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Research and Development of Highly Active and Durable Electrocatalysts Based on Multilateral Analyses of Fuel Cell Reactions

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ABSTRACT

In order to establish clear strategies for the design of electrocatalysts with high activity and high durability, fuel cell reactions have been analyzed by multilateral techniques. The use of monodisperse Pt or Pt-alloy nanocatalysts with uniform composition, which were highly dispersed over the whole surface of the carbon support by the nanocapsule method, contributed greatly in clarifying the effects of various properties (particle size, composition, and surface structure, etc.) towards the activity and durability for the anode and cathode in polymer electrolyte fuel cells (PEFCs). New catalyst layers have been developed in order to make the electrocatalysts work effectively specifically under low humidity. Several important concepts have been demonstrated for developing high-performance oxygen and hydrogen electrodes with high durability for a reversible solid oxide cell (R-SOC), which is expected to be a reciprocal direct energy converter between hydrogen and electricity with high efficiency.

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1. Introduction

Fuel cells convert chemical energy into electricity via electrochemical reactions with high efficiency and minimal emission of pollutants. Polymer electrolyte fuel cells (PEFCs) have been developed specifically for applications such as fuel cell vehicles (FCVs) and residential co-generation systems. Solid oxide fuel cells (SOFCs), which have been developed mainly for highly efficient stationary power generation, can be operated in the reverse mode [solid oxide electrolysis cell (SOEC)] to generate hydrogen via water vapor electrolysis, i.e., a reversible solid oxide cell (R-SOC).

In order to promote their large-scale commercialization toward a hydrogen-based society, it is crucial to reduce the system cost while maintaining high performance and durability. A single cell consists of an electrolyte (polymer electrolyte membrane, PEM, such as Nafion in the PEFC or a solid oxide electrolyte such as yttria-stabilized zirconia, YSZ, in the SOFC) sandwiched between two electrodes or electrocatalyst layers (usually denoted as catalyst layers, CLs). One of the most important subjects to be pursued is the further improvement of the activity and durability of the electrocatalysts, because the overpotential predominantly reduces the efficiency of fuel cells. However, as described below, clear strategies for the design of the electrocatalyst itself and its effective utilization in the CL have not been established yet.

We have engaged in the research and development (R & D) of electrocatalysts with respect to fundamentals and applications, intending to demonstrate new design concepts for realizing high activity together with high durability.^{1–4} For PEFC anode and cathode catalysts, the activity and its degradation have been analyzed by multilateral techniques such as X-ray photoelectron spectroscopy combined with an electrochemical cell (EC-XPS),^{2,5–8} in situ Fourier-transform infrared spectroscopy (FTIR),^{9–22} electrochemical quartz crystal microbalance (EQCM),^{23–26} in situ scanning tunneling microscopy (STM),^{27–31} in addition to conventional electrochemical measurements such as rotating disk electrode (RDE),^{32–34} channel flow electrode (CFE),^{21,35,36} and channel flow double electrode

(CFDE) methods.^{37–42} Based on these results, new practical catalysts have been synthesized.^{43–55} New catalyst layers or membrane-electrode-assemblies (MEAs) have been developed in order to make the electrocatalysts work effectively under widely varying operating conditions of relative humidity (RH) and temperature.^{56–72} Changes in the distribution of the specific resistance in the PEM and oxygen partial pressure at the CL/PEM interface during operation,^{73–75} as well as the degradation mechanism of the MEAs,^{59,63,64,76,77} were also analyzed to feedback information to the syntheses of PEMs and catalysts. For the R-SOC, high-performance, high-durability electrodes with novel architecture have been developed, while clarifying clues for the further improvement of activity and durability.^{78–100}

In the present comprehensive paper, these recent research works are reviewed.

2. PEFC Cathode Catalysts

Costly Pt and its alloys have been used as the cathode catalyst, having appreciable activity and durability under strongly acidic conditions (in contact with the polymer electrolyte binder) at low operating temperatures < 100°C. A sluggish oxygen reduction reaction (ORR) causes a large overpotential, even at the Pt cathode.

Hence, worldwide R & D has been focused on reducing the mass of Pt used in the cathode, for reasons of cost and supply limitation, while maintaining the durability.

The mass activity MA of Pt-based catalysts is the product of the area-specific activity j_s and the electrochemically active surface area ECA :

$$MA \text{ (A g}_{\text{Pt}}^{-1}) = j_s \text{ (A m}_{\text{Pt}}^{-2}) \times ECA \text{ (m}^2 \text{ g}_{\text{Pt}}^{-1}) \quad (2)$$

To increase the value of j_s (current density per ECA), Pt alloys (Pt-Fe, Pt-Co, and Pt-Ni) have been examined.^{101–103} Because the ECA value is inversely proportional to the diameter for spherical catalyst particles, it is an effective strategy for enlarging ECA to

disperse Pt or Pt-alloy nanoparticles (NPs) on high-surface-area supports such as carbon black (CB). However, for developing cathode catalysts having both high MA for the ORR and high durability, there has been long-standing controversy surrounding essential issues such as the types of alloys, the chemical composition, their optimum particle size, as well as the mechanism of enhancement of j_s at Pt-alloys. In the next two Sections, such important factors are demonstrated. All of the potentials in Chapters 2 and 3 will be referred to the reversible hydrogen electrode (RHE).

2.1 Effect of particle size and uniform dispersion on the activity and durability of Pt nanoparticles supported on carbon

The first issue is the particle-size effect of Pt NPs on j_s . It has been reported that the j_s values for the ORR decrease with decreasing average diameter d_{Pt} .^{104–106} For example, Gasteiger et al. have reported a strong particle-size effect on the kinetically-controlled j_s (denoted as j_k) on commercial c-Pt/CB catalysts for d_{Pt} ranging from 2 nm to bulk-Pt in O_2 -saturated 0.1 M $HClO_4$ by the use of the RDE technique only at 60°C, but the dependence of j_k on d_{Pt} was fairly small between 3 and 8 nm.¹⁰⁶ They evaluated j_k at 0.9 V from the hydrodynamic voltammograms measured with a sweep rate of 20 mV s⁻¹ to avoid electrode contamination by impurities in the electrolyte solution, although they recognized that the coverage of oxygen species (O_{ad} and OH_{ad}) cannot stabilize at such a high sweep rate, showing a large hysteresis between the positive-going and negative-going scans.

Then, in order to evaluate the steady-state j_k and H_2O_2 yield produced via the two-electron reduction of O_2 , $P(H_2O_2)$, of various Pt/CB catalysts (d_{Pt} = 1.6, 2.6, and 4.8 nm) and bulk-Pt in the practical temperature range of PEFCs (30 to 110°C), we measured hydrodynamic voltammograms by using a CFDE cell at a slow sweep rate (0.5 mV s⁻¹).⁴⁰ The use of 0.1 M $HClO_4$ electrolyte solution, which was purified in advance by a conventional pre-electrolysis method,^{107,108} allowed us to obtain steady-state ORR voltammograms with neither hysteresis nor interference by impurities at such a low sweep rate. Moreover, Pt/CB was uniformly dispersed on a gold substrate electrode at a constant loading of CB support, 5.5 $\mu\text{g cm}^{-2}$ (corresponding to approximately one monolayer of CB particles) and coated with a thin Nafion film (0.1 μm), in order to minimize the O_2 diffusion resistance within the thin catalyst layer.³⁹ We have demonstrated that the ORR rate constant (k_{app} , per unit ECA), its activation energy, and $P(H_2O_2)$ in O_2 -saturated 0.1 M $HClO_4$ were all independent of d_{Pt} from Pt_{1.6nm}/CB to bulk-Pt at 30 to 50°C, as well as from Pt_{2.6nm}/CB to bulk-Pt up to 110°C.⁴⁰

It was also found that the smallest (Pt_{1.6nm}) particles agglomerated at higher temperatures ($\geq 60^\circ\text{C}$). This result led our research to the second important issue regarding the Pt particle-size effect on the durability. A common view is that, the smaller the Pt particles are, the less durable they are with respect to load-cycling.^{109,110} It has been also noted that pristine Pt/CB catalysts prepared by conventional methods usually showed a broad distribution of sizes (standard deviation $\sigma_d \geq 20\%$). Considering the Ostwald ripening mechanism,¹¹¹ in which smaller particles predominantly dissolve and the resulting Pt^{n+} ions redeposit onto larger particles, it is necessary to examine the particle-size effect on the durability toward load-cycling by the use of Pt/CB catalysts with uniform Pt size.

Therefore, with an identical heat-treatment by the nanocapsule method,^{43,45} three kinds of catalysts (n-Pt/CB, d_{Pt} = 2, 3, and 4 nm, specific surface area of CB = 800 m²/g) were prepared with a very narrow σ_d (ca. 10%).⁴² Figure 1 shows changes in the MA_k and j_k at 0.85 V and 65°C on the n-Pt/CB and a standard c-Pt_{2nm}/CB (σ_d = 20%) in 0.1 M $HClO_4$ as a function of the number of potential-step cycles N during an accelerated durability test (ADT), according to a protocol recommended by the Fuel Cell Commercialization Conference of Japan (FCCJ).¹¹² At N = 0 (the beginning of testing,

Figure 1. (Color online) Changes in (a) kinetically-controlled area-specific activity, j_k , and (b) kinetically-controlled mass activity, MA_k at Nafion-coated n-Pt_{2nm}/CB (●), n-Pt_{3nm}/CB (▲), n-Pt_{4nm}/CB (■), and c-Pt_{2nm}/CB (▼) electrodes as a function of the number of potential step cycles, N . The values of j_k and MA_k were evaluated at 0.85 V vs. RHE in O_2 -saturated 0.1 M $HClO_4$ at 65°C. The ADT was performed in N_2 -saturated 0.1 M $HClO_4$ at 65°C according to the FCCJ protocol.¹¹² Reproduced from Ref. 42 with permission of Elsevier Ltd.

BOT), all catalysts exhibited the identical value of j_k , and the MA_k was proportional to the ECA (inversely proportional to d_{Pt}). With increasing N , the MA_k values of all catalysts decreased due to the reduction of the ECA , as a result of particle growth, but the j_k values were nearly unchanged, irrespective of such particle growth. After 30,000 cycles, at which each MA_k (or ECA) had reached a stable value (end of testing, EOT), the smallest Pt catalyst (n-Pt_{2nm}/CB) still maintained the highest MA_k , which was a factor of approximately two higher than those of n-Pt_{4nm}/CB and c-Pt_{2nm}/CB. Thus, contrary to the common view stated above, Pt NPs as small as 2 nm were found to be quite durable, maintaining high performance from the BOT to EOT, as long as they were uniform in size ($\sigma_d \leq 10\%$) and highly dispersed over the whole surface of the carbon support.

In addition to load-cycling, startup/shutdown-cycling in FCVs also causes severe degradation of Pt/CB cathode catalysts due to carbon corrosion at high potentials (1.3 to 1.5 V).¹¹³ The carbon corrosion was found to be mitigated significantly by the use of Pt NPs with uniform size and uniform dispersion on a corrosion-resistant graphitized CB (GCB) support,^{46–48} to which our nanocapsule method has contributed greatly.

We have been extending these concepts to alloy nanocatalysts, as discussed in the next Sections.

2.2 Mechanism of enhanced ORR activities at Pt skin layers formed on Pt-alloys and design of stabilized Pt skin catalysts

By the use of polycrystalline thin films Pt-Fe, Pt-Co, and Pt-Ni alloy RDEs, we clarified the composition-dependence of j_k values for the ORR in 0.1 M $HClO_4$ solution at room temperature.¹⁰² Based on EQCM, STM, and XPS analyses, we first clarified the mechanism for the enhancement of the j_k .^{1,3,4} It has been clearly demonstrated that nonprecious metal elements in these alloys are dissolved in acidic solution, followed by the spontaneous formation of a Pt skin layer, and the electronic state of the Pt skin is modified by the

Figure 2. Relation between the ORR current density and coverage of O_{ad}, θ[O_{ad}] and H₂O_{ad}, θ[H₂O_{ad}] for pure Pt, Pt skin/Pt₃₃Co₆₅ and Pt skin/Pt₆₃Fe₃₇ at 0.90 V vs. RHE in O₂-saturated 0.1 M HF measured by EC-XPS.^{2,6}

underlying alloy. The value of activation energy ε_a for the k_{app} on Pt skin/Pt alloys at temperatures $\leq 60^\circ\text{C}$ was found to be identical with that of pure Pt,³⁸ indicating that the enhanced ORR activities on Pt skin/Pt alloys can be ascribed to an increased pre-exponential factor in the Arrhenius equation. Such a result is completely inconsistent with the claim, based on density functional theory (DFT) calculations, that decreases in the O_{ad} and OH_{ad} bonding energies in the ORR on the Pt alloys result in a decrease in the ε_a .¹¹⁴

By EC-XPS technique, we have, for the first time, quantitatively identified oxygen-containing species (O_{ad}, OH_{ad}, and H₂O_{ad}) on Pt skin/Pt alloys in N₂- and O₂-saturated 0.1 M HF solution.^{2–4,6} The values of coverage of OH_{ad}, θ[OH_{ad}], on Pt-skin/Pt alloys and pure-Pt were at nearly the same level. This is completely inconsistent with the common view that the enhancement in the ORR activity on Pt alloys is due to a mitigation of blocking or “poisoning” of the surface by decreasing θ[OH_{ad}] or coverage of O_{ad}, θ[O_{ad}].^{114,115} As shown in Fig. 2, the ORR current density at 0.9 V increased with increasing θ[O_{ad}], measured after emersion of the electrode during the ORR, for pure Pt, Pt skin/Pt-Co, and Pt skin/Pt-Fe. A low θ[H₂O_{ad}] at Pt skin/Pt alloys suggests an increase in the number of sites available for the dissociative adsorption of O₂ at the Pt skin.

Such EC-XPS results provided a great impact, but several researchers have claimed that the emersion of the electrodes into ultrahigh vacuum is not suitable for the analysis. However, our recent series of measurements by EQCM and RDE, with a careful consideration on the specific adsorption of ClO₄[−] anions, have demonstrated strong evidence that the higher ORR activity on the Pt₃Co alloy is correlated with higher coverage of oxygen species.^{25,26}

2.3 Design of stabilized Pt skin/Pt alloy catalysts

By the use of the nanocapsule method, monodisperse Pt_xCo (atomic ratio X = 1, 2, and 3) alloy NPs supported on CB (n-Pt_xCo/CB) were prepared with well-controlled particle size and alloy composition.⁴⁴ The value of k_{app} for the ORR at X = 3 ($d = 1.9$ nm) at 30 to 70°C was found to be comparable to that for a bulk-Pt₆₈Co₃₂ (thin film) electrode,³⁸ which was higher by a factor of 2.2 than that for a c-Pt/CB ($d_{Pt} = 2.6$ nm), corresponding to an increase in MA_k by a factor of 3.3. However, the durability of both n-Pt₃Co/C and bulk-Pt₆₈Co₃₂ was insufficient, since the dealloying of Co was not fully suppressed at high temperatures $\geq 80^\circ\text{C}$, and the k_{app} values finally settled to a value comparable to those of c-Pt/CB or bulk-Pt.⁴⁴

We consider that an essential point is the well-controlled formation of a stable, uniform, thin Pt skin layer, which protects the underlying alloy from corrosion and maintains the modified electronic structure. Very recently, we have successfully prepared monodisperse PtCo alloy NPs, having approximately two atomic layers of stabilized Pt skin, dispersed uniformly on graphitized carbon black (GCB) or high-surface-area carbon black (Pt_xAL–PtCo/

Figure 3. (Color online) Changes in kinetically-controlled mass activity, MA_k at Nafion-coated Pt_xAL–PtCo/GCB (●), PtCo/GCB (▲), and c-Pt/CB (▼) electrodes as a function of (a) the number of potential step cycles, N , simulating load-cycles and (b) the number of potential cycles, N , simulating startup/shutdown-cycles. The values MA_k were evaluated at 0.85 V vs. RHE in O₂-saturated 0.1 M HClO₄ at 65°C. Replotted into log N -scale from Ref. 52.

GCB or Pt_xAL–PtCo/C, $1 < x \leq 2$ by more recent analysis).^{52,53} Figure 3 shows the variations in MA_k at 0.85 V on Pt_xAL–PtCo/GCB as a function of log N in potential changes at 65°C, simulating load-cycles and startup/shutdown-cycles of FCVs. The initial MA_k for both Pt_xAL–PtCo/GCB and PtCo/GCB was a factor of ca. 2.5 higher than that for c-Pt/CB. As a measure of the durability, we defined $N_{1/2}$, i.e., the value of N elapsed for the reduction of MA_k to 1/2 of the initial value for each catalyst ($MA_{1/2, c-Pt}$ and $MA_{1/2, PtCo}$). Assuming a Tafel slope of -70 mV for the ORR,³⁸ a halved MA results in a voltage loss of 21 mV ($= 70 \times \log 2$, 2.4%-loss from 0.85 V) for the same current output. The MA_k value for PtCo/GCB decreased steeply and approached that for c-Pt/CB after 30,000 cycles, mainly due to the dealloying of Co, since the j_k became identical with that of c-Pt/CB. In contrast, the degradation of MA_k for Pt_xAL–PtCo/GCB was suppressed considerably: the $N_{1/2}$ values were 14 and 128 times longer, respectively, than those for PtCo/GCB and c-Pt/CB. It is noteworthy that the j_k value on Pt_xAL–PtCo/GCB was maintained at a constant value to 30,000 cycles, suggesting that the stabilized Pt skin layers protected the PtCo core perfectly from the dissolution of Co.⁵² A very high durability of Pt_xAL–PtCo/GCB versus high potentials (simulating startup/shutdown-cycles of FCVs) is clearly seen in Fig. 3(b). Carbon-supported Pt_xAL–Pt-M (M = Fe, Co, and Ni) also exhibited superior performances both in the MA_k and the durability.⁵³ A collaborative effort with a catalyst company is under way to establish an industrial preparation method of these new catalysts.

3. Anode Catalysts for Residential PEFCs and Direct Oxidation Fuel Cells

The overpotential for the hydrogen oxidation reaction (HOR) is very small at Pt/CB anode catalysts operated with pure H₂, as in FCVs.⁶⁵ However, for residential PEFCs, the HOR at Pt/CB is severely poisoned by CO, even at low concentrations, in the

reformat, which is produced by the reforming of fuels (CH_4 or C_3H_8), followed by a series of reactions to reduce the CO concentration. Thus, CO-tolerant catalysts such as Pt-Ru alloys have been employed.

3.1 CO-tolerant HOR mechanism at Pt-alloys

It has been well-known for Pt-Ru alloys that the oxidation of CO molecules adsorbed on Pt sites ($\text{CO}_{\text{ad}}\text{-Pt}$) is facilitated by oxygen-containing species on Ru sites (so-called bi-functional mechanism),¹¹⁶ a ligand (electronic) effect,¹¹⁷ or both. For example, the onset-potential E_{onset} for the oxidation of CO_{ad} on bulk-Pt electrode (ca. 0.5 to 0.6 V) is shifted to a less positive potential (around 0.3 V) on Pt-Ru alloys at room temperature.^{5,18,24} The CO_{ad} oxidation rate is enhanced further by elevating the temperature or employing an oxide support (e.g., 0.21 V on $\text{Pt}_2\text{Ru}_3/\text{Sb-SnO}_2$ at 70°C).²¹ On the other hand, we found that Pt skin/Pt-M alloys ($M = \text{Fe}, \text{Co}, \text{Ni}$, etc.) exhibited moderate CO-tolerant HOR activities at temperatures $\leq 70^\circ\text{C}$.^{1,32,35} It has been clarified by a series of experiments that excellent CO-tolerance on various alloy (including Pt-Ru) catalysts at practical potentials $E < 0.1$ V for residential PEFCs is not ascribable to the increase in the oxidation activity of CO_{ad} , because CO_{ad} cannot be oxidized at such potentials.^{32,35,36}

By using EC-XPS technique, we have demonstrated, for the first time, clear and direct evidence for the modified electronic structure of surface Pt atoms of Pt skin/Pt-Co and Pt-Ru, i.e., positive core-level shift (CL-shift) of $\text{Pt}4f_{7/2}$.^{2,5} Changes in surface CL-shifts (ΔSCLS s) induced by CO_{ad} were related to CO adsorption energy $E_{\text{ads}}(\text{CO})$. The relationship between the CL-shifts and $E_{\text{ads}}(\text{CO})$ was found to be linear so that the CO adsorption becomes weaker in the order pure Pt > Pt skin/Pt-Co > Pt-Ru, as shown in Fig. 4. Hence, the CO-tolerant HOR activity at Pt skin/Pt-Co or Pt-Ru at $E < 0.1$ V can be ascribed to weaker CO adsorption, due to the modified electronic structures of the Pt surface.

3.2 Effect of particle size and composition on CO-tolerance at Pt-alloy nanocatalysts

For the cost reduction of residential PEFCs, it is essential to increase the MA for the HOR of the anode catalysts in the presence of CO at higher concentrations. In order to find clear strategies for the design of highly CO-tolerant catalysts, we have examined the effect of particle size and composition on the MA in the presence of CO_{ad} and analyzed the mechanism by in situ attenuated total reflection FTIR spectroscopy (ATR-FTIR) for monodisperse n- $\text{Pt}_2\text{Ru}_3/\text{CB}$ catalysts with uniform composition prepared by the nanocapsule method.^{17,19}

It was found that the CO-tolerance at n- $\text{Pt}_2\text{Ru}_3/\text{CB}$ was greatly improved by a heat treatment in 5% H_2 at 200°C and was superior to that of a commercial c- $\text{Pt}_2\text{Ru}_3/\text{CB}$ catalyst at an apparent coverage of CO (θ_{CO}) of 0.95.¹⁷ Figures 5(a), (b), and (c) shows in situ FTIR

Figure 4. Linear relation between core-level shifts (ΔCL) and surface core-level shifts ΔSCLS (CO adsorption energies, $E_{\text{ads}}(\text{CO})$). Reproduced from Ref. 5 with permission of the American Chemical Society.

Figure 5. (Color online) Changes in FTIR spectra of Nafion-coated $\text{Pt}_2\text{Ru}_3/\text{C}$ electrodes observed at 0.02 V in 1% CO (H_2 balance)-saturated 0.1 M HClO_4 solution at 25°C (dashed line) and 60°C (solid line) after $t_{\text{ad}} = 120$ min of CO adsorption. The spectra were normalized with respect to the value of $I[\text{CO}_L]$; (a) $d = 2.6$ nm, (b) 3.6 nm, and (c) 4.5 nm. Panels (d) and (e) show the particle size dependencies of CO-tolerance parameter $MA(\theta_{\text{CO}} \approx 0.9)/MA(\theta_{\text{CO}} = 0)$ and band intensities of $\text{I}[\text{CO}_B]$ and $\text{I}[\text{CO-Ru}]$ at 25°C (dashed line) and 60°C (solid line) after $t_{\text{ad}} = 120$ min. Reproduced from Ref. 19 with permission of the American Chemical Society.

spectra of CO_{ad} on n- $\text{Pt}_2\text{Ru}_3/\text{CB}$ with $d = 2.6, 3.6$, and 4.5 nm after CO adsorption. Since the θ_{CO} values became nearly constant at ca. 0.9 for all catalysts at 25 and 60°C, the values of $MA(\theta_{\text{CO}} \approx 0.9)/MA(\theta_{\text{CO}} = 0)$ were calculated as a measure of CO-tolerance and plotted as a function of d in Fig. 5(d). The CO-tolerance increased with decreasing particle size at 25 and 60°C. The integrated intensities of three bands (linearly adsorbed on Pt, CO_L ; bridged on Pt-Pt pair sites, CO_B ; CO_B on Ru-Ru and Ru-Pt sites, CO-Ru) changed with temperature and particle size d , as shown in Fig. 5(e). At 25°C, the suppression of CO-Ru was a dominant factor to maintain the electronic modification effect that decreases the $E_{\text{ads}}(\text{CO})$. Based on the hydrogen adsorption charge for the CO-free surface in the cyclic voltammograms, it was found that the atomic ratio of Pt/Ru on the top surface increased with decreasing d : a Pt-rich top-surface and a Ru-rich core was essential for high CO-tolerance at 25°C. In contrast, at 60°C, the coverage of CO_B on Pt sites was the lowest on the smallest Pt_2Ru_3 particles. Because CO_B blocks two active sites for the HOR, the largest number of HOR active sites can be available at the smallest particle. It was also found at 60°C that n- $\text{Pt}_2\text{Ru}_3/\text{CB}$ exhibited higher CO-tolerance than that at n-PtRu/CB (50 atom%-Ru) with the identical $d = 2.6$ nm, probably due to the Ru-rich core that modifies the electronic structure of the Pt surface.¹⁹

Very recently, we have developed novel anode catalysts $\text{Pt}_{\text{xAL}}\text{-Pt-M/C}$ ($M = \text{Fe}, \text{Co}, \text{Ni}$), which were originally synthesized for the cathode catalysts (see Sect. 2.3) supported on high-surface area carbon. They showed superlative CO-tolerance and high robustness with respect to air exposure at 70 to 90°C.^{54,55} The $\text{Pt}_{\text{xAL}}\text{-PtFe/C}$ catalyst exhibited the highest CO-tolerant HOR activity (j_s and MA), followed by $\text{Pt}_{\text{xAL}}\text{-PtCo/C}$ and $\text{Pt}_{\text{xAL}}\text{-PtNi/C}$. In situ ATR-FTIR,²² in situ X-ray absorption spectroscopy,¹¹⁸ and DFT calculations⁵⁵ clearly demonstrated the weakening of CO adsorption on the Pt_{xAL} .

3.3 Anode catalysts for direct oxidation fuel cells

Direct oxidation fuel cells (DOFCs) have the unique advantages of a simple system and ease of maintenance, which are suitable for the application to portable electronic devices, wheelchairs, vehicles, and robots. Aqueous solutions of methanol, formaldehyde, formic

acid, and methoxy compounds are directly fed to the anode and electrochemically oxidized. We have investigated the methanol oxidation reaction (MOR) and the CO_{ad} oxidation at various catalysts.^{119–123} The E_{onset} for the MOR was found to coincide well with that for the CO_{ad} oxidation reaction (CO_{ad}OR) at Pt and Pt-Ru alloys,^{121,122} because CO_{ad} is the intermediate in the MOR, with a facile dehydrogenation reaction. Among various catalysts examined in acidic media, Pt-Ru alloys have exhibited the highest activity for the MOR or CO_{ad}OR from 20 to 120°C.^{120,123} By in situ ATR-FTIR for CO-adsorbed Pt/CB, Pt₃Co/CB, and PtRu/CB from 23 to 60°C, a sharp band around 3630 cm⁻¹ was observed, which was assigned to $\nu(\text{OH})$ of non-hydrogen bonded, isolated water (co-adsorbed with CO).^{13,18,121} Changes in the $\nu(\text{OH})$ during the CO_{ad}OR clearly indicated that the dominant factor for determining the oxidation activity was the E_{onset} for the oxidation of the isolated water to provide an oxygen species (Pt-OH or Ru-OH). The values of $E_{\text{onset}}(\text{H}_2\text{O})$ at PtRu/CB were lowest among the three catalysts. Furthermore, the CO_{ad}OR rate at PtRu/CB was facilitated by both the bi-functional mechanism and the weakened CO adsorption due to the modification of the Pt electronic structure. The $E_{\text{onset}}(\text{H}_2\text{O})$ values shifted to less positive potentials with increasing temperature, resulting in an increase in the CO_{ad}OR activity, specifically at Pt/CB and Pt₃Co/CB.¹⁸

We also examined the electrooxidation of poly-oxymethylene-dimethylethers (CH₃-O-(CH₂-O)_n-CH₃, POMMs), which are alternative liquid fuels with lower toxicity and lower vapor pressure compared with methanol.^{50,124} The POMMs are hydrolyzed easily in acidic media to provide methanol and formaldehyde. While PtRu/CB was the active catalyst for the oxidation of hydrolyzed POMM, the activity was enhanced greatly by the use of an Sb-SnO₂ support (PtRu/Sb-SnO₂), probably due to an electronic modification effect.⁵⁰

4. Design of Catalyst Layers with High Effectiveness of Pt

As described above, in addition to the R&D of highly active, highly durable catalysts, it is very important to establish the strategies for the design of catalyst layer (CL) structures with increased utilization (effectiveness)¹²⁵ of Pt-based NPs. In a typical CL, Pt/CB or Pt-M alloy/CB catalysts are coated with the electrolyte binder (ionomer, typically, perfluorinated sulfonic acid (PFSA) polymers such as Nafion), which acts as the proton-conducting network. The proton conductance σ_{H} increases with increasing binder thickness coated on the Pt-based NPs, but, in turn, the O₂ gas diffusion rate decreases. We developed a novel preparation procedure of Nafion-coated Pt/CB for the CL with high Pt effectiveness.⁶⁰ Very uniform distribution of the binder in the CL was demonstrated, for the first time, by an electron tomography (3D-TEM).⁶¹ However, we still need to improve the CL performance further under widely ranging operating conditions of relative humidity (RHs) and temperature.

4.1 SiO₂-containing catalyst layers for low humidity operation

It is effective for cost reduction to avoid the use of an external humidifier for H₂-fuel gas and/or air and to operate at low RH. However, the σ_{H} values in both the PEM and the binder decrease at low RH, resulting in increases in both ohmic loss and overpotential. In order to increase the effectiveness of Pt NPs at low RH, we prepared CLs containing hygroscopic SiO₂ NPs (SiO₂-CLs).^{69,70} The cell performance at low RHs was improved with increasing SiO₂ content (volume ratio of SiO₂ to carbon, $V_{\text{SiO}_2}/V_{\text{C}}$). The ohmic resistances of the cell R_{cell} decreased with increasing $V_{\text{SiO}_2}/V_{\text{C}}$, indicating an increase in water content. However, the I - E performance gain was much larger than that expected for the reduction of ohmic loss. For the SiO₂-CL with $V_{\text{SiO}_2}/V_{\text{C}} = 0.39$ at 80°C and 30% RH, the value of $MA_{0.85\text{V}}$ was 2.6 times larger than that without SiO₂, as shown in Fig. 6(a). The cyclic voltammograms of the SiO₂-CLs (Fig. 6(b)) clearly indicated that the effectiveness of the Pt cathode

Figure 6. (Color online) Effect of SiO₂ addition in the CLs on (a) mass activity at 0.85 V ($MA_{0.85\text{V}}$) obtained from polarization curves at 80°C for H₂/air fuel cell under various RHs and (b) cyclic voltammograms of CLs measured at 80°C in N₂ with 30% RH at the sweep rate of 20 mV s⁻¹. The loading amount of Pt in the CLs was 0.56 ± 0.02 mg cm⁻². While the volume ratio of dry Nafion to carbon black support and SiO₂, $V_{\text{Nafion}}/(V_{\text{C}} + V_{\text{SiO}_2})$, was maintained constant at 0.77, in order to obtain a constant thickness of Nafion binder on the Pt catalyst particles, the volume ratio of SiO₂ to carbon ($V_{\text{SiO}_2}/V_{\text{C}}$) was changed from 0 (without SiO₂) to 0.39. Identical CLs were used for the anode and the cathode. Reproduced from Ref. 70 with permission of Elsevier Ltd.

catalyst increased, not only due to the increased electrochemically active area (ECA, based on hydrogen adsorption charge, Q_{H}) resulting from a good proton-conducting network, but also to the suppression of the specific adsorption of the sulfonate anions in the electrolyte binder on the Pt surface (increase in $Q_{\text{Pt oxide}}$), which is often a serious problem of low RH operation. It was also found that the use of an SiO₂-containing anode CL promoted the back-diffusion of water from the cathode to the anode, leading to an increase in the water content in the PEM (the reason for the lower ohmic drop), as well as increasing the oxygen partial pressure in the cathode CL (by suppressing the counter-flow of generated water vapor).⁷⁰

4.2 Cathode catalyst layers with sulfonated hydrocarbon electrolyte binders

PFSA polymers such as Nafion have been widely used as both the PEM and the binder because of their high σ_{H} as well as chemical and thermal stability. Recently, non-fluorinated hydrocarbon (HC) electrolyte membranes have been developed to reduce cost, to elevate the operating temperature, and to avoid environmental pollution due to fluoride on disposal. Specifically, the elevation of operating temperature ($\geq 100^\circ\text{C}$) leads to a significant cost reduction by increases in the MA values for the ORR⁴⁰ of the cathode catalysts and the CO-tolerant HOR of the anode catalysts,^{36,55} together with a down-sizing of the heat exchanger (radiator) in FCVs (due to increased ΔT).

The σ_{H} values in HC electrolytes so far are high enough at high RH but decrease more steeply with decreasing RH than that in the case of Nafion. In contrast, sulfonated poly(arylene ether) ionomers containing sulfofluorenyl groups (SPAIE, as shown in Fig. 7(a)), which were prepared by Miyatake and coworkers in our laboratory,

Figure 7. (Color online) (a) Chemical structure of the sulfonated poly(arylene ether) (SPAE) ionomer, (b) steady-state cathode polarization curves in air for the CLs of SPAE(1.8)-Pt68 ($\blacktriangle$), SPAE(2.5)-Pt68 ($\blacktriangle$), and SPAE(2.5)-Pt48 ($\bullet$) at 60% RH and 80°C. SPAE(1.8) and SPAE(2.5) mean the SPAE binder with the ion exchange capacity of 1.8 and 2.5 meq g⁻¹, respectively. Commercial Pt/CB catalyst with Pt-loadings of either 48 wt% (Pt48) or 68 wt% (Pt68) was used. The mass ratio of SPAE binder (dry basis) to carbon black (SPAE/C) was adjusted to 0.70. NRE212 was used as the electrolyte membrane in the fuel cell with H₂ and air (200 mL min⁻¹) under ambient pressure. Reproduced from Ref. 66 with permission of Elsevier Ltd.

showed σ_H values comparable to that of Nafion at RH $\geq$ 58% and 80°C.¹²⁶ The performances of the cathode CLs containing SPAE binder (SPAE-CL) were examined from 60 to 100% RH at 80°C.^{65,66} The values of MA at 0.9 V (measure of the catalyst utilization) in air and O₂ at the SPAE-CL reached a maximum at 88% RH and decreased steeply below 78% RH. By a series of experiments, the decrease in the performance at the SPAE-CL was ascribed to a decrease in the O₂-diffusion rate by excessive swelling of SPAE at high RH and a specific adsorption of functional groups (probably sulfonate groups) in the SPAE on the Pt catalyst surface at low RH. Then, the SPAE-CL performance was successfully improved over the whole range of current densities by using a high Pt-loading for the Pt/CB catalyst (68 wt%-Pt) in place of the conventional 48 wt%-Pt for the reduction of CL thickness, which enabled us to increase the O₂-diffusion rate and to suppress the adsorption of SPAE binder on the Pt surface (via effective utilization of generated water within a thin CL). As shown in Fig. 7(b), the performance at low RH (60% RH) was improved further by employing an SPAE binder with a lower ion exchange capacity (IEC) of 1.8 meq g⁻¹ [SPAE(1.8)] to suppress the specific adsorption of SPAE, in place of that with IEC = 2.5 [SPAE(2.5)]. Hence, for the SPAE-CLs, the use of a high Pt-loading catalyst, together with a binder with an appropriate IEC, is very important.⁶⁶

5. High Performance and Durable Electrodes for Reversible Solid Oxide Cell (R-SOC)

The R-SOC acts as an efficient, reciprocal direct energy converter between hydrogen and electricity.^{127–129} Large-scale amounts of electricity generated from photovoltaics or wind power can be stored as H₂ gas when the SOC is operated as an SOEC, while electric power is generated by the reverse operation mode (SOFC) to match the supply with demand. The high operating temperature of the R-SOC indeed provides the great advantage of reduced overvoltage without the use of noble-metal electrocatalysts, but its disadvantage is the rapid degradation of materials. Thus, a reduced temperature

operation (600–800°C) is a good option to decrease not only the degradation rates but also costs of materials and their manufacturing.

We have engaged in the R & D of high-performance electrodes with novel architecture for reduced temperature SOFCs since the 1990's,^{78,79} when such research was quite rare, but it has become more common nowadays. In order to enlarge the effective reaction zone (ERZ, in which gases, ions, and electrons are transported smoothly), we proposed a new concept of catalyzed reaction layers.⁷⁹ Mixed ionic and electronic conducting samaria-doped ceria (CeO₂)_{0.8}(SmO_{1.5})_{0.2} (denoted as SDC) with highly dispersed metal electrocatalysts exhibited very high performance as the hydrogen electrode at reduced temperatures. It was found that the Ni or Ni-Co NPs played a highly active role in the hydrogen oxidation/evolution reactions.^{91–95,98} The activity of the hydrogen electrode in the SOEC was found to increase with an increase in the ionic conductivity σ_{ion} of the zirconia electrolyte,⁹⁵ similar to the case of SOFC electrodes.^{78,81,84,86} the use of high-performance electrodes in combination with the a solid electrolyte having high σ_{ion} is essential to achieve high performance R-SOCs.

Very recently, we have developed double-layer (DL) hydrogen electrodes, consisting of an SDC scaffold with highly dispersed Ni or Ni_{0.9}Co_{0.1} NPs as the catalyst layer and a thin Ni-SDC current collecting layer, as shown in Fig. 8. The DL H₂ electrode exhibited highly reversible performance in both anodic and cathodic operation modes at 800°C.^{130,131} For the oxygen electrodes, a composite of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃ (LSCF) and SDC with SDC interlayer, in which SDC acted as a high oxide ionic conductor in oxygen atmosphere, exhibited very reversible performance and high durability.^{96,99,100} An IR-free electrolytic cell potential E_{cell} of 1.21 V for a full cell with the configuration of DL H₂ electrode | YSZ electrolyte | SDC interlayer | LSCF–SDC O₂ electrode was achieved at $j = -0.5$ A cm⁻² and 800°C with $p[H_2O] = 0.4$ atm (cathode) and pure O₂ (anode). If we add the ohmic loss of the scandia-stabilized zirconia electrolyte with a thickness of 50 μ m,¹³² the E_{cell} value is calculated to be 1.23 V, which is quite superior to that reported for an electrolyte-supported cell.¹³³ Durability tests of the full cell, as well as the fabrication of a large test cell, are in progress.

6. Conclusions and Outlook

Based on the analyses of fuel cell reactions by multilateral techniques, clear strategies for the design of electrocatalysts with high activity and high durability have been demonstrated. A key factor for high durability with high MA for the ORR was found to be the uniformity in the size ($\sigma_d \leq 10\%$) and high dispersion state of Pt on the support, so that we can avoid any adverse “particle-size effects.” The ORR activity was improved noticeably by alloying with transition metals (Fe, Co, and Ni), where the surfaces consist of a Pt skin with modified electronic structure. The increase in $\theta[O_{ad}]$ at the Pt skin was clearly demonstrated by EC-XPS and EQCM measurements, contrary to the common view of simple suppression of “OH poisoning.” We have clarified for Pt_xAL–PtCo that a very important factor for superior ORR activity and durability in the ADT is well-controlled formation of a stable, uniform, thin Pt skin layer, which protects the underlying alloy from corrosion and maintains the modified electronic structure. The optimization of composition and particle size of Pt-Ru anode catalysts was found to be effective in enhancing the CO-tolerance, while the Pt_xAL–PtCo/C catalysts open up the possibility of developing a new class of anode catalysts with superior performance. New catalyst layers and MEAs have been developed in order to make the electrocatalysts operate effectively, specifically under low RH conditions. Several important concepts have been demonstrated for developing oxygen and hydrogen electrodes with high performance and durability for R-SOCs.

Figure 8. (Color online) (a) Schematic representation of double-layer (DL) hydrogen electrode composed of highly-dispersed Ni or NiCo/SDC as a catalyst layer (CL) and Ni–SDC cermet as a current collecting layer (CCL), (b) cross-sectional SEM images of DL hydrogen electrodes (low magnification), (c) high magnification BSE (back-scattered electron) image of Ni–SDC (60 vol% Ni) CCL, and (d) high magnification SEM image of $\text{Ni}_{0.9}\text{Co}_{0.1}/\text{SDC}$ (8 vol% $\text{Ni}_{0.9}\text{Co}_{0.1}$) CL.

For the results described above, research efforts ranging from fundamentals to applications are seen to be very important. In our group, various researchers and students work together on the preparation and evaluation of electrocatalysts, PEMs, MEAs, and their multilateral analyses (mechanisms of operation and degradation). Rapid feedback of the information can greatly accelerate the PDCA (Deming) cycles for developing materials and analysis techniques. We are hopeful that our efforts might contribute to the development of fuel cells with high performance and high durability in the near future.

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