Investigation of the Effect of Hydrophilicity on Oxygen Reduction Reaction Property with Measurement of Water Vapor Specific Surface Area

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This is the final version of an authors’ manuscript, submitted by the author(s) and accepted for publication after peer review and technical editing by the Editorial Board of The Electrochemical Society of Japan. This manuscript may contain minor errors or incomplete designs that do not affect the judgment for publication. It is the responsibility of the authors to correct any errors in the Just Accepted manuscript during galley proof review.
In reaction rate-determining range

Large three-phase interface
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Abstract

For oxygen reduction reaction of an air battery which uses oxygen and water as reactants, it is important to control not only gas diffusivity but also hydrophilicity. In this study, the effect of hydrophilicity was investigated quantitatively. Various hydrophilic reaction layers were prepared with different amounts of Nafion as hydrophilic binder. The hydrophilicity was evaluated by measuring water vapor adsorption and nitrogen adsorption isotherms and calculating specific surface area by Brunauer-Emmett-Teller (BET) method. Polarization curves of oxygen reduction reaction revealed that the hydrophilicity effect differs between the reaction rate-determining range and the diffusion rate-determining range. In the reaction rate-determining range, the oxygen reduction current increased in proportion to the amount of water in the reaction layer, indicating the extension of the three-phase interface as the reaction field. In the diffusion rate-determining range, oxygen reduction current decreased with increasing the hydrophilicity, which demonstrates that high hydrophilicity suppressed oxygen diffusion.

Keywords: Hydrophilicity, Oxygen reduction, Three-phase interface, Air battery
1. Introduction

Metal-air batteries have received attention as electrical energy storage due to their high energy density.\textsuperscript{1-3} However, the problem of sluggish kinetics of the oxygen reduction reaction (ORR) needs to be solved in order to enhance their output and practical application. Numerous studies have been conducted to develop highly active, low-cost catalysts.\textsuperscript{4-8} Optimization of microstructure and surface properties of cathode is also investigated to promote mass transfer. So far, influences of micro-pore characteristics,\textsuperscript{9-11} amount of hydrophobic polymer,\textsuperscript{12-14} and hydrophilic polymer\textsuperscript{15,16} have been reported. These results revealed that gas diffusion promoted by high hydrophobicity, micropores and mesopores can increase ORR current density. In addition, it was reported that the use of hydrophilic-polymer binders could increase ORR current.\textsuperscript{15}

Reaction pathway\textsuperscript{17} for ORR in alkaline solution is known as follows:

\begin{align}
    \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^{-} & \rightarrow \text{HO}_2^- + \text{OH}^- \\
    \text{HO}_2^- + \text{H}_2\text{O} + 2\text{e}^{-} & \rightarrow 3\text{OH}^- 
\end{align}

These indicate that ORR requires the formation of a three-phase interface.\textsuperscript{12,18,19} Then, controlling hydrophilicity and hydrophobicity to extend the interface is important for improving electrode performance.\textsuperscript{20,21}
In this study, the effect of hydrophilicity was quantitatively evaluated to construct the optimum electrode condition for ORR. Gas diffusion electrodes (GDE) which have a gas diffusion layer and a reaction layer were used for the measurement of ORR properties. The reaction layer with different Nafion contents were prepared to evaluate the hydrophilicity by measuring the amount of water vapor adsorption and nitrogen adsorption. Although Nafion is an expensive material, it was selected in this study because it is mechanically robust and can sustain hydrated domains. In addition, it has been reported that the electrochemical surface area can be maintained without blocking the pores of the porous in the electrode material.

2. Experiment

2.1 Preparation of reaction layer

The powders for reaction layers were prepared with various amounts of Nafion (1100 EW, Dupont), hydrophilic carbon (KETJEN BLACK ECP600JD, LION Specialty Chemicals; surface area of 1270 m² g⁻¹) and polytetrafluoroethylene (PTFE) dispersion (D-210C, DAIKIN). The materials were mixed in purified water containing 1 % n-butanol, stirred and then filtered. Finally, these were milled to obtain uniform powders. One of the obtained powders was put in a beaker, heated to 120 °C by a hot plate, and
then sprayed with an alcohol solution containing Nafion. Reaction layer powders with different amounts of Nafion were prepared by changing the amount of the alcohol solution. The powder was placed in a mold and formed a layer by hot-pressing 20 MPa, at 140 °C. The reaction layer without Nafion was prepared by hot-pressing at 360 °C. The composition of constituent materials for the reaction layers is summarized in Table 1.

2.2 Fabrication of gas diffusion electrode (GDE)

Gas diffusion electrodes (GDE) with a reaction layer and a gas diffusion layer were fabricated to measure ORR current. The powder for the gas diffusion layer was prepared by mixing a hydrophobic carbon (HS-100, Denka) and PTFE dispersion (D-210C, DAIKIN) in aqueous solution with a surfactant (Triton X-100, Roche) at a ratio of carbon: PTFE: surfactant = 2: 3: 3 and filtered after being frozen and thawed. Then, it was heated at 280 °C for 3 hours to remove its surfactant. The powder was placed on a nickel mesh in a mold and integrated by 20 MPa hot-press at 360 °C to form a gas diffusion layer. Then, the powder of reaction layer was placed on the gas diffusion layer in a mold and integrated by hot-pressing 20 MPa, at 140 °C. The GDE without Nafion was prepared by hot-pressing at 360 °C.

2.3 Physical characterization
To measure adsorption isotherm curves, the reaction layers without a gas diffusion layer and nickel mesh were formed by a hot press. Nitrogen adsorption isotherm curves of the reaction layers were measured with an automated gas sorption analyzer (Autosorb-1c, Quantachrome) at –196 °C. The isotherm curves were analyzed to obtain pore distribution characteristics by a density functional theory (DFT) method.\textsuperscript{24–26} The values of the specific surface area (S. A. \textsubscript{N2}) were calculated by a Brunauer-Emmett-Teller (BET) method. Water vapor sorption isotherms were measured with an automated water vapor sorption analyzer (BELSORP-18, Microtrac MRB) at 50 °C. The values of the specific surface area for water adsorption (S. A. \textsubscript{H2O}) were calculated by the BET method. The hydrophilicity of the layers was determined as the ratio of S. A.\textsubscript{H2O} to S. A.\textsubscript{N2}. Morphology of the reaction layers was observed using a field emission scanning electron microscope (JSM-6701, JEOL).

2.4 Measurements of ORR current

The ORR current was measured using a three-electrode system, a potentiostat (HAL-3000, HOKUTO DENKO), and a function generator (HB-305, HOKUTO DENKO). The three-electrode system has a GDE, a Pt plate, and a reversible hydrogen electrode as working electrode, counter electrode, and reference electrode, respectively. The electrodes were immersed in 5 mol L\textsuperscript{−1} KOH electrolyte at 70 °C. Pure oxygen gas or
synthetic air (O₂ 21 % and N₂ 79 %) was supplied to GDE from the gas diffusion layer side at a flow rate of 80 cc min⁻¹. A potential was changed by 25 mV at 3 minute intervals.

3. Results and Discussion

The specific surface areas obtained from nitrogen sorption (S. A. N₂) and water sorption (S. A. H₂O) of the reaction layer with various amounts of Nafion are summarized in Table 1. SEM images of the surfaces of R1, R5, and R6 layers are shown in Fig. 1. It was found that the specific surface area of R1 layer without Nafion was smaller than those of other layers containing Nafion. SEM images revealed that R1 layer was formed by the melted PTFE which bound the carbon particles together, while R5 and R6 layers were constructed from fine particles and small spaces created by them. Since R1 layer was pressed at 360 °C, the melting point of PTFE, while R5 and R6 layers were pressed at 140 °C which is evaporation temperature of alcohol contained in the Nafion, the surface area and microstructure of these layers were very different.

Fig. 2 presents the relationship between the values of BET surface area (S. A. N₂ and S. A. H₂O) and Nafion content, and the relationship between the hydrophilicity of layers and Nafion content. Nitrogen adsorption is physical adsorption, therefore S. A. N₂ can be
regarded as a geometric surface area. It peaked at around 30 % Nafion content and slightly decreased at 36 %. On the other hand, S. A. H2O increased approximately linearly with increasing Nafion content over the entire measured range. The hydrophilicity increased in a similar pattern, but its rate of increase was different.

The pore distribution curves of the reaction layers and carbon powder (ECP 600JD) are shown in Fig. 3. Carbon powders have micropores with diameters of 1–2 nm or smaller than 1 nm and mesopores with diameters of 3 nm or 4–5 nm. The curve of R1 layer pressed at 360 °C was significantly different from that of the carbon powder; it seems that the pores were closed by melted PTFE. The layers pressed with Nafion have fewer micropores below 1 nm and mesopores at 3 nm than the carbon powder. In particular, the volumes of 3 nm mesopores were small in R2 and R3 layers which have high PTFE content. The pore characteristics of R4, R5, and R6 layers with high Nafion content are similar to those with carbon in the mesopore range.

Polarization curves of the GDEs that had reaction layers (R1–R6) with various Nafion contents under pure oxygen and air (O2 21 % and N2 79 %) conditions are shown in Fig. 4 (a) and (b). These results indicated that suitable composition of the reaction layer for ORR differs between pure oxygen and air supply condition. The current of GDE having
R1 (GDE-R1) showed the lowest value under pure oxygen flow, while GDE-R6 showed the lowest current value under air flow.

Among the electrodes measured, those with moderate hydrophilicity showed high current densities over wide potential range, regardless of gas supply conditions.

Tafel plots obtained from the polarization curves are shown in Fig. 4 (c) and (d). It appears that the ORR on GDEs is reaction rate-determining above 750 mV vs RHE and diffusion rate-determining below this potential.

Figure 5 shows the dependence of Nafion content on the ORR current under pure oxygen and air flows at different potentials. At 800 mV vs RHE, the ORR current increased with increasing Nafion content under both oxygen and air flow. In addition, the increasing trend of this value was similar to the increasing tendency of S. A. H2O. The reaction layer was in contact with the aqueous electrolyte solution during the ORR measurement, and the mobility of water to the layer should depend on the S. A. H2O. Therefore, this result shows that ORR depends on the amount of water in the layer.

That is, the ORR depends on the magnitude of three-phase interface in the reaction rate-determining range.

In contrast, in the diffusion rate-determination range, the ORR current value of GDE with high Nafion content was low. In particular, a decrease in the current under air flow
was confirmed as the Nafion content increased. This tendency was noticeable under higher overvoltage conditions, and seems to be due to the decrease in oxygen diffusion rate with increasing Nafion content. This indicates that increased hydrophilicity suppresses the gas diffusion. In the case of pure oxygen flow at 700 mV, the current increased with increasing Nafion content when the Nafion content was less than 29%. This appears the effect of extending the three-phase interface. These results indicate that the supply of oxygen was sufficient under this condition.

4. Conclusion

Reaction layers with various Nafion contents were prepared to quantitatively examine the effect of hydrophilicity on the ORR of air battery. In order to evaluate the hydrophilicity of the reaction layer, the isotherms of water vapor adsorption and nitrogen adsorption were measured, and the BET specific surface area was determined. The hydrophilicity was quantified as the ratio between specific surface area for water and nitrogen.

Polarization measurements were performed using GDEs with reaction layers containing various amounts of Nafion to evaluate ORR characteristics. It was found that the effect of hydrophilicity differs between the reaction rate-determining range and the
diffusion rate-determining range. ORR current in the reaction rate-determining range is proportional to the specific surface area of the water vapor adsorption. Thus, we conclude that it increased with the expansion of the three-phase interface. In the diffusion rate-determining range, the ORR current decreased with increasing the hydrophilicity, which should indicate that oxygen diffusion was suppressed.

From these results showed that the influence of hydrophilicity is different between the reaction rate-determining range and the diffusion rate-determining range. This information is important in deciding on which elements are needed to optimize the ORR electrode composition and improve the capacity of the air battery.

**Acknowledgements**

This work was supported by JSPS KAKENHI Grant Number JP18K05301.
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Fig. 1 SEM images of the cross-sectional view of the reaction layers of (a) R1, (b) R5, and (c) R6.

Fig. 2 Relation between Nafion content and (a) the BET specific surface areas for H₂O (S. A.₇₂₀) or N₂ (S. A.₇₂₂) and (b) the hydrophilicity (S. A.₇₂₀ / S. A.₇₂₂).

Fig. 3 Pore size distribution of carbon powder and reaction layers with various amount of Nafion.

Fig. 4 Polarization curves and Tafel plots of GDEs with a reaction layer (R1–R6) under pure O₂ flow (a), (c) and Air flow (b), (d) in 5 mol L⁻¹ KOH.

Fig. 5 ORR current densities of GDEs with various Nafion content (a) 800 mV, (b) 700 mV, and (c) 600 mV vs RHE in 5 mol L⁻¹ KOH.
Fig. 1
Fig. 2

(a) BET S. A. N$_2$ / m$^2$ g$^{-1}$ vs. Naflon content / %

(b) Hydrophilicity vs. Naflon content / %
Fig. 3
Fig. 4
Fig. 5

(a) 800mV
- O2
- Air

(b) 700mV
- O2
- Air

(c) 600mV
- Air
Table 1. Values of hydrophilicity, specific surface areas, and composition for reaction layers.

| Reaction layer | Hydrophilicity $(S. A_{H2O} / S. A_{N2})$ | $S. A_{H2O}^{*1}$ $m^2 g^{-1}$ | $S. A_{N2}^{*2}$ $m^2 g^{-1}$ | Nafion mg (wt%) | Carbon mg (wt%) | PTFE mg (wt%) |
|----------------|------------------------------------------|-------------------------------|-------------------------------|----------------|---------------|---------------|
| R1             | 0.0101                                   | 2.2                           | 218.6                         | 0.0 (0)        | 23.8 (56)     | 18.8 (44)     |
| R2             | 0.0301                                   | 8.8                           | 292.4                         | 6.9 (14)       | 23.8 (48)     | 18.8 (38)     |
| R3             | -                                        | -                             | 375.1                         | 13.8 (25)      | 23.8 (42)     | 18.8 (33)     |
| R4             | 0.0348                                   | 15.4                          | 442.8                         | 17.4 (29)      | 23.8 (40)     | 18.8 (31)     |
| R5             | -                                        | -                             | 456.1                         | 20.9 (33)      | 23.8 (37)     | 18.8 (30)     |
| R6             | 0.0554                                   | 21.4                          | 386.6                         | 24.4 (36)      | 23.8 (36)     | 18.8 (28)     |

*1) S. A. $H2O$: Specific surface area measured with $H2O$

*2) S. A. $N2$: Specific surface area measured with $N2$