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Nanostructured electrocatalytic materials and porous electrodes for direct methanol fuel cells



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ABSTRACT

Direct methanol fuel cells (DMFCs) are promising for use in portable devices because of advantages such as high fuel energy density, low working temperature and low emission of pollutants. Nanotechnology has been used to improve the performance of DMFCs. Catalytic materials composed of small, metallic particles with unique nanostructure supported on carbons or metal oxides have been widely investigated for use in DMFCs. Despite our increased understanding of this type of fuel cell, many challenges still remain. This paper reviews the current developments of nanostructured electrocatalytic materials and porous electrodes for use in DMFCs. In particular, this review focuses on the synthesis and characterization of nanostructured catalysts and supporting materials. Both computational and experimental approaches to optimize mass transportation in porous electrodes of DMFCs, such as theoretical modeling of internal transfer processes and preparation of functional structures in membrane electrode assemblies, are introduced.

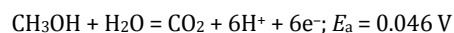
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1. Introduction

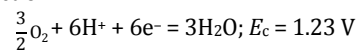
Direct methanol fuel cells (DMFCs) have been attracting extensive attention for many years as alternative energy devices. DMFCs are promising for use in portable electronic devices and field equipment, as well as light electric vehicles, because of their high fuel energy density, simplicity, rapid start-up, easy fuel recharging and low pollution. California-based Oorja Protonics launched its “ultra-powerful” DMFC technology in 2008. This company has also unveiled a variety of commercial products, such as Oorja Model 3 for the materials handling market and Oorja Model T-1 for stationary applications. Danish company IRD also has developed 500-W and 800-W DMFCs for use in lighthouses and telecommunication towers.

The maximum thermodynamic voltage of a DMFC at 25 °C is 1.18 V, as defined by its electrocatalytic redox reactions [1]:

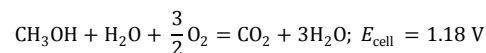
Anode reaction:



Cathode reaction:



Overall reaction:



However, because of the different types of voltage loss caused by the complexity in DMFCs, the actual cell voltage is lower than the theoretical value. In particular, methanol crossover (MCO) from the anode to the cathode causes a mixed potential in the cathode, making the overall cell voltage much lower than that of hydrogen fuel cells. Although considerable improvement has been realized, DMFCs are still far from widespread commercial application. At present, electrocatalytic materials are a major obstacle limiting DMFC technology. Con-

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ventional Pt catalysts suffer from several issues including catalyst deactivation, low catalytic efficiency and high cost. Thus, current research focuses on the development of inexpensive catalysts that display high stability, durability, and performance.

Besides the catalysts, DMFCs also face issues related with the microstructure and electrochemical characteristics of the membrane electrode assembly (MEA), where the chemical energy is converted to electrical energy by electrocatalytic redox reactions. MEAs are typically composed of an anode diffusion layer (DL), an anode catalyst layer (CL), a proton exchange membrane (PEM), a cathode CL, and a cathode DL. MEAs provide a complex conductive environment for electron/proton conduction, reactant/product transportation and interfacial redox reactions. Normally, methanol diffuses into the anode DL from the anode flow field, and reaches the anode CL, where it takes part in the methanol oxidation reaction (MOR). Excess methanol will be transported to the cathode by osmotic pressure and electromigration across the PEM, and then reacts with oxygen (O_2) as soon as it arrives at the cathode. Although the exact kinetics of this process are the subject of debate, the end result is a decrease of the cell voltage. At the cathode, O_2 from the surrounding air is transferred through the cathode DL to the cathode CL, where it is reduced to water. At the same time, free electrons from the anode reactions flow through the external circuit to the cathode, which allows the reaction at the cathode to continue. Before the electrons reach the current collector, they must be able to flow through the cathode CL and DL. By optimizing every layer in a MEA, limitations such as transport and management issues and MCO can be overcome, and conduction and distribution can be enhanced [2].

2. Nanostructured electrocatalytic materials for use in DMFCs

The catalytic efficiency can be enhanced by optimizing the structure or composition of electrocatalytic materials. For instance, numerous studies have shown that constructing an appropriate porous network or ordered nanoparticle array in the CL can lead to enhanced catalytic performance and improved Pt utilization because of an increase of electrochemically active surface area (EASA) [3]. Regarding composition modification, many researchers have focused on introducing other metals or metal oxides into Pt catalysts to modify their interface electronic state [4,5]. During such modification, the ligand effect can influence the poison tolerance of Pt by weakening the interaction between Pt and some adsorbates such as protons (H^+), hydroxide ions (OH^-) or adsorbed carbon monoxide (CO_{ads}), and thus improve catalytic efficiency. For example, it is well known that Pt-Ru bimetallic catalysts can activate H_2O at lower potential than Pt, the adsorbed OH^- species on Ru can oxidize the CO_{ads} on the surface of the Pt atoms to CO_2 and thus increase the anti-poisoning ability of Pt; this process is usually called the bifunctional mechanism [6].

2.1. Pt-based nanostructured catalysts

The three-dimensional (3D) network structure is considered suitable for constructing high-efficiency CLs because it facilitates internal transport by providing continuous passages and decreasing diffusion distances. The porous structure composed interspaces between separated branches can also provide sufficiently accessible active sites at interfaces to allow electrocatalytic reactions. The gaps between nanoparticles have been proved effective at preventing grain rearrangement and growth, improving the working life and durability of fuel cells [7]. Among various catalysts, Pt-based catalysts with advanced nanostructures are of particular interest for use in DMFCs.

As an example of a CL with a 3D network structure, Yamachi et al. [8] used a soft template method with lyotropic liquid crystals (LLCs) to form highly ordered mesoporous materials with lamellar, two-dimensional hexagonal, 3D cubic, and other nanostructures. They also developed a very simple one-step method to prepare Pt nanodendrites at room temperature within 5 min using block copolymer as a structure-directing agent [9]. Transmission electron microscopy (TEM) images of these Pt nanodendrites are shown in Fig. 1. The block polymer with amphiphilic nature mediated the growth of branched nanostructures through physical and chemical interactions with Pt precursors. The Pt nanodendrites displayed not only a large active Pt surface area, but also favorable electrochemical performance. The mass-normalized current densities for Pt nanodendrites and commercially available Pt black were 0.52 and 0.11 A/mg, respectively, in the positive direction sweep. The current density of the Pt nanodendrites was 4.7 times higher than that of Pt black.

Recently, Fan et al. [10] reported a one-pot hydrothermal synthesis of porous Pt-Cu alloy networks using the block copolymer Pluronic-F127 as a structure-directing agent. A scan-

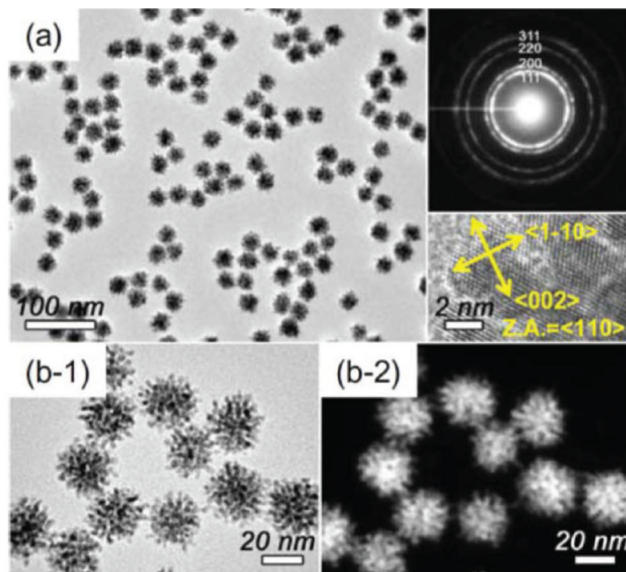


Fig. 1. (a, b-1) TEM images of Pt nanodendrites at low magnification. The inset images in (a) are selected-area electron diffraction patterns recorded for several particles and crystalline lattice fringes observed on the particle edge. (b-2) High angle annular dark field scanning transmission electron microscopy image of the same region as (b-1) [9].

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