Advances and challenges of methanol-tolerant oxygen reduction reaction electrocatalysts for the direct methanol fuel cell

Muhammad Aizaz Ud Din[a], Muhammad Idrees[b], Sidra Jamil [c], Syed Irfan[d], Ghazanfar Nazir,[e]Muhammad Ahmad Mudassir,[f]Muhammad Shahrukh Saleem,[g]SaimaBatool[h], Nanpu Cheng*[a], Rahman Saidur*[IJ]

[a]School of Materials and Energy, Southwest University, Chongqing 400715, China.

[b] Additive Manufacturing Institute, College of Mechatronics and Control Engineering, Shenzhen University, Shenzhen 518060, Guangdong, China.

[C] Chongqing Key Lab for Advanced Materials and Clean Energies of Technologies, School of Materials and Energy, Southwest University, Chongqing 400715, China.

[d]School of Materials Science and Engineering, Dongguan University of Technology, Dongguan 523808, Guangdong,China.

[e]Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 05006, Republic of Korea.

[f] Department of Chemistry, Khawaja Fareed University of Engineering and Information Technology, Rahim Yar Khan 64200, Pakistan.

[g]Laboratory for High Performance Ceramics, Empa, Swiss Federal Laboratories for Materials Science and Technology, 8600 Dübendorf, Switzerland.

[h]Institute for Advanced study, Shenzhen University, Shenzhen 518060, Guangdong, China.

[I]Research Centre for Nano-Materials and Energy Technology, School of Engineering and Technology, Sunway University, Bandar Sunway, Malaysia.

[J] Department of Engineering, Lancaster University, Lancaster, United Kingdom (U.K).

* Corresponding authors. E-mail addresses: saidur@sunway.edu.my (RahmanSaidur);

cheng_np@swu.edu.cn (Nanpu Cheng).

Abstract

Methanol cross-over effects from the anode to the cathode are important parameters for reducing catalytic performance in direct methanol fuel cells. A promising candidate catalyst for the cathode in direct methanol fuel cells must have excellent activity toward oxygen reduction reaction and resistance to methanol oxidation reaction. This review focuses on the methanol tolerant noble metal-based electrocatalysts, including platinum and palladium-based alloys, noble metal-carbon based composites, transition metal-based catalysts, carbon-based metal catalysts, and metal-free catalysts. The understanding of the correlation between the activity and the synthesis method, electrolyte environment and stability issues are highlighted. For the transition metal-based catalyst, their activity, stability and methanol tolerance in direct methanol fuel cells and comparisons with those of platinum are particularly discussed. Finally, strategies to enhance the methanol tolerance and hinder the generation of mixed potential in direct methanol fuel cells are also presented. This review provides a perspective for future developments for the scientist in selecting suitable methanol tolerate catalyst for oxygen reduction reaction and designing high-performance practical direct methanol fuel cells.

Keywords: Oxygen reducing reaction, Methanol tolerant electrocatalyst, Portable power sources, Direct methanol Fuel cell.

1. Introduction

Fuel cells have recently received much more attention as a portable power source because of their high efficiency and low environmental pollution compared to other energy conversion technologies [1–3]. Fuel cells are expected to be commercialized for various applications, including transportation, space technology, and portable electronic devices that will help to solve the global problem of energy supply [4]. Fuel cells are based on the principle that converts chemical energy into electrical energy through a sustainable process. Still, their efficiency is dependent on the kinetics of the cathode oxygen reduction reaction (ORR) process [5]. Among various types of fuel cells, (PEMFC) offers wide range of applications due to their quick startup, cheap price, high energy density, and smaller size [6]. Direct methanol fuel cells (DMFCs) are an important class of PEMFCs that use liquid methanol as fuel rather than gaseous hydrogen thus, they don’t require complicated configuration [7]. Fuel cell based automobiles have been regarded as the final solution for pollution-free vehicles and have a preference on battery based electric vehicles. The direct methanol fuel cell (DMFC) is considered the most efficient technology due to its low working temperature, high power density, and ease of fuel storage make it an alternative technology to expensive Li-ion batteries for application in electronic devices [8]. DMFC has been used as the power source for commercial applications, such as energy source for laptops, forklifts, unmanned aerial vehicles, automobiles, drone technology, stationary power plants, and military proposes [9]. Intensive efforts have been made recently that led to the development of cheap and more abundant electrocatalyst for the DMFC [10,11]. These include the fabrication of noble metal-based alloys catalyst, transition metal oxides and chalcogenides, and carbon-based composite electro-catalysts [12–16]. The DMFCs principle is based on the electrochemical reactions of methanol and oxygen at anode and cathode, respectively. The theoretical potential of DMFC at 25°C is 1.21 V as measured through thermodynamic calculations, and the conversion efficiency of methanol in DMFC could be as high as 96.4% through these measurements [17]. However, the practical working potential of a DMFC is lower than the theoretical value because methanol oxidation reaction (MOR) and methanol cross-over effects have slow reaction kinetics, which decreases cell efficiency [18]. The methanol cross-over effect was observed in DMFC due to methanol concentration gradient, hydraulic pressure gradient, and electro-osmotic drag by proton transport that causes methanol cross-way from the anode to the cathode through the electrolyte membrane [19]. The methanol arrives at the cathode because the cross-over effect will be oxidized with ORR, which can lead to cathode depolarization, which seriously drops the cell voltage potential as well as the power output of DMFC, due to MOR [20]. A significant reduction of overall cell potential was observed when they fed DMFC with a concentrated (over 1M) methanol solution [21]. The methanol oxidation reaction (MOR) can occur in both acidic or alkaline conditions so the choice of acidic or alkaline electrolyte will not effects methanol tolerance in DMFC [22]. There are various possible ways to solve methanol cross-over effects: fabrication of novel proton-exchange membranes or increasing catalyst loading at anode and cathode of the fuel cell, but it can enhance cost due to the massive utilization of noble metal that has commercially unacceptable. The thickness of the membrane is a key parameter in controlling methanol cross-over in DMFC. The methanol cross-over rate can be reduced by making a thicker membrane, but it lowers proton conductivity, thus decreasing overall cell performance by hindering ORR performance [23]. The membrane thickness should be controlled for effective ORR, while inhibiting the methanol cross-over effects in DMFCs. One possible strategy is the fabrication of a methanol-tolerant cathode electrocatalyst that overcomes the drawbacks of sluggish reaction kinetics and methanol crossover, and engineering these materials has become the hot topic of research in DMFCs and has drawn the attention of scientists [24–26]. The fabrication of cathode catalysts to overcome the methanol tolerance effects of the DMFC without hindering its performance as well as controlling its price, still remains a challenging task [27]. Shoa et al. summarize advances in ORR catalyst also provide progress of catalyst supports very thoroughly, but their review does not focus on methanol tolerate electrocatalyst, [28] to commercialize direct methanol fuel cell as an alternative source of energy, detail study about methanol tolerate catalyst is an urgent need. The methanol tolerance effects through feeding different modified electrocatalysts in DMFC are summarized in Fig. 1.

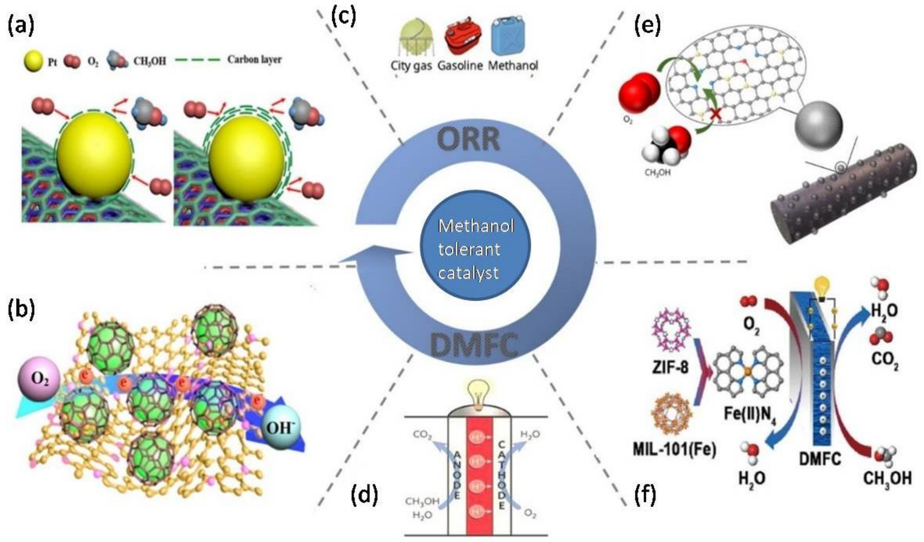


Fig.1. A summary of the effects of methanol feeding on the electrocatalyst.(a) Pt based catalyst and carbon coating for methanol tolerance, reproduced with permission from Ref. [57]. Copyright from American Chemical Society 2017. (b) graphene-wrapped iron carbide NPs supported on N-doped graphene, reproduced with permission from Ref. [93]. Copyright 2019 by Elsevier.(c) various energy sources.(d)production of electricity from DMFC.(e) Pt-aniline complex-coated carbon nanofibers, reproduced with permission Ref.[56]. Copyright 2020 by the American chemical society. (f) Fe-N-C catalyst derived from ZIF-8 and used as methanol tolerant catalyst, reproduced with permission from Ref. [94]. Copyright 2019 by Elsevier.

2. ORR catalyst for methanol tolerance

One drawback of a compact DMFC is that to run them continuously without recharging, a high methanol concentration is needed. However, higher methanol concentration will lead to enhance the rate of fuel cross-over, consequently lower accessibility of oxygen to the active sites of the catalyst; thus, methanol cross-over effects decrease the overall efficiency of the DMFC. The possible solution to these problems is the fabrication of a membrane with low methanol permeability, or an alternative approach is a methanol-tolerating cathode catalyst. To commercialize direct methanol fuel cells as an alternative source of energy, development of an ORR catalyst with desired performance requires more research attention [29,30]. Therefore, we need to explore methanol tolerate catalysts through rational engineering of nanostructures and interfaces that have a high surface area, larger electronic conductivity, abundant exposed active sites, can withstand harsh strong acidic media, limits CO poisonings, mixed potential as well as methanol poisoning. This review aims to summarize recent advances and challenges in the fabrication of methanol tolerant electrocatalysts in the ORR, with a particular focus on noble metal alloys based catalysts, their composites, carbon-based catalysts, and transition metal-based catalysts.

2.1 **Noble metal alloys based catalysts**

Noble metal-based alloy catalysts have been getting increased attention in fuel cell due to their higher electrocatalyst performance, structural stability, and resistance to CO poisonings [31–34]. However, the noble metal-based alloy catalysts encounter difficulties during their application in DMFC because they exhibit methanol poisoning in the fuel cell. In fuel cell, the small organic molecule such as methanol and formic acid can cross over from anode to the cathode by polymer electrolytic membrane, which hampered the cell performance [35,36]. However, commercial Pt/C catalysts do not exhibit tolerance toward these organic fuels thus, to address the durability issues of the fuel cell, scientists need to control parameters such as membrane, catalyst layer, gas diffusion layer, and bipolar plate during fuel cells operations [37]. Guo group synthesis PtBi nanoplates with a hexagonal structure to obtain high-performance ORR catalysis with high tolerance over the methanol oxidation as well as formic acid oxidation and CO-poisonings [38]. The excellent anti-poisoning tolerance for small organic fuels was attributed to their unique bonding structure, which can reduce bridge sites and buffer adsorption sites. By employing continuous-flow microfluidics, Zhang et al. report a method for preparing size-controlled intermetallic PtBi nanoparticles (NPs) (Fig. 2a-d) [39]. Their Pt-Bi intermetallic NPs display methanol tolerance capacity and high electro-catalytic activity for ORR (Fig. 2e-and f). The addition of Bi increases the Pt-Pt distance in the Pt_1Bi_2 catalyst which hinders the formation of intermediate products during methanol oxidation.

Furthermore, the Pt_1Bi_2 phase produces charge redistribution that hinders the oxygen-containing species from water dissociations. The resistance of the Pt_1Bi_2 catalyst to methanol poisoning could enhance the performance of ORR in commercial DMFC. Xun's group developed tetra-metallic PtAgBiCo nanoplates that display higher catalytic activity and long-term stability and are resistant to methanol cross-over effects in fuel cells [40]. (Fig. 2g, and h). There is no obvious methanol oxidation peak observed in the cyclic voltammetry (CV) plot of the PtAgBiCo nanoplates catalyst (Fig. 2i-and j), which proves that the nanoplates structure catalyst has improved selectivity for the ORR rather than for the methanol oxidation reaction. The excellent electro-catalytic performance of the as-prepared catalyst was attributed to the surface-based morphology of the nanoplates (Fig. 2 k-m) during the ORR reaction. The enhanced methanol tolerance in their catalyst was driven due to presence of the Bi species that is catalytically inert for the methanol oxidation reaction in an acidic medium, as three adjacent Pt sites in a proper geometry are regarded as an important parameter for methanol oxidation reaction to happen.

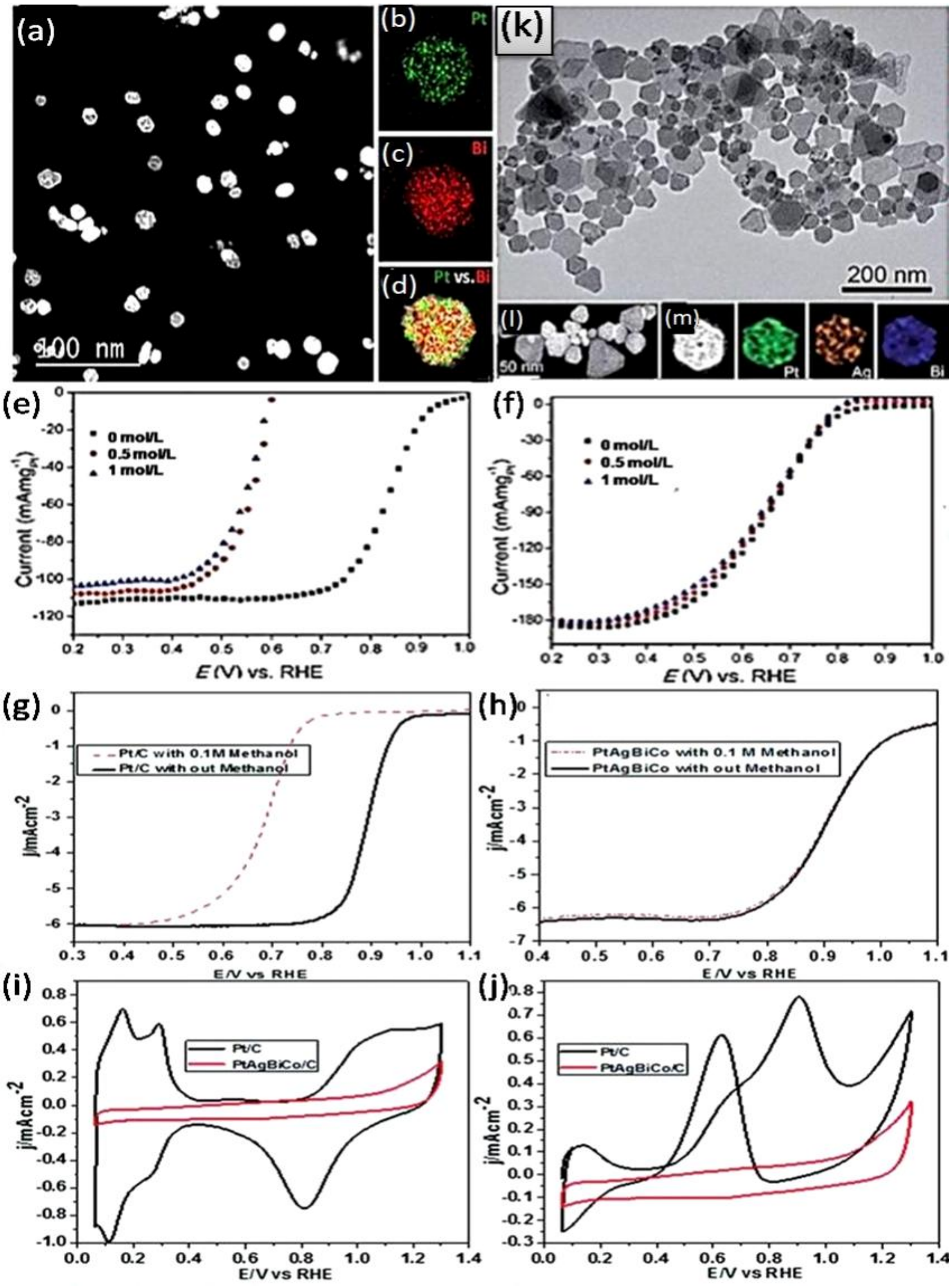


Fig. 2. (a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image of Pt_1Bi_2 nanoparticles (NPs). (b-d) EDX elemental mapping images of Pt and Bi. (e and f) methanol tolerance test for Pt/C catalyst and Pt_1Bi_2/XC-72 NPs in 0, 0.5, and 1.0 m/L

methanol solution at a rotation rate of 1600 $rmin^{-1}$. Reprinted with permission from Ref. [38]. Copyright from American Chemical Society 2015. (g and h) methanol tolerance test of Pt/C and PtAgBiCo/C catalysts with 0.1 M methanoland methanol free.(i and j) CV plots of Pt/C and PtAgBiCo/C catalysts with 0.1 M methanol and methanol free.(k) Transmission electron microscopy (TEM) of PtAgBiConanoplates.(l and m) HAADF-STEM and corresponding EDX elemental mapping images.Reprinted with permission from Ref.[39]. Copyright from Royal Chemical Society 2017.

Ud Din et al. prepared porous PtCuBiMn nanosheets with a thickness of almost 3-4 nm through the one-step hydrothermal method [41]. Our prepared PtCuBiMn nanosheets show high catalytic performance and long-term stability for the ORR as well as improved tolerance for methanol oxidation in DMFC. The enhanced tolerance of PtCuBiMn catalyst was attributed to the special geometric effects that arise due to the distortion of the three Pt sites. Zhao et al. prepared ultrathin PdAuBiTe quaternary nanosheets through the visible-light-induced template method [42]. Their nanosheets can act as high-performance ORR catalyst and shows improved methanol tolerance and anti-CO poisoning properties. The methanol tolerant ORR electro-catalyst needs a special surface electronic structure of Pt, which should promote the adsorption of oxygen and CO species as well as decreases the production of intermediate products (e.g. *O). Garcia and his co-worker synthesized Pd-based catalyst and then utilized it as the cathodic catalyst for ORR application [43]. They determine that PdFeIr/C shows excellent ORR performance compared to PdIr/C, PdFe/C, and Pd/C catalysts regardless of methanol concentration. However, PdFe/C and PdFeIr/C were the best methanol tolerant catalysts, among others. Their results demonstrate that the insertion of Fe into the PdIr material promotes methanol tolerance in their catalyst. Thus they suggest that doping of Fe can be considered in various noble-metal based catalysts as an efficient and cheap method for the synthesis of methanol tolerant ORR electrocatalyst. Wu et al. prepared core/shell based AgNi/PtAgNi nanoparticle through the seed-mediated growth method in an organic solvent that shows high ORR performance and inhibits methanol oxidation reaction in a basic solution [44]. As three neighboring Pt atoms in the crystal structure were essential to promote the oxidation of methanol. However, on the surface of PtAgNi shell the probability of three adjusting Pt-atoms was fewer, which was the key factor for the methanol tolerance of AgNi/PtAgNi catalysts. Liu et al. synthesized PtM (M= Fe, Ni, Co) nanoclusters through the impregnation-reduction method with diameters of about 2-5 nm [45]. Due to the lack of any protective agent on the catalyst surface their prepared material exhibits excellent ORR performance. However, PtNi shows the best ORR performance and resistance to methanol poisonings among various as-prepared catalysts due to unique electronic effects, smaller particle size, and excellent adhesion with the substrate. The presence of Ni on the catalyst surface reduces three adjacent Pt sites, which inhibits the methanol oxidation reaction and thus improves the performance of DMFC. Through the modified polyol method, Liu et.al synthesized PtPd nanoclusters for use as electrocatalyst in ORR [46]. Their PtPd nanoclusters exhibit 2.5 times higher specific activity and 4.1 times higher mass activity than that of commercial Pt/C catalyst as well as resistance to methanol oxidation. A chronoamperometric test was conducted to find durability in the presence of methanol solution, by adding methanol into an electrolyte solution. The addition of methanol decreases 5.8% ORR activity for PtPd nanoclusters catalyst however, for commercial Pt/C the activity reduced up to 39.2 during the chronoamperometric test. Their PtPd nanoclusters catalyst shows higher methanol tolerance due to the presence of Pd around the Pt active sites. Kim et al. fabricate a novel hierarchical cathode catalyst for DMFC consisting of Pt black as the inner layer and Pt/C as the outer layer and it shows high catalytic activity for ORR [47]. To find methanol cross-over effects the anode was fed with different methanol concentrations solution ranges from 1 to 3 M. At the methanol concentration 3M, their prepared catalyst shows maximum ORR performance, and they conclude that the hierarchical structure of the catalyst is very effective in decreasing the methanol cross-over effects on DMFC performance. Guan et al. prepared FePt@PtBi core–shell nanoparticles through the surface-engineering approach. Their prepared material exhibited excellent ORR activity, durability and behave as a methanol tolerate electrocatalyst in DMFC [48]. They suggested that, the presence of Bi species in their catalyst promotes resistance to methanol cross-over effects as well as hinder carbon monoxide poisoning. Wang et al. prepared intermetallic Pd_3Pb square nanoplates (SNP) through wet-chemical method that exhibits higher electrocatalytic activity for ORR and methanol tolerance (Fig. 3 a, and d) [49]. It was found that Pd_3Pb SNP shows ORR mass activity of 0.78 A/mg of palladium at 0.9 V, which was about 7.1 fold than that of conventional Pt/C catalyst. After the 5000th potential cycles for the durability test, there were no sharp structural and compositional changes observed, thus as-prepared catalyst was highly stable (Fig. 3b, and c). The DFT calculation reveals the possible reasons for the methanol tolerance of Pd_3Pb SNP in fuel cell. The theoretical study results demonstrate that presence of Pb plays a significant role in decreasing the adsorption strength of methanol in Pd_3Pb SNP. It was concluded that Pd_3Pb has the 3d orbital that is closer to Fermi level than Pd and Pt; thus

(100) orientation state in Pd_3Pb SNP shows weaker methanol adsorption energy, which might be the key reason for its methanol tolerance capacity (Fig.4e, and f). An alternative approach to regulate the electro-catalyst activity and selectivity inhibiting the particular reaction was tuning the electronic properties of surface atoms. The methanol tolerance in their catalyst was arisen due to polymer coating on the Pd surface that acts as barrier nanosieves to hinder the access of methanol molecules on active Pd sites. Sun et al. synthesized Rh-doped PdAg alloy nanoparticles (NPs) through a wet-chemical approach and utilized them for ORR application [50]. They prepared PdAgRh alloy NPs with different compositions and tested for methanol tolerance (ORR half-wave potential and mass activity) at various methanol concentrations (Fig. 3g and h) and maintained 92.4% mass activity during ORR in alkaline electrolyte upon feeding 0.1 M methanol, as compared to 100% decay for commercial Pt in same conditions. Also, their results indicate that the ORR mass activity and methanol tolerance of PdAg NPs can be optimized by Rh-doping; thus Rh-doping could be possibly used to control methanol cross-over effects in noble metal based catalysts.

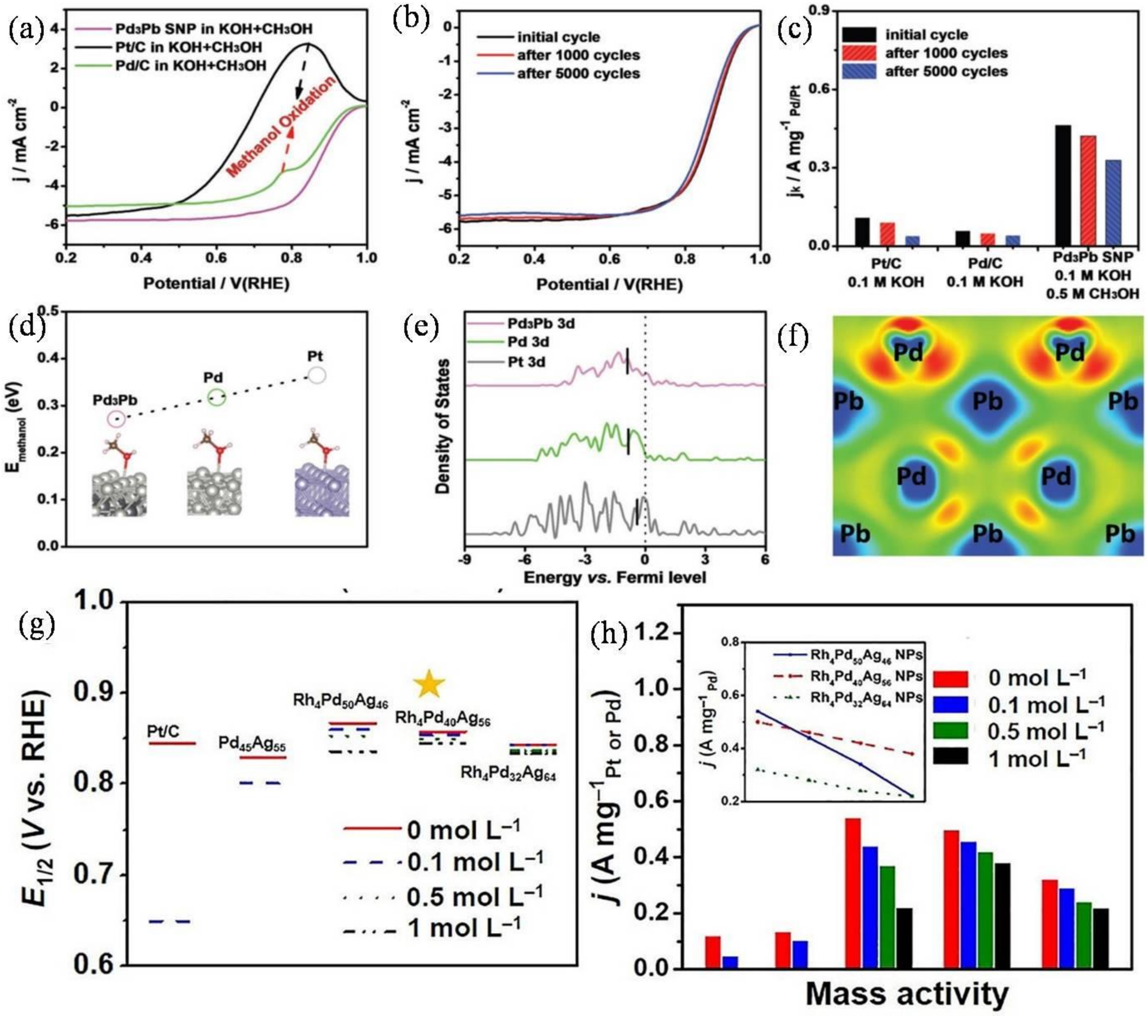


Fig.3. (a) LSV plots of PdPb, Pd/C, and Pt/C catalysts in 0.1 M KOH +0.5 M methanol feeding.(b) LSV plots of Pd3Pb SNP in 0.1 m KOH+0.5 M methanol feeding before and after stability test. (c) Changes in mass activities. (d) Trend in adsorption energy of methanol over Pd_3Pb (100), Pd (111), and Pt (111). (e) Density of States of Pd_3Pb, Pd, and Pt. (f) Differential charge density of the side view of Pd_3Pb (100) surface model. Reprinted with permission from Ref.[49]. Copyright from Willey2018. (g) Half-wave potential values for Pt/C, PdAg, RhPdAg catalysts with different compositions upon feeding various methanol concentration solutions in alkaline electrolyte. (h) ORR mass activity histograms of $Rh_4Pd_{50}Ag_{46}$, $Rh_4Pd_{40}Ag_{56}$, $Rh_4Pd_{32}Ag_{64}$, $Pd_{45}Ag_{55}$ and Pt/C

catalyst before and after feeding different methanol concentration solutions (0.1, 0.5,1 M). The inset in (b) is the mass activities line graph of Rh-doped PdAg. Reprinted with permission from Ref. [50]. Copyright from Elesvier and Science China Press 2018.

Vargas-Ordaz et al. prepared PtAg bi-metallic material through the electro-deposition method and explored for ORR. [51] The PtAg catalyst was elevated for fuel cross-over effects during ORR by feeding 0.1 M of methanol, ethanol, ethylene glycol, and glycerol in the electrolyte solution. Their PtAg material shows ORR activity and performs as a multi-fuel tolerant catalyst. The fuel tolerance of PtAg catalyst was arisen due to its high affinity to adsorb oxygen molecules rather than fuel (methanol, ethanol, and ethylene glycol) molecules. However, their PtAg catalyst adsorbs glycerol molecules, thus reducing active sites for ORR as well as generating low current density. Franca et al. prepared AgPt nanotubes through the galvanic replacement method using Ag nanowires as templates [52]. The AgPt nanotubes employed as electrocatalysts for ORR show high methanol tolerance in concentrated methanol solution (upto 7.5 M). The DFT study reveals that Ag atoms were responsible for methanol tolerance as it causes the reaction to be less favorable on the catalyst surface. Thus, the random configuration of AgPt nanotubes reduces the poisoning of methanol. Vecchio et al. synthesized Pd-Co alloys-based catalysts by the sulphite complex route that shows improved methanol tolerance in the half cell setup and resistance to corrosion phenomena [53]. Their Pd-Co alloys-based catalyst exhibits high activity and stability in single-cell DMFC than that of Pt-based catalyst due to the synergistic effects and provides better performance at high methanol concentration (>5 M). They conclude that Pd-based catalyst are more suitable for their application as cathode catalysts in DMFC due to less expensive as compared to Pt metal-based electrodes as well as high energy density because they have the tolerance to methanol poisonings effects. Xue et al. synthesized Au nanowires@Pd core−shell nanohybrids functionalized by polyethylenimine (Au-NWs@Pd@PEI) through the chemical reduction method and applied as electrocatalyst for ORR in alkaline electrolyte [54]. The enhanced methanol tolerance of their catalyst was arisen due to a loose-packed PEI polymer layer on the Pd surface that act as barrier nanosieves to hinder the access of methanol on Pd active sites. The main factor for ORR selectivity of their catalyst during methanol cross-over effects was hindering methanol access on active sites. Zhang et al. synthesize PdTe hexagonal nanoplates (HPs) for alkaline DMFC that simultaneously overcome the activity and methanol-tolerance issues [55]. The PdTe HPs exhibit high ORR activity, durability as well as good methanol tolerance and anti-poisoning stability in DMFC. The unique surface structure of their catalyst optimizes the adsorption of oxygen molecules and notably suppressed the unfavorable intermediates products such as methanol molecule. Huang et al. synthesized bimetallic palladium-copper (PdCu) nanoplates through one step facile oil bath method [56]. Their PdCu nanoplates exhibit excellent ORR performance as well as inert toward methanol oxidation. The theoretical calculation proves that methanol tolerance in their catalyst was arisen due to weak adsorption of methanol molecules, produced from the lower downshift of the d-band center, and electronic interaction between Pt and Cu components. Li et al. prepared interface-rich Au-doped PdBi (PdBiAu) branched one-dimensional (1D) alloyed nanochains through the single-step liquid phase method [57]. Their PdBiAu nanochains catalysts show excellent ORR performance and also demonstrate high methanol resistance. The methanol tolerance in their catalyst was due to the introduction of Au or/Bi, which increases their selectivity for ORR in DMFC. The summary of various parameters for noble metal-based methanol tolerate catalyst are presented in supporting information table S1.

Through a geometric design, the enhanced ORR selectivity of the noble metal-based catalyst could be achieved instead of relying on the intrinsic properties of the catalytic metal. Alternating the geometric structure of Pt-based catalyst, can reduce catalyst poisoning because methanol adsorption on the catalyst requires three proper adjacent Pt atoms, so doping or alloying Pt-based catalysts with some metals (Bi, Au) that can alter their geometry are the more effective way to enhance methanol tolerance. The selectivity of the methanol oxidation reaction depends on the crystalline orientation of catalysts. Therefore, engineering crystal orientation for selectively decreasing the methanol oxidative property can control methanol cross-over effects in DMFC. In the futures, by fabricating various porous core-shell nanostructures, noble metal based catalysts can have superior methanol tolerance due to the different diffusion behavior of methanol and oxygen in the porous metallic shell and core. Effective composite nanostructure synthesis for noble metal-based catalysts is urgently needed to improve the ORR activity and overcome the methanol poisonings in the DMFC.

2.2 **Noble metal-carbon composite based catalyst.**

Methanol cross-over effects are addressed in DMFC using noble metal with carbon composite-based catalysts that exhibit high resistance to methanol oxidation and excellent

ORR activity. Noble metals-carbon based composites were developed to protect the metal from dissolution by layering a thin carbon layer around the Pt or Pd sites. Carbon layers inhibit Pt or Pd nanoparticles aggregations and allow passage of oxygen, thus facilitating ORR reactions, and by adjusting the three Pt-sites on the catalyst surface, methanol oxidation reaction could be reduced. Lee et.al prepared Pt-aniline coated carbon nanofibers through simple heat treatment [58]. The catalyst exhibits high performance for ORR meanwhile, it inhibits methanol oxidations because the outer carbon layer buffer to access Pt core. However, this outer layer of carbon coating on the catalyst allowed oxygen to permeate for ORR, so the catalyst can be utilized for effective ORR reaction with high methanol resistance in DMFC. Tong et.al synthesized a novel hybrid ORR electrocatalyst that consists of Pt nanoparticles supported on carbon nanotubes and coated with a graphitic layer through the polymer encapsulation-graphitization method (Fig. 4a-e)[59]. Their polymer-encapsulated Pt/CNTs catalyst demonstrates higher catalytic activity for ORR and long-term stability for 3,000 cycles (Fig. 4f) and inhibits methanol oxidation reaction as compared to commercial Pt/C (Fig. 4g). The thickness of the graphitic layer of catalyst was optimized for ORR performance and methanol tolerance. The outer carbon layer should be sufficiently thick to reduce Pt nanoparticles detachment or aggregation and allows oxygen molecule to permeates on the catalyst surface as well as inhibit methanol oxidation (methanol molecule is too large as compared to oxygen molecule). However, if the outer graphitic layer is too thick, then it can inhibit ORR reaction as well as hinder the methanol oxidation reaction (Fig. 4h), thus reducing the electro-catalytic performance of the cathode catalyst for DMFC. The TEM characterization shows that Pt/CNTs aggregated after the stability test (Fig. 4i), while polymer-encapsulated Pt/CNTs do not agglomerate after the stability test (Fig. 4j).

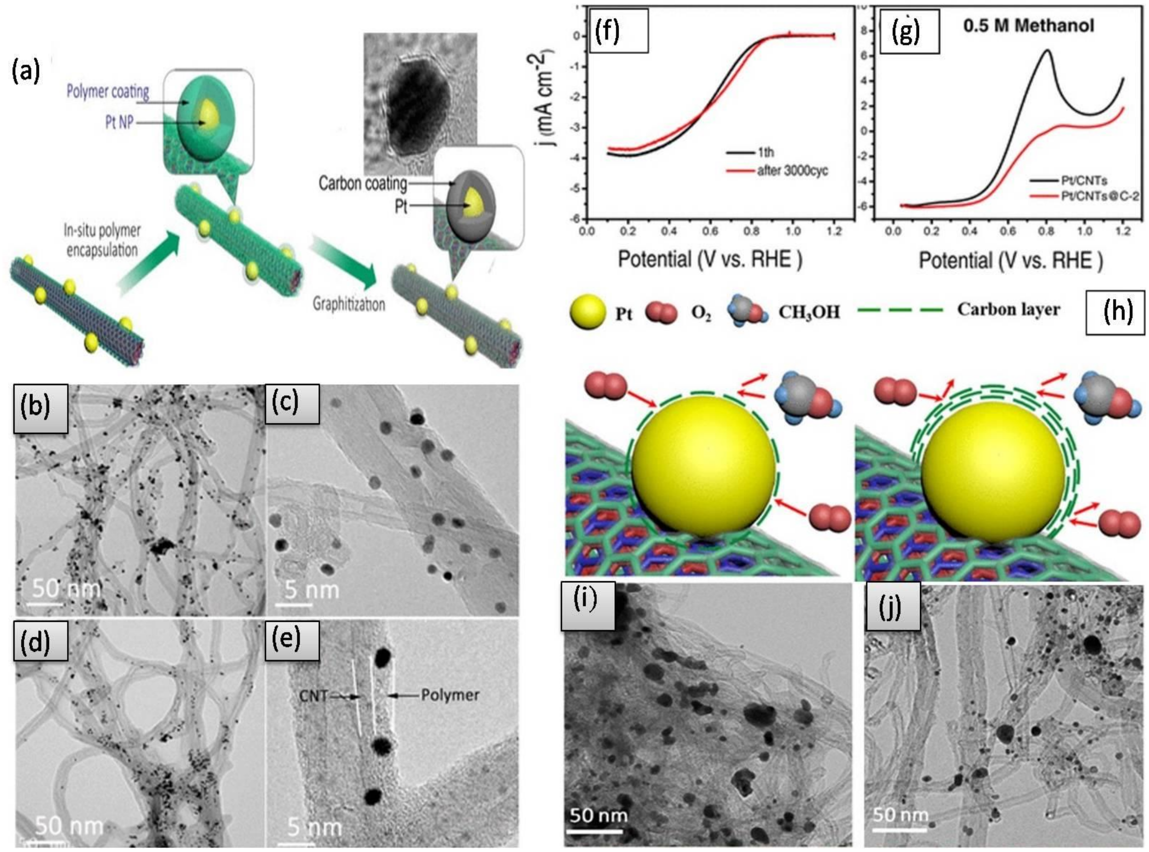


Fig.4. (a) Schematic illustration of the preparation of Pt nanoparticle supported on carbon nanotubes and coated with graphitic layer through polymer encapsulation-graphitization method.TEM images of Pt/CNTs and polymer-encapsulated Pt/CNTs (b and c) before graphitization and (d and e) after graphitization.(h) Schematic illustration of ORR on the catalyst surface with a different carbon layer. (i and j) TEM image of Pt/CNTs and polymer-encapsulated Pt/CNTs after stability test. Reprinted with permission from Ref.[59]. Copyright from American Chemical Society 2017.

A hydrothermal method was used by Faraji et al. to prepare Palladium-doped graphitic carbon nitride nanosheets (Pd-g-C_3N_4) decorated with nitrogen-doped carbon quantum dots (NCQD) [60]. Their two-dimensional Pd-g-C_3N_4 / NCQD catalyst shows excellent ORR performance and tolerance for methanol cross-over effects in DMFC. They suggest that methanol tolerance in their catalyst was arisen due to the presence of Pd. Pan et al. fabricate Pt-WSe_2/C composite through the modified borohydride reduction technique as a high-performance methanol-tolerant catalyst for ORR in DMFCs (Fig. 5 a) [61]. Their prepared Pt-WSe_2/C were optimized at various temperatures (600-1000◦C), while Pt-WSe_2/C-800 catalyst shows the best specific activity (4.57 mA cm^{-2}) for ORR as compared to WSe_2/C (2.45 mA cm^{-2}) and commercial Pt/C (2.69 mA cm^{-2}) catalysts. The doping of Se in the carbon structure can enhance the dispersion of active Pt, which increases the ORR performance, and decreases methanol cross-over poisoning effects. The RDE measurement for Pt-WSe_2/C and Pt/C catalysts was conducted in an acidic electrolyte solution with or without methanol feeding to determine the ORR kinetics and electron transfer number (Fig. 6b and d).The n value of Pt-WSe_2/C-800 catalyst is 3.84, while Pt/C is 4.05, in the methanol-free electrolyte solution, which was close to the theoretical value ($n = 4.0$), exhibits that their catalyst and Pt/C adopt 4-e^- path-way. The Pt/C LSV plot shows the sharp anodic current peak in methanol added electrolyte solution at 0.6 V due to the oxidation of methanol, however, LSV plot for Pt-WSe_2/C catalysts exhibits negligible changes after methanol feeding (Fig. 6c and 6e). The above-mentioned electrochemical test displays the methanol tolerance and ORR selectivity of Pt-WSe_2/C-800 catalyst. Methanol tolerance of Pt-WSe_2/C catalyst is produced due to the protective role of WSe_2 embedded in the carbon structure, synergistic effects among different components, exposed edge sites, porous morphology, and oxygen-contained functional groups on the catalyst. Guo et al. fabricate Pt decorated RuFeSe/C core-shell based catalyst through the reduction of Pt precursor and employed for ORR application [62]. The RuFeSe@Pt/C catalyst exhibits 4 electron pathways during ORR and excellent tolerance for methanol cross-over effects. Their RuFeSe@Pt/C catalyst selectively decreases the oxygen during the methanol oxidation reaction; thus methanol tolerance of the catalyst can be promoted due to the unique core-shell morphology and the ensemble effects. Zhang et al. fabricated PtRh alloy nanocrystal nanohybrids supported on carbon nanobowls (CNBs) and functionalized with 1-butyl-3-methylimidazolium tetrafluoroborate ionic liquid (BmimBF4) through precipitation–reduction strategy.[63] The electrochemical measurement reveals that CNBs perform advanced supporting materials, which reduce the particle size of PtRh nanocrystals and enhanced their dispersion. Their Pt_1Rh_1@- $BmimBF_4$/CNBs nanohybrids catalyst shows high ORR performance in acidic media as well as selectivity-reduced methanol oxidation. The improved methanol tolerance in their catalyst was due to $BmimBF_4$ molecules at the PtRh alloy nanocrystal surface, which block the access of methanol molecules at the catalyst surface because of the steric effect. Their work shows that chemical functionalization could effectively increase ORR activity and selectivity of noble metal nanocrystals.

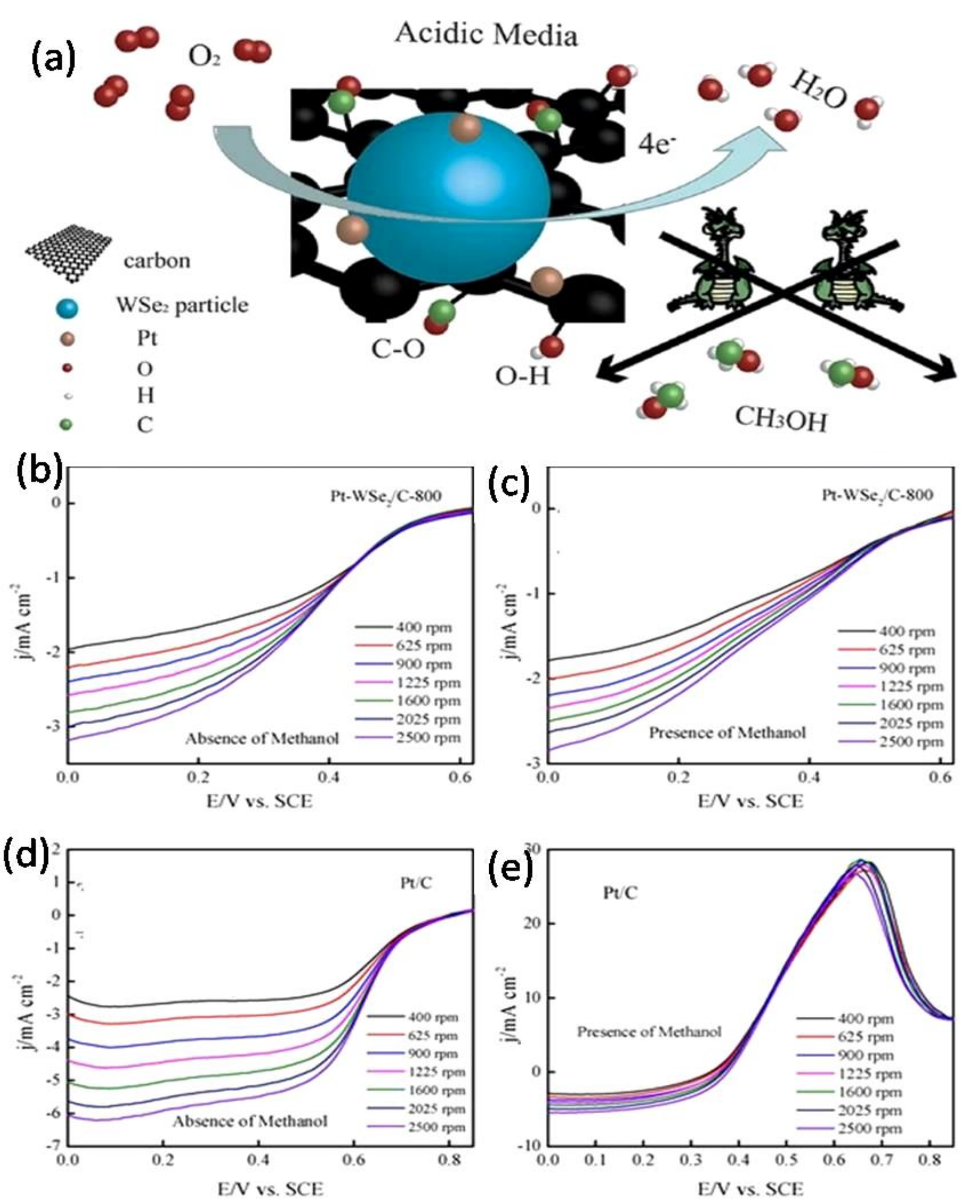


Fig.5. (a) Schematic illustration of the Pt-WSe$_2$/C catalyst in acid electrolyte solution upon feeding of methanol. (b and c) Linear sweep voltammetry (LSV) plots at different potentials (inset) of Pt-WSe2/C-800, and Pt/C. (d and e) in 0.5 M $H_2SO_4$with or without 0.5 M methanol addition at various RDE rotation speed. Reprinted with permission from Ref.[61]. Copyright from Elsevier 2017.

There are several drawbacks associated with using noble-metal based catalyst and their composites in DMFCs. The primary drawback is using expensive noble metal-based catalysts and their composites at both the anode and cathode, which can catalyze both methanol oxidation and oxygen reduction reactions. For DMFCs, efforts are currently being made to reduce the Pt/Pd loading or replace the expensive noble metal-based composites while maintaining the same performance as the existing one. The summary of various parameters for noble metal composite-based methanol tolerate catalyst are presented in supporting information table S2.

The material development technologies and theoretical calculations can be helpful for the tuning of the electronic properties of surface atoms which is a key approach to regulating the activity and selectivity of catalysts for ORR. Therefore designing thin layer carbon film coatings on the noble-metal based composites, can allow oxygen molecules to penetrate the catalyst surface but hinder large methanol molecules, thus enhancing methanol tolerance in DMFC. In the future, the development of various polymer coated noble metal-composite catalysts is expected to show an increase in ORR activity and a decrease in methanol adsorption, thus reducing the effects of cross-over with methanol. Furthermore, noble metal composite catalysts madeup from mxene also exhibit high electrocatalytic activity due to their high surface area, abundant active sites, and oxygen-diffusion dominant mesostructures, which can show high ORR performance and low methanol cross-over effects.

2.3 Carbon-based metal free catalysts.

Despite the tremendous achievements in DMFCs and availability of their pre-commercial instruments, many challenges still exist, such as low performance, insufficient stability, and utilization of expensive noble metal-based cathode catalysts that hinder their large-scale production [64,65]. Fabrication of methanol tolerant catalysts with comparable activity, non-precious, and increased stability to noble metal-based electrocatalyst is an urgent need for commercialization of DMFCs technology [66]. Farzaneh et al. prepared nitrogen-doped reduced graphene oxide (NRGO) through to hydrothermal method for utilization as a low cost cathode catalyst for ORR [67]. They find the effects of different parameters (fuel concentration, fuel efficiency, temperature, and current stability) on the performance of passive DMFCs. Their nitrogen-doped reduced graphene oxide catalyst shows methanol oxidation resistance even at higher methanol concentration (3.0 M), which promotes volumetric energy density of fuel cells. However, they concluded that further increasing methanol concentration (>3.0 M) will enhance methanol cross-over effects that lead to the blocking of active sites of catalyst as well as promoting mixed potential (which decreases cell potential) on the fuel cell. Mohmad et al. fabricate nitrogen-doped graphene-polypyrrole (NG-PPy) material through chemical exfoliation of graphene and by cationic intercalation of acid and pyrrole [68]. The NG-PPy material was utilized as a catalyst for ORR and Zn-air batteries. Their NG-PPy catalyst demonstrates improved ORR half-wave potential in the alkaline electrolytes as well as good tolerance for methanol poisoning. According to their proposed mechanism for ORR, oxygen molecule is adsorbed on the carbon atom that is adjacent to nitrogen doped graphene, which acts as the active site and promotes ORR. The CV plot for NG-PPy catalyst was evaluated by the addition of 1 M methanol, and it showed no obvious shift in the reduction peak current, and CV curves overlap. Moreover, the chronoamperometric test was performed by feeding methanol in the alkaline electrolyte; the reduction potential plot for their NG-PPy catalyst exhibited negligible changes, whereas after feeding methanol for 600 seconds, the Pt/C catalyst displayed a sudden shift from negative to positive current density. The above mentioned test shows that NG-PPy catalyst has high selectivity for methanol as compared to commercial Pt/C. Shi et al. synthesized nitrogen, phosphorus, and sulfur-doped three-dimensional porous graphite (NPS G) material through the pyrolysis method (Fig. 6a-e) and applied it as an electrocatalyst for ORR in alkaline electrolyte [69]. Their non-precious NPS G_2 (N, P & S amount optimized by mass ratio of graphene) catalyst shows excellent ORR performance and tolerance to methanol poisoning in an alkaline electrolytes (Fig. 6f and g). The excellent ORR activity and tolerance to methanol cross-over effects of metal-free NPS G_2 catalyst were ascribed because of its 3D porous structure and optimized content of nitrogen, phosphorus, and sulfur. Dar et al. have developed an innovative hybrid catalyst that combines polyphosphaze microspheres wrapped in carbon nanotubes with N, P, and O atoms (C-PCTNB@CNTs) (Fig. 6h-j) [70]. Our prepared composite catalyst shows excellent ORR activity (on set potential 0.94 V).The methanol tolerance was measured in oxygen saturated acidic solution that contained 0.1 M methanol, and half-wave potential for ORR measurement exhibited no obvious degradation (Fig. 6k and l). The C-PCTNB@CNTs show no acidic corrosion during electrolysis because carbon is anti-corrosive to acids as compared to transition metals. Hence, C-PCTNB@CNTs can be employed as anonprecious efficient and stable electrocatalyst for ORR in DMFC with tolerance for methanol poisoning.

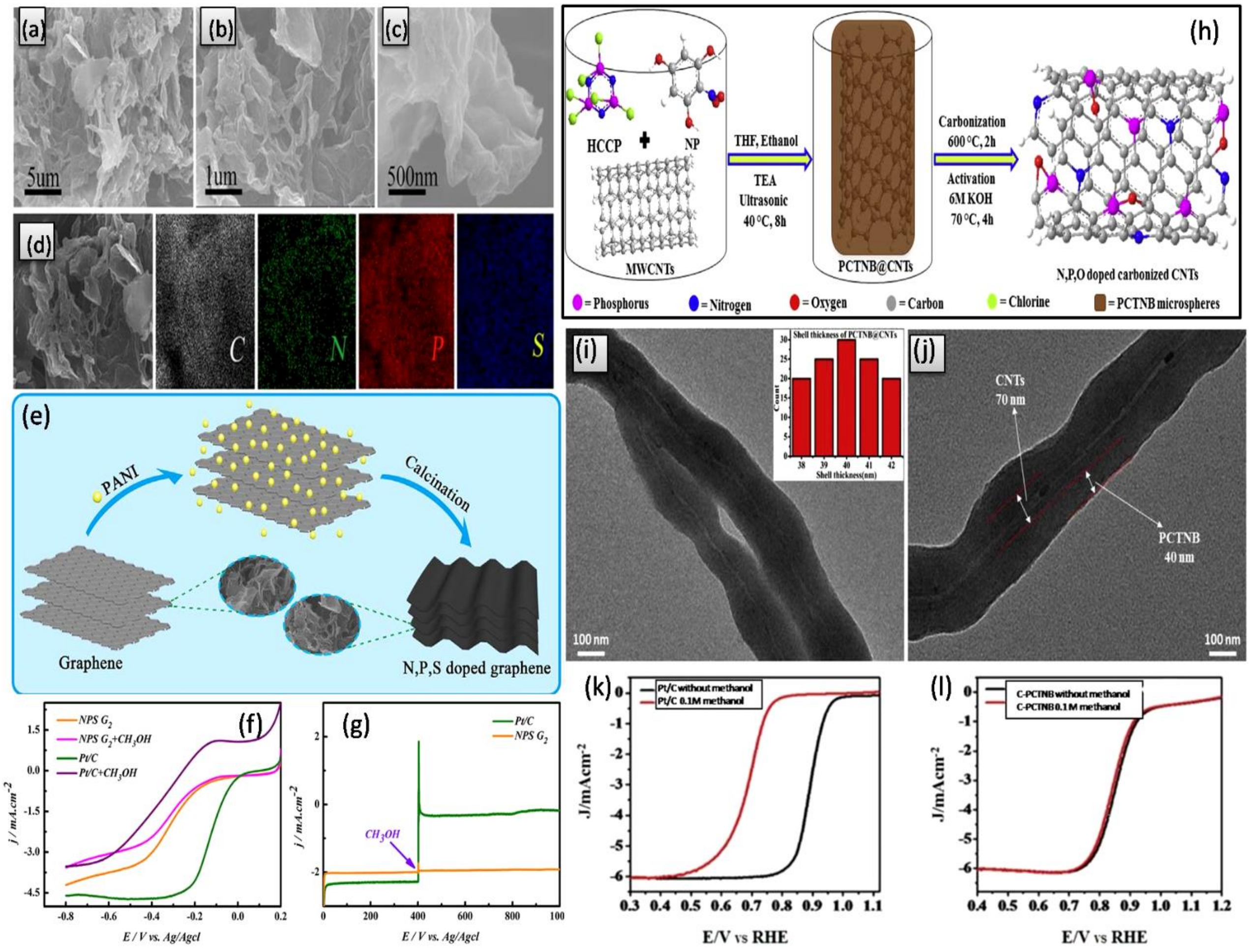


Fig. 6. (a-c) and SEM image of NPS G_2. (d) Elemental mapping images for C, N, P and S.(e) Schematic illustration of the sulfur-doped three-dimensional porous graphite (NPS G) material.(f) LSV plots of NPS G and Pt/C catalyst with and without methanol.(g) the Chronoamperometric plot of Pt/C and NPS G upon addition of methanol into the electrolyte. Reprinted with permission from Ref.[69]. Copyright from Elsevier 2020.(h) Schematic illustration of the synthesis of polyphosphaze microspheres wrapped in carbon nanotubes. (i and j) TEM images of C-

PCTNB@CNTs. (k and l) LSV plots of C-PCTNB@CNTsand Pt/C catalyst with and without methanol feeding. Reprinted with permission from Ref. [70]. Copyright from Elsevier 2017.

Sauid et al. prepared nitrogen-doped hierarchical porous carbon obtained from textile waste (TCPB).[71] The textile waste was impregnated with calcium chloride and urea, before heat treatment in the nitrogen environment. Their TCPB material is applied as the catalyst for ORR and shows high activity and stability in alkaline media. The TCPB catalyst exhibits methanol tolerance in highly concentrated methanol solution (3M). The summary of various parameters for carbon-based methanol tolerate catalyst are presented in supporting information table S3.

Through the application of innovative synthetic approaches, carbon-based nanomaterials possessing favorable compositions and porous structures, which, in conjunction with their low methanol crossover effects, represent a promising alternative ORR catalyst. This strategy has the potential to significantly reduce the cost of noble metal-based catalysts and facilitate their commercialization. An effective way to reduce the adverse effect of methanol crossover is designing a hierarchical carbon-based nanostructure, which can minimize the detrimental effect of the permeated methanol at the cathode in the DMFC. In the future, we believe researchers will be able to synthesize carbon nanomaterials with different dimensions by doping transition metal-based nanoparticles. Functionalization of transition metal-based nanoparticles on carbon nanomaterials demonstrates increased ORR activity and tolerance to methanol poisoning. Further exploration of more effective approaches for the fabrication, it will be possible to prepare heterodoped (N, O, S, B, or P) distinct 3D porous carbon-based electrocatalyst, and by doing so, the mechanism of how heteroatom functionality affects ORR will finally be understood. Such understanding will facilitate the development of ORR electrocatalysts with low methanol cross-over.

2.4 Transition metal-based Catalysts

Noble metal-based materials have been considered the excellent catalysts for the ORR, but their high price, low durability, limited availability, and poor methanol tolerance hampered their commercial application as cathode catalysts in DMFC, thus exploring high performance, cheap and abundant electrocatalyst for ORR with methanol resistance is necessary for DMFC [72–74]. Transition metal-based catalyst and their composites are promising alternatives to noble metal-based catalysts because of their higher activity, low cost, good stability, and resistance to methanol oxidation in DMFC [75]. Li et al. prepared the Fe-N-C catalyst through small uniform Fe/N-rich polymer spheres, and it exhibits high ORR performance as well as good methanol tolerance [76]. Furthermore, the effects of various sintering atmospheres (NH_3, Ar, and H_2) on the morphology, active sites, and ORR performance of the as-prepared catalyst were measured, and they found that the Fe-N-C-NH_3 based-catalyst shows comparable ORR performance and higher methanol resistance as compared to commercial Pt/C based catalyst. Park et al. synthesized graphene-based Fe/Co-N-C catalyst for ORR through the heat-treatment and subsequent chemical modification of the ball-milled graphene oxide [77]. Their prepared graphene and transition metal-based catalyst show comparable ORR performance and a high tolerance for methanol poisoning. They found the effect of methanol concentration on their graphene-based catalyst, and it can tolerate up to10 M methanol concentration;

however, maximum power density of the cell (32 mW cm^{-2}) was achieved with 1 M methanol concentration and by optimizing other parameters like ionomers content and catalyst loading. Liu et al. fabricate novel flower shape Fe-embedded N-doped carbon catalyst (Fig. 7a–f) through Cd^{2+}coordination with p-phenylenediamine and employed it for ORR as well as cathode for zinc-air batteries [78]. Furthermore, they leach out Cd through carbonization, and a porous flower-like N-doped carbon catalyst was obtained, and Fe was also embedded on the surface of the catalyst by the calcinations (Fe/NPC-2) as shown in the schematic diagram (Fig. 7g). Their Fe/NPC-2 catalyst shows the best ORR activity as compared to Pt/C and NPC (without Fe) catalysts. The chronoamperometric test was conducted (with or methanol-free) to elevate the stability of the Fe/NPC-2 and Pt/C catalyst (Fig. 7h and i). Fe/NPC-2 catalyst demonstrates resistance to methanol cross-over effects even at higher methanol concentrations (2M). Usually non-platinum group metal catalysts do not exhibit activity towards methanol oxidation while they are active towards ORR [79–81]. Sebastian et al. synthesized iron-based nitrogen-rich organic precursor amino-benzimidazole(Fe-ABZIM) material through heat treatment of iron nitrate [82]. The Fe-ABZIM has 3-D porous structure and can be applied as ORR catalyst. Their Fe-ABZIM catalyst has abundant catalytic actives sites and shows high ORR performance and methanol tolerance as compared to their prepared ferric amino antipyrine (Fe-AAPyr) and commercial Pt/C catalysts. The effect of methanol (concentration ranges from 0.001 M to 0.5 M) on ORR half-wave potential for Fe-ABZIM and Pt/C catalysts by keeping other parameters constant was determined as shown in Fig.3m. The ORR half-wave potential for non-platinum based catalysts (Fe-ABZIM, Fe-AAPyr) and Pt/C catalysts with methanol concentration (logarithmic scale) was plotted as shown in Fig.7j. The non-platinum based catalysts show constant half-wave potential plots over various methanol concentrations (logarithmic scale). In contrast Pt/C catalyst indicates sharp potential change at methanol concentration> 0.01 M, which arises due to the increased activity of Pt to the methanol oxidation reaction. The increase in methanol concentration in the electrolyte (sulfuric acid) doesn’t exhibit a significant change in the half-wave potential for Fe-ABZIM. The ORR half-wave potential plots for the commercial Pt/C catalyst exhibits peak shifts toward methanol oxidation reaction (Fig. 7k). Akram et al. prepared iron-nitrogen co-doped mesoporous carbon (Ex-FeN-MC) material through pyrolysis of the unique ureidopyrimidinone and applied it as bi-functional catalyst for Oxygen evolution reaction (OER) and ORR. [83] Our non-platinum based catalyst shows ORR activity comparable to commercial Pt/C with tolerance for methanol oxidation. The ORR half-wave potential plot for Ex-FeN-MC catalyst has almost no obvious degradation in the presence of 1 M methanol solution in an alkaline electrolyte, while commercial Pt/C catalyst displays sharp degradation in ORR half-wave potential when fed with 1 M methanol (keeping other parameters constant), the above results suggest our prepared catalyst has good selectivity for ORR rather than for methanol oxidation reaction.

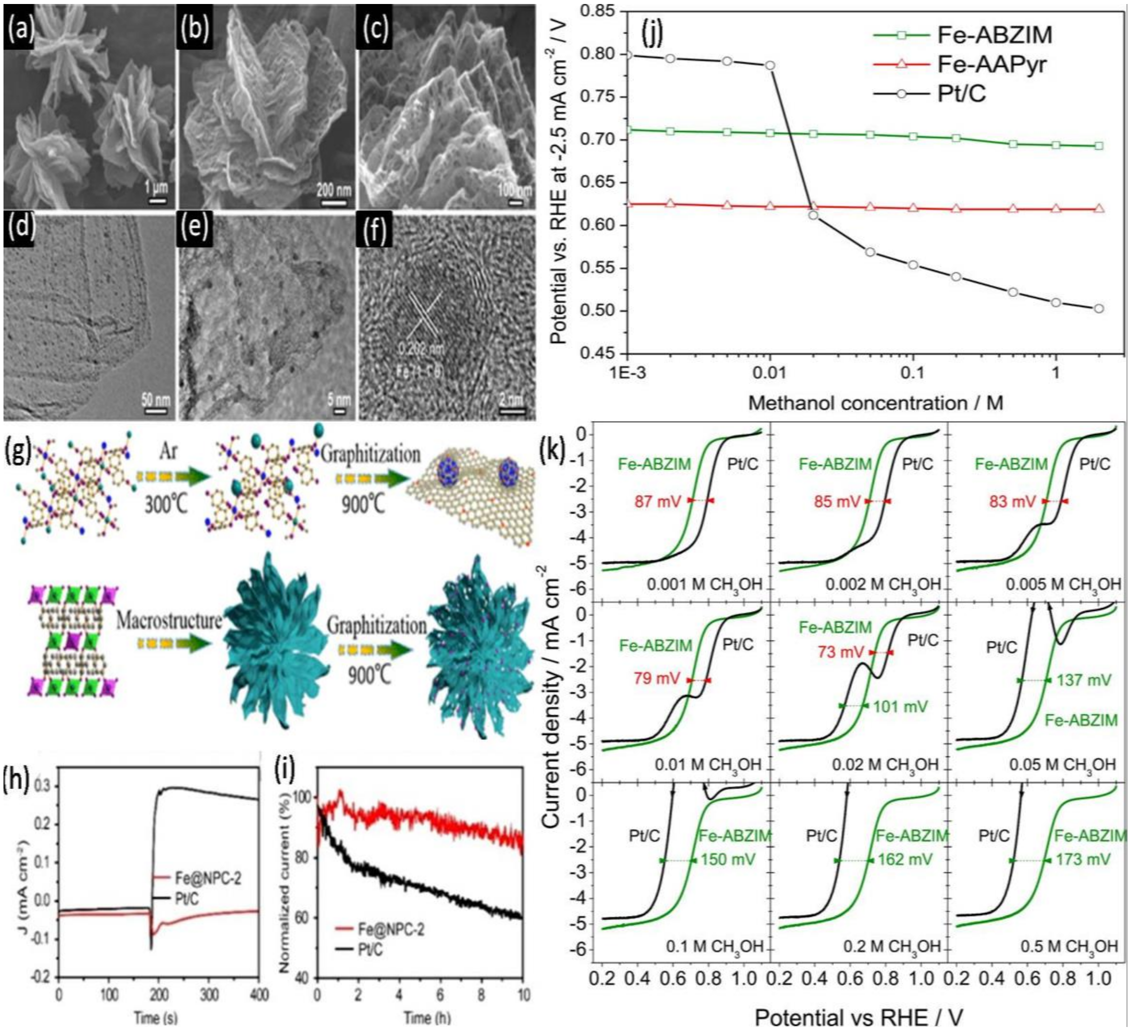


Fig.7. (a and b) SEM images, (c and d) TEM images, and (e,f) high-resolution TEM image of Fe@NPC-2. (g) Schematic illustration of the metal vaporization and escape from volatile metal–organic complexes in inert atmosphere at elevated Temperatures. (h) The chronoamperometric plot of Fe@NPC-2 and Pt/C upon feeding of 2 M methanol. (i) Chronoamperometric plots for Pt/C and Fe@NPC-2 at 0.7 V in 0.1 M KOH. Reprinted with permission from Ref.[78]. Copyright from American Chemical Society 2019. (j) Analysis of variation in half-wave potential (*E*½) with methanol concentration for Fe-ABZIM, Fe-AAPyr and Pt/C catalysts.(k) ORR plots measurement at various methanol concentrations with O_2-saturated

0.5 M H_2SO_4 solution for the Fe-ABZIM and the Pt/C catalysts Reprinted with permission from Ref.[82]. Copyright from Elsevier B.V 2016.

Shi et al. fabricated atomically dispersed M–N–C material M = Fe, Co, Mn), which contains FeN_4 active sites, and is applied as the catalyst for ORR in methanol-containing acid electrolyte [84]. They find that catalyst possessing FeN_4 sites that shows the best methanol poisoning during ORR as compared to pyridinic N, CoN_4, and MnN_4 active sites containing catalyst. The methanol cross-over effects become dominating if methanol concentrations exceed 2.0 M. Martinaiou et al. prepared Fe-N-C based catalyst through polyaniline, dicyandiamide and iron acetate precursors and find its ORR performance and methanol cross-over effects as non-precious metal catalyst in acidic electrolyte [85]. The methanol tolerance of their catalyst was elevated by feeding 0.1 M, and 1.0 M methanol to the acidic electrolyte. Their ORR onset potential plots show negligible changes after 1.0 M methanol addition, but their half-wave potential plots shifted almost 20 V. Sebastian et al. reported that such potential changes were aroused due to oxygen-concentration as well as diffusion variation in the electrolyte by methanol feeding [82]. They also measured durability test under load cycle conditions in the presence of methanol and found that methanol addition does not affect the stability of their non-precious Fe-N-C based catalyst thus, their catalyst as alternative of precious Pt or noble metal alloy based catalyst in DMFC with high tolerance for methanol cross-over effects. Their results display that ORR performance of the Fe-N-C catalyst was hampered due to the demetallation of FeN_4 sites and the creation of iron oxide clusters in the active sites. Videla et al. synthesized a Fe-N-C catalyst by hard template technique and iron phthalocyanine was employed as a source for iron/nitrogen/carbon [86]. Their selfstanding Fe-N-C framework was used as the catalyst for ORR by feeding methanol with various concentrations ranging from 0.01 to 10 M into the acidic electrolyte solution. Furthermore, their Fe-N-C catalyst was employed in DMFC, and it does not change by the methanol cross-over effects, exhibiting only a 12% decrease in maximum power density upon feeding methanol concentrated solution of 10 M. Their Fe-N-C material demonstrates a methanol tolerant catalyst as well as active enough for electronic applications.Hu et al. fabricated a series of non-precious metal Fe$_x$NC catalysts through pyrolysis method (Fig. 8a) and utilized them for ORR application [87]. Among their Fe-N-C based series of catalysts, Fe$_{1.5}$NC-900 electrocatalyst exhibits high stability and resistance to methanol cross-over effects in an alkaline electrolyte (Fig. 8b and c). The methanol tolerance effects were tested by adding methanol during the chronoamperometric test, and the current density of their Fe$_{1.5}$NC-900-2 catalyst was reduced by 8%, while the current density of Pt/C catalyst was sharply decreased upon methanol feeding (46%). Significant ORR activity and methanol resistance of Fe$_x$NC based catalyst was attributed to the abundant Fe$_3$N active sites produced during pyrolysis. The methanol tolerance effects were tested by adding methanol during the chronoamperometric test, and the current density of their Fe$_{1.5}$NC-900-2 catalyst was reduced by 8%, while the current density of Pt/C catalyst was sharply decreased upon methanol feeding (46%). Significant ORR activity and methanol resistance of Fe$_x$NC based catalyst was attributed to the abundant Fe$_3$N active sites produced during pyrolysis.

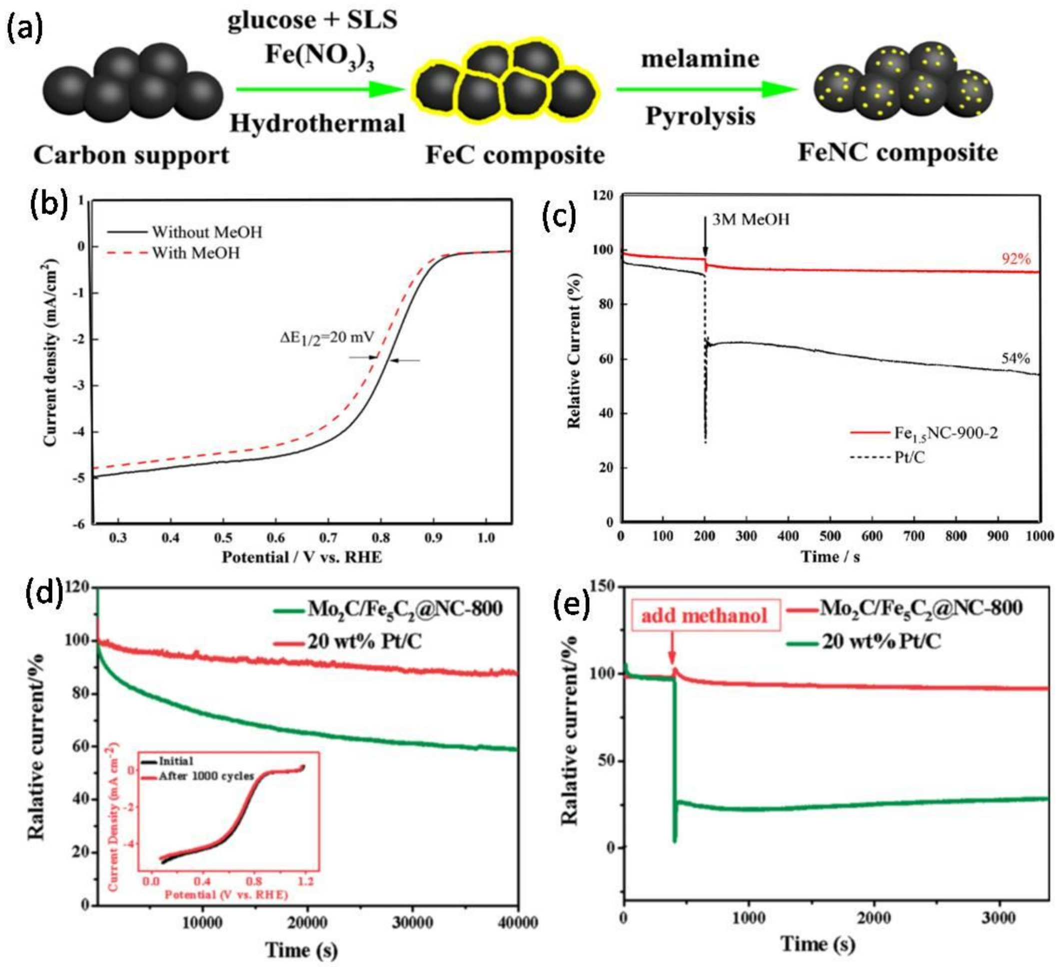


Fig. 8. (a) Schematic illustration of the preparation of Fe_xNC through pyrolysis method. (b and c) Linear sweep voltammetry (LSV) plots of $Fe_{1.5}NC$-900-2 electrocatalyst with or without methanol. Reprinted with permission from Ref.[87]. Copyright from Wiley 2019. (d) Chronoamperometric test of Mo_2C/Fe_5C_2@NC-800 and Pt/C catalyst in O_2-saturated 0.1 M KOH electrolytes and inset is LSV plot. (e) Methanol stability test of Mo_2C/Fe_5C_2@NC-800 and Pt/C in O_2-saturated 0.1 M KOH electrolyte. Reprinted with permission from Ref.[88]. Copyright from Elsevier 2019.

Li et al. prepared Mo_2C/Fe_5C_2 embedded in N-doped carbon through the pyrolysis method and employed it as a catalyst for ORR in alkaline electrolyte [88]. Their catalyst shows long-term stability for ORR (Fig. 8d).The addition of methanol during the stability test hardly affected the current density of Mo_2C/Fe_5C_2@NC catalyst; however, the current density of Pt/C was sharply affected by methanol injection (Fig. 8e), due to the inherent poison of carbon monoxide in the Pt-based catalyst [89]. The enhanced ORR performance of their Mo_2C/Fe_5C_2@NC catalyst was ascribed due to porous graphite-based carbon coating that increases the adsorption of O_2 and hinders the aggregation of Mo_2C and Fe_5C_2; also promotes stability of the catalyst for methanol cross-over effects. Li et al. prepared Fe-N/S−C material through the chemical vapor deposition method and employed it as the cathode to replace the noble metal-based catalyst for the ORR [90]. Moreover, kaliumpolyacrylate hydrogel (PAK gels) were synthesized through a single-step polymerization reaction and utilized as a quasi-solid electrolyte in DMFC. The methanol tolerance of Fe-N/S-C catalyst was elevated by methanol addition during the chronoamperometric test. Their Fe-N/S-C catalyst exhibits high methanol tolerance in DMFC, and the current density of the chronoamperometric curve does not produce any sudden changes by adding methanol. Fabrication of high methanol concentrated setup in DMFCs can lead to a high energy density; however, methanol cross-over effects produce mixed potential in the cell that decreases the overall efficiency, which is accelerated with high methanol concentration. Zuo et al. prepared non precious metal-free ORR catalyst, which contains Co/CoO/SnO encapsulated in N-rich mesoporous carbon (CCS@NPC) nanocubes [91]. During the ORR, their CCS@NPC catalyst can tolerate high concentrations of methanol due to the low catalytic activity of the functional components and the weak competition reaction of methanol oxidation that was induced by the compositional effect. As their catalyst is highly methanol-tolerant, they could feed more fuel (methanol) at the anode, which would certainly facilitate the development of commercial DMFCs. Feng et al. design hetero-structured Fe_2O_3/Mn_2O_3 material as the cathode catalyst for DMFC (Fig. 9a) [92]. The synergistic effect between α-Fe_2O_3 and α-Mn_2O_3 matrix in Fe_2O_3/Mn_2O_3 catalyst increases ORR performance of their catalyst in an alkaline solution (Fig. 9b). Their chronoamperometric test displays that Fe_2O_3/Mn_2O_3 catalyst has high stability and resistance to methanol poisoning in an alkaline solution (Fig. 9c). A polymer fiber membrane (PFM) has also been developed in place of traditional PEM in their DMFC. Fuels and electrolytes can easily pass through the PFM membrane, and the membrane is permeable; thus, it produces high performance for DMFC.As a zinc-based carbon precursor, ZIF-8 shows great potential because Zn vaporizes at 900 °C, forming homogeneous pores carbon structure, which promotes catalytic reactions by allowing reactants to diffuse [93–95]. Wang et al. synthesized single-atom Fe embedded nitrogen-doped carbon (Fe–N–C) porous material through high temperature pyrolysis by utilizing precursor ZIF-8 [96]. The Fe–N–C catalyst derived from Fc@ZIF-8 shows higher current densities (38.15 mA cm^{-2}) for ORR and a half-wave potential of 0.9044 V while operating at 0.85 V in an alkaline electrolyte. Methanol tolerance ability was measured by feeding methanol in an electrolyte during the chronoamperometric test; the Fe–N–C catalyst shows high tolerance against methanol poisoning as compared to Pt/C catalyst. The abundant FeN_x sites in the Fe–N–C catalysts contribute high ORR performance as well as methanol tolerance.

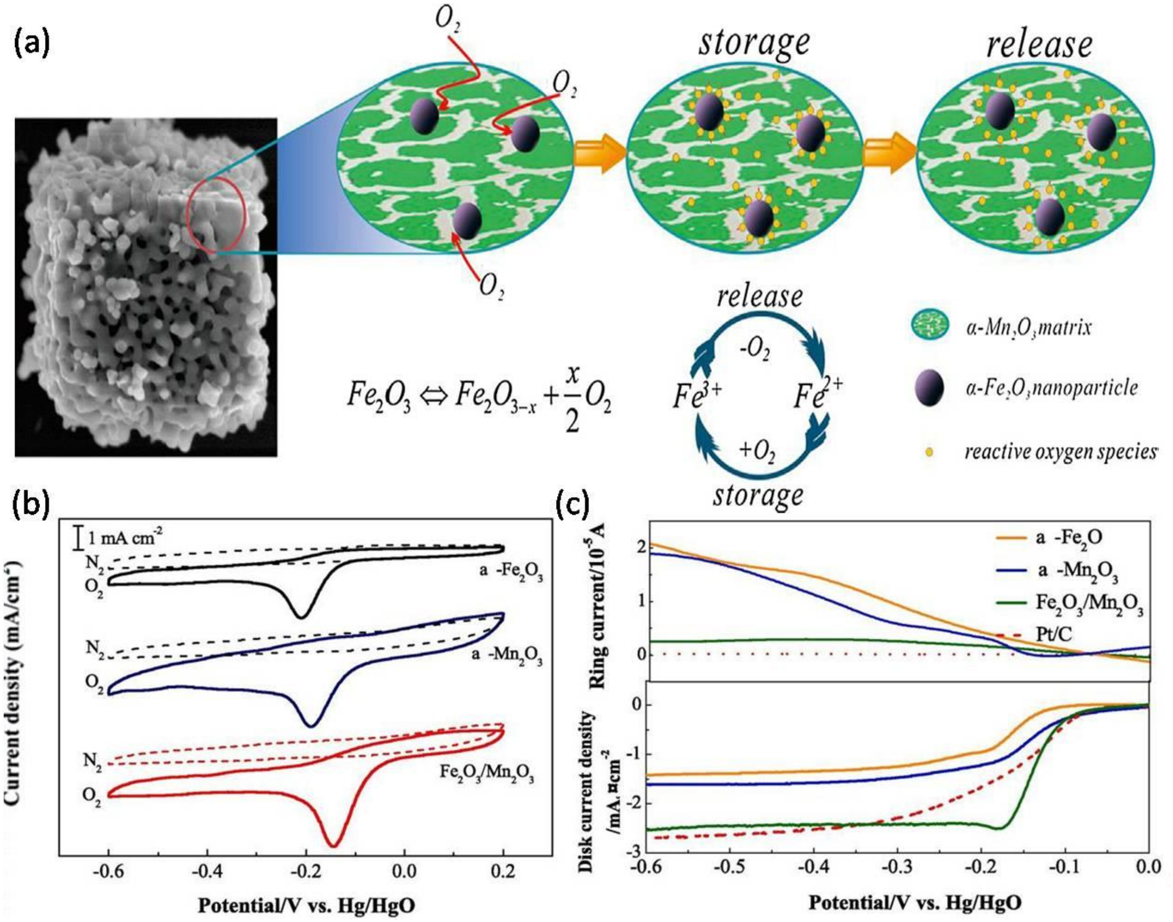


Fig. 9. (a) Schematic illustration of the oxygen adsorption, storage and release mechanism of Fe_2O_3/Mn_2O_3 catalyst for ORR (b) LSV plot of Fe_2O_3/Mn_2O_3 catalyst (c) Methanol tolerance test of Fe_2O_3/Mn_2O_3 and Pt/C in KOH electrolyte. Reprinted with permission from Ref.[92]. Copyright from Elsevier 2019.

Wen et al. prepared graphene-wrapped iron carbide (Fe_7C_3) nanoparticles supported on hierarchical N-doped graphene that has mesoporous morphology (Fe_7C_3/NG) that act as an efficient non-precious metal catalyst for ORR with strong methanol tolerance [97]. During the methanol tolerance test, their Fe_7C_3/NG-800 catalyst shows negligible changes in the current densities after the feeding of 1 M methanol into the alkaline electrolyte. The higher methanol tolerance of Fe_7C_3/NG-800 catalyst is due to the effective protection of the inner Fe_7C_3 by the external graphitic carbon shell. Xu et al. prepared atomically dispersed Fe-N-C catalyst for ORR through mechanical grinding of ZIF-8 with MIL-101(Fe) [98]. The abundant FeN_4 sites attributed high activity as well as good stability for ORR, [99–101] and were also responsible for higher methanol tolerance. Dual MOFs are therefore an ideal approach for preparing methanol tolerant cathode catalysts for DMFCs, and other devices that contain O_2 based cathode [102–104]. Abdulrehman et al. prepared the transition-metal-based Fe-N-C ORR electrocatalyst through metal organic framework precursors (Fe-MOF) [105]. Their Fe-N-C catalyst exhibits high ORR performance, which was arisen because of FeN_4 active sites embedded into the porous carbon matrix, and also tolerance to methanol cross-over effects. The methanol tolerance in their catalyst was due to the immunity of M-N-C catalyst sites to the methanol oxidation property produced by their atomic structure. They find that their Fe-N-C cathode catalyst has low sensitivity to higher methanol concentrations up to 6 M than the commercial Pt/C. The summary of various parameters for the Transition metal-based methanol tolerate catalyst are presented in supporting information table S4.

From experiments as well as density functional theory (DFT) calculations, it was found that transition metal-based catalysts can give excellent ORR activity and methanol tolerance. Transition metal-based materials will need to be explored in the future because they are the most attractive and promising cathode catalysts for high-performance DMFCs because of their geological abundance, and environmental friendliness.

Researchers can focus their future efforts on the following aspects when developing transition metal-based ORR electrocatalysts. In situ characterization techniques that can provide surface-sensitive insights must be developed to investigate the changes in catalyst surface electronic structure that occur during ORR and methanol adsorption. Because of their compositional and structural flexibility, perovskites type catalysts have attracted considerable interest and must be investigated for their capability to inhibit methanol cross-over effects in DMFC. It is possible to use strategies including core-shell design, space confinement, and hierarchical structures to improve the ORR activity and hinder methanol adsorption on the catalyst surface. As a result of strong coupling synergetic effects on functionalized carbon supports such as mxzenes and transition-metal catalytic active sites, the issues of low electrical conductivity can be effectively solved. The development of cathode catalyst with non-platinum group metals M-Nx-C type (M = Fe, Co, etc.) is highly recommended for designing cheap methanol tolerant electrocatalyst because they show high ORR activity and extremely low methanol oxidation property.

5. Conclusions and perspective

Almost all research developments on methanol tolerate electrocatalysts for oxygen reduction reactions in acidic and basic media are summarized. The first step in commercializing direct methanol fuel cells will be to solve the methanol cross-over effects, which will make fuel cell technology a more efficient and sustainable energy source. In order to alleviate the mixed potential caused by methanol permeation from anode to cathode through the membrane, intensive research efforts have been needed to hinder the intermediate methanol adsorption on the cathode catalysts to boost the ORR performance. One of the main advantages of the methanol tolerate catalyst is that it can reduce the formation of the carbon monoxide, which produce during the electro-oxidation of methanol; the adsorbed carbon monoxide intermediates degrade the cathode catalyst lifetime in DMFC. The design of catalyst materials must be complemented by engineering approaches to mitigate methanol crossover. To maintain reasonable energy density and stability as well as hindering mixed potential due to methanol cross-over effects in DMFCs, must address several challenges, and major compromises are required. The key conclusions are as follows:

1. Platinum, palladium, and several other noble metal-based catalysts are widely used as ORR catalysts because of their high catalytic performance. Despite their huge potential as ORR catalyst, noble metal-based catalysts still suffer from a number of disadvantages, including their high cost, scarcity in nature, and poor methanol tolerance. However, several studies have been conducted to investigate methanol-tolerant ORR catalysts without using noble metals, but their ORR activity is still considerably lower than that of noble metal-based catalysts. As a consequence, it is still difficult to implement DMFC technology for commercial propose using non noble metal based catalysts. Scientist urges to reducing the amount of Pt or other noble metals for commercial application of catalyst, the possible solution is doping cheap metals such as bismuth, ferric and nickel in the catalyst, which reduces three adjacent Pt sites, also lattice contraction effect of the alloy inhibits the methanol oxidation reaction, and cathode depolarization slow down; thus, it improves the overall performance of DMFC as well as decreases their cost.

2. Several approaches are discussed in this review to prepare methanol-tolerant support materials that can reduce the risk of methanol poisoning on the noble metal-based catalysts. Through the synthesis of composite-based noble metal materials, the electro-catalytic activity for ORR is promoted, and their tolerance to methanol crossover effects is also increased. There are different protective layers available for noble-metal based catalysts, but the carbon shells have proven to enhance catalyst stability as well as methanol tolerance. However, several issues, such as too thin carbon coating, will not protect noble-metal based catalyst effectively, while too thick ones will block the active surface of the catalyst, which hinders oxygen permeation and reduces ORR activity. The carbon layer can be controlled precisely so that it can allow oxygen molecules, but it should hinder methanol molecules on the catalyst surface, also noble metal nanoparticles can be firmly anchored at the surface of the catalyst. In particular, reduced graphene oxide (rGO) is an ideal support for catalytic reactions. A large number of functional groups on the surface of rGO provide many adsorption points, allowing different nanoparticles to adhere to the surface, and preventing aggregation. Many challenges have yet to be overcome, such as the oxidation of the carbonaceous support of the catalyst, which results in the loss of ORR catalytic sites, which are known to be integrated in the carbonaceous support of the catalyst for Fe/N/C and CN_x. For the commercialization of DMFC, the scientist needs to focus their attention on the lack of durability of non-noble metal and metal-free catalysts and its possible causes.

3. To design methanol-tolerant catalysts, non-precious materials such as carbon-based catalysts or metal-free catalysts are another viable option. In general, metal free catalysts are less active; however, they do not suffer from CO or methanol poisoning. Carbon-based catalysts (both pyrolyzed and non-pyrolyzed) exhibit high ORR activity in DMFCs and have appropriate methanol tolerance, through the non-pyrolyzed catalyst is questionable in terms of their durability. Nitrogen-doped carbon exhibits high catalytic activity compared with other metal-free catalysts because of its enhanced electro-negativity, resulting in a net positive charge on the nearby carbon atoms. Furthermore, it has been determined that nitrogen-doped heterostructure, including graphene, carbon nanotubes (CNTs), and mesoporous carbon structures, offer the best ORR performances as well as high methanol tolerance. Many problems need to be resolved, such as micro-porosity of carbon material having an effect on the flooding of the catalyst layer, which limits the efficiency of DMFCs: accumulation of water causing blockage of pores on the catalyst surfaces causes poor fuel cell performance. The mxene-based catalyst was employed recently for ORR in acidic and basic media, so Mxene-based catalyst or metal supported on Mxene can be studied in the future as methanol tolerates catalyst.
4. Exploring and developing non-precious metal ORR catalysts with low cost, abundant resources, commercial efficiency and durability is crucial. There have been significant efforts in recent years to develop noble-metal-free catalysts such as transition metal phosphides, chalcogenides, oxides, carbides, nitrides, and nitrogen-containing transition metal complexes. Contrary to the elemental-doping

> strategy that only allows low-content dopants to maintain catalytic properties of noble metal-based catalysts, transition metal-based materials have a wide range of elements that can improve ORR and decrease methanol poisoning. The heterostructure catalyst made up of transition-metals could be used to improve the efficiency of direct methanol fuel cells by overcoming CO poisoning and high oxygen mass-transfer over-potential produced by the methanol cross-over. In order to demonstrate transition metal-based catalyst feasibility in large-scale fuel cell applications with high performance and durability, it still needs to be focused on finding appropriate support materials for them.

Finally, the essential strategies to enhance the methanol tolerance of ORR catalyst are summarized as (1) Through designing the porous core-shell based nanostructures that can promote methanol tolerant property of the catalyst due to the different diffusion behavior of oxygen and methanol in the porous shell. (2) By designing a modified Pt-based ORR catalyst through doping metals (e,g Se, Bi) can alter three adjacent Pt sites, so it can inhibit methanol adsorption. (3) In noble-metal based catalyst, the protective carbon layers can change the diffusion behavior and thus improve the methanol tolerance. (4) By engineering the crystalline orientation of the electrocatalyst for selectively reducing the methanol oxidative property can control methanol cross-over effects in DMFC. (5) Through promoting the research on the synthesis of cheap transition-based nanomaterials such as M-N-C (M=Fe,Co) catalyst because M-N_4 and M-N_2C_2 active sites preferentially adsorb oxygen with much higher energy than the methanol. The development of high-efficiency and methanol-tolerant ORR electrocatalysts for application as cathodes in DMFCs is an important and challenging area of research. The focus of this review is to provide an update on the rapid development of studies of methanol-tolerated ORR electrocatalysts over the last few years, with special attention being paid to phenomenological understanding and the topics under discussion.

6. Acknowledgments

The current work was supported by the National Natural Science Foundations of China (22150410340) and the Chongqing Science & Technology Commission (catc2018jcyjax0582).

References.

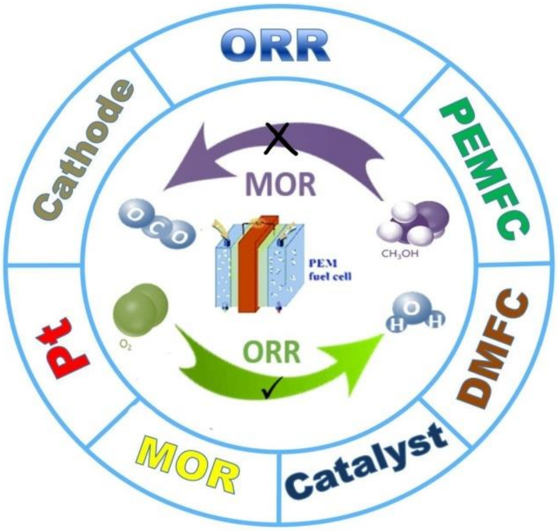
[1] Y.J. Wang, J. Qiao, R. Baker, J. Zhang, Chem. Soc. Rev. 42 (2013) 5768-5787.
[2] M.M. Mohideen, A.V. Radhamani, S. Ramakrishna, Y. Wei, Y. Liu, J. Energy Chem. 69 (2022) 466-489.
[3] J. Zhou, H. Xiao, W. Weng, D. Gu, W. Xiao, J. Energy Chem. 50 (2020) 280-285.
[4] M.A. Zeb Gul Sial, M.A. Ud Din, X. Wang, Chem. Soc. Rev. 47 (2018) 6175-6200.
[5] Q.H. Meng, C. Hao, B. Yan, B. Yang, J. Liu, P.K. Shen, Z.Q. Tian, J. Energy Chem.71 (2022) 497-506.
[6] Z. Shangguan, B. Li, P. Ming, C. Zhang, J. Mater. Chem. A, 9 (2021) 15111-15139.
[7] J. Chang, G. Wang, W. Zhang, Y. Yang, J. Energy Chem. 68 (2022) 439-453.
[8] J.-X. Chen, X.Q. Zhang, B.Q. Li, X.M. Wang, P. Shi, W. Zhu, A. Chen, Z. Jin, R. Xiang, J.-Q. Huang, Q. Zhang, J. Energy Chem. 47 (2020) 128-131.
[9] H. Beydaghi, L. Najafi, S. Bellani, A. Bagheri, B. Martín-García, P. Salarizadeh, K. Hooshyari, S. Naderizadeh, M. Serri, L. Pasquale, B. Wu, R. Oropesa-Nuñez, Z. Sofer, V. Pellegrini, F. Bonaccorso, J. Mater. Chem. A, 9 (2021) 6368-6381.
[10] Q. Liu, L. Xu, S. Liu, Z. Xiang, J. Energy Chem. 64 (2022) 129-135.
[11] J. Mao, P. Liu, J. Li, J. Yan, S. Ye, W. Song, J. Energy Chem. 73 (2022) 240-247.
[12] E. Luo, Y. Chu, J. Liu, Z. Shi, S. Zhu, L. Gong, J. Ge, C.H. Choi, C. Liu, W. Xing, Energy Environ. Sci. 14 (2021) 2158-2185.
[13] Y. Wang, M. Wu, K. Wang, J. Chen, T. Yu, S. Song, Adv. Sci. 7 (2020) 2000407.
[14] Z. Ji, J. Chen, Z. Guo, Z. Zhao, R. Cai, M.T.P. Rigby, S.J. Haigh, M. Perez-Page, Y. Shen, S.M. Holmes, J. Energy Chem. 75 (2022) 399-407.
[15] Z. Ji, J. Chen, M. Pérez-Page, Z. Guo, Z. Zhao, R. Cai, M.T.P. Rigby, S.J. Haigh, S.M. Holmes, J. Energy Chem. 68 (2022) 143-153.
[16] Y. Xu, R. Wang, J. Wang, Y. Zhang, T. Jiao, J. Energy Chem. 71 (2022) 36-44.
[17] H. Burhan, K. Cellat, G. Yılmaz, F. Şen, Chapter 3 - Direct methanol fuel cells (DMFCs), in: R.G. Akay, A.B. Yurtcan (Eds.) Direct Liquid Fuel Cells, Academic Press2021, pp. 71-94.

[18] A. Casalegno, R. Marchesi, J.Power Sources, 185 (2008) 318-330.
[19] M.U. Karaoglan, A.C. Ince, A. Glüsen, C.O. Colpan, M. Müller, D. Stolten, N.S. Kuralay, Int. J. Hydrog. Energy, 46 (2021) 4844-4856.
[20] C.Y. Du, T.S. Zhao, W.W. Yang, Electroch. Acta, 52 (2007) 5266-5271.
[21] A.S. Mathew, B. Naigil, E. George, E. Benny, R. Baby, Mater. Today: Proc., 58 (2022) 400-406.
[22] A. Yuda, A. Ashok, A. Kumar, Catal. Rev., 64 (2022) 126-228.
[23] S.S. Munjewar, S.B. Thombre, R.K. Mallick, Renew. Sus. Energy Rev., 67 (2017) 1087-1104.
[24] M. Lei, J. Wang, J.R. Li, Y.G. Wang, H.L. Tang, W.J. Wang, Sci.Reports, 4 (2014) 6013.
[25] M. Geethalakshmi, M. Ganeshbabu, S. Surendran, A. Stephen, Ionics, 28 (2022) 1347-1357.
[26] K. Huang, K. Bi, C. Liang, S. Lin, R. Zhang, W.J. Wang, H.L. Tang, M. Lei, Sci. Reports, 5 (2015) 11351.
[27] H. Ren, X. Meng, Y. Lin, Z. Shao, J. Energy Chem. 73 (2022) 588-598.
[28] M. Shao, Q. Chang, J.-P. Dodelet, R. Chenitz, Chem. Rev., 116 (2016) 3594-3657.
[29] Y. Feng, K. Song, W. Zhang, X. Zhou, S.J. Yoo, J.-G. Kim, S. Qiao, Y. Qi, X. Zou, Z. Chen, T. Qin, N. Yue, Z. Wang, D. Li, W. Zheng, J. Energy Chem. 70 (2022) 211-218.
[30] Y. Liu, S. He, B. Huang, Z. Kong, L. Guan, J. Energy Chem. 70 (2022) 511-520.
[31] W. Jiao, C. Chen, W. You, X. Zhao, J. Zhang, Y. Feng, P. Wang, R. Che, Adv. Energy Mater., 10 (2020) 1904072.
[32] M.A. Ud Din, F. Saleem, M. Zulfiqar, X. Wang, Nanoscale, 10 (2018) 17140-17147.
[33] Y. Yao, S. Wang, Z. Li, Y. Wu, J. Energy Chem. 63 (2021) 604-624.
[34] X. Huang, G. Yang, S. Li, H. Wang, Y. Cao, F. Peng, H. Yu, J. Energy Chem.68 (2022) 721-751.
[35] P.J. Kulesza, I.S. Pieta, I.A. Rutkowska, A. Wadas, D. Marks, K. Klak, L. Stobinski, J.A. Cox, Electroch. Acta, 110 (2013) 474-483.
[36] Q.T. Phan, K.C. Poon, H. Sato, Int. J. Hydrog. Energy, 46 (2021) 14190-14211.
[37] J. Wu, X.Z. Yuan, J.J. Martin, H. Wang, J. Zhang, J. Shen, S. Wu, W. Merida, J. Power Sources, 184 (2008) 104-119.
[38] Y. Feng, Q. Shao, F. Lv, L. Bu, J. Guo, S. Guo, X. Huang, Adv. Sci., 7 (2020) 1800178.
[39] D. Zhang, F. Wu, M. Peng, X. Wang, D. Xia, G. Guo, J. Am. Chem. Soc., 137 (2015) 6263-6269.
[40] A. Mahmood, N. Xie, M.A. Ud Din, F. Saleem, H. Lin, X. Wang, Chem. Sci., 8 (2017) 4292-4298.
[41] M.A. Ud Din, F. Saleem, B. Ni, Y. Yong, X. Wang, Adv.Mater., 29 (2017) 1604994.
[42] F. Zhao, L. Zheng, Q. Yuan, X. Yang, Q. Zhang, H. Xu, Y. Guo, S. Yang, Z. Zhou, L. Gu, X. Wang, Adv. Mater., 33 (2021) 2103383.
[43] L.M. Rivera-Gavidia, M. Luis-Sunga, J.L. Rodríguez, E. Pastor, G. García, Int. J. Hydrog. Energy, 45 (2020) 20673-20678.
[44] D. Wu, D. Cheng, Electroch. Acta, 180 (2015) 316-322.
[45] J. Liu, J. Lan, L. Yang, F. Wang, J. Yin, ACS Sustainable Chem. Eng., 7 (2019) 6541-6549.
[46] J. Liu, J. Yin, B. Feng, F. Li, F. Wang, Appl. Surf. Sci., 473 (2019) 318-325.
[47] S. Kim, J.E. Park, W. Hwang, Y.-H. Cho, Y.-E. Sung, Appl. Catal. B Environ., 209 (2017) 91-97.
[48] J. Guan, S. Yang, T. Liu, Y. Yu, J. Niu, Z. Zhang, F. Wang, Ang. Chem. Int. Ed., 60 (2021) 21899-21904.
[49] K. Wang, Y. Qin, F. Lv, M. Li, Q. Liu, F. Lin, J. Feng, C. Yang, P. Gao, S. Guo, Small Methods, 2 (2018) 1700331.
[50] Y. Sun, B. Huang, N. Xu, Y. Li, M. Luo, C. Li, Y. Qin, L. Wang, S. Guo, Sci. Bulletin, 64 (2019) 54-62.
[51] M. Vargas-Ordaz, I. Velázquez-Hernández, J.A. Bañuelos, J. Ledesma-García, L. Álvarez-Contreras, N. Arjona, M. Guerra-Balcázar, Mater. Today Energy, 14 (2019) 100335.

[52] M.C. França, R.M. Ferreira, F. dos Santos Pereira, F.A. e Silva, A.C.A. Silva, L.C.S. Cunha, J.d.J.G. Varela Júnior, P. de Lima Neto, A.A. Takana, T.S. Rodrigues, M.A.S. Garcia, J. Mater. Sci., 57 (2022) 8225-8240.
[53] C. Lo Vecchio, D. Sebastián, C. Alegre, A.S. Aricò, V. Baglio, J. Electroanalytical Chem., 808 (2018) 464-473.
[54] Q. Xue, J. Bai, C. Han, P. Chen, J.-X. Jiang, Y. Chen, ACS Catal., 8 (2018) 11287-11295.
[55] Y. Zhang, B. Huang, G. Luo, T. Sun, Y. Feng, Y. Wang, Y. Ma, Q. Shao, Y. Li, Z. Zhou, X. Huang, Sci. Adv., 6 (2020) eaba9731.
[56] S. Huang, J. Wang, H. Hu, Y. Li, F. Xu, F. Duan, H. Zhu, S. Lu, M. Du, J. Colloid Interface Sci., 630 (2023) 375-384.
[57] X. Li, K.X. Yao, F. Zhao, X. Yang, J. Li, Y. Li, Q. Yuan, Nano Research, 15 (2022) 6036-6044.
[58] D. Lee, S. Gok, Y. Kim, Y.-E. Sung, E. Lee, J.-H. Jang, J.Y. Hwang, O.J. Kwon, T. Lim, ACS Appl. Mater. Interfaces, 12 (2020) 44588-44596.
[59] X. Tong, J. Zhang, G. Zhang, Q. Wei, R. Chenitz, J.P. Claverie, S. Sun, Chem. Mater., 29 (2017) 9579-9587.
[60] M. Faraji, S. Moradi Dehaghi, Inorg. Chem. Commun., 123 (2021) 108328.
[61] S. Pan, Z. Cai, Y. Duan, L. Yang, B. Tang, B. Jing, Y. Dai, X. Xu, J. Zou, Appl. Catal. B Environ., 219 (2017) 18-29.
[62] H. Gao, S. Liao, Y. Zhang, L. Wang, L. Zhang, Int. J. Hydrog. Energy, 42 (2017) 20658-20668.
[63] Z.-N. Zhang, B.-Q. Miao, Z.-Q. Wu, P. Chen, X. Xiao, S.-N. Li, Y. Chen, J. Mater. Chem. A, 9 (2021) 25621-25628.
[64] D. Liu, L. Tao, D. Yan, Y. Zou, S. Wang, ChemElectroChem, 5 (2018) 1775-1785.
[65] D. Liu, Y. Tong, X. Yan, J. Liang, S.X. Dou, Batteries & Supercaps, 2 (2019) 743-765.
[66] M. Zhou, H.-L. Wang, S. Guo, Chem. Soc. Rev., 45 (2016) 1273-1307.
[67] A. Farzaneh, E.K. Goharshadi, H. Gharibi, N. Saghatoleslami, H. Ahmadzadeh, Electroch. Acta, 306 (2019) 220-228.
[68] G. Mohmad, S. Sarkar, A. Biswas, K. Roy, R.S. Dey, Chem. Euro. J., 26 (2020) 12664-12673.
[69] C. Shi, X. Maimaitiyiming, Int. J. Hydrog. Energy, 46 (2021) 10247-10258.
[70] S.U. Dar, M.A. Ud Din, M.U. Hameed, S. Ali, R. Akram, Z. Wu, D. Wu, J. Power Sources, 373 (2018) 61-69.
[71] S.M. Sauid, S.K. Kamarudin, N.A. Karim, L.K. Shyuan, J. Mater. Research Tech., 11 (2021) 1834-1846.
[72] Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu, H.J. Fan, Adv. Sci., 3 (2016) 1500286.
[73] J. Xie, Y. Xie, Chem. Euro. J., 22 (2016) 3588-3598.
[74] Z. Chen, D. Higgins, A. Yu, L. Zhang, J. Zhang, Energy Environ. Sci., 4 (2011) 3167-3192.
[75] D. Zhao, Z. Zhuang, X. Cao, C. Zhang, Q. Peng, C. Chen, Y. Li, Chem. Soc. Rev., 49 (2020) 2215-2264.
[76] Q. Li, H. Liu, L.-C. Zhang, H. Chen, H. Zhu, Y. Wu, M. Xu, S.-J. Bao, J. Power Sources, 449 (2020) 227497.
[77] J.C. Park, C.H. Choi, J.Power Sources, 358 (2017) 76-84.
[78] H. Liu, Z. Deng, M. Wang, H. Chen, L. Zhang, Y. Zhang, R. Zhan, M. Xu, S.-J. Bao, ACS Appl. Mater. Interfaces, 11 (2019) 21481-21488.
[79] A. Serov, C. Kwak, Appl. Catal. B Environ., 90 (2009) 313-320.
[80] D. Banham, S. Ye, K. Pei, J.i. Ozaki, T. Kishimoto, Y. Imashiro, J. Power Sources, 285 (2015) 334-348.
[81] M.K. Jeon, C.H. Lee, G.I. Park, K.H. Kang, J. Power Sources, 216 (2012) 400-408.

[82] D. Sebastián, A. Serov, K. Artyushkova, P. Atanassov, A.S. Aricò, V. Baglio, J. Power Sources, 319 (2016) 235-246.
[83] R. Akram, M.A. Ud Din, S.U. Dar, A. Arshad, W. Liu, Z. Wu, D. Wu, Nanoscale, 10 (2018) 5658-5666.
[84] Q. Shi, Y. He, X. Bai, M. Wang, D.A. Cullen, M. Lucero, X. Zhao, K.L. More, H. Zhou, Z. Feng, Y. Liu, G. Wu, Energy Environ.Sci., 13 (2020) 3544-3555.
[85] I. Martinaiou, A.H.A. Monteverde Videla, N. Weidler, M. Kübler, W.D.Z. Wallace, S. Paul, S. Wagner, A. Shahraei, R.W. Stark, S. Specchia, U.I. Kramm, Appl. Catal. B Environ., 262 (2020) 118217.
[86] A.H.A. Monteverde Videla, D. Sebastián, N.S. Vasile, L. Osmieri, A.S. Aricò, V. Baglio, S. Specchia, Int. J. Hydrog. Energy, 41 (2016) 22605-22618.
[87] H.-S. Hu, R.-J. Liu, S. Si, D.-S. Kong, Y.-Y. Feng, Int. J. Energy Research, 43 (2019) 7107-7119.
[88] P. Li, Y. Qiu, S. Liu, H. Li, S. Zhao, J. Diao, X. Guo, Euro.J. Inorg. Chem., 2019 (2019) 3235-3241.
[89] P. Trens, R. Durand, B. Coq, C. Coutanceau, S. Rousseau, C. Lamy, Appl. Catal. B Environ., 92 (2009) 280-284.
[90] X. Li, T. Chao, Y.-e. Duan, Y. Qu, Y. Liu, Q. Tan, ACS Sustainable Chem. Eng., 9 (2021) 15138-15146.
[91] Y. Zuo, M. Huang, W. Sheng, Q. Xu, W. Tao, Z. Li, Int. J. Hydrog. Energy, 47 (2022) 917-927.
[92] Y. Fang, T. Zhang, Y. Wang, Y. Chen, Y. Liu, W. Wu, J. Zhu, Appl. Energy, 259 (2020) 114154.
[93] T.J. Bandosz, Carbon, 188 (2022) 289-304.
[94] W. Tian, H. Zhang, X. Duan, H. Sun, G. Shao, S. Wang, Adv. Funct. Mater., 30 (2020) 1909265.
[95] C. Du, P. Li, Z. Zhuang, Z. Fang, S. He, L. Feng, W. Chen, Coordination Chem. Rev. 466 (2022) 214604.
[96] J. Wang, G. Han, L. Wang, L. Du, G. Chen, Y. Gao, Y. Ma, C. Du, X. Cheng, P. Zuo, G. Yin, Small, 14 (2018) 1704282.
[97] G.-L. Wen, H.-J. Niu, A.-J. Wang, Z.-Z. Yin, Q.-L. Zhang, J.-J. Feng, J. Colloid Interface Sci., 556 (2019) 352-359.
[98] X. Xu, Z. Xia, X. Zhang, R. Sun, X. Sun, H. Li, C. Wu, J. Wang, S. Wang, G. Sun, Appl. Catal. B Environ., 259 (2019) 118042.
[99] N. Zhang, T. Zhou, M. Chen, H. Feng, R. Yuan, C.a. Zhong, W. Yan, Y. Tian, X. Wu, W. Chu, C. Wu, Y. Xie, Energy Environ.Sci., 13 (2020) 111-118.
[100] G. Chen, Y. An, S. Liu, F. Sun, H. Qi, H. Wu, Y. He, P. Liu, R. Shi, J. Zhang, A. Kuc, U. Kaiser, T. Zhang, T. Heine, G. Wu, X. Feng, Energy Environmen.Sci., 15(2022) 2619-2628.
[101] H. Yang, X. Wang, S. Wang, P. Zhang, C. Xiao, H. Maleki Kheimeh Sari, J. Liu, J. Jia, B. Cao, J. Qin, W. Xiao, Z. Zhou, X. Li, Carbon, 182 (2021) 109-116.
[102] H. Wang, Q.L. Zhu, R. Zou, Q. Xu, Chem, 2 (2017) 52-80.
[103] Y. Ren, G.H. Chia, Z. Gao, Nano Today, 8 (2013) 577-597.
[104] Y. Jia, Z. Xue, Y. Li, G. Li, Energy Environ. Mater., 5(2022) 1084-1102.
[105] M.E. Abdelrahman, H. Zhang, G. Wu, X. Li, S. Litster, Electroch. Acta, 416 (2022) 140262.

Graphical Abstract



This review summarizes recent advances and challenges in the methanol tolerant catalysts for the ORR, with a focus on modification of cathode catalyst to improve methanol tolerance in DMFC.