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Progress in nanostructured (Fe or Co)/N/C non-noble metal electrocatalysts for fuel cell oxygen reduction reaction

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ABSTRACT

The high cost and limited supply of platinum for Pt-based catalysts in proton exchange membrane fuel cells (PEMFCs) have driven intensive research into the use of non-noble metal catalysts in recent years. As the most promising non-noble metal catalysts for PEMFC oxygen reduction reactions (ORR), metal/N/C class of catalysts has been extensively explored. Earlier efforts (1964–2004) were mainly focused on the exploration of various synthesis routes and the investigation of active site mechanisms. During recent years (2005–2010), great progress in the development of these types of non-noble metal catalysts in real PEMFC environments has been achieved both in terms of catalytic activity and stability. From 2011 to present, several new synthetic approaches have been explored to produce highly dense catalytically active sites decorated within micropores using rationally designed zeolite imidazolate frameworks (ZIFs) and porous organic polymers (POPs). Currently, the most active non-noble metal catalysts are derived using this method and are able to deliver a kinetic volumetric current density of 450 A/cm^3 at 0.8 V under fuel cell operating conditions. These results are superior to the US DOE 2020 target of 300 A/cm^3. In terms of fuel cell maximum power density, the best non-noble metal catalysts for cathodes can achieve results as high as 0.98 W/cm^2 and 0.41 W/cm^2 with feeds of pure O_2 and air respectively. In terms of stability, some non-noble metal catalysts have remained stable for over 1000 h with only minor degradation under PEMFC conditions. Nonetheless, activity and stability still remain major challenges for non-noble metal catalysts when compared to Pt-based ones in PEMFCs. Improvements in the structure of both catalysts and catalyst layers are urgently needed to realize the activity targets established for automobile fuel cell applications as well as the US DOE Hydrogen and Fuel Cell (H&FC) program. In the long term and the sustainable commercialization of fuel cells, replacing Pt-based catalysts with non-noble metal catalysts is, in the present authors' opinion, the most sustainable solution. Therefore, further intensive research into fundamental studies is critical to uncovering the workings of active site mechanisms. Once controllable design and synthesize of non-noble metal catalysts with high active site densities and utilization can be achieved, the goal of cost-effective, non-noble metal catalysts in automobile fuel cells can become reality.

1. Introduction

As one of the most promising and sustainable clean energy technologies, proton exchange membrane fuel cell (PEMFC) technology has made great progresses in the past several decades in terms of technological maturity and commercialization. This technology is already providing sufficient performance and durability to be competitive with alternative technologies in applications such as distributed power, auxiliary power units, material handling equipment, and specialty vehicles [1]. Among these early market applications, fuel cell automobiles appear to be the most important in terms of economy, energy sustainability, and environmental benefits. Major challenges still hinder PEMFC commercialization however, including high costs, insufficient durability, and hydrogen fuel related technologies. Of these challenges, cost reduction should be the priority in fuel cell research and development due to the fact that high costs are the predominate hindrance to

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commercialization. In a current state-of-the-art fuel cell system, Pt-based catalysts represent almost half of the entire PEMFC stack cost at high production rates and can represent as much as 20% of the overall system cost [2]. In2016, the US DOE Hydrogen and Fuel Cells Program (H&FC program) launched the Electrocatalysis Consortium (ElectroCat) to accelerate the development of catalysts made without platinum group metals for use in automotive fuel cell applications [3]. Therefore, developing high-performing, cost-effective electrocatalysts is key to successful fuel cell commercialization.

There are two methods to reduce the cost of electrocatalysts: one is to reduce the Pt loading in a unit membrane electrolyte assemble (MEA) without compromising performance; the other is to replace Pt with non-noble metals. In previous decades, most research and development efforts have been focused on the first approach rather than the second because non-noble metal catalysts possess inherent difficulties when competing with Pt catalysts in terms of both activity and stability. However, with commercialization becoming more realizable in other respects, the fuel cell community has realized that low-cost, high-performance non-noble metal catalysts, rather than noble metal catalysts, is the long-term solution for the ultimate cost-reduction goal of PEMFC technology. During the past 30 years, Pt loading in PEMFC MEAs has been reduced from 2.0 mg/cm^2 to 0.134 mg/cm^2 without compromising fuel cell performance [2]. Further reduction of Pt loading however leads to high risks of losing catalyst durability. In addition, technical advances in Pt loading reduction cannot match the pace of rising Pt prices due to the scarcity of Pt and the continuously increasing demand from other industries. Thus, developing non-noble metal catalysts to replace Pt-based catalysts is necessary to achieve sustainable commercialization of PEMFCs.

In the last several decades, non-noble metal catalysts for ORR in acidic mediums (PEMFC environment) have been extensively investigated and several review papers have been published in recent years to evaluate the progress in this research area [4–14]. Major candidates evaluated include transition metal oxides, carbides, nitrides, xynitrides, chalcogenides, metal/N/C catalysts. Although non-noble metal carbides, nitrides, oxides, and oxynitrides have high chemical and thermal stability, their ORR activities toward PEMFC cathode reactions are limited to low temperatures. Thus, only metal chalcogenides and metal/N/C class of catalysts is considered to be potential low-cost substitutes for Pt-based catalysts in PEMFCs. For example, Ru-based chalcogenides have attracted much attention because of their high catalytic activity toward ORR (30–40% inferior to Pt catalysts) and their high tolerance toward methanol oxidation reaction (MOR). Although Ru is much cheaper than Pt, it is more rare than Pt due to its low production volume and thus, these Ru-based catalysts cannot be considered as promising substitutes for Pt-based catalysts. Non-noble metal chalcogenides have also been explored in recent years as ORR catalysts for PEMFCs, but their low activity and stability make them unviable Pt alternatives based on current technology. Subsequently, metal/N/C class of catalysts has become the predominant focus of non-noble metal catalyst research and development, a trend indicated by published journal papers and patents on non-noble metal catalysts over the past decades. Although publications on metal/N/C class of catalysts are not comparable to those of Pt-based catalysts, research on transition metal/N/C class of catalysts has attracted much activity and is rapidly increasing since 2005, outnumbering studies on chalcogenides. This increased research into non-noble metal/N/C class of catalysts have made great strides in recent years with Fe-based and Co-based catalysts being demonstrated as the most promising non-noble metal catalysts to date for PEMFCs. Fig. 1 shows a schematic of PEMFC with metal-Nx moieties as active sites in non-noble Fe-based catalysts.

In this paper, transition metal (Fe or Co) metal/N/C class of catalysts as non-noble metal catalysts for ORR in PEMFCs is specifically focused on. This review will present a clear picture of the past (1964–2004), the period between 2005 and 2010, the present (2011–2016), and the future of this class of non-noble metal catalysts. First, a brief history of the evolution of macrocycle based non-noble metal catalysts for ORR will be present. Next, the current research and development status of these catalysts since 2005 will be reviewed, highlighting representative milestones achieved in this area. Finally, existing challenges facing these catalysts will be analyzed and future research directions will be explored.

2. History

Jasinsky first reported the discovery of transition metal macrocycles with catalytic activity toward ORR in 1964 [15] having found that cobalt phthalocyanine demonstrated oxygen reduction activity in alkaline electrolyte at room temperature. In the nearly five decades since then, researchers have extensively explored this class of materials as ORR catalysts in low-temperature fuel cells with Fe based catalysts later emerging [16]. Dodelet reviewed the history of this work in his book chapter (2006) titled “Oxygen reduction in PEM fuel cell conditions: heat-treated non-precious metal-N4 macrocycles and beyond” [4]. In this book chapter, major milestones in the development of metal/N/C class of catalysts-based ORR catalysts are summarized. More details can be found in Dodelet's chapter and other review papers [4–7].

In the early stages of this research (1960s and 1970s), most studies focused on exploring various metal macrocycles for oxygen reduction in both basic and acidic conditions. Aside from metal phthalocyanines, studies have also explored metal porphyrins and other metal-N4 structured molecules (e.g., cobalt tetraazaannulene) as oxygen reduction catalysts. The effects of parameters such as macrocycle types, metal types, ligands, and molecular configurations were extensively examined. For example, central metal ions were found to play a decisive role in metal macrocycle electrocatalysts in which the ORR activity of metal phthalocyanines follows the order: Fe > Co > Ni > Cu ≈ Mn [17]. The ORR mechanism for metal macrocycles was also systematically investigated, and it was generally believed that this catalytic oxygen reduction process was directly related to the redox of the central metal ions [18]. Much of the studies during this period were carried out on unsupported or carbon-supported macrocycle catalysts and it was observed that the ORR activity of these catalysts degraded rapidly, demonstrating that catalyst stability was a problem. One of the major achievements during this period was the discovery of the positive effects of heat treatment on catalyst activity and stability. It was found that after thermal treatment at 500–900 °C in inert gas atmospheres, carbon-powder-supported metal macrocycles showed enhanced catalytic activity toward hydrogen peroxide decomposition and thereby longer operation times in ORR conditions [19]. This discovery, along with its methanol tolerance, drew more attention to this class of catalyst for practical applications in low-temperature fuel cells and especially in direct methanol fuel cells. The study of heat-treated metal macrocycles has continued to dominate research on non-noble metal catalysts for ORR in PEMFCs.

In the following two decades (1980s and 1990s), research had two focuses: (1) to explore the structures of the catalytic active sites in heat-treated metal macrocycles (and thereby address the question of what happens to the metal macrocycles during heat treatment and what is the active site in the final catalysts); and (2) to optimize synthesis conditions and explore new synthesis routes to address the issues of catalyst activity and material/process cost. The

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