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Review (Special Column on Electrocatalysis for Fuel Cells)

Nano-electrocatalyst materials for low temperature fuel cells: A review



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ABSTRACT

Low temperature fuel cells are an attractive technology for transportation and residential applications due to their quick start up and shut down capabilities. This review analyzed the current status of nanocatalysts for proton exchange membrane fuel cells and alkaline membrane fuel cells. The preparation process influences the performance of the nanocatalyst. Several synthesis methods are covered for noble and non-noble metal catalysts on various catalyst supports including carbon nanotubes, carbon nanofibers, nanowires, and graphenes. Ex situ and in situ characterization methods like scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy and fuel cell testing of the nanocatalysts on various supports for both proton exchange and alkaline membrane fuel cells are discussed. The accelerated durability estimate of the nanocatalysts, predicted by measuring changes in the electrochemically active surface area using a voltage cycling method, is considered one of the most reliable and valuable method for establishing durability.

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1. Introduction

Unlike conventional power generating systems which rely on the thermal expansion of gases to drive electro-mechanical generators, fuel cells do not have moving parts except for blowers and controllers. Direct conversion avoids mechanical frictional losses and leads to increased fuel conversion efficiency. In addition, fuel cells are not limited by the thermodynamic constraints imposed by Carnot efficiency [1,2].

The choice of the electrolyte determines the range of operating temperature and physico-chemical properties of the other cell components (catalysts, electrodes, interconnectors and

current collectors) [3]. For example, a proton exchange membrane fuel cell (PEMFC) is typically operated below 100 °C and hence could be a potential system for automotive applications. In contrast, the molten carbonate fuel cell requires temperatures exceeding 800 °C which makes it slow to start up and it should be run continuously rather than intermittently. While low temperature fuel cells are better suited for periodic on and off usage patterns, the slow electrochemical kinetics at low temperature requires the use of catalysts to achieve the type of performance required for typical transportation applications.

Fig. 1 illustrates the schematic of a single PEMFC configuration and its main components including the bipolar plate, gas

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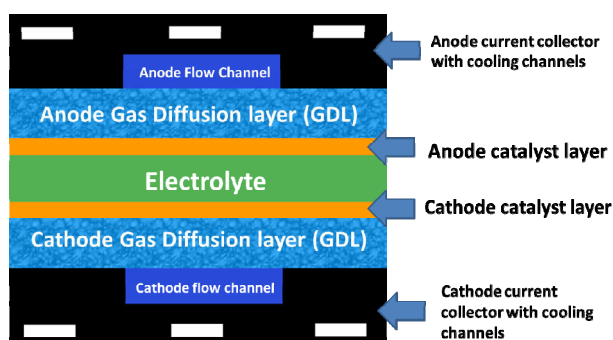


Fig. 1. Schematic diagram of a fuel cell showing the gas flow plates, gas diffusion layers, catalyst layers and electrolyte.

diffusion layer (GDL) electrode, electrocatalyst layer, polymer electrolyte membrane and sealant. The hydrogen oxidation reaction (HOR) occurs at the anode catalyst layer, while the oxygen reduction reaction (ORR) takes place at the cathode catalyst layer. Protons generated at the anode are transported through a humidified electrolyte membrane and they combined with pure oxygen (or oxygen from air) at the cathode to form water and heat. The membrane prevents electrons from passing through, so they move through an external circuit to drive the load. Nafion (DuPont™) is a commercially available electrolyte membrane for PEMFCs and it is based on a chemically stabilized perfluorosulfonic acid/PTFE (Poly-tetra-fluoro-ethylene) copolymer in acid form, which provides a relatively high ionic conductivity (e.g., 0.16 S cm^{-1} for $117 \mu\text{m}$ thickness membrane) [4]. As seen in Fig. 1, the electrolyte is sandwiched with the electrocatalyst and GDL layers and the assembly is generally referred to as a membrane electrode assembly (MEA).

Since the 1960s, much progress has been made in PEMFC development in terms of increasing the stack conversion efficiency and reducing the overall system cost. However, there are several technical barriers which limit the commercial viability of PEMFCs. These include issues associated with hydrogen generation, storage and distribution, system cost and fuel cell reliability and durability [5]. Electrocatalysts such as platinum or other highly active materials play a critical role in the cost and durability of PEMFCs [6]. With the Pt-based anode and cathode catalysts used in PEMFCs, the cost of the electrocatalysts accounts for 35%–42% of the total cost of the PEMFC stacks [7]. Furthermore, the sensitivity of Pt-based catalysts to contamination, carbon corrosion and particle agglomeration has shifted the technical burden to a high purity hydrogen supply and the development of advanced support materials. A recent publication highlights the various approaches in developing Pt-based nanocatalysts with the focus to improve performance as well as durability [8]. The major objective of this review is to examine advanced nanomaterials and the synthesis techniques used to enhance electrocatalyst properties and electrochemical performance to promote cost-effective catalyst use in PEM and alkaline fuel cells. In particular, advanced electrocatalyst support nanomaterials, durable Pt nanocatalyst synthesis, advanced non-platinum electrocatalyst fabrication, core-shell nanocatalyst development and catalyst characterization (including the evaluation of catalyst degradation, analysis

of fuel cell performance and failure mode diagnosis) are discussed in detail.

2. Electrocatalyst support structures

The electrochemical activity of catalysts depends on the size of the catalyst particles and their dispersion on the support network. The ideal support material should have the following properties: high surface area, optimum pore size and distribution, good electrical conductivity, good physico-chemical stability, oxidative stability and cost effectiveness [9,10]. Commercially available carbon black-supported Pt catalyst (Pt/C) is widely used due to its simple synthesis process as well as the high surface area of the carbon particles. However, it is well known that a Pt/C catalyst shows a relatively low Pt utilization due to the poor mass transfer characteristics of carbon black. Carbon black is also sensitive to electrochemical oxidation under many fuel cell service conditions such as H_2 starvation, stack start-up/shut-down and a high cell potential, leading to carbon corrosion and Pt detachment from the support material [11]. Advanced support materials with nanostructures such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), nanowires (NWs) and graphenes are discussed and consolidated in the following sections.

2.1. Carbon nanotube supports

Significant progress has been made in CNT synthesis and property improvement since its first discovery by Iijima in 1991 [12]. CNTs have extraordinary mechanical and electrical properties and have been extensively applied in various research fields (including nanocomposite materials, nanoelectrode materials, field emitters and nanoscale sensors) [13,14]. There are many special issues of journals and books documenting the potential applications of CNTs [15–17]. CNTs can be classified into two main types: single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). The common synthesis techniques of CNTs include arc discharge, laser ablation and chemical vapor deposition (CVD). The first two methods use a high energy input to release carbon atoms from precursors, whereas CVD applies catalytic decomposition from a precursor onto the surface of transition metal particles. This technique enables the scale-up to industrial level for high volume CNT production. Fig. 2(a) shows vertically aligned CNTs produced using a photo-thermal CVD technique by a Ti/Fe bilayer film as the catalyst, which was obtained by the research group of Shang *et al.* [18].

Prior to introducing the catalyst onto the CNT support, many non-covalent and covalent modification methods can be employed to functionalize the CNTs and create active sites around the inert CNT walls for improving catalyst dispersion and molecular interactions. To incorporate carboxyl, carbonyl and hydroxyl groups on the surface of the CNTs, a strong acid treatment (e.g., HNO_3 , $\text{HNO}_3 + \text{H}_2\text{SO}_4$) has been used [19]. A mild and facile method using citric acid prevents the degradation of the CNT nanostructure during the functionalization process [19,20]. In fact, citric acid functionalization of MWCNTs

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