Stability characteristics of Pt_1Ni_1/C as cathode catalysts in membrane electrode assembly of polymer electrolyte membrane fuel cell

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ABSTRACT

To understand the difference in degradation characteristics between carbon-supported platinum (Pt/C) and platinum–nickel alloy (Pt_1Ni_1/C) cathode catalysts in membrane electrode assemblies (MEAs) of a polymer electrolyte membrane fuel cell (PEMFC), constant current operation of MEA in a single cell was conducted for 1100 h. A significant change in cell potential for the Pt_1Ni_1/C MEA was observed throughout the test. High-resolution transmission electron microscopy showed that sintering and detachment of metal particles in the Pt_1Ni_1/C catalyst occurred more sparingly than in the Pt/C catalyst. Instead, X-ray photoelectron spectroscopy element mapping revealed dissolution of Ni atoms in the Pt_1Ni_1 catalysts even when the Pt_1Ni_1/C catalyst used in the MEA was well synthesized.

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1. Introduction

Studies on the lifespan of membrane electrode assemblies (MEAs) have been conducted extensively over the past decade for the purpose of polymer electrolyte membrane fuel cell (PEMFC) commercialization. From prior investigations, it is obvious that decay of MEA cathode catalysts is one of the most crucial factors in the life expectancy of the PEMFC [1–3]. Use of carbon-supported Pt alloy (Pt alloy/C) in conjunction with transition metals such as Co, Ni, and Fe as cathode catalysts in PEMFCs reduces Pt consumption and increases the oxygen reduction reaction (ORR) activity. Therefore, minimizing the degradation of MEA performance caused by deactivation of the Pt alloy is necessary for commercializing PEMFCs [4,5]. The half-cell test and accelerated durability test (ADT) are important for evaluating the electrochemical catalyst performance. Previous studies on catalyst degradation have been based primarily on the half-cell test and on ADTs such as load cycling, start/stop cycling, and RH cycling [6,7]. Those studies examined the effect of Pt alloy/C on the degradation of PEMFC performance, but they provided inconsistent results [8–12]. Those inconsistencies may result from the different operating conditions of each durability test. Nevertheless, it is widely accepted that Pt alloy/C catalysts are electrochemically unstable compared to carbon-supported Pt (Pt/C) catalysts under half-cell and ADT conditions. From a practical standpoint, the MEA test is the ultimate evaluation criterion for characterization of catalysts [13–15]. Investigations of the durability of catalysts in MEAs are more complex and difficult than those in half-cells because the temperature, pressure, and gas flow conditions play pivotal roles in determining accurate MEA performance. Generally, constant current test has been recognized as traditional durability test mode. In this paper, to overcome prior limitations, catalyst-coated membranes (CCM) used as MEAs were fabricated using Pt/C or Pt_1Ni_1/C as cathode catalysts, and they were operated for 1100 h in constant current mode using a single cell. A comparison is reported between the performance degradation behaviors of MEAs containing Pt/C or Pt_1Ni_1/C as cathode catalysts. In addition, X-ray photoelectron spectroscopy element mapping was used to characterize degradation of the catalyst layer over a wide area (above 0.78 mm^2); this is a novel approach for analyzing degradation of the catalyst layer in a PEMFC. The unique transition of cell

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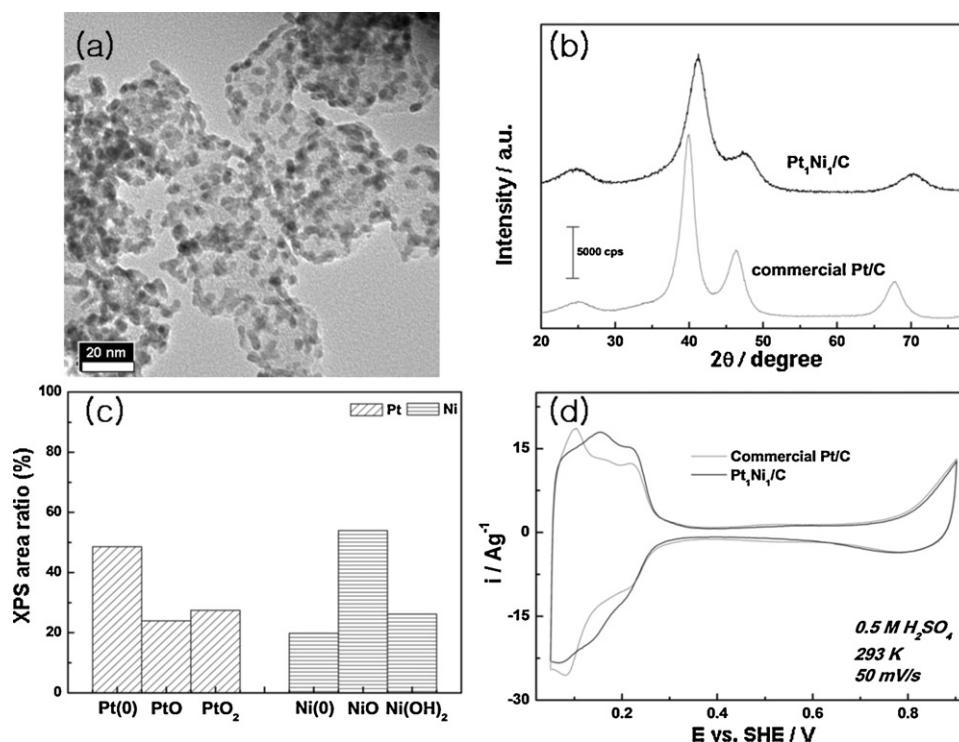[1] International Society of Electrochemistry member.

Fig. 1. (a) TEM image of the carbon-supported Pt–Ni alloy nanoparticles, (b) powder X-ray patterns and (c) area ratios of various states fitted with XPS spectra of Pt 4f and Ni 2p of Pt_1Ni_1/C. (d) Cyclic voltammograms obtained in 0.5 M H_2SO_4 solution at a scan rate of 50 mV s^{-1}.

potential as a function of time on the Pt_1Ni_1/C MEA will be discussed in comparison with the Pt/C MEA.

2. Experimental

Pt/C (40 wt.%, Johnson Matthey) and Pt_1Ni_1/C (40 wt.%, synthesized) were used as cathode catalysts in order to compare their performance degradation behaviors. Pt/C was also used as an anode catalyst in both MEAs. The 40 wt.% Pt_1Ni_1/C electrocatalyst was synthesized by borohydride reduction in anhydrous ethanol containing dissolved sodium acetate ($C_2H_3NaO_2$), as described in our previous report [16]. The prepared Pt_1Ni_1/C and as-received Pt/C were analyzed using X-ray diffraction (XRD, Rigaku D/Max2500) with Cu Kα radiation (40 kV, 200 mA). High-resolution transmission electron microscopy (HR-TEM) using a JEOL EM-2000 EXII microscope at a 200 kV accelerating potential was conducted to measure changes in the size and distribution of Pt/C and Pt_1Ni_1/C particles. XPS was used using an Al Kα source (ESCALAB 250 XPS spectrometer, VG Scientifics) to determine chemical states of the synthesized Pt_1Ni_1 alloy. Binding energies were calibrated with respect to C (1s) at 285 eV. Experimental data were curve-fitted using XPSPEAK4.1 software. For the electrochemical characterization of synthesized Pt_1Ni_1/C and as-received Pt/C powders, the catalyst slurry for the half-cell test was ultrasonically prepared using 200 μl of deionized water, 572 μl of 5 wt.% Nafion solution (Aldrich), and 8 ml of isopropyl alcohol per 0.1 g of catalyst. Cyclic voltammogram for half-cell tests was performed in a three-electrode electrochemical cell that consisted of a glassy carbon electrode coated with catalyst slurry for the working electrode, saturated calomel electrode (SCE) for a reference electrode, and Pt wire for a counter electrode. A cyclic voltammogram was examined in argon-saturated 0.5 M H_2SO_4 with a 50 mV s^{-1} scan rate at 20 °C in order to determine the electrochemical active surface area (ESA). The catalyst inks for MEAs were blended ultrasonically

with Nafion solution (5 wt.%, Aldrich), deionized water, and iso-propyl alcohol. The CCMs for MEAs were fabricated as a polymer electrolyte through a spraying method using Nafion 212 (Dupont), as reported previously [17]. The active area of the electrode was 5 cm^2, and the metal catalyst loading was 0.2 mg cm^{-2}. The MEAs were assembled from gas diffusion layers (GDLs), including a micro-porous layer and gaskets, using a single cell (CNL-PEM005-01, CNL Energy). The long-term test as a function of time was performed for 1100 h using a fuel cell test station (CNL Energy) at a constant current density of 400 mA cm^{-2}, and the load was not disconnected during the experiment duration without replacing the reactant gases (H_2 or air). The single-cell was operated using fully humidified H_2 gas and air on the anode and cathode with a stoichiometric ratio of 2:2.5, respectively, and the cell temperature was maintained at 70 °C under ambient pressure. The MEAs used with the Pt/C and Pt_1Ni_1/C cathode catalysts are hereafter referred to as Pt/C MEA and Pt_1Ni_1/C MEA, respectively. XPS element mapping of Pt_1Ni_1/C MEA was performed to determine atomic ratios of Pt and Ni on the catalyst layer surface before and after the long-term operation in an ultra high vacuum (UHV) multipurpose surface analysis system (SIGMA PROBE, Thermo, UK) at base pressures <10^{-10} mbar. The photoelectron spectra were excited by an Al Kα (1486.6 eV) anode operating at a constant power of 100 W (15 kV and 10 mA). The mapping area of catalyst layer surfaces in the Pt_1Ni_1/C MEA was 0.78 mm^2 (975 μm × 800 μm), and the number of pixels was 1248 (39 × 32). Beam size pixel sizes were 15 μm and 625 μm^2 (25 μm × 25 μm), respectively.

3. Results and discussion

As-prepared Pt_1Ni_1/C powder was characterized by HR-TEM, as shown in Fig. 1(a). Pt_1Ni_1 nanoparticles were well dispersed on the carbon support with an average particle size of approximately 2.5 nm. As seen in Fig. 1(b), the (2 2 0) peak of the as-prepared