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Research Report

Strategies for Designing Ideal Pt/Ionomer Interfaces in Polymer Electrolyte Fuel Cells

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■ABSTRACT■ To design ideal structures of the interface between Pt surface and ionomer in the cathode catalyst layer of polymer electrolyte fuel cells (PEFCs), Pt single crystal electrodes were modified with various materials and the effects of the foreign materials on the oxygen reduction reactions (ORR) and stabilities of the surfaces were experimentally analyzed. Stepped Pt single crystal electrodes where Au atoms have been selectively deposited on the step sites exhibited higher ORR activities and stabilities against potential cycles than the bare electrodes. Thus, protecting or replacing vulnerable low-coordinated Pt atoms with stable materials is a promising strategy to improve both the ORR activity and durability of Pt catalysts. The effects of a Nafion thin film on the ORR activity on Pt surface were quantitatively analyzed with a Pt(111) electrode, and it was found that the activity is suppressed by Nafion coating by up to over 80% through the adsorptions of sulfonate moieties in the molecules. Changing anion structures as well as the flexibility of side-chain was found effective for reducing the ionomer-induced catalyst poisonings. Thus, the fundamental researches with Pt single crystals provided useful information for developing desirable catalysts and ionomers for PEFCs.

■KEYWORDS■ Pt Catalyst, Ionomer, Pt Single Crystal, Oxygen Reduction Reaction, Activity, Durability, Edge Protection, Side Chain, Anion, Modification

1. Introduction

In catalyst layers of polymer electrolyte fuel cells (PEFCs), Pt nanoparticles used as electrocatalysts are usually covered by ionomer as shown in **Fig. 1**.⁽¹⁾ Recent studies⁽²⁻⁴⁾ have demonstrated that the cell

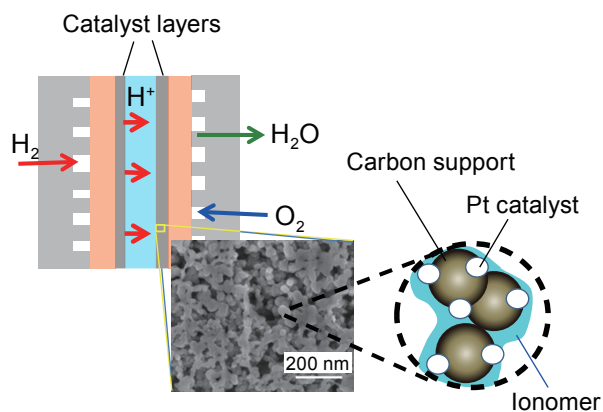


Fig. 1 Composition of a PEFC with enlarged views of a catalyst layer.

performance is significantly affected by the property of the interface between the Pt surface and ionomer in the cathode catalyst layer, where oxygen reduction reaction (ORR) takes place. For obtaining guidelines for designing the Pt/ionomer interface, understanding the ORR mechanisms (e.g. the locations of reaction site and the role of spectator species) in atomic and molecular scales is essential. In this respect, experimental studies using Pt single crystal electrodes are a powerful approach because their controlled surface structures exhibit site-specific signals in electrochemical measurements depending on the plane orientations of (hkl) and quantitative information about the effect of spectator species adsorbed on specific sites on the faradaic reactions can be obtained.^(5,6) Here, our recent works with such analytical methods⁽⁷⁻¹⁰⁾ will be reviewed.

The article is divided into two parts. In the first part, the focus is on the Pt-catalyst side of the interface. We will demonstrate an ideal surface structure of Pt catalyst for achieving the compatibility between the activity and durability of the catalyst. In many cases, those two

properties have a trade-off relation.^(11,12) Modifying the catalyst surface in an atomically-controlled way, however, was found possible to improve both the activity and durability. In the second part, the focus is on the ionomer (electrolyte) side of the interface. From the analyses with a well-defined Pt/ionomer interface prepared using a Pt single crystal electrode, the effects of ionomers on the catalytic activity for ORR were quantitatively clarified. It was found that ionomers significantly suppress ORR activities of Pt catalysts through the adsorptions of the anionic moieties of the polymer. For mitigating the catalyst poisonings, key factors determining the anion adsorptivity of the ionomer are discussed.

2. Activity and Durability Improvements of Catalysts

As the catalysts in PEFCs, Pt nanoparticles supported on high-surface-area carbons are most widely used.⁽¹³⁾ The surfaces of Pt nanoparticles consist of various sites including facets, edges and corners.⁽¹⁴⁾ Those sites have different catalytic properties and the key differences are summarized as follows:

- 1) The low-coordinated edge and corner sites are blocked strongly by oxygenated species during ORR, and therefore, have negligible activities compared to facet sites.^(15,16)
- 2) Pt atoms at edges and corners are easier to dissolve into electrolytes than those at facets⁽¹⁷⁾ and can initiate the degradation of the Pt nanoparticle.

These observations suggest that masking or replacing Pt atoms at edges and corners of Pt nanoparticles with stable substances can improve the durability without deteriorating the ORR activity. Actually, theoretical studies by Wei and Liu⁽¹⁸⁾ and Jinnouchi et al.⁽¹⁹⁾ predicted that both the activity and durability of Pt nanoparticles are improved by replacing Pt atoms at edges and corners with Au atoms. This “edge-protection” concept has also been proposed in experiments, where the durabilities of Pt nanoparticles were improved without significantly affecting the ORR activities by partially masking the surfaces with Au atoms.⁽²⁰⁻²²⁾ In those experiments, however, direct evidences of the edge-protection mechanisms were not presented because of the difficulty to identify locations of the Au atoms on Pt nanoparticles, whose surface morphologies are generally uncontrolled and complex. This issue was effectively addressed by using Pt single

crystal electrodes as follows.

The analyses were carried out using stepped Pt single-crystal surfaces modified with Au.⁽⁹⁾ The deposition sites can be identified by comparing the cyclic voltammograms (CVs) with and without the Au modification. **Figure 2** shows the CVs for Pt(111), Pt(755), and the Au-modified Pt(755) (denoted as Au/Pt(755) below). For Pt(111), the reversible plateaus (0.05–0.4 V) and butterfly peaks (0.6–0.9 V) are observed, and they are ascribed to the desorption/adsorption of underpotentially deposited hydrogen (H_{upd}) and formation/reduction of Pt hydroxide (OH(ads)), respectively.^(23,24) For Pt(755), which consists of (111) terraces with the width of six atoms separated by monoatomic (100) steps and is noted as Pt [6(111) × (100)] as well, sharp peaks due to (100) steps are observed at 0.29 V as well as the plateaus due to (111) terraces in the H_{upd} region.⁽²⁵⁻²⁷⁾ By the Au modification, the Pt(100) step peaks have disappeared, whereas the Pt(111)-terrace contribution has remained essentially intact. These results suggest that Au atoms selectively mask the Pt(100) step sites as depicted in the inset of Fig. 2. The selective depositions of Au atoms on the step sites have also been confirmed using X-ray photoelectron spectroscopy as discussed in Ref. (9).

Figure 3 summarizes the effect of the Au modification on the ORR activities measured by the rotating disk electrode (RDE) technique for Pt(755) ([6(111) × (100)]), Pt(322) ([5(111) × (100)]) and Pt(211) ([3(111) × (100)]). The ORR-improving

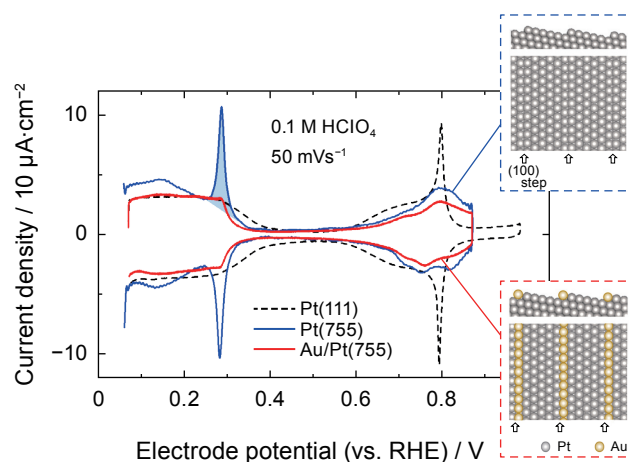


Fig. 2 CVs for Pt(111), Pt(755), and the Au-modified Pt(755). The insets are the side and top views of the bare and Au-modified Pt(755).

effect is clearly observed on Pt(755) and Pt(322), whereas it is not observed on Pt(211). The non-proportionality of the increase in ORR activity by the Au modification (Δi_K) against the step density implicates that the ORR-active sites contributing to Δi_K are located not on the one-dimensional Au atomic rows at the steps but on the Pt(111) terraces,⁽²⁸⁾ and that the local ORR activities on the Pt(111) terraces are enhanced by the Au modification. The Au atoms at the steps can affect the stabilities of ORR intermediates including OH(ads) at the terraces by modifying the H-bond networks surrounding the intermediates or by making the (111)-terrace sites near the step sites available for ORR by suppressing the oxide formation near the steps.^(18,19) Further studies are, however, necessary for clarifying the mechanisms in more detail.

Figure 4 shows the changes in the CVs for the bare and Au-modified Pt(755) after 10 cycles between 0.07–1.0 V. On bare Pt(755), the features of the CV both in the regions for H_{upd} (0.05–0.4 V) and OH(ads) (0.6–0.9 V; see the arrows) are changed after the potential cycles. This observation indicates a surface reorganization on the electrode surface during the potential cycles and thus the instability of bare Pt(755).⁽²⁹⁾ In contrast, the CV for the Au/Pt(755) exhibits no changes over the entire potential region (0.05–0.9 V) during the potential cycles, indicating that the Au modification stabilizes the Pt surface by protecting the low-coordinated (100) step sites.

In summary, Pt single crystal surfaces modified by

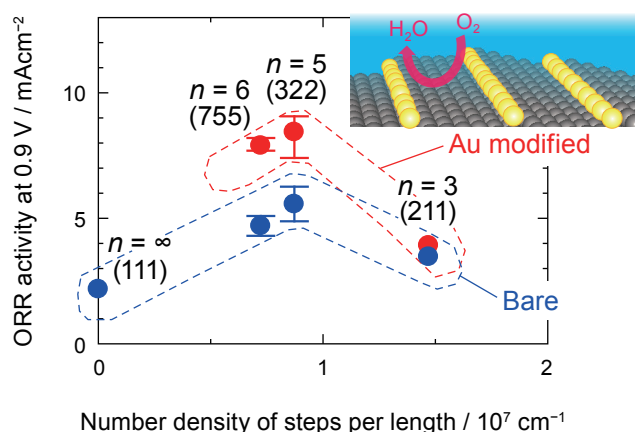


Fig. 3 ORR activities at 0.9 V (vs reversible hydrogen electrode (RHE)) on the bare and Au-modified Pt surfaces containing (100) steps. The locations of the ORR active sites are (111) terraces as depicted in the inset.

depositing Au atoms selectively on (100) step sites showed improvements in both the ORR activity and stability of the surfaces. This result proves the validity of the edge-protection concept, which can be applied to a wide range of inhomogeneous catalyst that suffers from a trade-off dilemma between the catalytic activity and durability.

3. Mitigating Catalyst-poisonings by Ionomers

For ionomers used as a binder and proton-conductor for the catalyst layer as well as electrolyte membranes, perfluorinated sulfonic acid polymers (e.g., Nafion) have been almost exclusively used owing to their high chemical stability and strong acidity. Although effects of sulfonate anions of Nafion on the kinetics of ORR have been discussed in various manners, reported experimental results were inconsistent (e.g., suppressions and accelerations of ORR).⁽³⁰⁻³⁴⁾ Recently, by using Pt single-crystal electrodes coated with Nafion thin films, Subbaraman et al.^(35,36) observed voltammetric features signaling the adsorptions of sulfonate moieties in the ionomer on the Pt surfaces and suppressions of ORR kinetics by the ionomer coatings. These Nafion effects were also examined for

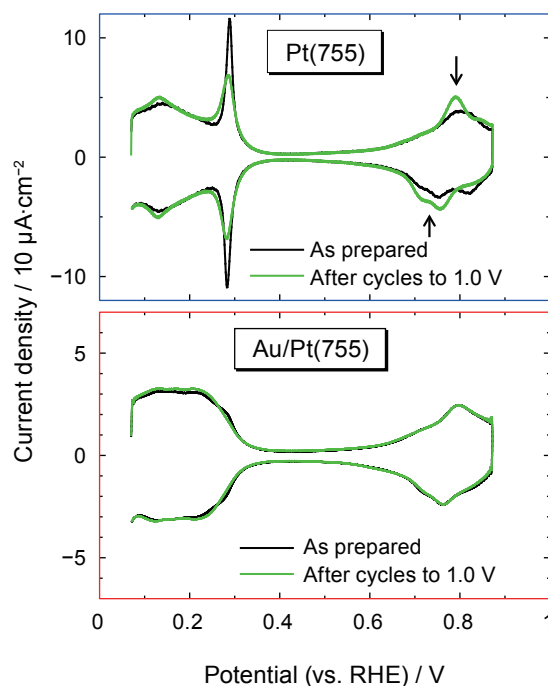


Fig. 4 Changes in the CVs on the bare and Au-modified Pt(755) after 10 cycles between 0.07–1.0 V.

Pt nanoparticles under well-controlled experimental conditions by Shinozaki et al.,⁽³⁷⁾ and suppressed ORR kinetics were confirmed. Thus, terminal sulfonate moieties on the side chains in Nafion are widely recognized to adsorb on Pt and to decrease the ORR activities, limiting the efficiency of PEFCs.

The method developed by Subbaraman et al.^(35,36) using Pt single crystals is a powerful tool for studying the Nafion effects because the anion adsorptions can be detected in the voltammetry. In their works, however, the uniformities of Nafion films on the Pt surfaces were not confirmed. For quantitatively evaluating the Nafion effects and the differences in the catalyst poisoning properties among various ionomers, the uniformities of the ionomer films are essential and therefore were examined in our laboratory. **Figure 5** shows the scanning electron microscope (SEM) images and energy-dispersive X-ray (EDX) spectra of the Nafion-coated Pt(111) surface that had been

prepared in the method described in Refs. (8), (35) and then subjected to electrochemical measurements. The surface composes of a bright thin periphery and a dark gray region in the inner part, which are assigned to a bare and a Nafion-coated Pt surfaces, respectively, from the EDX spectra. Thus, the entire Pt(111) surface except for the thin periphery was confirmed to be covered by the Nafion film. In the same way, the uniformities of ionomer thin films were confirmed for all ionomers discussed below.

Figure 6 shows the CV and ORR Tafel plot for the Pt(111) surface covered by the uniform Nafion film in comparison with those for a bare Pt(111) electrode. By the Nafion coating, sharp redox peaks appear in the double layer region (0.4–0.6 V) and OH formation (> 0.6 V) is suppressed, whereas the H_{upd} plateaus (0.05–0.4 V) are not affected. These observations indicate that sulfonate moieties in Nafion are adsorbed on the Pt surface in the potential range higher than that

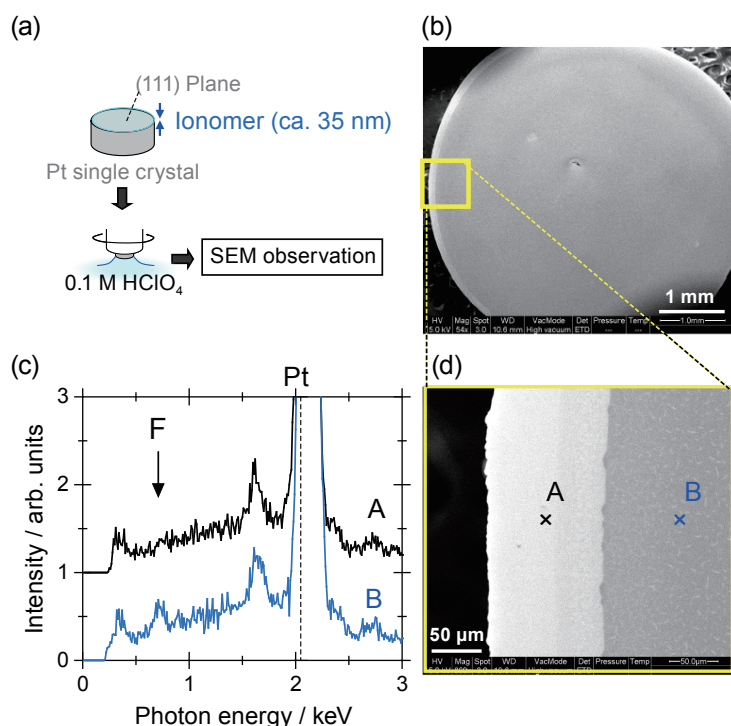


Fig. 5 (a) Experimental procedure of analysis with ionomer-coated Pt single crystals. (b) SEM image of the whole region of the Nafion-coated Pt(111) surface after the electrochemical measurements. (c) EDX spectra measured in the bright region ((A) in Fig. 5(d)) and in the gray region ((B) in Fig. 5(d)) on the SEM image of the Pt(111) surface. The peak position for fluorine is denoted by the down-pointing arrow. (d) Magnified SEM image for the square region in Fig. 5(b). The marks are the places where the EDX spectra were measured.

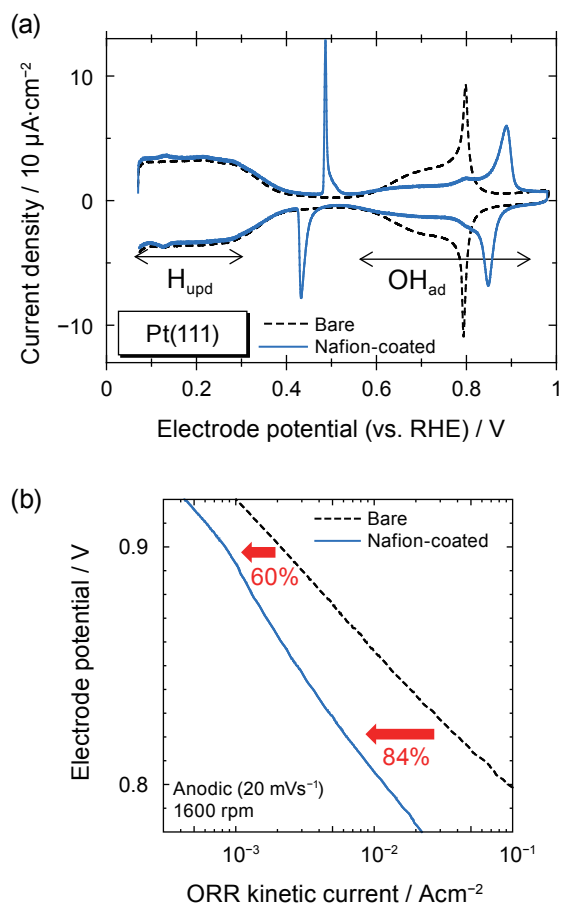


Fig. 6 (a) CVs and (b) ORR Tafel plots for the bare and Nafion-coated Pt(111) surfaces.

for the sharp redox peaks (ca. 0.45–0.5 V).

The coverage of sulfonate is estimated to be 0.09 ML from the peak charge by assuming that the adsorption is a one-electron-transfer process ($-\text{SO}_3^- + \text{Pt} \rightarrow -\text{SO}_3-\text{Pt} + e^-$). This result indicates that only 27 % of the electrode surface area is masked by the sulfonates, even if one sulfonate anion masks three Pt atoms via the three oxygen atoms of the functional group. The suppression of ORR, in contrast, is more significant (84% at 0.82 V and 60% at 0.9 V). For clarifying the origin of the gap, further analyses were carried out to obtain molecular scale information.⁽¹⁰⁾ **Figure 7** shows the infrared (IR) spectrum measured using the method of surface enhanced IR spectroscopy (SEIRAS) for a Pt polycrystalline electrode at the potential of 0.7 V in an aqueous electrolyte of perfluoro-(2-ethoxyethane) sulfonic acid (PESA, $\text{C}_2\text{F}_5\text{OC}_2\text{F}_4\text{SO}_3\text{H}$) as well as an IR spectrum of the bulk aqueous solution of PESA (1 M) with the band assignments.⁽³⁸⁾ The SEIRA spectrum exhibits strong asymmetric SO_3 stretching vibrations, which yield oscillating dipole moments perpendicular to the $\text{C}(\text{F}_2)-\text{S}(\text{O}_3)$ axis, indicating the adsorption of PESA anion on Pt surface through one or two O atom(s) on the basis of the surface selection rule in SEIRAS: Vibrations that yield oscillating dipoles perpendicular to the surface are selectively observable,⁽³⁹⁾ and if the sulfonate groups are adsorbed through three O atoms, the asymmetric SO_3 stretching vibrations should not be observed. One more notable feature is that the asymmetric C–O–C mode of the ether group in the SEIRA spectrum is weaker than that in the bulk-solution spectrum. Since this vibrational

mode yields oscillating dipole moment along C–O–C, the weakening of this mode in the SEIRA spectrum suggests the parallel orientation of the perfluoro-alkyl chain to the Pt surface, as depicted in the upper right schematic in Fig. 7. This orientation is presumably caused by the interaction of the ether group with the surface via the lone pair of the oxygen atom in addition to van-der-Waals interactions between the perfluorinated parts and Pt surface.⁽³⁾ The adsorption via both the terminal sulfonate moiety and ether group can explain the significant suppression of ORR at the Pt/Nafion interface despite the small coverage of sulfonate shown above: not only sulfonate moiety but also perfluoro-alkyl chain blocks the Pt sites for ORR. However, complete quantitative analyses based on the physical factor (the effect of the decrease in the ORR active area by the blockages by the molecular parts) are still underway, and it is an open question whether there also exist chemical factors such as the decrease in the local activity on adsorbate-free Pt sites due to the ionomer adsorptions.

The preceding discussion revealed the significant ORR suppression effect of Nafion through the adsorption of sulfonate moiety. Since the experiments were carried out with aqueous electrolytes, the conclusion is, however, limited to the condition where the ionomer is fully hydrated. Studies for dryer states of ionomers are also important because PEFCs are frequently operated in undersaturated conditions, and therefore, we newly devised a solid-state cell applicable to Pt single crystals.⁽⁷⁾ **Figs. 8(a)** and **(b)** show the configuration of the solid-state cell, where

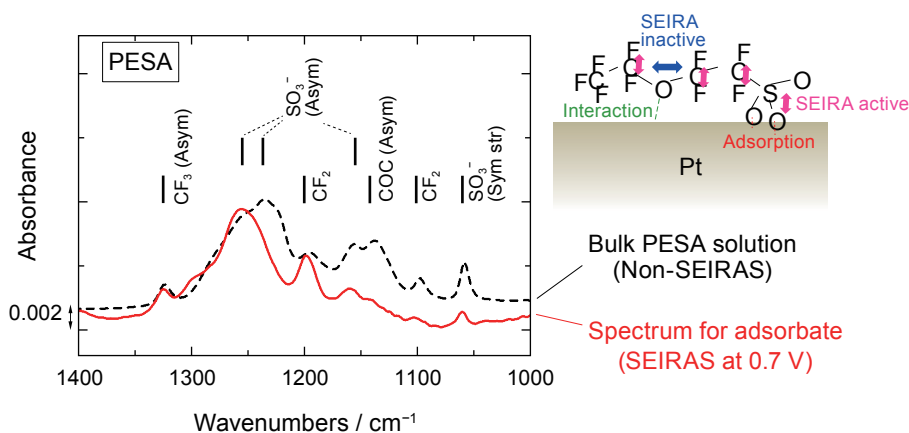


Fig. 7 SEIRA spectrum for a Pt polycrystalline electrode at the potential of 0.7 V in 0.1 M PESA as well as IR spectrum of the bulk aqueous solution of PESA (1 M). From the feature of the SEIRA spectrum, the adsorbed PESA anion is suggested to be oriented parallel to the Pt surface as depicted in the upper right schematic.

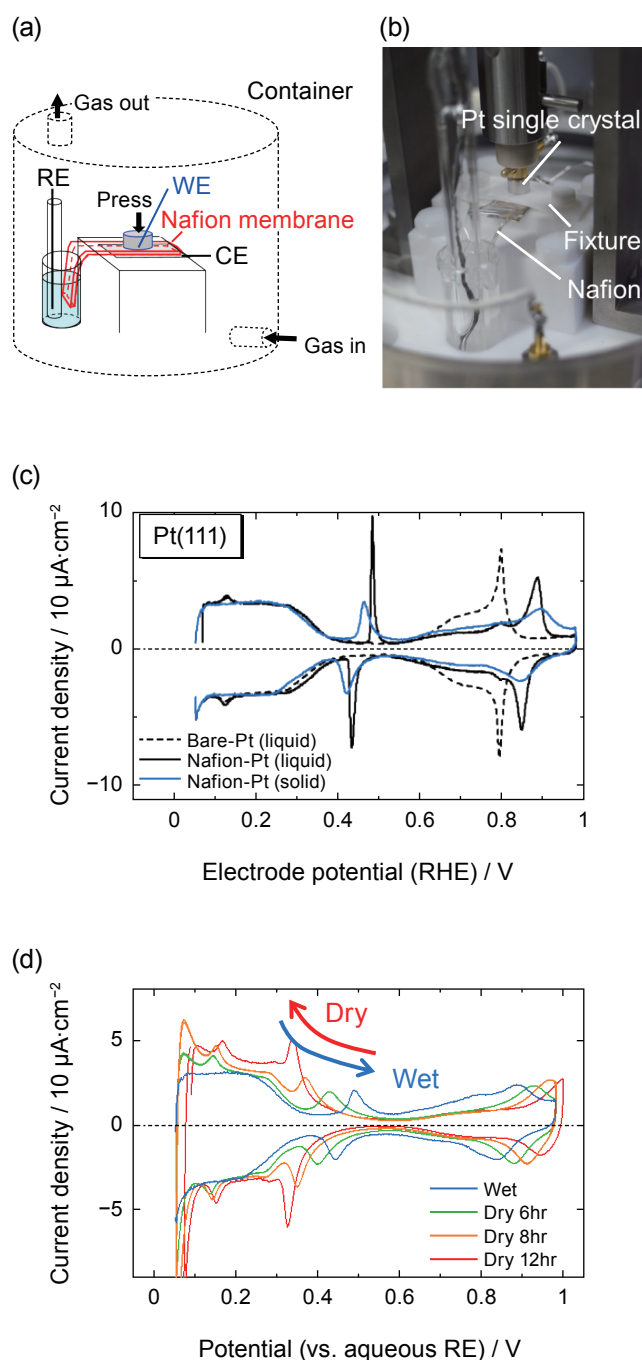


Fig. 8 (a) Illustration of the whole setup of the solid-state cell. (b) Magnified photograph of the cell. The fixture has a hole for the mounting of the Pt single crystal. (c) CVs for the Nafion-coated Pt(111) surfaces in the aqueous (liquid) electrolyte of 0.1 M HClO_4 (black solid line) and in the solid-state cell (blue solid line). The CV for a bare Pt(111) is also shown for comparison (black dashed line). (d) Changes in the CV for the Nafion/Pt(111) interface in the solid-state cell after the switching to the dry-gas flow. This peak shift is reversible as indicated by the shift back to higher potentials after re-switching to the wet-gas flow.⁽⁷⁾

a Nafion-coated Pt(111)-surfaced single crystal as the working electrode (WE) is pressed onto a cast Nafion membrane having a thickness of 1 mm, and the whole cell is placed in a gas atmosphere container. A platinized Pt mesh in a hydrogen-reserved glass tube immersed in 0.1 M HClO_4 connected to the Nafion membrane is used for the reference electrode (RE), whereas a Pt plate is used for the counter electrode (CE).

Figure 8(c) shows the CVs for a Nafion-coated Pt(111) surface in an aqueous electrolyte (0.1 M HClO_4) and in the solid-state cell at a room temperature under fully humidified condition (the flow gas was humidified with water at a room temperature). The well-defined features of a Nafion-coated Pt(111) (reversible H_{upd} plateaus (0.05–0.4 V) and redox peaks due to sulfonate adsorption/desorption (0.4–0.5 V)) are observed in the solid-state cell. After the measurement under the fully humidified condition, the fully humidified gas flow was switched to a non-humidified gas flow. Figure 8(d) shows the change in CVs after the switching. The anion-adsorption/desorption peaks are shifted to lower potentials as indicated by the red arrow. (This peak shift is reversible as indicated by the shift back to higher potentials after re-switching to the fully humidified gas flow.⁽⁷⁾) The decrease in the anion adsorption potential indicates the increase in the anion adsorptivity with drying the ionomer. The higher adsorptivity of the dehydrated ionomer can be explained by higher chemical potential of the hydrated (desorbed) sulfonate anion, which is probably caused by two reasons: decrease in the hydration stabilization energy of ionomer and increase in the anion concentration in water channels in ionomer.

As a summary of Nafion-effects on ORR on Pt(111) surface, significant ORR-activity suppressions by sulfonate adsorptions at a small coverage, and the increase in the anion adsorptivity with drying the ionomer were confirmed. The gap between the ORR suppression degrees and sulfonate coverage was explained by the blockages of active sites not only by the sulfonate moieties but also by perfluoro-alkyl chains. In addition to the activity, such large deactivation domains can suppress the oxygen transport in the Pt/Nafion interface region,⁽⁴⁾ and therefore, reduce the power density of the cell. Therefore, mitigating ionomer-induced catalyst poisonings is being recognized as one of the most important issues in the development of PEFCs. Promising methods for

the mitigation are presented in the following sections.

We evaluated the catalyst poisoning properties of three ionomers, which have different anion structures and side-chain lengths (**Fig. 9(a)**).^(8,10) For the sulfonimide acid ionomer (NBC4), which has bulky acid groups terminated by an inactive perfluorinated

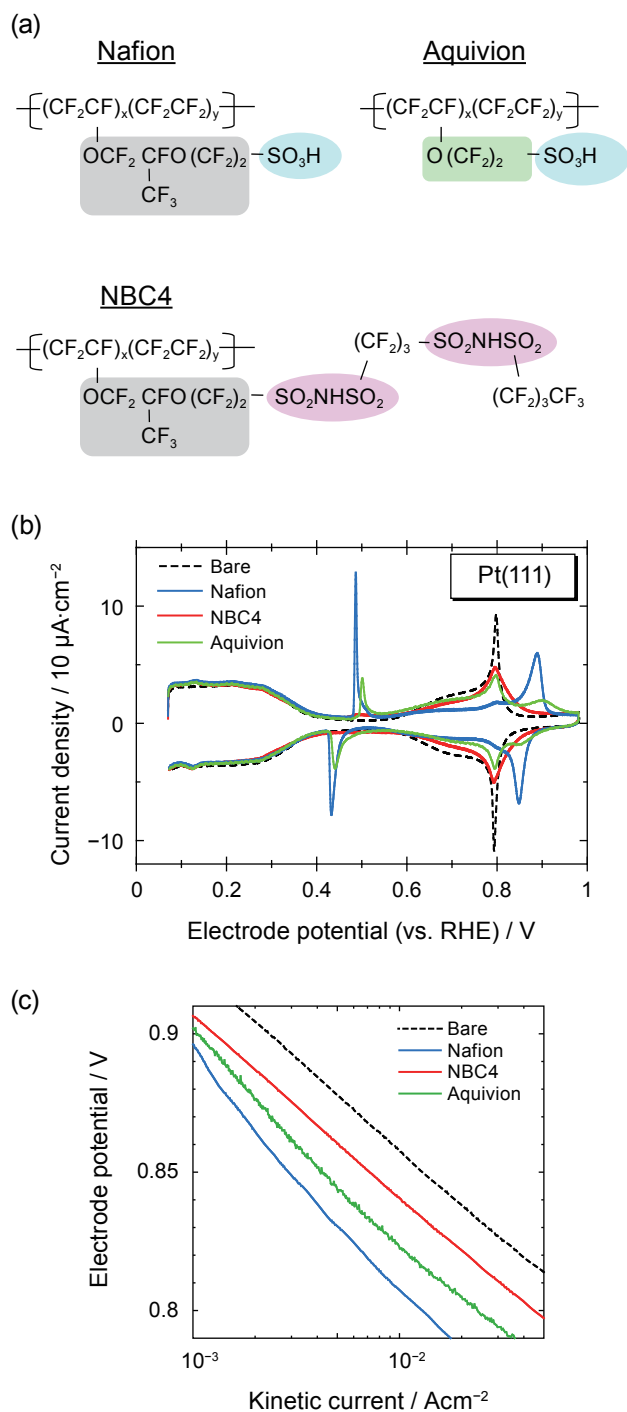


Fig. 9 (a) Molecular structures of Nafion, Aquivion, and NBC4. (b) CVs and (c) ORR Tafel plots for Pt(111) surfaces coated with and without the ionomers.

part, as shown in Figs. 9(b) and (c), the anion adsorption/desorption peaks are broader and weaker, and the ORR activity is higher than for the sulfonic acid ionomers (Nafion and Aquivion). Thus, the poisoning by the sulfonimide anions is judged to be weaker than that by the sulfonate anions. This result is consistent with a prediction from a density functional theory combined with a continuum electrolyte theory,⁽⁸⁾ which showed that the adsorption is weaker for a low-molecular-weight perfluorinated sulfonimide anion than for a low-molecular-weight perfluorinated sulfonate anion on Pt(111) surface. The steric effect due to the inactive perfluorinated terminal in the side chain of NBC4, which was not included in the theoretical calculation, may also play a role for the weaker anion adsorption.

Another factor affecting the anion adsorptivity is the flexibility of side chains.⁽¹⁰⁾ As shown in Figs. 9(b) and (c), the short-side-chain ionomer (Aquivion) exhibits smaller peaks for the anion adsorption/desorption and a higher ORR activity than Nafion although they have the same anion structure. In addition to the shorter length, the side chain of Aquivion has a smaller number of ether groups (one) than that of Nafion (two). These two differences most likely make the side chain of Aquivion less flexible than that of Nafion, and the adsorption of the side chain, via either the terminal sulfonate moiety or ether group, should be suppressed because it requires larger deformation of the perfluoro-alkyl backbone (**Fig. 10**).

In summary, catalyst poisonings by ionomers were found to be mitigated by changing the flexibility of side chain and anion structure of the molecule. This information can provide guidelines for developing desirable ionomers for PEFCs.

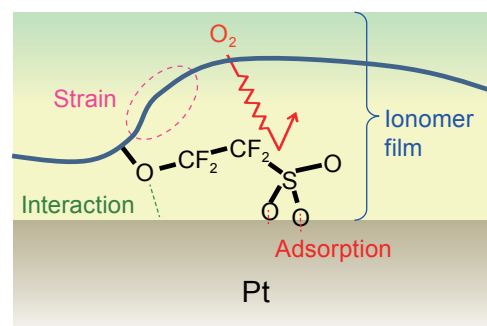


Fig. 10 Adsorption state of ionomer (Aquivion) on Pt surface suggested by the analyses in this work.

4. Conclusions

Experimental analyses were carried out using model catalytic surfaces of Pt single crystals for obtaining guidelines in designing the structures of Pt/ionomer interfaces in PEFCs. Stepped Pt single crystal electrodes were modified by depositing Au atoms selectively on vulnerable step sites and their electrocatalytic activities for ORR were examined. The result indicated that the ORR activities are improved and the surfaces are stabilized against potential cycles. Thus protecting vulnerable sites with stable substances is a promising method to enhance both the ORR activity and durability of the catalysts. Analysis with Pt single crystals was also applied to the study of catalyst poisonings by ionomers. Significant ORR-activity suppressions for Pt(111) surface by the coating with Nafion thin film were confirmed and ascribed to side chain adsorptions via the interactions between Pt and sulfonate and also between Pt and ether groups in the ionomer side chains, leading to the blockages of active sites. In addition, the anion adsorptivity was found increasing with drying the ionomer. The effect of molecular structure of ionomer was examined, and changing the flexibility of side chain and anion structure of the molecule was found effective to mitigate the catalyst poisoning. In this way, the well-defined model experiments successfully provided useful strategies for developing highly active and durable catalysts as well as less-poisoning ionomers.

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Figs. 2-4

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Figs. 5(b)-(d)

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Figs. 7 and 10

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Figs. 8(a)-(c)

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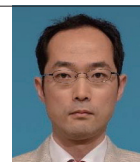
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