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High-surface-area CoTMPP/C synthesized by ultrasonic spray pyrolysis for PEM fuel cell electrocatalysts

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Abstract

Ultrasonic spray pyrolysis (USP) was used to synthesize a high-surface-area CoTMPP/C catalyst for oxygen reduction reaction (ORR). SEM micrographs showed that the USP-derived CoTMPP/C consists of spherical, porous and uniform particles with a diameter of 2–5 μm, which is superior to that with a random morphology and large particle sizes (up to 100 μm) synthesized by the conventional heat-treatment method. BET results revealed that the USP-derived catalyst had a higher specific surface area ($834\,m^2\,g^{-1}$) than the conventional one. Cyclic voltammetric, rotating ring-disk electrode (RRDE) and H_2-air PEM fuel cell testing were employed to evaluate the USP-derived CoTMPP/C. The kinetic current density of the USP-derived catalyst at 0.7 V versus NHE was two times higher than that of the conventional catalyst. Compared to Pt/C catalyst, the USP-derived CoTMPP/C catalyst showed a strong methanol tolerance and a higher ORR activity in the presence of methanol. In a H_2-air PEM fuel cell with USP-derived CoTMPP/C as the cathode catalyst, the cell performance was much higher than that with conventional heat-treated CoTMMP/C as the catalyst.

Keywords: Ultrasonic spray pyrolysis; CoTMPP; Macrocycles; Electrocatalyst; Oxygen reduction; PEM fuel cell

1. Introduction

In recent years, proton exchange membrane fuel cells (PEMFCs), including direct methanol fuel cells (DMFCs), as high-efficient and clean power sources in transportation and stationary applications, have drawn great attention worldwide in resolving energy demanding and environmental pollution issues. The major challenges towards PEMFC commercialization are cost and reliability/durability. With respect to the cost, the component materials such as electrocatalyst, membrane and bipolar plates are dominant, among which the electrocatalyst is the most expensive one [1].

Currently, the most practical catalysts are platinum-based. The platinum-based catalysts are not only expensive, but also suffer from possible supply shortage in the future. Moreover, if used in a DMFC application, platinum-based cathode catalysts have no methanol tolerance. In DMFC operation, the methanol can cross through the membrane from the anode to the cathode, and then reacts with the cathode Pt or Pt-based catalyst, leading to a cathode potential drop, which lowers the operating cell voltage. This activity of cathode Pt catalyst towards methanol oxidation is not desirable [2].

There has been significant activity in recent years in oxygen electrochemistry to develop new and low-cost non-noble metal-based electrocatalysts, which would be capable of selectively catalyzing the four-electron reduction of oxygen to produce water with low overpotential and low H_2O_2-production, a greater tolerance of contaminants, and the ability to remain inert towards methanol oxidation in DMFCs. With respect to this, some metal macrocyclic complexes such as Fe and Co porphyrins or phthalocyanines have been tested as PEMFC and DMFC cathode catalysts. They showed remarkable selectivity to O_2 reduction and inertness to methanol oxidation [3,4]. Although a variety of cobalt and iron macrocycles have been demonstrated to have high oxygen reduction activity, the catalyst durability still remains as a major barrier in the applications. This is mainly due to the presence of corrosive peroxide, which is the intermediate of the catalyzed oxygen reduction reaction (ORR) [5–7].

In the effort to improve the catalytic activity and stability, heat-treatment to the transition metal macrocycles has been

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carried out and approved to be an effective way to improve performance in fuel cell operation conditions [8–10]. With respect to the fundamental understanding of catalytic performance enhancement in terms of activity and stability, the importance of active catalytic sites after the heat-treatment has been identified although there are still some controversies on the origin of enhanced activity [10]. However, the generation of as many catalytic activity sites as possible through the interaction between macrocycles and the carbon support surface active sites, which can promote four-electron oxygen reduction mechanism, is always the right direction. For further development, more works have concentrated on exploring new catalyst systems and carbon support strategies, and optimizing the heat-treatment conditions [11–19]. Furthermore, some recent works have focused on the development of novel routes to synthesize ORR catalysts by heating up the mixture of simple metal salts, nitrogen containing molecules and carbon [20–24]. In addition, new heat-treatment strategies to synthesize active catalysts have always been attractive in terms of catalyst morphologic improvement in ORR activity. Bogdanoff et al. [25,26] developed a heat treatment method using metal oxalates as foaming agents to form highly porous catalysts, and a plasma thermal treatment method to suppress the particle aggregation. In this way, the electrochemical activity of the prepared catalysts was effectively improved.

Ultrasonic spray pyrolysis (USP) is an important approach to synthesize heat-treated solid-state materials, and is widely applied in the ceramic industry and the field of heterogeneous catalysis [27]. The USP method is a continuous, one-step and scalable method to prepare un-aggregated spherical and uniform particles with controllable particle size. This method has also been successfully used to prepare highly dispersed Pt-based catalysts such as Pt/C and PtRu/C for PEM fuel cells [28].

Cobalt tetramethoxyphenylporphyrin (CoTMPP), a typical macrocycle, is one of the effective non-noble catalysts for oxygen reduction reaction in acidic, basic and even neutral solutions [29]. Recently, Ma et al. [18] investigated the feasibility of heat-treated carbon-supported CoTMPP as a cathode catalyst in PEM fuel cell, and the results seemed promising in terms of performance and durability.

In this work, we adopted the USP method to prepare spherical and porous carbon-supported CoTMPP catalysts, aiming at developing a new heat-treatment approach to synthesize high-surface-area carbon-supported macrocycle catalysts and demonstrate the significant effect of morphology on the electrochemical activity of the synthesized catalysts.

2. Experimental

The catalysts were prepared by the ultrasonic spray pyrolysis method as well as a conventional heat-treatment method for comparison. Cobalt nitrate and tetramethoxyphenylporphyrin (H_2TMPP, Adrich) were used as the catalyst precursors. Black Pearls 2000 (Carbot Corp., 1500 $m^2\,g^{-1}$) was used as the carbon support. The loading of cobalt with respect to carbon was controlled at 3.0 wt%, which corresponds to a CoTMPP loading of 42.0 wt%. The preparation steps were as follows: Cobalt nitrate was dissolved in acetone, and BP2000 was added gradually into this solution to form a homogeneous mixture under stirring, into which a 3.0 M formic acid with dissolved H_2TMPP was then added to form the precursor ink. Finally, the ink was ultrasonically agitated overnight and then divided into three parts. The first part was placed in an 80 °C oven overnight to evaporate the solvent and then dried at 120 °C for 24 h. The sample obtained in this way was pulverized and assigned as non-heated CoTMPP/C catalyst (Sample 1). The second part was dried under the same procedure as that of Sample 1, and then heat-treated at 800 °C in a horizontal quartz tube under a continuous flow of nitrogen for 2 h. The obtained powder was then cooled down under the nitrogen atmosphere and pulverized by a grinder mill. This sample was assigned as conventional CoTMPP/C (Sample 2). The third part of ink was pumped into a 2.4 MHz atomizer (Sonaer Inc., USA) and converted into small droplets. The droplets were carried into a heated quartz tube (diameter: 2 in., length: 48 in.) by a continuous high-purity nitrogen flow (99.999%, 5.0 $dm^3\,min^{-1}$). The quartz tube was installed inside a split tube furnace (Thermcraft Inc., USA), which was controlled at 800 °C. The formed solid particles were collected in a high-pressure filter at the other end of quartz tube. The obtained powder was assigned as USP-derived CoTMPP/C (Sample 3).

The morphologies of the as-prepared Samples 1–3 were observed in a scanning electron microscope (SEM, Hitachi S-3500N) operated at 20 kV. The measurement of specific surface area was carried out by the BET method in a surface area analyzer (SA3100, Beckman Coulter).

The electrochemical activities of the as-prepared catalysts were evaluated by cyclic voltammetry (CV) and rotating ring-disk electrode (RRDE) techniques. The measurements were performed in a multi-potentiostat (Solartron 1480) and a single-compartment, three-electrode cell with a MSR rotator (Pine Research Inc.). A glassy carbon disk (disk diameter of 4.57 mm)–platinum ring (ring width of 5.38–4.93 mm) electrode (Pine Research Inc.) was used as the working electrode. Platinum wire was used as the counter electrode. A standard Hg/$HgSO_4$ reference electrode (CH Instruments, Inc.) was used as the reference electrode. The potentials presented in this work are referenced with respect to normal hydrogen electrode (NHE).

The catalysts were applied onto the disk electrode by an ink-coating technique. The catalyst ink (5.0 $mg\,ml^{-1}$) was prepared by ultrasonically blending the mixture of catalyst powder and isopropanol for 10 min. Ten microlitres of the ink was coated onto the glassy carbon disk gradually by a micro syringe. After the evaporation of the solvent, 10 μl of diluted Nafion solution (0.1 wt%, Aldrich) was added onto the catalyst layer. The Nafion film was dried naturally at room temperature. The total catalyst loading is 305 $\mu g\,cm^{-2}$. The CVs were recorded by scanning the disk potential from 0.84 to 0.04 V versus NHE with a scan rate of 5 $mV\,s^{-1}$ in oxygen-saturated 0.5 M H_2SO_4 solution. Before recording the CV curves, several potential scanning cycles were carried out to rule out the effect of possible contamination of the electrode surface. For the RRDE measurements, the ring potential was fixed at 1.2 V versus NHE to oxidize any peroxide produced during the potential scan of the disk electrode from open circuit potential (OCP) to 0.04 V versus NHE