and Pd electrodes in alkaline media. They found the oxidation of ethylene glycol more active than methanol and more stable than both methanol and ethanol oxidation. They concluded from their results that the mixture of methanol and EG is an encouraging applicant being fuel in DAFCs. Amongst all the several potential alcohols, methanol is the most promising fuel due to its numerous advantages in aqueous electrolytes such as accessible at an

economical price, easy to handle/ stocked and the tremendous general density of power equivalent to that of gasoline [87-89]. Many researchers have investigated the electro-oxidation of alcohols on Platinum supported composites in alkaline media and found that DMFCs exhibit quite high performance and durability [90-92]. Now the researchers are focusing towards the replacement of Pt electrocatalysts to Pd supported composites and based on the outcomes they have concluded that Pd can act as a suitable electrocatalyst for ethanol as well as C3-alcohols oxidation in alkaline media [85, 93].

Liu *et al.* [94] have focused their study on methanol electro-oxidation into tetrahexahedral Pt nanocrystals (THH Pt NCs) electrodes and investigated by an aggregate of electrochemical procedures. The adornment of the tread surfaces by Ru atoms improved the susceptibility to poisoning and thus decreased the opening potential towards methanol oxidation. When they examined PtRu metal nanoparticle composite, the Ru fabricated THH Pt NCs show significantly better catalytic currents and CO_2 production at smallest possible scale. Meher and Rao [95] synthesized a single shuttle-shaped CeO_2 in gram range by an uncomplicated polymer-assisted uniform precipitation technique. In this work, the first time they reported and confirmed that CeO_2 with an appropriate microstructure could recover the electrocatalytic movement of Pt/C as for methanol oxidation, and also can be used for inventing different electrocatalysts for fuel cell employment.

Li *et al.* [96] reported a simple method to prepare Pt nanoparticles supported on non-covalent functionalized graphene nanosheets during solvent-shedding extended graphite with the assistance of supercritical CO_2 and 1-pyrenamine. After that, they applied platinum as shielding materials to examine the possible utilization of the acquired nanocomposite in DMFCs. Researchers also showed that graphene could be scaled and functionalized [97, 98]. Many researchers have reported different support catalyst such as Yang *et al.* [99] reported an easy procedure for fabricating mesoporous chromium nitride (CrN) via the ammonolysis of a substance ternary oxide ($K_2Cr_2O_7$) as high-concert catalyst aid in favour of methanol electro-oxidation. Though, in requisites of fuel cell application, some research articles trafficking includes metal nitrides as reactant chains. The activity of a tungsten nitride held at carbon black (W_2N/C) being a non-noble electrocatalyst in support of ORR in PEMFCs has been accounted. Here the article summarized the performance of the W_2N/C catalyst approaching the ORR and it was lower to that of commercially accessible Pt/C catalysts previously broadly employed in PEMFCs [100]. Most of the researchers done their study on titanium nitride (TiN), but it goes through loss and deterioration in acidic conditions [101-103]. On the other hand, CrN has

elevated immunity to fatigue and corrosion [104, 105]. CrN has been applied as a covering material for bipolar plates in fuel cells that are a significant part of PEMFC heaps [106, 107]. Habibi and co-workers [108] have carried out proper investigations of CH_3OH, CH_3CH_2OH, $CH_3CH_2CH_2OH$ and $CH_3CH_2CH_2CH_2OH$ electro-oxidation on a carbon-ceramic electrode (CCE) potentiostatically mitigated by Pd nanoparticles. Huang and Wang [109] reported current progress on carbon-root aid resources for electrocatalysts of DMFCs. They summarized the current growth in the scheme and modification from novel carbon-root anode reactants through different approaches and their uses toward methanol oxidation reaction.

2.2 Direct Methanol Fuel Cell

Direct-methanol fuel cell (DMFC) works at low and transitional temperatures (vary up to 150 ºC) and supplied by a dilute aqueous solution of methanol. Cells process in gas phase further provides an excellent performance [30].

2.2.1 Generalities

Fundamentally, a proton exchange fuel cell is called DMFC that is supported through an aqueous suspension of methanol. Here both the catalytic electrodes that will be the CH_3OH oxidation and the reduction of oxygen are parted by an electrolyte film that conducts protons from anode to cathode, whereas other compounds prevent dissipation [110]. Every electrode is composed of a gas diffusion sheet and a catalytic sheet. The aqueous solution of methanol is supported by the anode side that spreads within the dispersion layer towards the catalytic layer, which will be electrochemically oxidized inside mostly CO_2 protons and electrons [111]. Protons appeared while the reaction scatters within the Nafion film near the cathode catalytic zone. All contribute to oxygen reduction headed to produce the water at the cathode surface. Oxygen can be absolute, but it can further get from the air. The electrons have been recovered via graphite bipolar plates that have the two sticks of the cell. The composition of this cell has been explained in given Fig. 1.

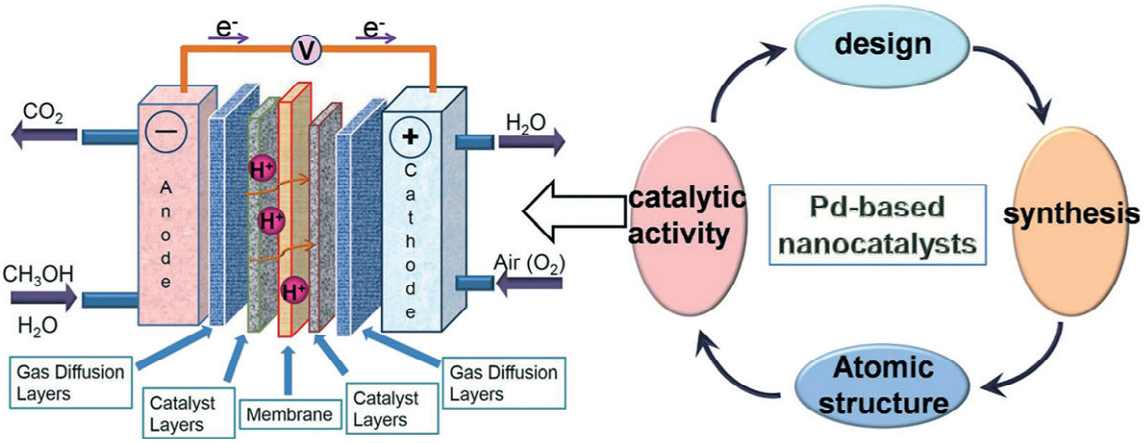

Fig. 1. Representative DMFC mechanism and the propose principles of the Pd-based nanocatalyst for these fuel cells. Reprinted with permission from Ref. [112]. Copyright 2014 Royal Society of Chemistry.

2.2.2 Reactions

$$\textbf{\textit{AT ANODE}}: \quad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$\textbf{\textit{AT CATHODE}}: {}^3/_2\, O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

$$\textbf{\textit{OVERALL REACTION}}: \quad CH_3OH + {}^3/_2\, O_2 \rightarrow 2H_2O + CO_2$$

At the anode side, the CH_3OH has oxidized in CO_2 and six protons and electrons. Further, all protons have developed counter at the cathode side, including oxygen to reach the water. The final reaction seems similar to a combustion effect and hence occasionally pointed because of cold combustion [113-115]. In fact, the cell is expected to manage this reaction and apply it to generate current instantly.

3. The impact of Direct Methanol Fuel Cell

3.1 Advantages

Arico *et al*. summarized both the basic and technological aspects of DMFCs. During methanol oxidation, it delivers six protons and electrons per atom. Its tremendous energy density helps methanol to be used as a fuel in fuel cells application[116]. DMFC works on low and mean temperatures (increase up to 150ºC) with a weak aqueous suspension of methanol as fuel. In fact, the extraordinary temperature improves kinetics and methanol crossover dropped beside

a gas phase supplies. Despite, the demand for vaporization may be a restriction for some purposes [117, 118]. Alkaline alcohol fuel cells (AAFCs) showed quite significant improvements when it was analyzed by PEMFCs: (i) the dynamics of the couple alcohol oxidation and oxygen reduction in an alkaline electrolyte as an alternative to an acidic one are advanced appreciably [119, 120], (ii) in alkaline evidence, less-Pt or also non-Pt catalysts positioned on Au [121] and Pd [122, 123] with anode, Ag [124] as well as perovskite-kind oxides [125] in the cathode may be employed including excellent electrocatalytic capability so the industrialization possibility of DAFC can increase (iii) in AFC the fuel crossover is bypassed as of the convey of hydroxyl accumulations of the cathode surface to the anode side via electro-osmosis.

3.2 Environmental affects

Fuel Cells are recognised as environmentally favourable because they do not generate toxic by-products. However, they generate carbon dioxide that is a greenhouse gas. It is additionally perfect for hydrogen that gives CO_2 obliquely during resolving level through the water-gas shift effect. Methanol and different alcohols too generate any other by-products similar to ketones, aldehydes and carboxylic acids still within small concentrations. It originated from the biomass; the CO_2 appeared through cell process would yet be restored via CO_2 used during photosynthesis. Subsequently, the concerning energy would no further contribute to the greenhouse effect and would be sustainable. In addition, the tremendous performance of fuel cells offers limited CO_2/ kW as compared to the standard route. In the present scenario, the energy crunch and environmental contamination are both critical hurdles encountered by human culture as of quickly rising power require and extensive ignition of fossil fuels. It is extensively supposed that the traditional assumptions of energy production and regeneration are not appropriate for the world's sustainable growth [126-129]. Consequently, an enormous opportunity for the study has been moved out to create spotless and sustainable energy roots as well as their tools [130-133]. Amongst these various energy methods, DMFCs hold an excellent power transformers that convert the chemical energy concerning methanol immediately into electrical energy [134].

3.3 Potential applications

There are fundamentally three significant classes regarding utilisations of fuel cells. Fuel cells are quite familiar for holding a substitute into enclosed combustion engines but further acknowledged for transportation and stationary purposes.

3.3.1 Stationary applications:

During the previous decade, enormous progress has been achieved in fuel cell science and technology, particularly in some employment fields such as transportation, and stable power roots [135]. Fuel cells can generate electricity immediately from fuel, including an excellent performance. For stationary purposes, they change the combustion supported electric-generating systems where energy failures take place in the hot engine, including the electric dynamo. They may be used in domestic, trade and manufacturing divisions for electricity plus heat generation [136]. As we know, DMFC does not require a few regenerations of methanol; there are no failures while the agitator.

3.3.2 Transportation applications:

Direct methanol fuel cell technology proposes a resolution for transportation purposes in the change close to a zero discharge prospect. By applying methanol being a fuel avoids one of the significant obstacles troubling PEMFC technology, so the evolution of economic and secure hydrogen transportation to substitute the gasoline/diesel combustible circulation channels. It has been enough recognized so the transportation for methanol shipping and storehouse can directly modify from the contemporary gasoline exhaustive transportation. An additional disadvantage in accepting a PEMFC system is necessity to save hydrogen (at quite excessive stresses) or take a great fuel worker to change the liquid fuel within hydrogen toward keeping the transportation. Methanol is a delightful fuel as its power density is approximately half of that of gasoline, and it is a liquid under atmospheric conditions[137]. Despite the gripping benefits of working DMFCs in transport purposes, the most significant barriers to their debut remain. Certain obstacles incorporate the essential values of substances utilized in forming DMFCs (mainly the massive price of Pt electrocatalysts), the crossover of methanol within the electrolyte film of the anode towards the cathode and, the lower conductivity and power density representation of DMFCs in corresponding to PEMFCs. Notwithstanding certain hindrances, some organizations (especially in the previous five years) have grown actively that are involved in the evolution of DMFCs for transportation purposes [138]. Even though new cars produce an economic volume of poisonous gases than their forerunners, transport is yet a significant cause of infection. Substituting an essential part with fuel cells would have a considerable impact lying on the atmosphere. Methanol fuel cells become delicately examined for transport purposes. The principal convenience is that storehouse and container refilling is simple for the aqueous methanol [135].

3.4 Transportable applications and micro-fuel cells:

There are some organizations energetically involved in the improvement of low energy DMFCs for mobile phones, laptops, transportable camera and electronic game purposes [139, 140]. The fundamental aim of investigation has been to build up evidence of DMFCs proficiency of substituting good-performance rechargeable batteries in the 6-billion US$ transportable electronic accessories business. Hypothetically, methanol has a better definite energy density among the enormous rechargeable battery, lithium polymer and lithium ion polymer arrangements. The most significant characteristic of a transportable or micro fuel cell is just a small object. A lessened dimension and mass of the cell ought to operate at atmospheric temperature. The low function temperature concerning the PEM fuel cell is a significant benefit for transportable purposes. In fact, it is the unique fuel cell competent in operating at an atmospheric temperature [141]. Since the objects parallel to conveying purpose, it performs on obviously that DMFC is also an appropriate comparison to the hydrogen fuel cells. The fuel cells system are yet growing and require enhancement in both technological achievements and price.

4. Issues in direct methanol fuel cell

4.1 Steady electro-oxidation kinetics

Numerous exterior intermediates are developed during methanol's electro-oxidation. Here, methanol is converted mainly to CO that is additionally oxidized to CO_2. Another CO corresponding classes further appears: COH_{ads}, HCO_{ads} and $HCOO_{ads}$ [13, 142]. Few of certain intermediates are not easily oxidizable and stay powerfully adsorbed to the catalyst exterior. Accordingly, others avoid new methanol units of adsorbing and supporting new reaction. Therefore electro-oxidation of intermediates is the rate restricting level. Here, the poisoning of the catalyst exterior is severely reduced under the oxidation reaction. Also, an exact percentage of the intermediates adsorbs in advanced from oxidized into CO_2 and thus decreases fuel performance but bearing within full oxidation. Consequently, a highly significant hurdle is to expand further electrocatalysts, which slow down the contamination and improve the reaction.

4.2 Methanol Crossover

4.2.1 Explanation:

During PEM fuel cells, to strike the electrode approaching the different side and support non-electrochemical oxidation is the main object of the membrane to prevent fuel and oxygen. Though, during DMFC, the fuel scatters within the electrolyte membrane [143]. Owing to the

hydroxyl assembly and their hydrophilic characteristics, methanol communicates including the ion swap positions and is pulled through hydronium ions within the extension towards diffusion essentially a decision of the concentration gradient within both electrode positive and negative. Methanol which passes overhead reacts directly with oxygen on the cathode surface.

4.2.2 Easy solutions to counter crossover:

Crossover can be improved by adjusting the concentration of electrolyte and pressure gradient among working and counter electrode. It may be quickly restricted through applying a low down methanol absorption within the anode supplies solvent and by improving cathode strain toward a particular size.

4.3 Gas management on anode side

Gas supervision towards the anode surface is an essential matter in DMFC scheme. However, towards the anode surface, CO_2 is conceived being a result of electrochemical methanol oxidation. If CO_2 droplets cannot remove efficiently, the anode tubes will be prevented, leading to insufficient mass transport. Argyropoulos *et al.* [144] recognized the two-phase flow model in the anode tube under several working states. That flow visualization towards the anode surface generates a proper recognition of droplet dynamics in DMFC. Maximum of the carbon dioxide is produced in methanol oxidation within the gas state. CO_2 is accumulated at the working electrode, catalytic film and scatters through the tip like the gas dissipation film. Wherever, CO_2 droplets are produced on the exit of the holes. The measurement depends upon the extent of the holes and the wet capability of the electrode support. Next, they enter an exact volume and these droplets are delivered in the methanol solution [145]. The leading concentration concerning droplets gives them to combine and grow slugs. Subsequently, the amount of methanol cannot be enough to preserve a coveted current density. This phenomenon is mainly a matter at unusual current densities wherever a significant volume of carbon dioxide is produced. Two procedures are measured to handle this obstacle. It is required to develop and applied concurrently. Firstly, the designs of the supplies carriers can be adjusted to support the rapid elimination of CO_2. Secondly, Lu and Wang [145] also reviewed the composition of the dissipation film and arrangement of droplets on the tip. Consistent with the results, short and consistently expanded holes would form small diameter droplets entirely in comparison to slugs. It may produce a foamy flow preferably than a laggard flow.

5. Catalysts

The catalyst film is formed of catalytic particles used over the dissipation sheet or straight at the membrane. There are several reaction initiative agents for both working and counter electrode.

5.1 Platinum group metal-based catalysts

Pt-group metals can work as excellent electrocatalysts for methanol oxidation reaction (MOR) or ethanol oxidation reaction (EOR) for DAFC applications[146]. Pt-based nanocatalyst's catalytic activities greatly depends on the configuration and size as well as the revealed surface facet. Numerous investigations have been carried out to deliver an optimized equilibrium among Pt and base metal, starting to greater fully recognition [147-149] [150]. Different morphologies of Pt-based electrocatalysts such as nanowire, nanotube, a nanoplates, and three-dimensional ordered macroporous arrangements have been reported [151-153]. Antoniassi *et al.* [154] synthesized Pt + SnO_2/C electrocatalyst holding cubic Pt nanoparticles through preferential (100) direction for DEFC application. The electrochemical consequences for DEFC showed in Fig. 2, that Pt + SnO_2/C electrocatalyst sustaining Pt nanoparticles by preferential (100) orientation gives a better action for EOR. Wang *et al.* have [146] synthesized ordered nanostructured cathodes based on controlled vertically aligned Pt nanotubes for DMFC via an approach linking sacrificial template outline and in-situ galvanic replacement.

5.2 The advanced representation of binary and ternary catalysts

Tremendous works have been devoted to developing Pt-based catalysts with least Pt loading or substitute catalysts based on transition elements by alloying and de-alloying of Pt for the synthesis of Pt-based core-shell catalysts [155]. Several compounds, for example, Pd-Pt, Pd-Ni, Pd-Ag, Pd-Au, Pd-Cu, and so on have been published with the shift of the d-band center, which generates an essential function in favor of the metal to adsorb, heading towards improved electro-oxidation of alcohol at the exterior of metals catalysts. Wang et al. (Fig. 3) summarized a simple production of Pt-Pd bimetallic nanodendrites through a Pd central and dendritic Pt surface with better electrocatalytic movement in contrast through industrial Pt electrocatalysts [156]. Liu *et al.* [157], demonstrated an uncomplicated and proficient wet chemical approach in favor of the production of consistent, ultrathin and ultra-long trimetallic PtAuCu alloy nanowires. They have reported the electrochemical characterizations of various alloys proportions by altering the percentage of a copper constituent within the alloy NWs. The

prologue of Cu notably enhances the electrocatalytic surface area and movement headed for methanol oxidation, which can be associated with the transformed structure and synergic effects.

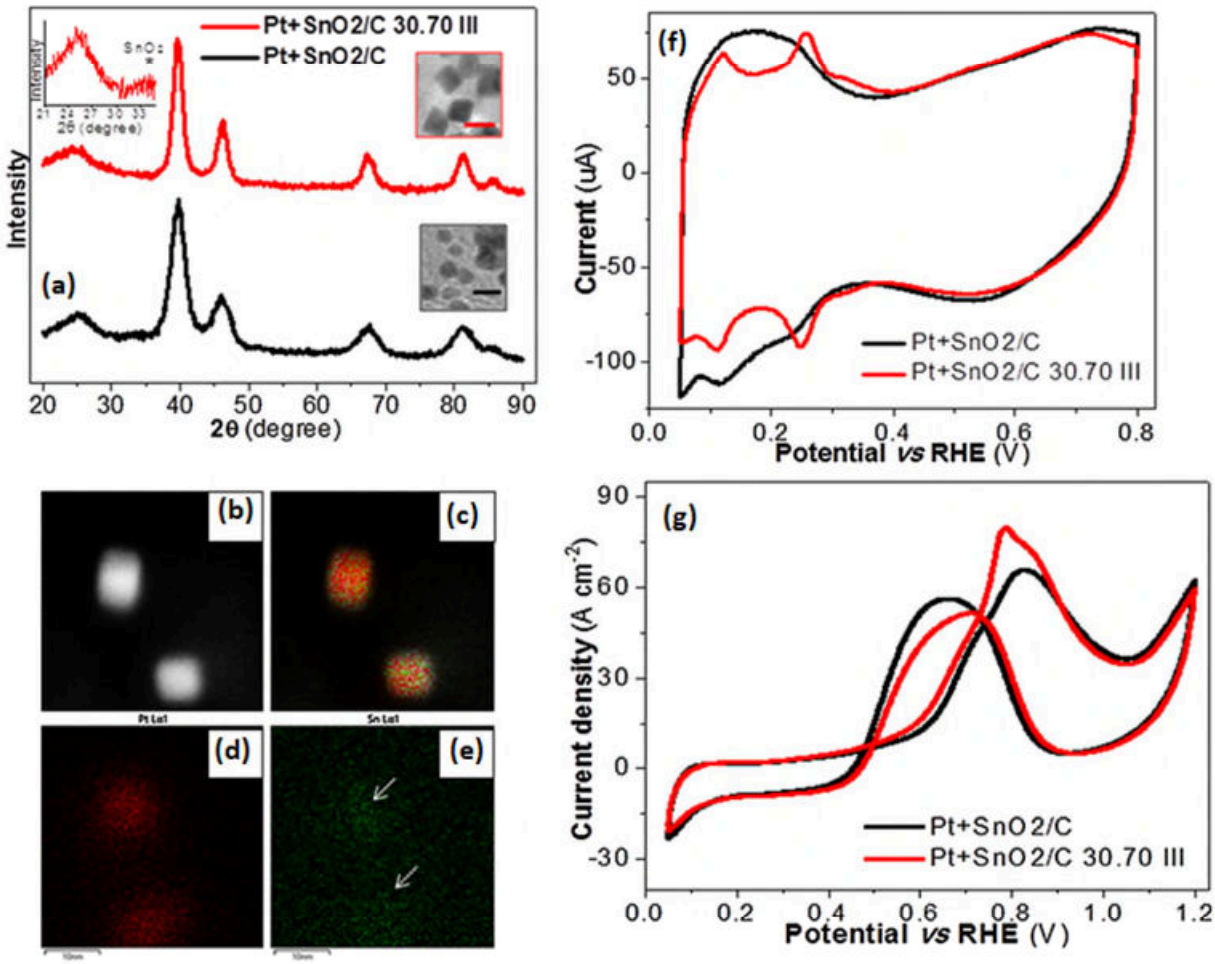

Fig. 2. (a) shows the X-ray diffraction pattern (TEM representation bar 10 nm), (b) shows the STEM-DF picture of cubic nanoparticles formed of Pt-SnO_2/C30.70 III substance, (c) XEDS chemical mapping on the Pt-SnO_2/C30.70 III nanoparticles, (d) and (e) Pt and Sn mapping of (b).
Electrochemical experiments (f) CV curves conceded in 0.5 M of H_2SO_4 at 50 mV s^{-1}, (g) CV with ethanol evidenced with a sweep rate of 10 mV s^{-1}.Reprinted with permission from Ref. [154]. Copyright 2017 Elsevier.

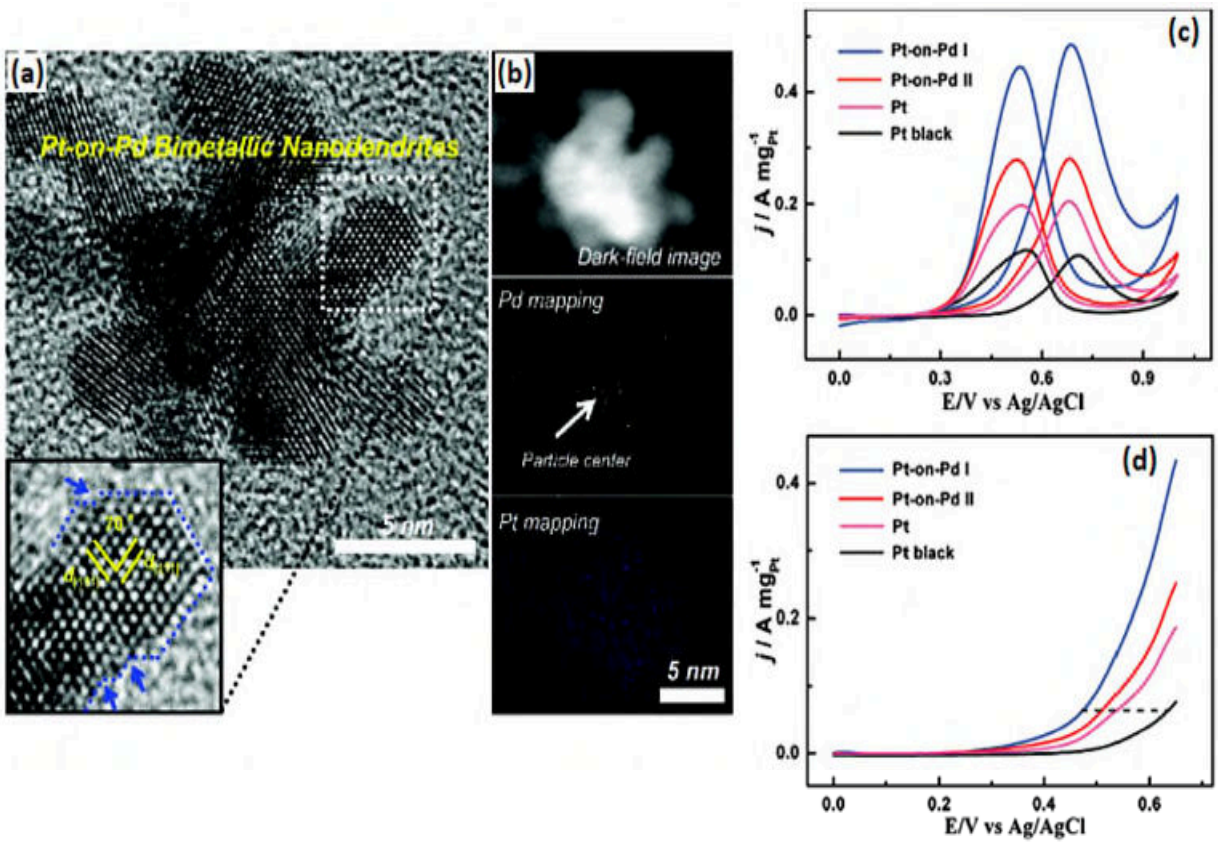

Fig. 3. (a) Shows the high exaggerated TEM image and (b) the equivalent EDS mapping pictures of single nanoparticle. The blue arrows in the inset figure of (a) point out numerous atomic ladders on the Pt bough exterior. (c) Cyclic voltammograms, (d) linear-sweep voltammograms graphs for methanol oxidation reactions catalyzed by Pt on Pd I (blue), Pt-on-Pd II (red), Pt nanodendrites with no Pd centers (pink), and normally accessible Pt black (black) in an aqueous solution including 0.5 M H_2SO_4 and 1 M CH_3OH.Reprinted with permission from Ref. [156]. Copyright 2011 American Chemical Society.

Xie *et al.* [158] have formed the carbon spheres festooned by nickel ruthenium layered double hydroxide and cerium-doped nickel ruthenium layered double hydroxide applying a straightforward solvothermal approach. Then a comfortable microwave-assisted polyol method is used for depositing Pt nanoparticles (NPs). Hong *et al.* revealed a facile technique for the synthesis of PtCu NWs with the high aspect ratio [159]. Wang *et al.* [160] have demonstrated the flourishing arrangement of highly available and well isolated Au-Pd nanoparticles, stabilized with 2D graphene oxide that itself is discrete by intercalated titanium particles to form ternary hybrid catalysts shown in Fig.4.

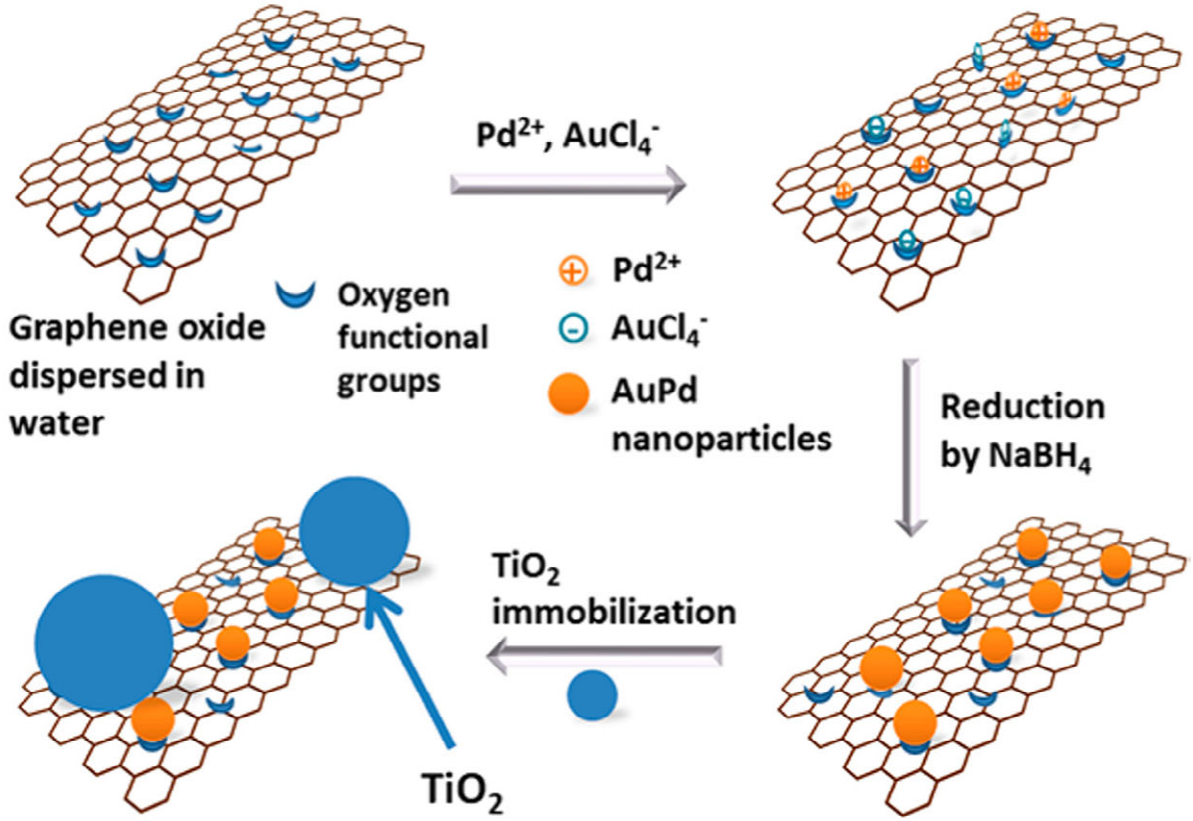

Fig. 4. Scheme of the method used for arranging GO alleviated Au-Pd NPs on TiO_2 (AuPd–GO/TiO_2) via a "Ligand-free" sol-immobilization-type method. Reprinted with permission from Ref. [160]. Copyright 2015 American Chemical Society.

5.3 Impact of the supporter on catalytic performance of electrocatalysts

The initial conditions of features to a proper fuel cell catalyst sustain should hold (i) large surface area, (ii) appropriate porosity, (iii) high electrical conductivity; and (iv) high endurance following fuel cell operational conditions [161]. It has been reported that the execution of a DMFC holding of a Pt-Ru positive electrode catalyst sustained at molybdenum carbide, and tungsten carbide (WC) showed larger current densities than the achieved for Pt-Ru synergist put on a carbon support. Molybdenum carbide and WC used as a catalyst promoting models were integrated by applying a straight carbonization technique. The aerial current densities received while utilizing the carbides when backer was owing toward the synergistic impact generated through the communication within Pt and metal carbides [162, 163]. Platinum and different carbon-supporting materials have been examined as an electrode catalyst ingredient of low-temperature fuel cells. Pt is generally employed as the reactant owing to its great electrocatalytic activity. Current study is now concentrated on applying either modified carbon-

based or non-carbon-based resources as catalyst supports to get better catalytic activity of Pt [164].

The catalyst nanoparticles are needed to be scattered on the conductive support which is typically a carbon-based material [165-167]. It is commonly believed that carbon support improves the catalyst materials scattering, electron transportation, and the kinetics of mass transfer at the electrode exterior [168]. Some carbon structures [169] are shown in Fig. 5.

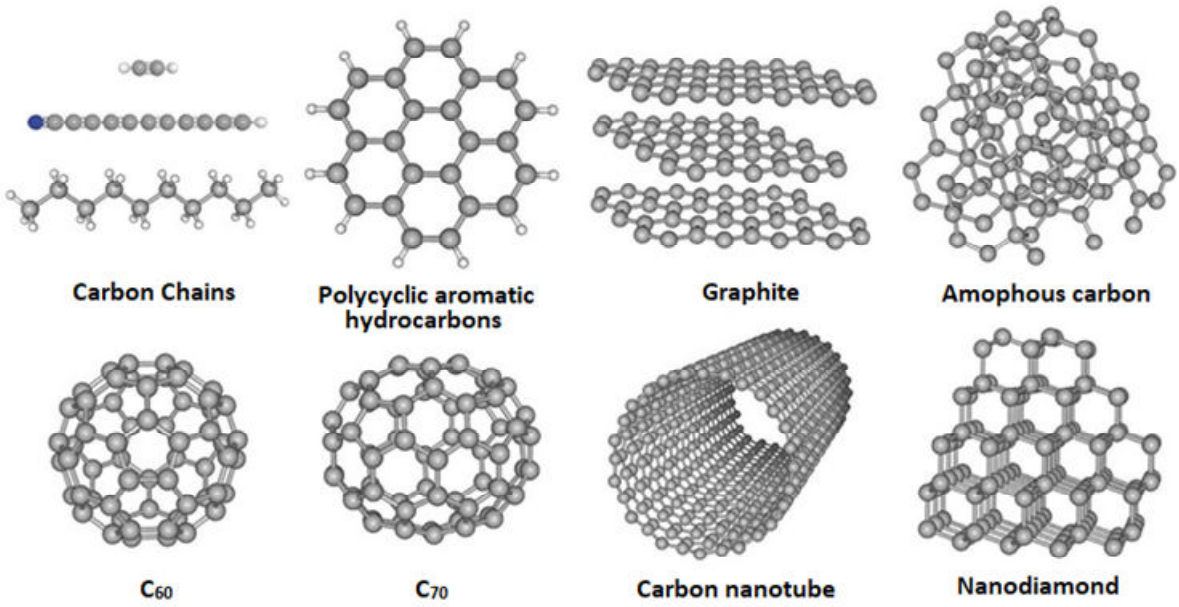

Fig. 5. Graphic illustration of the dissimilar type of carbon structure. Reprinted with permission from Ref. [169]. Copyright 2010 Science.

Watanabe et al. [170] have elucidated the effect of the size alone of Pt NPs supported on graphitized carbon black upon the durability in 0.1 M $HClO_4$ solution at 65^0C by the channel flow double electrode (CFDE) cell during accelerated durability tests protocols that simulated the practical start/stop operation and load-change cycles for fuel cell vehicles.

Graphene nanosheets (GNS) were amalgamated through the $NaBH_4$ reduction of recently developed graphite oxide and employed as catalyst rod of PdNPs used as the electro oxidation of ethanol and methanol. Home-prepared GNS were characterized via Raman spectroscopy and XRD. The investigation in table 2 has revealed that PdNPs scattered above GNS were extremely useful towards the electro oxidation of CH_3CH_2OH and CH_3OH in 1 M KOH [79].

Table. 2. Result of cyclic voltammetry of 20 wt% Pd/GNS, 20 wt% Pd/MWCNT and 20 wt% Pd/NC in 1 M KOH +1 M alcohol at 25^{0}C. Reprinted with permission from Ref. [79]. Copyright 2011 Royal Society of Chemistry.

	Methanol		Ethanol			I/mA mg$^{-1}_{Pd}$ at −10 mV		SA/mA cm^{-2}	
Catalyst	I_p/mA mg$^{-1}_{Pd}$	E_p/mV	I_p/mA mg$^{-1}_{Pd}$	E_p/mV	EASA/cm^2 mg$^{-1}_{Pd}$	Methanol	Ethanol	Methanol	Ethanol
20 wt% Pd/GNS	1179 ± 23	81 ± 15	1966 ± 26	89 ± 3	5169 ± 18	915 ± 12	1830 ± 25	0.18	0.36
20 wt% Pd/MWCNT	911 ± 3	70 ± 2	1581 ± 14	48 ± 12	4531 ± 20	800 ± 17	1510 ± 20	0.18	0.34
20 wt% Pd/NC	891 ± 10	22 ± 8	1276 ± 19	14 ± 16	2183 ± 20	850 ± 29	1236 ± 14	0.39	0.56

Reduced graphene-decorated carbon fiber (RGO-CF) and reduced graphene/carbon fiber composite (RGO/CF) are developed and applied as a supporting material of Pt NPs for electrocatalysis utilization. The compound fabrication performance of the acquired electrocatalysts is examined and correlated with the economic catalyst-Pt/C. The Pt NPs arranged on RGO/CF manifests improved catalytic durability in the methanol oxidation reaction.

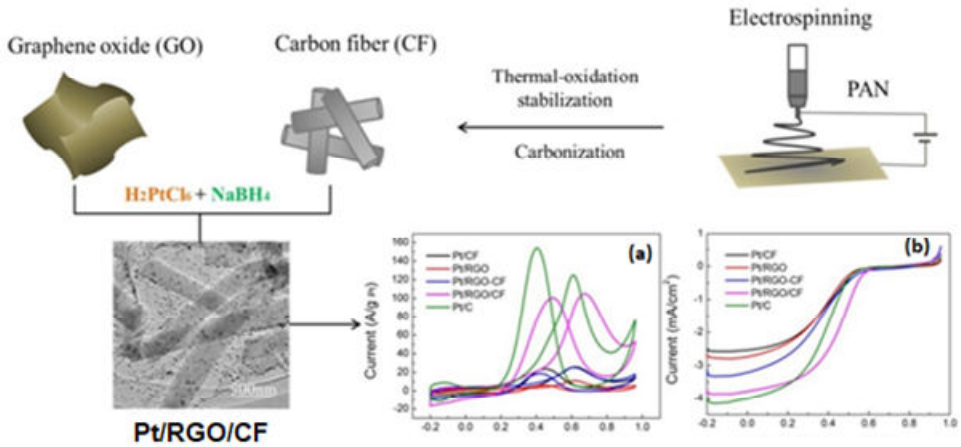

Fig. 6. Systematic route to synthesis of Pt/RGO/CF and (a) Cyclic voltammograms, (b) LSV graphs of Pt/CF, Pt/RGO, Pt/RGO-CF, Pt/RGO/CF and Pt/C in 0.5 M H2SO4 + 0.5 M CH3OH.Reprinted with permission from Ref. [171]. Copyright 2017 Elsevier.

Mohanraju et al. [172] used Pt-aniline complex to synthesize a high loaded Pt core/carbon shell catalyst and corresponding results are shown in Fig. 7. The Pt-aniline compound was actively incorporated by illuminating an ultrasound over the hexachloro platinic acid and aniline monomer blend. The extremely dense sort of aniline manages the regeneratable hexagonal plate-similar Pt-aniline network crystals.

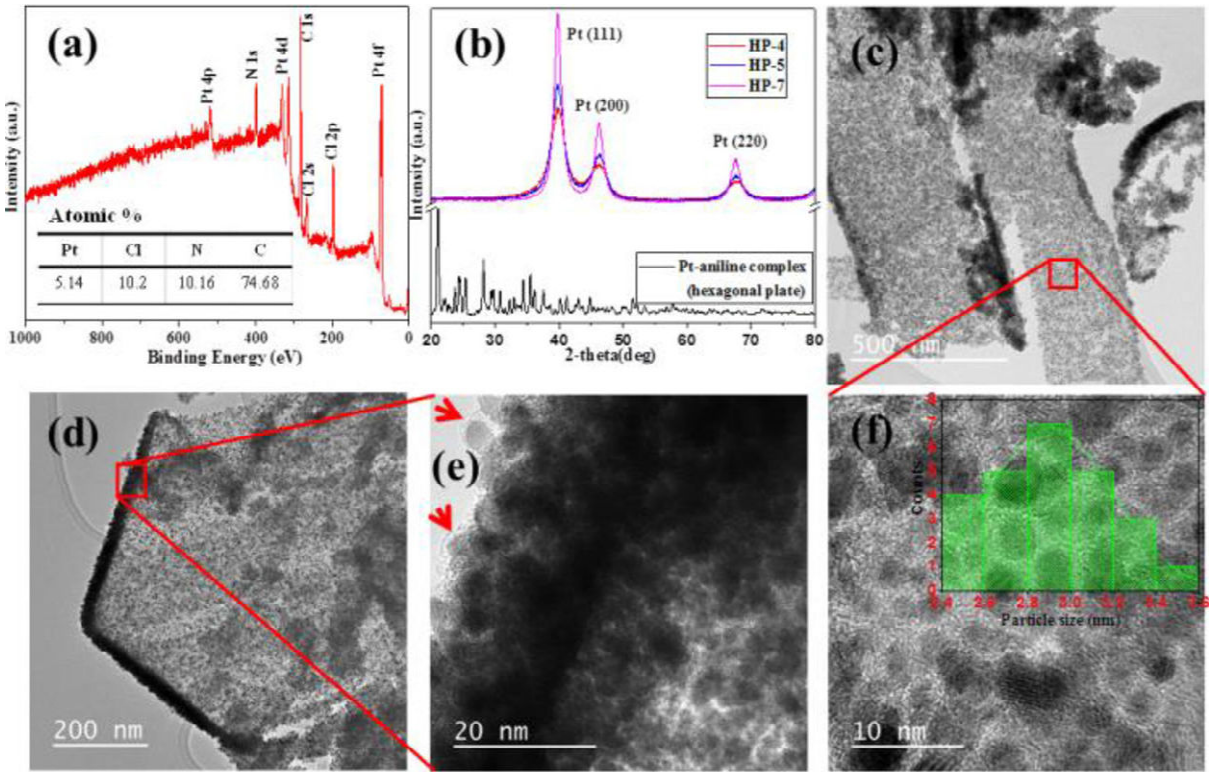

Fig.7. (a) Shows the XPS analysis spectrum through atomic proportion of Pt, N, Cl, and C ingredients in the recrystallized Pt-aniline complex, (b) XRD pattern of the Pt-aniline hexagonal plate acquired prior and past pyrolysis, (c-f) TEM images of HP-5 with diverse magnifications (inset in (f) demonstrates the histogram of Pt atom dimension allocation).Reprinted with permission from Ref. [172]. Copyright 2018 Wiley-VCH Verlag GmbH &Co.

5.4 The role of polymer based catalyst

Combination of metal nanoparticles in the polymer has grown as an impressive approach for forming the multifunctional composite materials where the features of the first polymer can be significantly modified [173]. In this interesting research, authors have discussed the polymer-based catalyst for fuel cell application. Individually, metal nanoparticle (MN) and conductive polymer (CP) have the excellent properties, but when they were combined, the resulting nanocomposite has a connection of both the properties. Conducting polymers, including nanostructures, are engaging as advanced materials due to their enhanced performance and versatile applications [174]. Some of them are shown in Fig. 8.

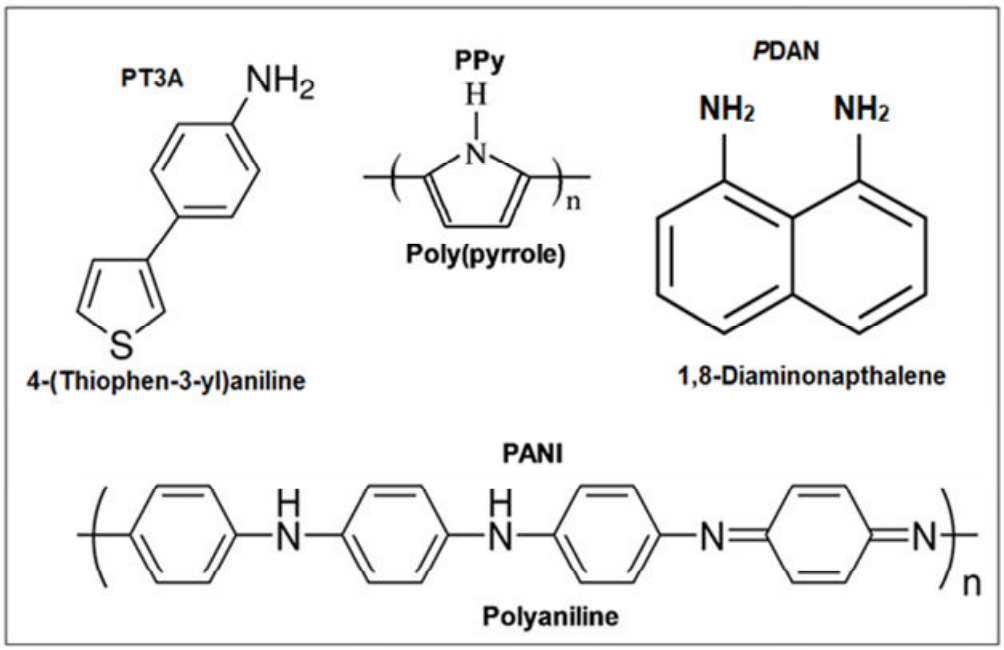

Fig. 8. Molecular configuration of a few conducting polymers.

The nanocomposites of noble metals and conducting polymers have shown various exceptional characterizations as of the amalgamation of different functional components [175]. Conducting polymers have been typically applied as supporting materials to incorporate the metal nanoparticles for electrocatalytic applications. Polymer-supported noble metal nanoparticles have shown good catalytic performance because of the active surface areas and the synergistic coupling impact among the two mechanisms [176]. MNs exhibit a high surface area that leads to consequential aggregation and poor colloidal stability. To overcome this issue, polymers have frequently been used as an outer shell coating of the metal nanoparticles [177] and provide a steric barrier for aggregation as shown in Fig. 9. Unique synthetic approaches can play a significant role to locate the MNs over the polymer web to avoid the collection of them. In this way, the polymer also collaborates with the catalytic properties of the MNs and enhances the catalytic activity. In this respect, lots of physical and chemical approaches accounted for the synthesis of the metal-polymer composites. Out of them, the IPCF technique [178] is more promising and performed an important role during the synthesis of metal nanoparticle-polymer composites with an increased catalytic response. In the composite synthesized by IPCF approach, the metal nanoparticles-polymer is formed together and come to an intimate contact with each other. In this method, metal salt act as an oxidizing agent that initiates the oxidative polymerization of monomer while beside it the direct reduction of metal salt generates the metal nanoparticles.

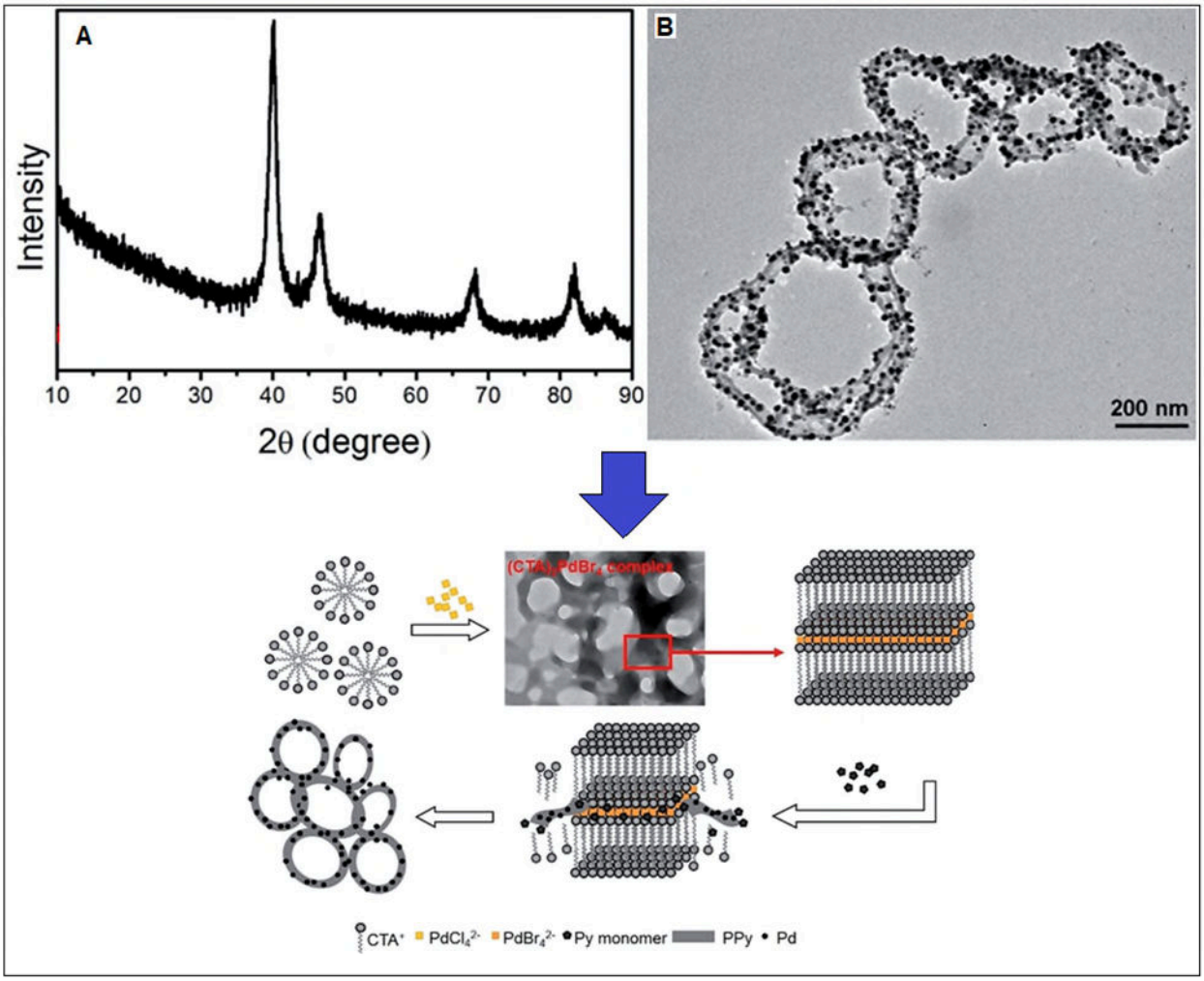

Fig. 9. XRD patterns (A)and TEM image (B) of Ppy/Pdcomposite nanorings. Schematic diagram of the manufacture of PPy/Pd composite nanorings. Reproduced with permission from the ref. [177], Copyright 2015 Royal Society of Chemistry.

Lots of work has been done to describe the IPCF method and also support the reduction of different dye as well as the synthesis of metal nanoparticle-polymer composite [179, 180]. It has been found that the synthesized metal nanoparticle encapsulated polymer by IPCF methods shows the excellent electro-oxidation of methanol [181]. Polymer sustained palladium nanoparticles have also been synthesized, which were effectively used as electrocatalysts for the methanol oxidation reaction in alkaline media [182]. A beneficial Pd catalyst at conducting polymer-carbon network was developed for electro-oxidation of ethanol and formic acid. A carbon-based polypyrrole compound was incorporated in the camphor sulfonic acid (CSA) [183] while the polymerization move of pyrrole at the ambient condition is shown in figure 10.

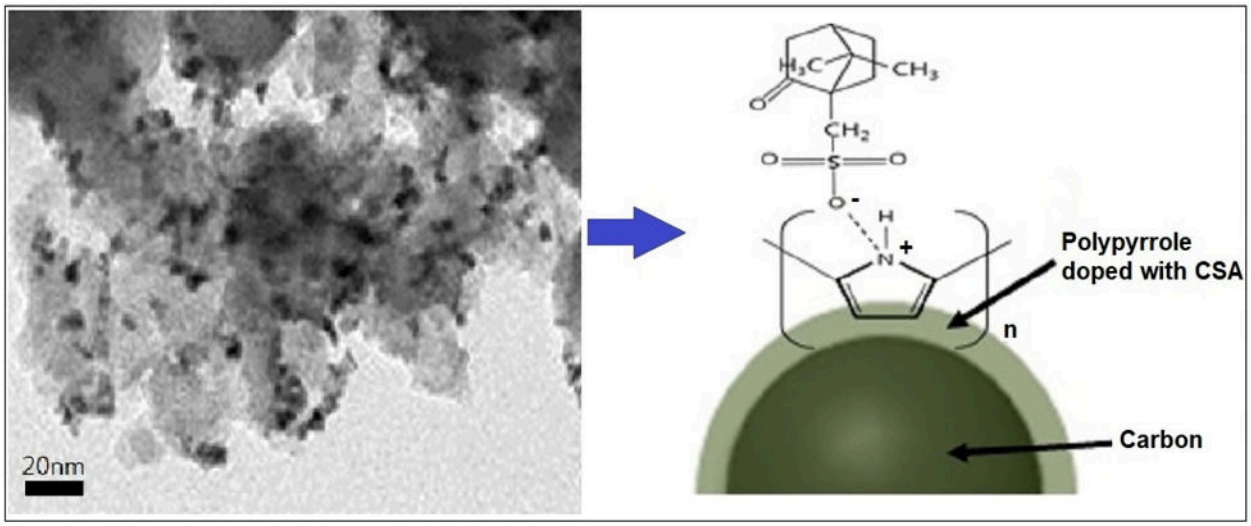

Fig. 10. TEM images of Pd/PPyCC. Schematic diagram of the CSA doped PPy-carbon support. Reproduced with permission from the ref. [183]. Copyright 2017 Wiley-VCH Verlag GmbH & Co.

The synthesized CSA-based polypyrrole-carbon catalyst (PPyCC) revealed notable improvement in the specific surface area and improved electrical conductivity correlated with a polypyrrole-carbon catalyst in the absence of PPyC. From the electrochemical analyses, it is noted that the Pd-sustained on CSA-based polypyrrole-carbon composite (Pd/PPyCC) showed considerable electrochemical surface area (ECSA), magnified catalytic performance and tremendous endurance to the oxidations of ethanol and formic acid [183]. Fard *et al.*[184] used in-situ emulsion polymerization technique to synthesize poly (pyrrole-co-aniline) (PPCA) hollow nanosphere (HN). Later they reported a template-free strategy to fabricate Pd NFs on a PPCA HN spread glassy carbon electrode through a simplistic electrochemical technique. The PPCA sustained Pd NFs, including huge surface area manifests the remarkable electrocatalytic performance than additional electrodes to the electro-oxidation reaction in alkaline electrolyte. It could be attributed to the automatic charge transfer towards conductive copolymer interfaces, large electrochemically available surface areas and electric conductivity. Those tactics give an assuring principle for direct alcohol fuel cells. Liu *et al*. [64] in an excellent review article summarized that the anode catalysis during the direct methanol fuel cell and clarified two main obstacles related to new DMFC anode catalysts, that is, the enforcement, covering activity, dependability and endurance, and cost improvement. It has been established that in rate discovering levels of methanol oxidation, an adsorbed hydroxyl group is essential [116]. This group develops from water separation at the catalyst exterior that takes place just on large electrode potential at Pt. This forms electro-oxidation of methanol complicated towards an absolute Pt catalyst. On the other hand, water removal happens on greatly lowering potential

upon ruthenium. This the reason that a bimetallic reaction initiative agent holding Pt and Ru both usually applied on anode electrode. The chemisorption's method for methanol is recommended support at Pt positions. Therefore, the levels involving the hydroxyl groups may take place near Pt and Ru positions. It should be noted in number through the catalyst formation [185]. The optimized junction region among both catalysts is required. There has been much work done on anode catalyst and **table 3** reviewed some work as given in below table:

Table: 3 A comparison of different results of typical anode catalysts including several combinations towards fuel cell applications.

Catalyst Composition	**Experimental Conditions**	**Specific/mass activity**	I_F/I_R	**Ref.**
PtNi/C	1 M NaOH and 1 M CH_3OH	48.5 mA/cm^2	-	[186]
Pt/C	0.5 M H_2SO_4 and 1 M CH_3OH	575 mA/mg	-	[88]
Pt/MC	0.5 M H_2SO_4 and 0.5 M CH_3OH	250 mA/mg	-	[187]
PtRu/MC	0.5 M H_2SO_4 and 1 M CH_3OH	487.9 mA/mg	3.3	[78]
Pt/graphene	0.5 M H_2SO_4 and 1 M CH_3OH	-	0.83	[188]
PtRu/graphene	0.5 M H_2SO_4 and 1 M CH_3OH	205.7 mA/mg	4.7	[189]
PtPd/graphene	0.1 M $HClO_4$ and 1 M CH_3OH	198 mA/mg	1.61	[190]
Pd/graphene	0.5 M NaOH and 1 M CH_3OH	61.6 mA/cm^2	-	[191]
Pd/MnO_2/CNT	0.5 M NaOH and 1 M CH_3OH	432.02 mA/mg	18.3	[192]
Pd/MnO_2/graphene	0.5 M KOH and 1 M CH_3OH	20.4 mA/cm^2	4.3	[193]
Pd/MnO_2/graphene	0.5 M NaOH and 1 M CH_3OH	838 mA/mg	-	[194]
Pt/TiO_2/graphene	0.5 M $H_2SO_4$and 1 M CH_3OH	83.1 mA/cm^2	-	[195]
Pt/TiO_2/C	0.5 M H_2SO_4 and 0.5 M CH_3OH	102.8 mA/mg	-	[196]
Pd/PPY/graphene	0.5 M NaOH and 1 M CH_3OH	359.8 mA/mg	7.30	[197]
Pt/PDDA/graphene	1 M $H_2SO_4$and 2 M CH_3OH	2.53 mA/cm^2	1.9	[198]
Pt/PDDA/GO	1 M H_2SO_4 and 2 M CH_3OH	3.82 mA/cm^2	3.32	[199]

Pd/C	0.5 M NaOH and 1 M CH_3OH	0.36 mA/cm^2	-	[200]
Pd/rGO	0.5 M NaOH and 1 M CH_3OH	1.6 mA/cm^2	-	[201]
Pd/PANI	1 M NaOH and 1 M CH_3OH	0.82 mA/cm^2	2.1	[202]
Pd(I)/*p*T3A	0.5 M KOH and 1 M CH_3OH	5.03 mA/cm^2	2.48	[181]
Pd-pDAN	0.5 M KOH and 1 M CH_3OH	1.7 mA/cm^2	7.98	[182]
Pd/PPyC	1 M KOH and 1M C_2H_5OH	983 mA/cm^2.mg Pd	-	[183]
Pd NFs/PPCA HN	0.5 M KOH and 1 M CH_3OH	1.79 mA/cm^2	-	[184]
Pd-NPLs/PDPB-nf	1 M KOH and 1M C_2H_5OH	3.53 mA/cm^2	3.41	[203]
Pt/PPy	1 M H_2SO_4 and 1 M CH_3OH	14.1 mA/cm^2	-	[204]
Pd/PPy PNCs	1 M KOH and 1M C_2H_5OH	13.08 mA.cm^2	1.37	[205]
Pd/MWCNT	0.5 M NaOH and 1 M CH_3OH	315.1 mA/mg	1.39	[206]
PdNi/MWCNT	0.5 M NaOH and 1 M CH_3OH	482.2 mA/mg	2.16	[206]
PdCo/RGO	1 M KOH and 1 M CH_3OH	303.8 mA/mg	0.89	[207]
Pd/polypyrene/GO	0.5 M H_2SO_4 and 1 M CH_3OH	4.36 mA.cm^2	1.62	[173]
Pt/NG	0.5 M H_2SO_4 and 1 M CH_3OH	296.3 mA/mg	0.99	[208]
Pt/MWCNT	0.5 M H_2SO_4 and 1 M CH_3OH	970.2 mA/mg	1.02	[209]
Pd-gC_3N_4	0.5 M H_2SO_4 and 1 M CH_3OH	2.29 mA/cm^2	1.63	[210]
Pd/GN	1 M KOH and 1 M CH_3OH	215.5 mA/mg	2.04	[211]
Pd/MWCNT	1 M KOH and 1 M C_2H_5OH	0.663 A/mg	0.62	[212]
Pt/MWCNT	1 M KOH and 1 M CH_3OH	0.73 A/mg	11.77	[213]
Pd/NG	1 M KOH and 1 M CH_3OH	19.7 mA/cm^2	1.63	[214]
Au-gC_3N_4	0.5 M KOH and 1 M CH_3OH	49.5 mA/cm^2.mg Au	1.47	[215]

6. Challenges and alternative approaches:

For the successful commercialisation of the technologies in the field of Direct Alcohol Fuel Cell several crucial challenges exist and they must be overcome. Some of these include the expansion of existing DAFC operations with fuel supplies variations, removal of poisonous outcomes, two-phase flow, impurities of pollutants, heat and water control. Many studies have been done on DMFC methods owing to the fewer articles about the DAFCs. Investigations towards the new kinds of alcohols have been essentially concentrated on basic features owing to the sluggish kinetics concerning electro-oxidation reactions including low energy production. Alternatively, DMFC growth has reached its plethora level, at which conventional cell aim and resources are well-known. Though, it is predictable to facilitate the projected advances for DMFCs, they can be always modified or prolonged to further DAFC schemes. Furthermore, for fuel cells to fight realistically including modern power production technology, all must grow more competitively with the viewpoint from both capitals, including installed price. Particular areas where cost decreases are being studied include:

1. Materials decrease with search for low-cost substitutes,
2. Plummeting the complication of an integrated structure,
3. Reducing temperature limitations (which put in complication as well as cost to the method),
4. Upgrade assembly to increase the advantage of economies of level (volume) during augmented market penetration.

Fuel cells need to be improved to employ generally accessible fossil fuels, control changes within fuel composition plus work without harmful influence on the environment. The thrust towards working with renewable materials and technologies including fuels decay is crucial to achieve business possibilities toward fuel cells.

7. Conclusion and future prospects

This review article has been focused mainly on different catalysts and their aggregates for application in DAFC. Pt-based catalyst, binary, tertiary, different supports and polymer-based catalysts have been considered, together with particular importance on the new aims in catalyst usage. To overcome the catalyst loading while increasing or at least to have the fuel cell execution is a very critical hurdle that can be accomplished by getting better Pt utilization and the catalytic movement. The progress in the field of fuel cell catalyst has attracted widespread consideration to explore substitute energy sources. The rapid development of

nanotechnology creates highly stable and dynamic supported catalysts. Moreover, the working principles of the fuel cells and the different types of fuel cells with operating condition have been reported. This is due to the patent operational advantages the system can deliver regarding new anode catalysts, specifically, the performance, including activity, consistency, stability and cost reduction. The technique to change the appearance of metal nanocrystals, commonly with a perception of the structure-dependent catalytic characteristics, gives an excellent chance to design new catalysts with enhanced performance logically. Furthermore, managing the gap on carbon-based shielding materials may also give a possibility to tailor the catalytic features of nanocrystals. This article has highlighted the research gaps through detailed review of the current state of the art experimental study. Furthermore, it is clear that in coming years, many nano-sized electrocatalysts and backer materials will be revealed for the fuel cells applications. The representation of the as-received catalysts in terms of activity, stability and the cost is yet not competent for the broad-scale utilization. Future research works should be dedicated to the wide-scale synthesis of durable, low-cost, multi-metallic nanocrystals with various size, appearance, and composition. This type of study would assist in recognising the most significant potential incorporation of catalysts for fuel cell purposes. Though this should be known, this is unrealistic to suppose that a particular kind of catalyst component may fit the all conditions for a decent functioning of a DAFC, particularly in various running states for several utilization. Hence, broad and advanced investigation ventures are expected together in the laboratory and automation in order to assure a possibility for DAFCs approaching its path to commercialization in times to arrive.

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