

Article

CO-Tolerant Pt–BeO as a Novel Anode Electrocatalyst in Proton Exchange Membrane Fuel Cells

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Abstract: Commercialization of proton exchange membrane fuel cells (PEMFCs) requires less expensive catalysts and higher operating voltage. Substantial anodic overvoltage with the usage of reformed hydrogen fuel can be minimized by using CO-tolerant anode catalysts. Carbon-supported Pt–BeO is manufactured so that Pt particles with an average diameter of 4 nm are distributed on a carbon support. XPS analysis shows that a peak value of the binding energy of Be matches that of BeO, and oxygen is bound with Be or carbon. The hydrogen oxidation current of the Pt–BeO catalyst is slightly higher than that of a Pt catalyst. CO stripping voltammetry shows that CO oxidation current peaks at ~0.85 V at Pt, whereas CO is oxidized around 0.75 V at Pt–BeO, which confirms that the desorption of CO is easier in the presence of BeO. Although the state-of-the-art PtRu anode catalyst is dominant as a CO-tolerant hydrogen oxidation catalyst, this study of Be-based CO-tolerant material can widen the choice of PEMFC anode catalyst.

Keywords: fuel cells; anode; beryllium oxide; hydrogen oxidation; CO tolerance

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are very promising technologies for various applications such as stationary and automotive power sources. A PEMFC anode is usually comprised of Pt-based catalysts, and hydrogen oxidation reaction (HOR) occurs on Pt particle surfaces. Because hydrogen for anode fuel is a practically reformed gas, CO inevitably exists in reformed hydrogen on the anode side and irreversibly adsorbs on the active sites of the Pt catalyst. The presence of CO in reformate gas is a major problem for the state-of-the-art PEMFC operating below 100 °C because a very small amount (about 10 ppm) of CO can poison the Pt catalyst [1,2]. For this reason, CO oxidation or CO tolerance of Pt has been an important scientific issue. The best CO-tolerant anode catalyst is generally known to be a PtRu alloy, and its CO oxidation behavior was well characterized [3]. The improved CO tolerance of PtRu is attributed to the bifunctional character of PtRu, which includes the ability of Ru atoms to provide nucleation sites for hydroxyl species at low potentials and the oxidation of CO migrating to these sites from either Pt or Ru sites nearby.

Meanwhile, other CO-tolerant materials based on metal alloys or metal oxides that can be coupled with Pt particles in a form of co-catalyst or support have been reported. Pt was alloyed with noble

metals such as Au [4] and Pd [5] or with Sn [6,7]. Oxides of noble metals such as RhO₂ [8] and RuO₂ [9] were also reported as having a CO-tolerant effect. Among transition metal oxides, WO_x [10–12] is one of frequently reported CO-tolerant materials along with MoO_x [13,14] and CeO_x [15,16]. Whether a co-catalyst or support for making a Pt catalyst CO-tolerant is alloying metal or metal oxide, the underlying mechanism for CO tolerance is usually adopted from the aforementioned bifunctional mechanism. Otherwise, a change in electronic state of Pt resulting from a coupling with RhO₂ [8] or a spillover effect of CeO₂ [15] is stated as the CO tolerance mechanism.

In this study, a novel CO-tolerant metal oxide, BeO, is introduced for use as HOR anode catalysts in PEMFCs. BeO is coupled with Pt particles on a carbon support, and the CO tolerance of Pt–BeO is investigated by using electrochemical techniques.

2. Results and Discussion

2.1. Physicochemical Properties of Carbon-Supported Pt–BeO

The morphology of carbon-supported Pt–BeO (Pt:Be mole ratio of 1:2.3) was investigated by TEM, as shown in Figure 1. Pt particles with an average diameter of 4 nm are distributed on a carbon support. Although the existence and amount of Be can be confirmed by either ICP or XPS, locating the position of BeO in the TEM image is not straightforward because the heat treatment temperature was not so high as to render BeO to a crystalline form, and it is assumed that amorphous BeO was formed on the carbon support. Indeed, although their system is not exactly the same as ours, Lim *et al.* [17] reported that amorphous Be-rich oxide layer becomes crystalline BeO in between 500 and 600 °C. In contrast, the morphology of Pt–BeO (1:11.5) was fairly different from that of Pt–BeO (1:2.3) in that Pt nanoparticles were hardly seen with merely the detection of amorphous layers (the inset in Figure 1 is a TEM image of Pt–BeO (1:11.5) on carbon support). For the purposes of comparison, we synthesized carbon-supported BeO without Pt to examine the morphology of BeO more easily. The morphology of Pt–BeO (1:11.5) was very similar to BeO on carbon support, and we understand that the amorphous nature of BeO can make it difficult to distinguish BeO particles from the underlying poorly-crystallized Ketjenblack.

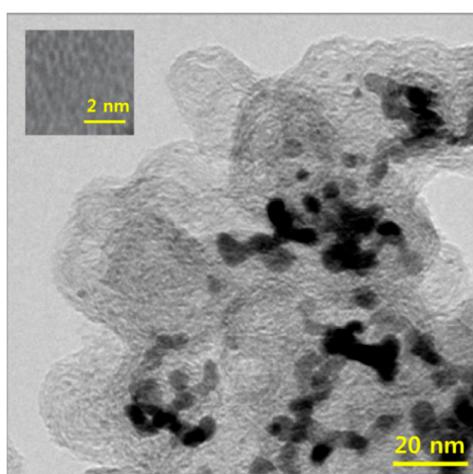


Figure 1. TEM image of carbon-supported Pt–BeO (the inset is the surface of Pt–BeO (1:11.5) on carbon support).

The XPS analysis in Figure 2 shows that a peak value of the binding energy of Be matches that of beryllium oxide, and oxygen can be bound with Be or carbon. This could indicate that Be exists as an oxide rather than forming an alloy with Pt.

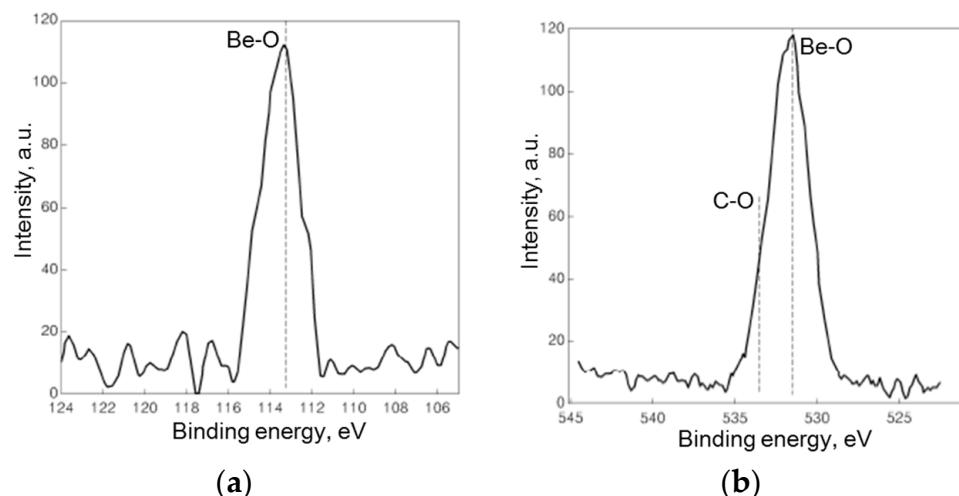


Figure 2. XPS spectra of Pt–BeO: (a) Be 2s and (b) O 2p.

2.2. Electrochemical Properties of Carbon-Supported Pt–BeO

Figure 3 is a linear sweep voltammetry result comparing the HOR activity of carbon-supported Pt and Pt-BeO with different BeO content (Pt-2.3BeO and Pt-11.5BeO). The HOR current of the Pt-2.3BeO catalyst is slightly higher than that of the Pt catalyst, indicating that the Pt-BeO catalyst can be used as an anode catalyst of PEMFCs. However, if an excessive amount of BeO is around Pt as in the case of Pt-11.5BeO, the HOR current is significantly reduced to an impractical level of HOR activity. This reduction in HOR activity can be attributed to a loss in electrochemical surface area (ESA) of Pt blocked by the excessive amount of BeO, as can be confirmed in Figure 4, where the ESA of Pt-11.5BeO is indeed negligible compared to that of Pt-2.3BeO. The BET specific surface area (SSA) and ESA of the catalysts are summarized in Table 1. Regarding the stability of an anode catalyst in a PEMFC environment, the catalyst stability at potentials close to 0 V vs. RHE is usually important considering anode operating potential ranges. However, the catalyst stability at potentials above 1 V would need to be confirmed in case of a potential reversal incident. The current level of both Pt-2.3BeO and Pt-11.5BeO at potentials between 0.05 V and 1.05 V in Figure 4 was maintained for the first 50 cycles, which could indicate the stable nature of BeO in the PEMFC environment.

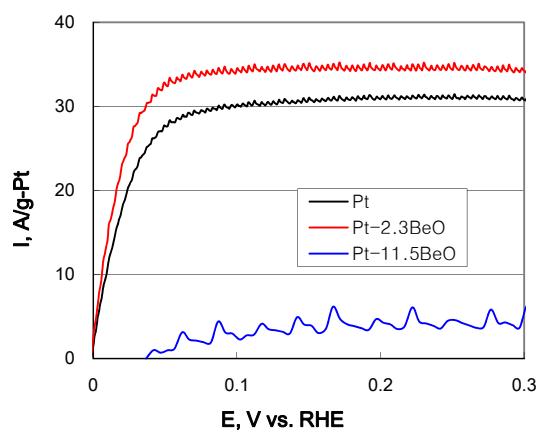


Figure 3. Linear sweep voltammogram of carbon-supported Pt and Pt–BeO.

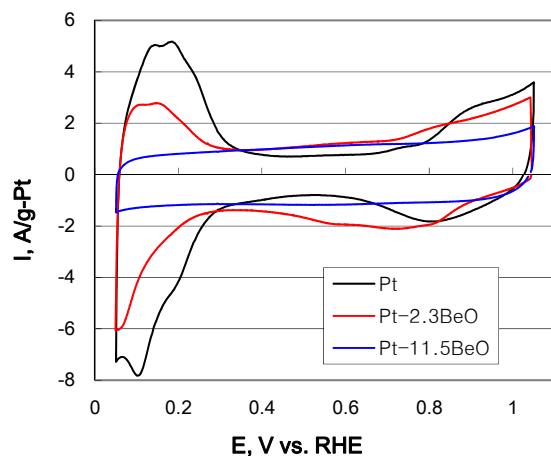


Figure 4. Cyclic voltammogram of carbon-supported Pt–BeO with different amounts of BeO.

Table 1. BET specific surface area and electrochemical surface area of Pt and Pt–BeO.

Catalyst	BET SSA (m^2/g)	ESA (m^2/g) ¹
Pt/C	180	91
Pt-2.3BeO/C	79	39
Pt-11.5BeO/C	74	0
PtRu/C ²	215	-

¹ ESA was estimated by using the theoretical electrical charge ($0.210 \text{ mC}/\text{cm}^2$) for monolayer desorption of hydrogen on Pt (anodic currents from 0.05 to $\sim 0.4 \text{ V}$ with the correction of a double-layer charging current were used); ² commercial PtRu/C from Tanaka Kikinzoku Kogyo.

Figure 5 is a CO stripping voltammetry result, which compares the CO tolerance of carbon-supported Pt, Pt-2.3BeO, Pt-11.5BeO, and PtRu. Initially adsorbed CO on the catalysts at 0.05 V is oxidized by increasing potential, and their oxidation peak or onset potentials are compared. First, Pt shows a peak oxidation potential around 0.85 V , which is a similar value to Schmidt *et al.* [18], and that of Pt-2.3BeO is $\sim 0.75 \text{ V}$, which is lower than the peak oxidation potential of Pt by 100 mV . However, Pt-11.5BeO with excessive BeO has no oxidation peak, which would indicate that there are no available Pt sites for CO adsorption, resulting in absent CO oxidation peaks. On the other hand, the oxidation peak potential of a commercial PtRu is measured to be 0.55 V , which is the most CO-tolerant among the samples. Although Pt–BeO is not so CO-tolerant as PtRu, it is evident that an addition of an optimum amount of BeO to Pt makes Pt–BeO CO-tolerant compared to Pt.

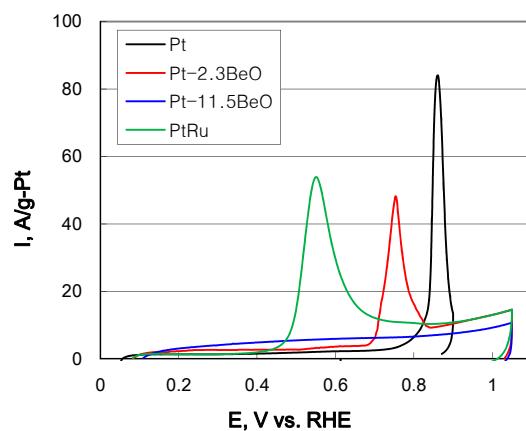


Figure 5. CO stripping voltammetry of carbon-supported Pt, Pt–BeO, and PtRu.

Meanwhile, while a significant amount of hydrogen can adsorb on Pt–BeO (as seen in the hydrogen oxidation current in Figure 3), the lower coverage of CO is simultaneously observed as deduced by the lower CO oxidation peak. This can be more significant than the shift of the oxidation potential as compared to Pt. The latter is not always related to the strength of the bond of CO with the Pt surface but also to the potential at which the oxidic species are formed on the surface. In fact, the lower CO coverage accompanied by the increase in hydrogen coverage can be a strong indication of the lower binding strength of CO on the Pt surface, which is affected by the BeO deposits. Kolla *et al.* [16] also pointed out that the direct removal of CO from the Pt surface dominates the sequential CO oxidation process, where hydroxyl species surface diffusion is involved when metal oxides are introduced to PtRu/C.

The origin of BeO-induced CO tolerance is not clear yet, but the following possibilities could be considered. First, the bifunctional mechanism could operate as in other CO-tolerant metal oxides such that the adsorption of hydroxyl species is enhanced on the BeO side, and CO on the Pt side is combined to CO_2 through surface diffusion. Another CO conversion scheme to formaldehyde in the presence of BeO has also been suggested [19]. Stoffelsma *et al.* [20] reported that CO oxidation at Pt is promoted in the presence of Be ions in alkaline solutions, which would be more or less related to the origin of BeO-induced CO tolerance in this study.

3. Materials and Methods

3.1. Preparation of Catalysts

In order to prepare the carbon-supported Pt–BeO catalyst in a Pt:Be mole ratio of 1:2.3, 1 g of Ketjenblack carbon support and a Be precursor solution where 0.443 g of BeCl_2 was dissolved in 2 mL of water/acetone mixture (volume ratio = 1:1) were first mixed in a vinyl bag. After the mixture was dried at room temperature for 5 h, a Pt precursor solution (1.131 g of H_2PtCl_6 in 3 mL of acetone) was added to the dried mixture. The composition of carbon-supported Pt-2.3BeO on a wt. % basis was 24.8 wt. % Pt, 9.1 wt. % BeO, and 66.1 wt. % C. After the resulting mixture was dried at 60 °C overnight, the mixture was reduced under hydrogen atmosphere with increasing temperature to 200 °C and subsequently maintaining for 2 h at that temperature. The reduced sample was finally heat-treated to 250 °C and maintained for 5 h in a nitrogen atmosphere. The carbon-supported Pt–BeO catalyst in a Pt:Be mole ratio of 1:11.5 was synthesized similar to Pt-2.3BeO, except the different amount of Be precursor. The composition of carbon-supported Pt-11.5BeO on a wt. % basis was 18.1 wt. % Pt, 33.5 wt. % BeO, and 48.4 wt. % C. Additionally, carbon-supported BeO particles without Pt were prepared for the morphological characterization of BeO. Carbon-supported PtRu (atomic ratio = 3:2) was purchased from Tanaka Kikinzoku Kogyo.

3.2. Electrochemical and Physicochemical Characterization

Catalysts were fabricated into a thin-film rotating disk electrode (RDE) on a glass carbon substrate. Electrochemical characterizations such as cyclic voltammetry, linear sweep voltammetry, and CO stripping voltammetry were performed at room temperature using a three-electrode system with a Pt foil counter electrode, a Ag/AgCl reference electrode, and a 0.1 M HClO_4 solution as an electrolyte. HOR activity was evaluated by linear sweep voltammetry, where potential was increased from an open-circuit voltage in the hydrogen-saturated electrolyte at a scan rate of 5 mV/s and a rotation of 900 rpm. Cyclic voltammetry was conducted in the nitrogen-saturated electrolyte. The CO tolerance of catalysts was evaluated by CO stripping voltammetry, where potential was increased to detect CO stripping oxidation currents after CO was first adsorbed on the catalysts at 0.05 V in the CO-saturated electrolyte. Currents were normalized based on the Pt content in catalysts and expressed in ampere per gram of Pt, and potential was displayed *vs.* reversible hydrogen electrode (RHE). Details on thin-film RDE electrode fabrication and the RDE evaluation of HOR activity and CO tolerance can be found elsewhere [18,21,22]. The amounts of Pt and Be were confirmed by ICP (ICAP 6500), and the

morphology, oxidation state, and alloying degree of samples were analyzed by TEM, XPS, and XRD respectively. TEM used a JEOL JEM-2100F microscope at an accelerating voltage of 200 kV. XPS spectra were recorded with a monochromatic Al K α X-ray source using a Thermo Fisher K-Alpha instrument. XRD patterns of samples were taken with a Rigaku D/Max 2500 V/PC X-ray diffractometer equipped with a Cu K α source at 40 kV and 200 mA.

4. Conclusions

CO-tolerant HOR catalysts are essential in securing the price competitiveness of PEMFCs, where reformed hydrogen fuel is practically adopted. In addition to some known CO-tolerant materials based on alloying metals or metal oxides that can be coupled with Pt in the form of a co-catalyst or support, amorphous BeO is here suggested. CO desorption at Pt–BeO initiates at a potential that is lower than Pt by 100 mV, but an addition of excessive BeO to Pt can reduce the electrochemical surface area of Pt. Thus, the composition optimization of BeO with respect to Pt for the maximization of CO tolerance will soon be under way.

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Abbreviations

The following abbreviations are used in this manuscript:

PEMFC	Proton exchange membrane fuel cell
HOR	Hydrogen oxidation reduction
RDE	Rotating disk electrode
RHE	Reversible hydrogen electrode

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