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## Technical Communication

# Performance and stability characteristics of MEAs with carbon-supported Pt and Pt<sub>1</sub>Ni<sub>1</sub> nanoparticles as cathode catalysts in PEM fuel cell

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### ABSTRACT

Polarization curves of membrane electrode assemblies (MEAs) containing carbon-supported platinum (Pt/C) and platinum–nickel alloy (Pt<sub>1</sub>Ni<sub>1</sub>/C) as cathode catalysts were obtained for durability test as a function of time over 1100 h at constant current. Charge transfer resistance was measured using electrochemical impedance spectroscopy and postmortem analysis such as X-ray diffraction and high-resolution transmission electron microscopy was conducted in order to elucidate the degradation factors of each MEA. Our results demonstrate that the reduced performance of MEAs containing Pt<sub>1</sub>Ni<sub>1</sub>/C as a cathode catalyst was due to decreased oxygen reduction reaction caused by the corrosion of Ni, whereas that of MEAs containing Pt/C was because of reduced electrochemical surface area induced by increased Pt particle size.

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## 1. Introduction

The use of Pt alloys was investigated in polymer electrolyte membrane fuel cells (PEMFCs) for the reduction of Pt load and the increase of oxygen reduction reaction (ORR) activity. Although Pt alloy catalysts have higher electrochemical activity in the ORR compared to pure Pt catalyst, their low

stability in electrochemical and physical properties are obstacles to the commercialization of these catalysts in MEAs. Several mechanisms have been offered that explain how Pt alloys increase ORR activity and why they cannot be applied as MEAs. However, inconsistent results have brought about confusion. These inconsistencies may result from varying operating conditions between each durability test [1–5]. For

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example, some prior studies were conducted using a half-cell test while others employed the accelerated durability test (ADT) for the degradation of electrocatalysts in fuel cells [6–8]. This paper shows the reduced performance of MEAs containing carbon-supported platinum (Pt/C) and carbon-supported platinum nickel alloy (Pt<sub>1</sub>Ni<sub>1</sub>/C) as cathode catalysts based on a long-term single-cell test. The causes of the decreases in MEA performance were explained using electrochemical impedance spectroscopy (EIS), X-ray diffraction (XRD), and high-resolution transmission electron microscopy (HR-TEM).

## 2. Experimental

Pt/C and Pt<sub>1</sub>Ni<sub>1</sub>/C were used as cathode catalysts for the preparation of Pt/C MEA and Pt<sub>1</sub>Ni<sub>1</sub>/C MEA, respectively. 40 wt.% Pt/C was purchased from Johnson-Matthey Co. while Pt<sub>1</sub>Ni<sub>1</sub>/C (40 wt.%) electrocatalysts were prepared by borohydride reduction in anhydrous ethanol containing dissolved sodium acetate (C<sub>2</sub>H<sub>3</sub>NaO<sub>2</sub>), as described in our previous report elsewhere [9]. Pt/C also was introduced as the anode catalyst in both MEAs. The catalyst powders were ultrasonically mixed with Nafion solution (5 wt.%, Aldrich), deionized water, and isopropyl alcohol for the preparation of catalyst ink. Catalyst-coated membranes (CCMs) for MEAs were fabricated using Nafion 212 (Dupont) as polymer electrolyte by spraying method as described in our previous paper [10]. The active area of the electrode was 5 cm<sup>2</sup>, and the loading of metal catalyst was 0.2 mg cm<sup>-2</sup> in all electrodes. The MEAs were assembled with gas diffusion layers (GDL), including a microporous layer and gaskets using a graphite plate engraved flow field (CNL-PEM005-01, CNL Energy) [11]. A 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 of 400 mA cm<sup>-2</sup>, and polarization curves were obtained at 0 h, 330 h, 780 h, and 1100 h. 100% humidified hydrogen gas and air were supplied to the anode and cathode with a stoichiometric ratio of 2:2.5, respectively. The cell temperature during the single-cell test was maintained at 70 °C under ambient pressure. Changes in mean Pt particle size before and after long-term test were determined by XRD at angles ranging from 30° to 80° at a rate of 2°/min with X-rays produced by a Cu K $\alpha$  source at room temperature. The crystallite size of Pt was calculated using the Scherrer equation based on the broadness of the (220) peak [12]. The distributions of Pt<sub>1</sub>Ni<sub>1</sub> nanoparticles on carbon supports in MEAs before and after long-term single-cell operation were confirmed by HR-TEM (JEOL2010) using a JEOL EM-2000 EXII microscope at a 200 kV accelerating potential. EIS was carried out at frequencies from 10 kHz to 100 mHz at a single-cell voltage of 0.7 V under the same the single-cell operating conditions with amplitude of 5 mV, and ten points per logarithmic decade were recorded.

## 3. Results and discussion

Fig. 1 shows the single-cell performances of MEAs containing (a) Pt/C and (b) Pt<sub>1</sub>Ni<sub>1</sub>/C as cathode catalysts at 0 h, 330 h, 780 h, and 1100 h during a long-term operation test at

constant current operation of 400 mA cm<sup>-2</sup>. As shown in Fig. 1, the current densities of (c) Pt/C MEA and (d) Pt<sub>1</sub>Ni<sub>1</sub>/C were normalized to initial performance with each voltage, respectively. The initial current densities at 0.6 V were 816 mA cm<sup>-2</sup> for the Pt/C MEA and 717 mA cm<sup>-2</sup> for the Pt<sub>1</sub>Ni<sub>1</sub>/C MEA. This difference in performance between the Pt/C and Pt<sub>1</sub>Ni<sub>1</sub>/C MEAs is reasonable since only catalyst ink has been optimized to Pt/C catalyst. Moreover, one of our prior publications demonstrates that the ORR kinetics of synthesized Pt<sub>1</sub>Ni<sub>1</sub>/C catalyst used in this study was slightly lower than that of purchased Pt/C catalysts because Pt<sub>1</sub>Ni<sub>1</sub>/C used in this study did not experience heat-treatment for removing oxide and separating a phase between Pt and Ni on synthesized catalyst surface [9]. After 330 h, the current densities at 0.6 V were 344 mA cm<sup>-2</sup> for the Pt/C MEA and 343 mA cm<sup>-2</sup> for the Pt<sub>1</sub>Ni<sub>1</sub>/C MEA. The performance of both the Pt/C and Pt<sub>1</sub>Ni<sub>1</sub>/C MEAs therefore dramatically declined over this time period. However, the current densities of the Pt/C MEA at 0.6 V after 780 h and 1100 h were 337 mA cm<sup>-2</sup> and 343 mA cm<sup>-2</sup>, respectively. This result indicates that Pt/C MEA performance was maintained after 330 h in constant current operating. On the other hand, the current densities of the Pt<sub>1</sub>Ni<sub>1</sub>/C MEA at 0.6 V after 780 h and 1100 h were 287 mA cm<sup>-2</sup> and 217 mA cm<sup>-2</sup>, respectively, which implies that Pt<sub>1</sub>Ni<sub>1</sub>/C MEA performance was continuously decreased with time. In summary, the performance of the Pt/C MEA was maintained at a steady-state after an initial decrease at 330 h and was not declined any further with time. In contrast, the performance of the Pt<sub>1</sub>Ni<sub>1</sub>/C MEA declined continuously with time. The XRD patterns of the Pt/C and Pt<sub>1</sub>Ni<sub>1</sub>/C MEAs before and after the long-term operation test (1100 h) are shown in Fig. 2. Average Pt particle size after the test was 6.3 nm for the Pt/C MEA, and this value was larger than the 4.0 nm Pt particle size of the Pt/C MEA before testing. No peak related to Ni phases in Pt<sub>1</sub>Ni<sub>1</sub>/C catalyst can be observed from Fig. 2. Besides, the peak (220) position of the Pt/C MEA before testing was a  $2\theta$  of 67.57°, whereas that of the fresh Pt<sub>1</sub>Ni<sub>1</sub>/C MEA was a  $2\theta$  of 68.80°. Pt<sub>1</sub>Ni<sub>1</sub> before testing had a higher peak position compared to the Pt of Pt/C MEA, which means that Pt<sub>1</sub>Ni<sub>1</sub> was well alloyed. Because Ni atom is 11% smaller in size relative to Pt, the substitutional solid solution usually occurs. It is natural that the average size of Pt<sub>1</sub>Ni<sub>1</sub> alloy particles is smaller than that of pure Pt particles [13,14]. As shown in Fig. 2(b), the full width at half maximum (FWHM) of (220) peak for the fresh Pt<sub>1</sub>Ni<sub>1</sub>/C MEA was smaller compared to that of the fresh Pt/C MEA. However, in the case of the Pt<sub>1</sub>Ni<sub>1</sub>/C MEA after testing, the diffraction peak (220) position of Pt<sub>1</sub>Ni<sub>1</sub> shifted to  $2\theta$  of 67.96°. These results imply that Pt<sub>1</sub>Ni<sub>1</sub> alloy metal was dealloyed in the catalyst layer, which is supported by the fact that Pt<sub>1</sub>Ni<sub>1</sub>/C MEA performance was decreased by non-noble metal corrosion. Nevertheless, the average metal particle size of the Pt<sub>1</sub>Ni<sub>1</sub>/C MEA after testing was slightly increased. The extent of the size increase was only 1.0 nm, which was lower than the 2.3 nm increase for the Pt/C MEA cathode catalyst. These results demonstrate that Pt alloy particles have more resistance to the sintering of metal particles compared to pure Pt particles. Analogous result was published to be so called “the anchor effects of Ni to Pt on carbon supports” by Popov et al. [15]. Moreover, as shown in Fig. 3, severe

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