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Hybrid cathode catalyst with synergistic effect between carbon composite catalyst and Pt for ultra-low Pt loading in PEMFCs

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ABSTRACT

Due to the high cost of Pt catalyst, reducing the amount of Pt in electrodes is one of the primary issues in polymer electrolyte membrane fuel cells. In this study, the hybrid cathode catalyst using the electrochemically active carbon composite catalyst and Pt catalyst is developed in order to reduce the amount of Pt and increase the overall catalytic performance. The carbon composite catalyst (CCC) is synthesized by pyrolysis of Fe-Co chelate compound followed by acid leaching. The current density of Pt/CCC is 1.5–6-fold higher than that of Pt/CB when employing ultra-low Pt loading (0.04 $mg_{Pt}\,cm^{-2}$). It is found that the Pt/CCC with the ultra-low Pt loading at tuned operating conditions exhibits a higher fuel cell performance than the Pt/CB and commercial Pt/C with four times higher Pt loading (0.16 $mg_{Pt}\,cm^{-2}$). The extensive activity of Pt/CCC is ascribed to the synergistic effect through (1) the combined activity of catalytic sites present in the CCC support and Pt, (2) the well-distributed nanoparticles and (3) the increased metallic Pt^0 concentration which indicated that the pyridinic-N played a role of oxide-cleanser.

1. Introduction

Recently polymer electrolyte membrane fuel cells (PEMFCs) are emerging as a promising candidate for automotive industries. Still, the cost reduction is critically necessary for commercializing PEMFCs. The activity of oxygen reduction reaction (ORR) catalyst should be further improved due to the slow kinetics and costly Pt. In this regard, one of the efforts has been focused on the development of various Pt-alloy cathode catalysts such as PtCo, PtNi, and PtCu [1–5]. They found that the Pt alloy with 3d transition metals enhances the kinetic activity for ORR due to a variety of factors such as the suppression of Pt oxide formation [6,7] and formation of new electronic structures with Pt 5d orbital vacancies [8]. The above-mentioned Pt-based catalysts have shown significant improvements in the activity and stability. However, the amount of Pt should be further reduced in order to meet the targets for the commercialization and the performance is varied with the compositional ratio of Pt to transition metals.

The other way is using the hybrid cathode catalyst (HCC) comprising of the electrochemically active N-doped carbon support and the Pt catalyst. The N-doped carbon as an inexpensive alternative material has been vastly investigated. Sevilla et al. prepared the N-doped mesoporous carbons using polypyrrole, SBA-15 and silica xerogel [9]. Its onset potential exhibited −90 to −70 vs.Ag/AgCl, and its current density exceeded that of a commercial Pt catalyst. They found that the N-doped mesoporous catalysts exhibited good tolerance to the methanol cross-over effect, unlike the commercial platinum catalyst. Leonard et al. studied a variety of structural and compositional properties of metal-nitrogen-carbon (MNC) catalysts using high-pressure pyrolysis [10]. They observed that the nitrogen content was linearly increased with the metal content and the substrates adsorbing the most nitrogen and metal showed the highest activity. Wang et al. obtained the non-precious metal electrocatalysts using the in-situ polymerization of dicyandiamide with different amount of Fe, followed by the pyrolysis at above 700 °C [11]. The rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) studies exhibit that the best performance was observed at 750 °C. The half-wave potential ($E_{1/2}$) was decreased by 12 mV during potential cycling from 0.6 to 1.0 V vs. RHE, while that of the commercial Pt/C catalyst exhibited 24 mV loss.

There are additional benefits for the use of nitrogen-doped carbon as a support. Doping the nitrogen produced the defects on carbon supports to anchor the Pt nanoparticles with high dispersion [12,13]. Chen et al. measured Carbon K-edge near-edge X-ray absorption fine structure (NEXAFS) and Raman spectroscopy to confirm the defects on carbon nanotubes [13]. They observed the sharp peak at 289.1 eV and high I_D/I_G comparing non-doped carbon nanotubes. It also influenced on the surface chemical property. It has one lone pair of electrons in addition to the one electron donated to the conjugated π bond system providing the carbon with Lewis basicity [14]. Consequently, the nitrogen-doped

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carbon showed $pH_{pzc} \approx 9$, while the carbon black is neutral. It is observed that strong Lewis basicity of carbons doped with pyridinic and graphitic nitrogens facilitates the reductive adsorption reaction of O_2 without the irreversible formation of oxygen functionalities, due to an increased electron-donor property of carbon [15]. Furthermore, the nitrogen-doped carbon-supported PtRu catalysts showed the higher catalytic activity and better CO tolerance than the carbon-supported PtRu and Pt-only catalysts [12]. Liu et al. found that PtRu on N-doped porous carbon nanospheres (PCNs) exhibited lower onset potential and higher mass activity than PtRu/C. Electrochemical impedance spectroscopy confirmed that PtRu/PCN suggested the faster dehydrogenation of methanol molecules and oxidation of intermediate CO_{ads} species. Cheng et al. reported that the N-self-doped 3-dimensional graphene-like networks (N-3D GNs) can be prepared by improved ion-exchange/activation method [16]. Pt/N-3D GNs showed 2.6 times higher catalytic activity than the commercial Pt/C catalyst. Perini et al. [17] prepared N-doped mesoporous carbon with high surface area prepared by an optimized hard template approach, employing NH_3 as the doping agent. They reported that Pt nanoparticles supported on N-doped support exhibit high activities for the ORR in acidic solutions, with better performances than those of commercial Pt on Vulcan XC-72. Furthermore, Pt nanoparticles on mesoporous carbon would be more stable than the commercial Pt on Vulcan XC-72 due to a better confinement effect inside the mesoporous structure. Nitrogen-doped onion-like carbon (N-OLC) prepared by arc discharge in a liquid phase in the presence of different ammonia concentrations was used as a support of Pt [18]. Pt/N-OLC catalyst with 1.7 at% nitrogen exhibited the higher electrochemically active surface area, specific current density and half-wave potential than the commercial Pt/C catalyst. The observed enhanced oxygen reduction could be ascribed to the defective outermost layers and the electronic modification. Recently, a research for the direct synthesis of a nitrogen-doped carbon aerogel (NCA) was reported [19]. Compared with a Pt on carbon aerogel synthesized by a conventional reduction method, the Pt/NCA showed enhanced electrochemical performance with a high electrochemically active surface area and electrocatalytic activity towards oxygen reduction. Jukk et al. studied the oxygen reduction activity of Pt on N-doped graphene nanosheets (Pt/NG) prepared using dicyandiamide precursor employing the RDE technique [20]. They showed that when the N-doped graphene-based material was used as a carbon support for Pt metals, platinum loading could be reduced and better nanoparticle distribution could be achieved.

In our previous papers [15,21–24], the CCC was developed for the ORR through the chelate compound of non-platinum group metal (PGM) and nitrogen followed by the treatment combination of pyrolysis and acid leaching. The CCC showed high onset potential for ORR and high performance in the fuel cell tests. In the long-term stability test, a very slow potential decay with as low as 40 $\mu V\,h^{-1}$ was observed for 1050 h fuel cell operation at a current density of 200 mA cm^{-2}.

In this study, a novel approach for the preparation of cost-effective and highly active HCC and its synergistic effect towards ORR is reported. HCC is a combination of pyridinic and quaternary nitrogen site-containing CCC and Pt catalytic sites for oxygen reduction. Besides its own contribution to the overall catalyst activity that is not present on conventional carbon black supports, the PGM-free CCC can also enhance the activity of the Pt through synergistic effects. To elucidate the intrinsic synergistic effects, in terms of the activity, we controlled the Pt particle size effect with the low Pt concentration on the supports since the Pt particle size plays an important role in the activity of ORR. To convert the activity study in half-cell into the practical fuel cell, the 30 wt% Pt on the supports was used to minimize the mass transport limitation since the low Pt concentration results in the thick electrode. The enhanced activity of HCC is characterized by various physico-chemical analyses and demonstrated both in half-cell using 0.1 M $HClO_4$ as electrolyte and in 25 cm^2 MEAs.

2. Experimental

2.1. Preparation of support and catalyst

For a typical CCC preparation [15,21–24], 2 ml of the ethylenediamine (EDA, Alfa Aesar) was chelated with iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, Sigma-Aldrich) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich) in isopropyl alcohol (IPA, BDH Chemicals). 0.4 g of pre-oxidized CB (Ketjen Black EC-300J, AkzoNobel) was added to the chelating solution followed by refluxing at 85 °C for 3 h. The solvent was removed by rotary evaporating and the product was dried in an air oven at 80 °C for 12 h. Subsequently, the resultant powder was pyrolyzed in a tube furnace under the pure nitrogen atmosphere for 1 h at 800 °C. After cooling down to room temperature, the sample was leached in 0.5 M H_2SO_4 at 80 °C for 3 h to remove the unnecessary transition metals present on the surface. The CCC was obtained after washing and drying at 80 °C overnight.

The Pt deposition on CCC and CB was carried out by the electroless deposition using sodium formate (Alfa Aesar) as a reducing agent. The desired amount of 4.0 mM H_2PtCl_6 (Sigma-Aldrich) solution was mixed with deionized (DI) water and supports under stirring. 2.0 M sodium formate solution was added dropwise to the reaction mixture at 70 °C, followed by refluxing at 70 °C for 12 h. The resulting catalysts were washed with DI water several times, and then dried in the vacuum oven at 80 °C for 12 h 5 wt% Pt on supports was used for characterization and half-cell test, while 30 wt% Pt on supports was prepared for fuel cell testing.

2.2. Physico-chemical characterization

The nitrogen adsorption/desorption isotherms were obtained at −196 °C using a Quantachrome NOVA 2000 BET analyzer. Specific surface area was determined by a multipoint Brunauer-Emmett–Teller (BET) analysis. Pore size distribution (PSD) curves were calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption/desorption branch. X-ray diffraction (XRD) analysis was performed using a Rigaku D/Max 2500 V/PC with a Cu Kα radiation. A tube voltage of 30 kV and a current of 15 mA were used during the scanning. To estimate the particle size of samples, we employed the following Scherrer equation [25]:

$$D = \frac{k\lambda}{10B\cos\theta}$$

where D is the crystallite size in nm, k is a coefficient (0.9), λ is the wavelength of X-ray (1.5404 Å), B is the line broadening at half the maximum intensity in radians, and θ is the angle at the position of the maximum peak known as Bragg angle. X-ray photoelectron spectroscopy (XPS) was carried out with a Kratos AXIS 165 high-performance electron spectrometer on samples to analyze the elemental oxidation state. High resolution transmission electron microscope (HR-TEM) was used to study the morphology and particles size distribution of the catalysts using Hitachi 9500 HR-TEM operated at 300 kV accelerating voltage. X-ray fluorescence (XRF, Fischer XDAL) was used to determine Pt loading with accuracy in the catalyst coated membrane.

2.3. Electrode preparation

In a typical RDE experiment, for the CCC, 8 mg of CCC was ultrasonicated in 1 ml of IPA. 15 ul of the ink was deposited on the glassy carbon electrode. In the case of Pt/CCC and Pt/CB, the catalyst ink was prepared by mixing the respective catalysts with absolute ethanol and DI water in an ultrasonicate bath. The catalyst ink was deposited onto the glass carbon electrode with a target Pt loading of 20 $\mu g_{Pt}\,cm^{-2}$. For all RDE tests, 5 µl of 0.25 wt% ionomer (Alfa Aesar) was additionally deposited on the catalyst layer to give a good adhesion of catalyst onto the glassy carbon electrode.