RuO2 Nanosheet Modified Pt3Co/C Cathode: Mitigating Activity Loss at High Temperature and High Potential Conditions

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Pt3Co/C is known as an active catalyst for the oxygen reduction reaction (ORR). The stability of this catalyst under high temperature and potential conditions is a concern for practical application in fuel cell systems. In this study, we have pursued the possibility of improving the performance of Pt3Co/C under such severe conditions by the addition of ruthenium oxide nanosheets. The initial mass activity of RuO2 nanosheets modified Pt3Co/C was higher compared to that of pristine Pt3Co/C. The improved mass activity is attributed to the increase in accessible active sites for ORR for the composite catalyst. The mass activity after accelerated durability test by potential step cycling between 0.6 and 1.2 V vs. RHE at 60 °C for RuO2-RuO2-Pt3Co/C was 243 A (g-Pt)−1, which is 1.9 times higher than non-modified Pt3Co/C (127 A (g-Pt)−1). Transmission electron microscopy analysis and energy dispersive X-ray spectroscopy of the catalyst after durability test showed that the particle growth and dissolution of cobalt was inhibited by the addition of RuO2 nanosheets.

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Manuscript received September 10, 2015. Published October 31, 2015.

Platinum-cobalt alloy nanoparticles supported on carbon (PtCo/C) shows high oxygen reduction reaction (ORR) activity, and is used as a practical catalyst in polymer electrolyte fuel cells for both residential and vehicle applications.1–4 Surface cobalt atoms of the PtCo alloy easily dissolve in hot acid solution, forming a Pt skeleton layer enriched with Pt, which is then either thermally5 or electrochemically treated6,7 to stabilize an active Pt skin surface layer. Such catalysts have higher ORR activity than Pt alone,8–10 owing in part to the modification of the electronic state of Pt by the alloying with cobalt. The ORR activity and durability of PtCo alloy are affected by various parameters including the surface structure,11–14 the atomic ratio of platinum and cobalt,15–19 as well as the nanoparticle size,20,21 which have been finely optimized to give maximum performance.

Despite these tremendous efforts, binary catalysts still suffer from durability issues. Although cobalt dissolution is protected by the Pt-skin layer,22–27 studies have underlined that dissolution of cobalt from PtCo core is accelerated at high temperature leading to severe loss in ORR performance.28–31 The stability of electrocatalyst under high load or high potential conditions is also problematical as a result of dissolution of both Pt and Co.29–32 In the case of PtCo alloy catalysts, once the protective Pt skin layer is lost, severe de-alloying of cobalt eventually leads to a thick Pt layer that has activity comparable to pure platinum.16,28–32 Based on these studies, electrocatalyst degradation under high temperature and severe potential cycling conditions may be one of the few problems associated with using PtCo alloys as an ORR catalyst in practical systems.

Many approaches have been proposed to mitigate electrocatalyst degradation, with one of the most well-studied methods being the addition of metal oxide to Pt/C. Oxide additives such as TiO2,33,34 SiO2,35,36 CeO2,37–39 and WO3,40 have been shown to inhibit particle growth and/or dissolution of the catalyst. For example, TiO2-Pt/C exhibited higher durability compared to Pt/C, which was attributed to the suppression of the aggregation of Pt nanoparticles.35,38 Similarly, particle growth and sintering of Pt nanoparticles was suppressed for Pt-CeO2/C composite catalyst.39–41 Although these are effective co-catalysts, one must take into consideration that the co-catalysts are poor electronic conductors and care must be taken so that the oxide additive does not cover or block the metal surface, which would result in loss of accessible surface area.

We have reported that the catalytic performance of Pt/C could be improved by the addition of RuO2 nanosheets.38–40 RuO2 nanosheets are 1 nm thick nanosheets derived by exfoliation of layered H2RuO4, nH2O, and is high electronically conductive and stable.41,42 Owing to the water-swelling property of RuO2 nanosheets, access of electrolyte to the Pt surface should not be disturbed in the presence of water. An increase in initial ORR activity and enhancement in long term performance was observed by the addition of RuO2 nanosheets to Pt/C18–40. Here, we extend our studies on the use of RuO2 nanosheets as a co-catalyst to the Pt3Co/C alloy system. We anticipate that this will allow us to take advantage of both the high ORR activity of Pt3Co alloy, and the durability/activity enhancing effect of RuO2 nanosheets to overcome the durability issue of Pt3Co/C under high temperature and high potential conditions. It should be noted that although much effort has been placed on increasing the performance of Pt/C with oxide additives, studies on oxide-PtCo composites are scarce. To the best of the authors knowledge, only one study has been reported, namely the CeO2-PtCo/C system, which exhibited enhanced activity.43 The durability of this catalyst was unfortunately not described. In this study, emphasis is placed on increasing the durability of Pt3Co/C at high temperature and high potential conditions. The ORR activity of RuO2 nanosheet modified Pt3Co/C (RuO2-nS-Pt3Co/C) after accelerated durability tests at three different potential windows (0.6–1.0, 0.6–1.1, 0.6–1.2 V vs. RHE) was investigated at 60 °C. We will show that the composite catalyst exhibited improved performance in terms of both initial ORR activity and stability especially at high potential regions.

Experimental

Pt/C (TEC10150E, 47 mass% Pt) and Pt3Co/C (TEC36E52, 52 mass% Pt3Co) were purchased from Tanaka Kikinzoku Kogyo K.K.. Pt3Co/C was used after acid-treatment with 0.1 M HClO4 (60 °C) for 12 hours to remove excess cobalt. The composite catalyst was synthesized following our previous recipe for RuO2 nanosheet modified Pt/C.38–40 RuO2 nanosheets were derived via exfoliation of layered H2RuO4, nH2O as reported previously.41,42 Briefly, 0.1 g of layered H2RuO4, nH2O was added to an aqueous solution of 10% tetrabutylammonium hydroxide (TBA+OH−), adjusted to a solid-liquid ratio of 4 g L−1 (TBA+ /H+ = 1.5). The mixed solution was shaken for 10 days and then centrifuged to remove any non-exfoliated material at 2000 rpm. RuO2 nanosheet colloidal was then mixed with a suspension of commercial Pt3Co/C catalyst to prepare the composite catalyst. In a typical synthesis, the RuO2 nanosheet colloidal, diluted to 1 g–RuO2 L−1, was added to an aqueous Pt3Co/C suspension with a molar ratio of RuO2/Pt/Co = 0.3/1/0.3 (9.0 mass% RuO2, 42.8 mass% Pt, 4.5 mass% Co). The dispersion was magnetically stirred and
ultrasonified to ensure homogenous reaction. After sedimentation, the composite was washed with water and dried at 120 °C to yield the RuO2ns-Pt3Co/C catalyst. The catalyst morphology was characterized by transmission electron microscopy (TEM, JEOL 2010) operated at an accelerating voltage of 200 kV. Particle size distribution was determined from at least 10 randomly chosen typical TEM images (total of 200 to 300 particles). The atomic ratio (Pt/Co) in the catalysts was estimated from energy dispersive X-ray spectroscopy (EDX, Horiba EX-200) operated at an accelerating voltage of 20 kV.

Electrochemical measurements were conducted with a rotating disk electrode (Nikon Keisoku). Pt/C and RuO2ns-Pt3Co/C catalyst suspensions were prepared by dispersing 18.5 mg of catalyst in 25 mL of 2-propanol/water solution (75/25 volume ratio). A 5 wt% Nafion solution (100 μL) was added to the catalyst suspension as a proton conducting binder to ensure adhesion. The working electrode was prepared by depositing 17.3 μg Pt cm−2 on a mirror-polished glassy carbon rod (6 mm diameter) and vacuum dried at 60 °C for 30 min. A carbon fiber (Toho Tenax Co., HTA40 E13 3K 200tex) was used as a counter electrode, and a reversible hydrogen electrode (RHE) was used as a reference electrode. Initial break-in cycles were conducted in de-aerated 0.5 M H2SO4 (25 °C) at 50 mV s−1 for 70 cycles between 0.05 and 1.2 V vs. RHE to electrochemically stabilize the active Pt skin surface layer. The electrochemically active surface area (ECSA) was estimated from the hydrogen adsorption charge, excluding the hydrogen evolution area, and the Coulombic charge necessary for oxidation on polycrystalline Pt as 210 μC cm−2. Linear sweep voltammetry was measured in O2-saturated 0.5 M H2SO4 at rotation rates of ω = 2500, 2200, 1600, 1200, 800, and 400 rpm. Background subtraction was conducted by subtracting the linear sweep voltammograms collected under de-aerated conditions (N2 gas) at the respective rotation rates from the voltammograms taken in O2-saturated 0.5 M H2SO4. The potential was swept at 10 mV s−1 from 0.05 to 1.2 V vs. RHE. Oxygen reduction reaction (ORR) activity was obtained by extrapolation of Koutecky-Levich plots at 0.85 V vs. RHE to ω = ∞, which gives the kinetically controlled current. Mass activity will be reported as the kinetically controlled current at 0.85 V vs. RHE divided by the mass of Pt. Three different Accelerated durability test (ADT) conditions were applied to elucidate the impact of stepping to high potentials. After accumulation of initial ORR activity, the potential was stepped between 0.6 and 1.0 V vs. RHE (3 s hold each) at 25 or 60 °C for 2000 cycles (ω = 0). For the second protocol, 2000 cycles were applied between 0.6 and 1.1 V vs. RHE. The upper potential limit was increased to 1.2 V vs. RHE for the third protocol. The three durability test protocols will be abbreviated as ADT(0.6–1.0), ADT(0.6–1.1) and ADT(0.6–1.2). The reported initial ORR activity values are averaged from 3 individual runs. The ORR activity after ADT(0.6–1.0), ADT(0.6–1.1) and ADT(0.6–1.2) are averaged from two measurements for each ADT condition. All water used was ultrapure grade (Milli-Q, > 18 MΩ cm).

Results and Discussion

ORR activity of fresh Pt3Co/C and RuO2ns-Pt3Co/C catalyst.—Figure 1 shows typical TEM images of Pt3Co/C and RuO2ns-Pt3Co/C. The RuO2 nanosheets have lateral dimension of a few hundred nanometers in size with ∼1.0 nm thickness. The corresponding particle size distribution is also shown. The average diameter for Pt3Co/C and RuO2ns-Pt3Co/C were 4.2±0.7 nm and 4.2±0.8 nm, respectively. The addition of RuO2 nanosheets has no negative impact on the Pt3Co particle size distribution, in other words, aggregation of Pt3Co nanoparticles is negligible.

The ECSA of fresh RuO2ns-Pt3Co/C was 47 m2 (g-Pt)−1, which is comparable or slightly higher than pristine Pt3Co/C (43 m2 (g-Pt)−1) (Table I). The mass activity of the catalysts increased with increasing temperature, as shown in Figure 2. This is attributed to an increase in ORR kinetics with increasing temperature, agreeing well with previous reports.12,16,28 The mass activity of RuO2ns-Pt3Co/C is comparable or slightly higher than pristine Pt3Co/C (43 m2 (g-Pt)−1) (Table I). The mass activity of RuO2ns-Pt3Co/C was higher than Pt3Co/C for all temperatures studied (Table II). The enhancement effect was more pronounced at higher temperatures; the

| Catalyst          | ADT Condition | ECSA/m2 (g-Pt)−1 | Mass activity/A (g-Pt)−1 |
|-------------------|---------------|------------------|-------------------------|
|                   |               | initial | after ADT | initial | after ADT |
| Pt/C              | 0.6–1.0 V     | 80 ± 6  | 59 ± 6 (74%) | 285 ± 22 | 235 ± 12 (82%) |
|                   | 0.6–1.1 V     | 48 ± 6 (60%) | 35 ± 6 (44%) | 179 ± 11 (63%) | 123 ± 13 (43%) |
|                   | 0.6–1.2 V     | 16 ± 5 (25%) | 12 ± 5 (18%) | 127 ± 6 (33%) |
| Pt3Co/C           | 0.6–1.0 V     | 43 ± 4  | 36 ± 3 (84%) | 385 ± 36 | 315 ± 8 (82%) |
|                   | 0.6–1.1 V     | 25 ± 2 (58%) | 18 ± 5 (32%) | 238 ± 10 (62%) |
|                   | 0.6–1.2 V     | 18 ± 5 (32%) | 12 ± 6 (33%) | 243 ± 22 (52%) |
| RuO2ns-Pt3Co/C    | 0.6–1.0 V     | 47 ± 2  | 44 ± 2 (94%) | 467 ± 39 | 422 ± 10 (90%) |
|                   | 0.6–1.1 V     | 39 ± 3 (83%) | 35 ± 7 (76%) | 357 ± 9 (76%) |
|                   | 0.6–1.2 V     | 33 ± 4 (70%) | 32 ± 5 (66%) | 243 ± 22 (52%) |

*Retention rates with respect to the initial mass activity of the corresponding catalyst are shown in parentheses.
clear at the moment, but the addition of conducting RuO2 nanosheets (Fig. 3). The reason for the increase in ORR accessible sites is not catalyst. may have a positive impact on the overall conductivity of the times higher than that of Pt3Co/C (385 A (g-Pt)−1) and ADT (0.6–1.0) for Pt3Co/C was 36 and 20 m2 (g-Pt)−1, respectively. The ECSA after ADT (0.6–1.0) and ADT (0.6–1.2) for RuO2ns-Pt3Co/C was 44 and 33 m2 (g-Pt)−1, respectively. The ECSA of RuO2ns-Pt3Co/C after both ADT protocols was higher than that of Pt3Co/C, suggesting that the addition of RuO2 nanosheets contributes to the enhancement in catalyst durability.

The mass activity of RuO2ns-Pt3Co/C after all ADT protocols was higher than that of Pt/C and Pt3Co/C, agreeing with the trend in ECSA retention. The degradation of the catalyst is accelerated by the high potential durability conditions; the mass activity after ADT (0.6–1.2) for all catalysts were lower than after ADT (0.6–1.0) (Fig. 5). Although, the mass activity of Pt3Co/C after ADT (0.6–1.0) and ADT (0.6–1.1) was higher than that of Pt/C, the superiority becomes less evident for Pt3Co/C at a high potential durability condition (ADT (0.6–1.2)). As shown in Fig. 5 and Table I, this drawback is mitigated by the addition of RuO2 nanosheets. The mass activity after ADT (0.6–1.2) for RuO2ns-Pt3Co/C was 243 A (g-Pt)−1, which is 1.9 times higher than that of Pt3Co/C. As shown in Figure 6, the addition of RuO2 nanosheets is particularly effective for enhancing the performance at high temperature. The results show that the addition of RuO2 nanosheets is especially effective to improve the catalyst durability under high potential conditions and high temperatures.

### Table II. ORR mass activity in 0.5 M H2SO4 at various temperatures before and after ADT for Pt/C, Pt3Co/C and RuO2ns-Pt3Co/C.

| Catalyst          | 25°C | 35°C | 45°C | 60°C | 25°C | 35°C | 45°C | 60°C |
|-------------------|------|------|------|------|------|------|------|------|
| Pt/C              | 205  | 264  | 328  | 285  | 135  | 180  | 167  | 123  |
| Pt3Co/C           | 238  | 309  | 381  | 385  | 164  | 224  | 258  | 127  |
| RuO2ns-Pt3Co/C    | 262  | 331  | 440  | 467  | 197  | 243  | 338  | 243  |

mass activity at 60°C for RuO2ns-Pt3Co/C was 467 A (g-Pt)−1, 1.2 times higher than that of Pt3Co/C (385 A (g-Pt)−1) and 1.6 times higher than that of Pt/C (285 A (g-Pt)−1). The higher mass activity of RuO2ns-Pt3Co/C may be interpreted as an increase in accessible sites for ORR compared to pristine Pt3Co/C. This is also supported by the fact that the limiting current for ORR in the linear sweep voltammograms was higher for RuO2ns-Pt3Co/C compared to Pt3Co/C at 60°C (Fig. 3). The reason for the increase in ORR accessible sites is not clear at the moment, but the addition of conducting RuO2 nanosheets may have a positive impact on the overall conductivity of the catalyst.

**ORR activity of RuO2ns-Pt3Co/C after accelerated durability tests under different potential windows.—** The durability of the catalysts was evaluated by potential step cycling tests with different potential windows (0.6–1.0, 0.6–1.1, and 0.6–1.2 V vs RHE) at 60°C. The retention in ECSA and mass activity of Pt3Co/C after the three different ADT protocols decrease with the increase in the upper potential limit (Table I). The durability of Pt3Co/C is higher than Pt/C which is evident from the slower loss of ECSA for Pt3Co/C compared to Pt/C (Fig. 4a). The decrease in ECSA was further retarded for RuO2ns-Pt3Co/C (Fig. 4b). The ECSA after ADT (0.6–1.0) and ADT (0.6–1.2) for Pt3Co/C was 36 and 20 m2 (g-Pt)−1, respectively. The ECSA after ADT (0.6–1.0) and ADT (0.6–1.2) for RuO2ns-Pt3Co/C was 44 and 33 m2 (g-Pt)−1, respectively. The ECSA of RuO2ns-Pt3Co/C after both ADT protocols was higher than that of Pt3Co/C, suggesting that the addition of RuO2 nanosheets contributes to the enhancement in catalyst durability.

The mass activity of RuO2ns-Pt3Co/C after all ADT protocols was higher than that of Pt/C and Pt3Co/C, agreeing with the trend in ECSA retention. The degradation of the catalyst is accelerated by the high potential durability conditions; the mass activity after ADT (0.6–1.2) for all catalysts were lower than after ADT (0.6–1.0) (Fig. 5). Although, the mass activity of Pt3Co/C after ADT (0.6–1.0) and ADT (0.6–1.1) was higher than that of Pt/C, the superiority becomes less evident for Pt3Co/C at a high potential durability condition (ADT (0.6–1.2)). As shown in Fig. 5 and Table I, this drawback is mitigated by the addition of RuO2 nanosheets. The mass activity after ADT (0.6–1.2) for RuO2ns-Pt3Co/C was 243 A (g-Pt)−1, which is 1.9 times higher than that of Pt3Co/C. As shown in Figure 6, the addition of RuO2 nanosheets is particularly effective for enhancing the performance at high temperature. The results show that the addition of RuO2 nanosheets is especially effective to improve the catalyst durability under high potential conditions and high temperatures.
After ADT (0.6–1.2), the metal ratio for Pt3Co/C was Pt/Co = 5.9 ± 1.4 nm, whereas it was 4.6 ± 1.3 nm for RuO2ns-Pt3Co/C. Pt3Co/C composite catalyst is strongly correlated to the retention in particle size and Pt/Co composition. RuO2 nanosheets is effective to inhibit cobalt dissolution from catalyst. From TEM and EDX analysis, the enhancement in durability of RuO2ns-Pt3Co/C can be explained by the inhibition of particle size growth and Co dissolution. The better durability of the RuO2ns-Pt3Co/C composite catalyst is strongly correlated to the retention in the particle size and Pt/Co composition. RuO2 nanosheet model electrode studies have shown that there are chemical interactions with the RuO2 nanosheets and Pt0 ions as well as metallic Pt. Assuming a similar mechanism for the RuO2ns-Pt3Co/C system, the enhancement in durability for Pt3Co/C can be attributed to the suppression of the diffusion of dissolved ions from the catalyst and a strong metal support interaction. Finally, it should be noted that the initial activity of RuO2ns-Pt3Co/C is 1.6 times higher than a typical Pt/C catalyst. Moreover, the higher retention of mass activity is obtained for all ADT conditions, which leads to a 2 times higher ORR activity of RuO2ns-Pt3Co/C compared to Pt/C after different ADTs.

Conclusions

The durability of Pt3Co/C at high temperature and high potential condition was successfully improved by the addition of RuO2 nanosheets. The initial mass activity of Pt3Co/C at various temperatures between 25 and 60°C were improved by the addition of RuO2 nanosheets. The enhancement effect was more pronounced at higher temperatures. The catalyst durability was evaluated by potential cycling at 60°C with three different potential windows 0.6–1.0, 0.6–1.1, and 0.6–1.2 V vs. RHE. The mass activity of RuO2ns-Pt3Co/C was 1.9 times higher than Pt3Co/C after the potential cycling tests. Based on the TEM analysis, the increase in particle size was suppressed by the addition of RuO2 nanosheets. Additionally, the modification with RuO2 nanosheets also inhibited cobalt dissolution, which should also contribute to the enhanced durability. Based on our results on the impact of the lateral size of nanosheets to the ORR activity and influence of the nanosheet content, further enhancement in catalyst performance may be anticipated by optimization of catalyst structure and composition.

Acknowledgment

This work was supported in part by the “Polymer Electrolyte Fuel Cell Program” from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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Figure 6. The ORR activity of (circles) Pt/C, (squares) Pt3Co/C, and (triangles) RuO2ns-Pt3Co/C after ADT(0.6–1.2) (refer to text for detailed measurement conditions).

Figure 7. Typical TEM images and corresponding Pt3Co particle size histograms for (a−c) Pt3Co/C and (d−f) RuO2ns-Pt3Co/C after ADT(0.6–1.2).
