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Self-humidifying Pt-C/Pt-TiO_2 dual-catalyst electrode membrane assembly for proton-exchange membrane fuel cells

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ABSTRACT

A high-performance Pt-C/Pt-TiO_2 dual-catalyst electrode was prepared and found to exhibit excellent water production and retention in self-humidifying proton-exchange membrane fuel cells. Different weight fractions of xPt-C/(1–x)Pt-TiO_2 dual-catalyst layer were applied to both anode and cathode with fixed total Pt loadings of 0.2 mg/cm^2 and 0.3 mg/cm^2. The dependence of cell performance on the Pt-TiO_2 content in dual-catalyst electrode was highly affected by the relative humidity (RH): When the RH was lower than 60%, the cell performance was significantly affected by the Pt-TiO_2 content. The ability to produce and retain water of the Pt-TiO_2 catalyst layer on the anode side was very important for the zero-RH cell performance. A visual cell experiment clearly revealed that water production at the anode was highly dependent on the Pt-TiO_2 content in the Pt-C/Pt-TiO_2 dual layer on the anode side. A half dual-layer experiment involving the Pt-TiO_2 on the cathode side alone strongly suggested that zero-RH operation is impracticable. The Pt-TiO_2 in the dual layer at the anode produces water consuming the H_2 and O_2 crossing the membrane from the cathode, resulting in excellent cell performance under zero RH. The Pt-C/Pt-TiO_2 ratio must be optimized in terms of the water-production and retention ability.

1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) are among the most powerful energy sources with the potential to replace fossil energy because they have several advantages, such as eco friendliness, high energy-conversion efficiency, and long lifetimes [1–4]. PEMFCs consist of an anode and a cathode with a Pt catalyst supported on carbon materials separated by a proton-exchange membrane (PEM) [5]. Perfluorosulfonic acid membranes, which are also known as Nafion membranes, are the most widely used PEMs because of their high proton conductivity and good oxidative and mechanical properties [6,7]. Unfortunately, Nafion has inherent problems, such as significant fuel crossover and poor proton conductivity under low-humidity conditions (including zero humidity) [8–11]. The system of reactions that occurs in PEMFCs is as follows: 1) H_2 oxidation at the anode, during which the electrons move through an external circuit from the anode to the cathode; 2) H^+ ion conduction through the PEM; and 3) O_2 reduction at the cathode, where O_2 reacts with H^+ ions and electrons to form water molecules [12]. However, the fuel cell requires humidity to facilitate proton transfer through the membrane. Water is transported along with the protons through the membrane from the anode to the cathode by electro-osmotic drag, which increases with the current density. Therefore, the humidification of the anode is critical; in the absence of humidity, the anode will become dehydrated. In addition, the back diffusion of water molecules from the cathode to the anode could occur because of the water concentration gradient caused by the water produced at the cathode. Two methods are available to humidify the fuel cell [13,14]: Humidify the fuel entering the cell using an external humidifying unit or modify the PEM to enhance its water-production and retention ability. The former makes the system complicated, bulky, heavy, and expensive, thus inhibiting commercialization [15]. In contrast, the latter method can be implemented using a composite membrane to which hydrophilic inorganic fillers, such as metal oxides, are added to enhance its water-retention ability [16–18]. Another interesting way to facilitate PEMFC operation even under zero humidity is to deposit Pt nanoparticles onto hydrophilic inorganic fillers, such as Pt-SiO_2 [19,20], Pt-TiO_2 [21], and Pt-ZrP [22], and incorporate these

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Pt-metal oxides into the Nafion membrane. In this case, Pt provides a reaction site for water production using the H_2 and O_2 crossing the membrane from the cathode, whereas the hydrophilic metal oxides provide water-adsorption sites, thereby helping to keep the membrane hydrated. Although Nafion/Pt-metal oxide composite membranes exhibit some advantages over Nafion membranes under low-humidity conditions, the content of the inorganic filler must be precisely controlled to achieve good cell performance. Recently, Yang et al. [19] described Nafion/various Pt-SiO_2 composite membranes with different order of sulfonation and reported that the cell performance decreased because of electron loss through the electrical conductive Pt network in the membrane. Some other drawbacks also have been noted: Uniformly dispersing inorganic fillers in Nafion is difficult because of the poor compatibility between these fillers and Nafion, and the use of Pt-metal oxides incurs an additional expense, which is required to purchase the Pt particles.

The objectives of this study is to investigate the possibility of dual catalyst electrode as an alternative to the conventional self-humidifying Nafion/metal oxide composite membrane and provide the fundamentals. In this study, to develop a self-humidifying PEMFC that is not affected by detrimental effects on cell performance, such as electron loss via the Pt network in composite membranes, significant fuel crossover, non-uniform dispersion of inorganic fillers within Nafion, and the expense of additional Pt, separate Pt-TiO_2 catalyst layers were sandwiched between gas-diffusion electrodes and Nafion membrane. Compared to the composite membrane, this dual-catalyst layer structure is expected to exhibit several advantages. The water production by the Pt-TiO_2 catalyst layer on the anode and cathode sides, the electrochemical properties, and the cell performance under low-humidity conditions are also discussed.

2. Experimental

2.1. Dispersion of Pt onto TiO_2

First, a 0.4-M NaOH solution (98%, Samchun Chemicals, Korea) was prepared with ethylene glycol (EG, 99.5%, Samchun Chemicals) as the solvent to which 1.0 g of H_2PtCl_6 (Sigma Aldrich, USA) was added and stirred under ambient atmosphere at 160 °C for 3 h. After 3 h of reduction, the color of the dispersion had changed from orange to dark brown. Then, 2 g of commercial TiO_2 (~21 nm, Sigma Aldrich, USA) was dispersed in 1-M HCl (35–37%, Samchun Chemicals). The TiO_2 was then collected by centrifugation and washed with acetone (99.5%, Duksan Chemicals). Then, the TiO_2 and 3 mL of acetone were added to a Pt solution, followed by sonication for 1 h. Finally, the Pt-TiO_2 particles were collected by centrifugation and dried for 12 h under vacuum [23].

2.2. Preparation of catalyst ink and electrodes

First, commercial Pt-C (40% Alfa Aesar, USA) or Pt-TiO_2 was added to isopropyl alcohol (IPA, 99.5 wt%, Samchun Chemicals, Korea) as a solvent, to which a Nafion dispersion (5 wt%, Dupont Chem. Co., USA) was added. The catalyst ink was then sonicated for 30 min. The Pt-TiO_2 catalyst ink was first brushed on both sides of a membrane (Nafion NRE 212, Dupont Chem. Co., USA) with an area of 3×3 cm^2, and subsequently, the Pt-C catalyst ink was brushed on top of the Pt-TiO_2 layer at 40 °C on a hot plate. The amounts of Pt-TiO_2 and Pt/C were varied as follows: xPt-C/(1–x)Pt-TiO_2, where x = 0.5, 0.6, 0.7, or 0.8. The total Pt loadings in the Pt-C and Pt-TiO_2 dual layers were fixed at 0.2 mg/cm^2 and 0.3 mg/cm^2 for the anode and cathode, respectively. For comparison, a half dual-catalyst layer (i.e., a dual layer of Pt-TiO_2 on the anode or cathode side only) was prepared and tested. This set-up consisted of a 0.7Pt-C/0.3Pt-TiO_2 dual layer at the cathode and a Pt-C single layer at the anode (hereinafter, PCTC) or a Pt-C single layer at the cathode and a 0.7Pt-C/0.3Pt-TiO_2 dual layer at the anode (hereinafter, PCTA). The membrane electrode assemblies (MEAs) were then assembled without hot pressing. Carbon fiber paper (SGL 10BCE, SGL Carbon Co., Germany) was employed as the gas-diffusion layer (GDL) for the fabrication of the MEAs. A schematic diagram of a MEA fabricated with the Pt-C/Pt-TiO_2 dual-catalyst layer is shown in Fig. 1.

Finally, a single-catalyst electrode was also prepared by mixing Pt-C and Pt-TiO_2 in different weight fractions, such as 0.6–0.4, 0.7–0.3, and 0.8–0.2. As in previous cases, the MEAs were fabricated, and the cells were tested and compared.

2.3. Characterization

Powder X-ray diffraction (XRD, Rigaku Model D/Max 2200) analyses were performed to identify the phase formed and the particle size using CuKα radiation operating at 40 kv and 30 mA with a scanning rate of 5° min^{-1} with an angular resolution of 0.04° over the 2θ scans. Energy-dispersive X-ray spectroscopy (EDS, Oxford Ins., INCA energy) was used to investigate the distributions of Pt, TiO_2, and carbon within the catalyst layer. Transmission electron microscopy (TEM, JEOL, JEM 2000EX) was conducted to identify the dispersion and particle size. The Pt content in the Pt-TiO_2 was evaluated by X-ray fluorescence (XRF, Panalytical, Epsilon3-XL) analysis.

2.4. Electrochemical measurement

Nyquist plots (IM6, Zahner) were collected in potentiostatic mode for each MEA after the cell test. The conditions were the same as those used in the cell test: O_2 was fed to the cathode, and H_2 was fed to the anode. The H_2 anode served as the dynamic hydrogen electrode, and the voltage of the single cell was fixed at 0.850 V to study the interface resistance of the MEA. The measurements were performed over a frequency range from 100 kHz to 0.1 Hz while the fuel cell was at steady state [24].

2.5. Visual cell test

To investigate the water production at the anode, a visual cell test was conducted using transparent cells. The MEA fabricated with a xPt-C/(1–x)Pt-TiO_2 dual-catalyst layer (x = 0.5, 0.6, 0.7, and 0.8) and a half dual layer was placed between visual serpentine flow channels, and the liquid-water produced on the anode side was photographed using a digital charge-coupled device (CCD) camera (Redlake MegaPlus II ES4020) with a micro lens (Nikon AF-MF 105 mm F2.8 EX DG MACRO F). Standard stainless steel 316 was used as the unipolar plate for both the anode and cathode sides. The area of the window was approximately 4.91 cm^2. A schematic diagram of the visual cell experiment is shown in Fig. S1.

2.6. Single-cell test and durability test

Single-cell tests were conducted using the fuel cell hardware of a fuel cell test station (Wona Tech smart II) at 80 °C. O_2 (99.99%) was introduced into the cathode inlet, and H_2 (99.999%) was fed into the anode inlet; both gases had a fixed flow rate of 100 cc/min and various relative humidity (RH) values (100%, 60%, 40%, and 0%). During the durability tests, the voltage was fixed at 0.5 V, and the current density was measured with 100 cc/min of H_2 and O_2 under 0% RH for 100 h.