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Editorial

Electrocatalysis in Fuel Cells

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1. Introduction

Low temperature fuel cells are expected to come into widespread commercial use in the areas of transportation and stationary and portable power generation, and thus will help solve energy shortage and environmental issues. Despite their great promise, commercialization has been hindered by lower-than-predicted efficiencies and the high cost of the electrocatalysts in the electrodes. The sluggish kinetics of the oxygen reduction reaction (ORR) are one of the main reasons for the high overpotential in a hydrogen proton exchange membrane fuel cell (PEMFC). The introduction of Mirai, the first mass-produced fuel cell vehicles (FCVs), by Toyota in Japan in 2014, and in North America in the following year, has accelerated the development of FCVs by other automotive companies. For instance, Honda and Hyundai announced the mass production of their own FCVs in 2016 and 2017, respectively. The current sale price of a new Mirai is about $57,000 US. One of the main reasons for the high sale price is the high Pt loading in the fuel cell stacks, especially at the cathode electrode, where the ORR occurs. The Pt loading at the anode, where the hydrogen oxidation reaction (HOR) occurs, can be reduced to as low as 0.05 mg cm^{-2} due to the extremely high reaction rate on Pt surfaces, while a much higher Pt loading ($\geq$0.2 mg cm^{-2}) at the cathode is required using Pt or Pt alloys as the ORR electrocatalysts in order to achieve a desirable cell performance. Pt is a costly and scarce metal. Thus, reducing its loading or even completely replacing it with abundant and cheap materials would be advantageous to lower the cost of FCVs. Recent research efforts have been focused on developing advanced Pt alloys, core-shell structures, shape-controlled nanocrystals and non-precious-metal (NPM) catalysts [1–4].

In addition to ORR activity, one must also consider the durability of the electrode during fuel cell operation in the harsh environment [5]. The life of a fuel cell stack in a FCV has to last at least 10 years in order to compete with the conventional combustion engine. It has been confirmed that the fuel cell performance gradually declined during operation [5]. The main reasons for the degradation of the catalyst layer are the dissolution of the Pt and the corrosion of the carbon support. As a consequence,

both catalysts and supports that are more stable than Pt nanoparticles and carbon black may be needed to meet the durability requirements. Promising supports include alternative carbon supports, carbides and oxides [6].

In other types of low temperature fuel cells, for instance direct alcohol fuel cells (DAFCs), the slow fuel oxidation reactions and fast performance decay caused by poisonous CO species adsorbed on catalyst surfaces are the other major contributions to their low performances [1]. Thus, the development of more active catalysts with higher tolerance to CO poisoning is required for high-performance and long-life DAFCs. The most promising DAFCs include DMFC, DEFC and DFAFC which use methanol, ethanol and formic acid as fuel, respectively.

2. This Special Issue

This Special Issue aims to cover recent progress and trends in designing, synthesizing, characterizing and evaluating advanced electrocatalysts and supports for both ORR and small organic molecule oxidation reactions, as well as theoretical understanding in fuel cell reactions. I am honored to be the Guest Editor for this Issue, which includes 34 high quality papers. The nine reviews together with 25 original research papers cover a very broad spectrum of electrocatalysis in fuel cells. The diversities of these contributions are illustrated in Figure 1.

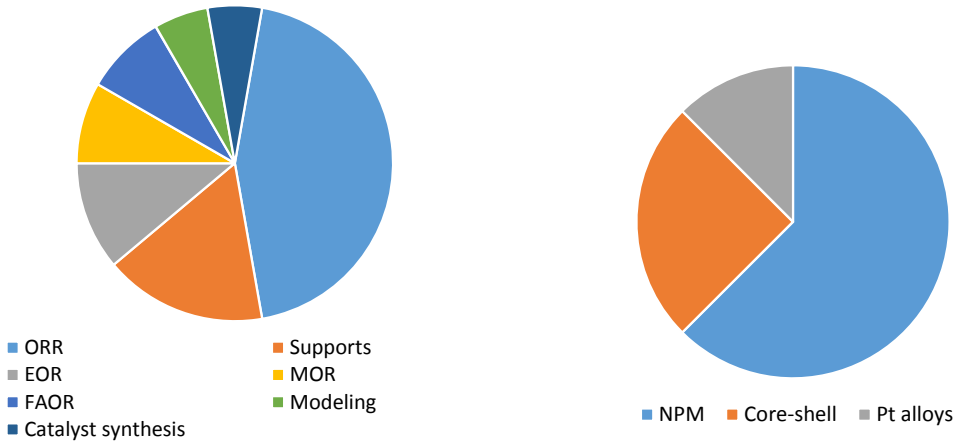

Figure 1. The distribution of the 34 contributions in this Special Issue (**a**) and the 16 contributions in oxygen reduction reaction; (**b**) in different research areas. ORR: oxygen reduction reaction; EOR: ethanol oxidation reaction; MOR: methanol oxidation reaction; FAOR: formic acid oxidation; NPM: non-precious metal.

From Figure 1a, it is obvious that the ORR is still the most important topic in fuel cell electrocatalysis. There are 16 papers that cover some important development of ORR electrocatalysts including NPM, core-shell and Pt alloy catalysts. As shown in Figure 1b, a significant effort is focused on completely replacing Pt in the ORR catalysts by developing novel NPM materials. Wei *et al.* summarized the recent progress in design and synthesis of metal-free nitrogen-doped carbon materials, including nitrogen-doped carbon nanotubes (NCNTs) and nitrogen-doped graphene (NG) for ORR in both acidic and alkaline media [7]. The Fe and N-doped carbon composites (Fe-N-C) are the most promising candidates, having comparable activity to Pt/C [4]. Liu *et al.* reviewed the progress made in the past five years in

the areas of Fe-N-C electrocatalysts for ORR and understanding the possible active sites in this type of catalyst [8]. The Fe-N-Cs prepared from Fe-doped zeolitic imidazolate frameworks (ZIFs) are among the most active ones in catalyzing the ORR [9]. Barkholtz *et al.* optimized the synthesis and post-treatment protocols of ZIF-based Fe-N-C nanocomposites, as well as the membrane electrode assembly (MEA) fabrication process, and achieved an impressive fuel cell performance of 221.9 mA cm^{-2} at 0.8 V [10]. Armel *et al.* [11] emphasized the importance of the morphology control of Fe-N-C on ORR activity by adjusting the crystal size of ZIF-8, milling speed and heating mode. With the smallest ZIF-8 crystal size (100 nm), the best H_2/O_2 fuel cell performance of 900 mA cm^{-2} at 0.5 V was obtained, which was double the value obtained with previous synthesis protocol [11]. Zhang and Chen developed a novel method to prepare Fe-N-C catalysts by using a cationic surfactant cetyltrimethylammonium bromide (CTAB) as the template and the negatively charged persulfate ions as the oxidative agent to stimulate the aniline polymerization, resulting in a unique one-dimensional (1D) semi-tubular structure of PANI [12]. On the other hand, SBA-15 was used as the template by Wan *et al.* in the synthesis of nitrogen-doped ordered mesoporous carbon [13]. Qiao *et al.* found that P, N dual-doped reduced graphene oxide synthesized by pyrolyzing a mixture of graphite oxide and diammonium hydrogen phosphate was very active for ORR [14]. Non-noble metal oxides and chalcogenides are also promising catalysts for ORR. Some interesting works on the synthesis and evaluation of Ti-Nb oxides [15], CoS [16] and $FeSe_2$ [17] were also included in this Special Issue.

Core-shell structures consisting of a cheaper core and an atomic thin Pt shell have attracted great attention due to their extremely high Pt utilization and activity enhancement from the core materials [18]. Hu *et al.* designed a core-shell catalyst with a nitride (PdNiN) alloy core and a Pt monolayer. Its stability was dramatically enhanced compared with that of the previously reported structure with a pure Pd core [19]. Inoue *et al.* developed a new method without using any surfactant to synthesize clean Pd nanoparticles as the core for Pt monolayer deposition [20]. On the other hand, Caballero-Manrique *et al.* used Cu nanoparticles as the sacrificing template to prepare core-shell catalysts consisting of Pt and Pt-Ru shells [21]. Amra *et al.* tried to explain the strain and ligand effects from the $Pd_{1-x}Cu_x$ alloy core on the Pt monolayer based on the first principles density functional theory (DFT) calculations [22].

Since the discovery of Pt alloys as superior ORR catalysts for fuel cells in the 1980s, they have been considered as the second generation fuel cell catalysts after pure Pt. Pt alloys not only significantly reduce the Pt loading, but also enhance the catalytic activity and stability in comparison with Pt. Shen *et al.* gave a nice review on some of the recent approaches in developing Pt alloy electrocatalysts for the ORR [23]. The particle size effect of Pt alloys on the fuel cell performance and decay rate is very important and has not been systematically studied. Gummalla *et al.* compared the initial performances and decay trends of Pt_3Co/C cathodes in PEMFCs with three different particle sizes (4.9 nm, 8.1 nm, and 14.8 nm), but with the identical Pt loading [24]. The initial mass activity of the 4.9 nm Pt_3Co-based electrode was the highest, as well as the performance decay rate. The impact of PEMFC operating conditions, including upper potential, relative humidity, and temperature, on the alloy catalyst decay trends were also carefully studied for the first time.

Some non-carbon-based materials have been explored as alternative supports for ORR catalysts [6]. Lori and Elbaz summarized the latest studies on ceramic supports including carbides [25], oxides, nitrides, borides, and some composite materials [26]. Alternative carbon supports including carbon nanotubes, ordered mesoporous carbon, and colloid imprinted carbon were reviewed by Banham *et al.* [27]. The importance of carbon wall thickness was highlighted. Functionalized graphitic supports with pyrene carboxylic acid also showed superior durability [28].

The performance of fuel cell catalysts is certainly dependent on the preparation methods. Holade *et al.* [29] and Job *et al.* [30] summarized the recent advances in the preparation of carbon-supported nanocatalysts based on colloidal methods. The correlation between the structure of the catalysts and their activities and the effects from the synthesis methods were discussed. In addition, the fuel cell performance is also strongly influenced by the composition and fabrication protocols of MEA. A semi-empirical model was developed by Myles *et al.* to understand the performance of the cell as a function of the ratio of Nafion ionomer to carbon support (I/C ratio) in high temperature PEMFCs [31].

There are three papers in this issue focusing on Pt-based nanocomposites for the methanol oxidation reaction (MOR). Pt/C-Mn_xO_{1+x} [32] and $H_3PMo_{12}O_{40}$-Pt/reduced graphene oxide [33] were found to have better performance than Pt/C and PtRu/C due to the synergetic effects between Pt nanoparticles and hybrid supports. Wu *et al.* synthesized a conductive copolymer based on indole-6-carboxylic acid and 3,4-ethylenedioxythiophene (EDOT) as the support for Pt particles [34]. This nanocomposite also showed good activity for MOR. Chen *et al.* prepared a multi-component nanoporous PtRuCuW electrocatalyst by chemical and mechanical dealloying [35]. The unique ligament/channel nanoporous structure showed an enhanced activity for MOR compared to PtRu/C.

The advances in the study of reaction mechanisms and electrocatalytic materials (mainly Pt- and Pd-based catalysts) for the ethanol oxidation reaction (EOR) were reviewed by Wang *et al.* [36]. PdW alloys [37] and hollow PdCu nanocubes [38], as well as PtMn alloys [39], showed some improvement over pure Pd or Pt toward EOR.

Meng *et al.* presented a comprehensive review on the Pd-based electrocataysts' formic acid oxidation reaction (FAOR), MOR, EOR and ORR [40]. The high activity of Pd-based materials toward FAOR was also supported by a couple of original research papers included in this issue [41,42].

Finally, I would like to thank Keith Hohn, Editor-in-Chief, Mary Fan, Managing Editor, and the staff of the Catalysts Editorial Office for their great support during the preparation for this Special Issue. I also thank all the authors for their great contributions and referees for their time reviewing the manuscripts. I believe these excellent papers collected in this Special Issue will make significant contributions to the electrocatalysis community.

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