

## Catalyst Poisoning Property of Sulfonimide Acid Ionomer on Pt (111) Surface

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## Introduction

In catalyst layers of polymer electrolyte membrane fuel cells (PEMFC), a solid polymer electrolyte, called "ionomer" to be distinguishable from the electrolyte membrane, is used to form electrochemical interfaces on catalyst surfaces. Recent studies, however, showed that a perfluorinated sulfonic acid polymer (e.g. Nafion), which is almost exclusively used for the ionomer, blocks active sites on Pt catalyst and, therefore, slows down the kinetics of oxygen reduction reaction (ORR) [1].

A plausible poisoning species is the sulfonic anion of the polymer molecule, the adsorption of which on Pt (111) surface is clearly seen in the cyclic voltammogram (CV) [1-3]. It is, therefore, expected to be effective for improving the ORR performance to use an ionomer with a functional group that is less adsorptive to Pt surface.

Recently, Shinohara et al. developed a novel ionomer having two sulfonimide acid groups in its side chain ended with a hydrophobic group, instead of a sulfonic acid group, NBC4 (Fig. 1), which has higher protonic conductivity and O<sub>2</sub> permeability than Nafion [4]. The new side chain likely has a stronger steric effect for anion adsorption, and NBC4 is expected to be less-poisoning and have improved properties not only for the proton conduction and O<sub>2</sub> transport but also for ORR kinetics. These expectations are examined experimentally in the present study.

## Experimental

A Pt single crystal was used for analyzing the interface [1-3]. Thin films of Nafion and NBC4 were formed on Pt (111) surfaces and electrochemical measurements were carried out in the configuration of hanging meniscus rotating disk electrode [5].

## Results and Discussion

Cyclic voltammograms of Pt (111) surfaces covered with and without the ionomers are shown in Fig.2. Nafion-coated Pt showed irreversible sharp peaks in the double layer region (0.4 – 0.6 V), which have been attributed to the oxidative adsorption and reductive desorption of

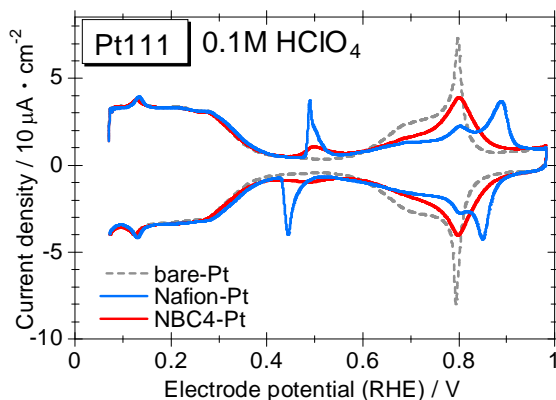


Fig. 2 The CVs for Pt (111) surfaces covered with and without the ionomers.

sulfonic anions [1-3]. Although the NBC4-coated Pt also has seemingly-anion-related peaks in the same potential range, they are much duller. Another difference in the nature of the anion adsorption is visible in the hydroxyl adsorption/desorption region (0.6 - 0.9 V). While both the ionomer-coatings suppress hydroxyl adsorption, the degree of suppression is much less with the NBC4-coating than with the Nafion-coating. These results show that the poisoning with the anions of NBC4 is weaker than that of Nafion.

Figure 3 shows that NBC4 exhibits a higher ORR kinetic current than Nafion by ca. 30% below 0.86 V and suggests that NBC4 has a better property for the ORR kinetics.

The kinetic current with NBC4, however, is still significantly less than that without any coating (60 % less at 0.82 V). Hence, the electrode surface should be still poisoned with some parts of NBC4 (the sulfonimide anion or fluorinated parts of the polymer chain), and this poisoning is required to be further lessened.

In addition, NBC4 shows, no longer, the ORR-improving effect above 0.86 V (see the results at 0.90 V). In that potential region, the coverage of Pt hydroxide seems too high for the ionomer to make a difference.

## References

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- [4] Shinohara et al., Japanese Patent, JP 2011- 40363.
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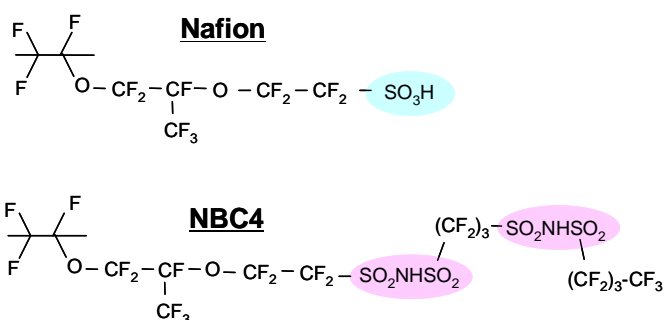


Fig. 1 Molecular structures of Nafion and NBC4.

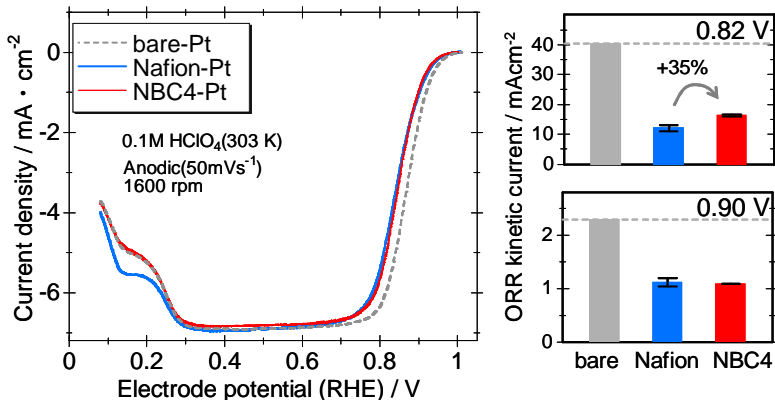


Fig. 3 The ORR curves and kinetic currents at 0.82 and 0.90 V on Pt (111) surfaces covered with and without the ionomers.