

# Enhancement of Catalytic Activity of Ultra-low Platinum Loading Electrode by Thickness Decrease of Ionomer Film

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## Abstract

The effect of viscosity of the ionomer solution on the catalytic mass activity and particle diameter of platinum in the Ultra-Low Platinum Loading Electrode (ULPLE<sup>®</sup>) has been investigated, since the solution is generally used as a precursor material for the preparation of ULPLE<sup>®</sup> to control its catalyst's loading level. The decreased viscosity from 73.4 mPa s to 10.4 mPa s using 2-propanol diluent was found out to lead to the improvement of catalytic mass activity by 16.5% with the decrease of particle diameter of platinum by 38.5%. This phenomenon is considered to be caused by deep infiltration of diluted ionomer solution with the lowered viscosity into both micro pores within the aggregate and voids within the agglomerate of carbon particles. The formation of thinner ionomer film on the carbon powders enables small-sized catalyst particles to deposit at the site of interface between the carbon and hydrophilic cluster of ionomer resulting in the enhancement of catalytic mass activity.

*Key words*: Ultra-low platinum loading electrode; Catalytic mass activity; Ionomer solution; Viscosity

## 1 Introduction

Both the utilization of platinum catalyst and its durability performance of ultra-low platinum loading electrode (ULPLE<sup>®</sup>) have been reported to be extremely high, because the nano-sized catalyst particles are selectively located on the interface between hydrophilic cluster of ionomer and carbon support.<sup>1,2)</sup> The ULPLE<sup>®</sup> is prepared by the very unique procedure comprising the adsorption process to exchange the counter ion in cluster of ionomer located on the surface of carbon for  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  complex cation, followed by the reduction process under hydrogen atmosphere at low temperature condition such as 180

°C for 6 hours. In the reduction process, the adsorbed complex cations are thought to migrate toward the interface to be reduced successively; therefore, the particle diameter of platinum catalyst is estimated to be proportional to the cubic root of thickness of ionomer film on carbon. In this paper, we report the effect of viscosity of ionomer solution as a precursor material for the preparation of ULPLE<sup>®</sup> on its catalytic mass activity.

## 2 Experimental

### 2.1 Preparation of ULPLE<sup>®</sup>

The ULPLE<sup>®</sup> was prepared with the following process: dilution process of ionomer solution of 10 mass% by the addition of 2-propanol to the ionomer

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solution; preparation process of mixture composed of the diluted ionomer solution with concentration of 1.0, 2.5, and 5.0 mass% and carbon powders (Cabot, Vulcan XC-72) by using of rotary blade beater and ultrasonic irradiation; concentration process of the mixture up to 20 mass% by evaporation of the solvent at 60 °C; application process of the mixture to a titanium sheet by using knife coater; dry process of the mixture in the dryer at 80 °C result in the formation of composite sheet as precursor for electrode; immersion process of the composite sheet comprising carbon of 60 mass% and ionomer of 40 mass% in  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  complex cation solution of 50 mmol l<sup>-1</sup> at 60 °C for 12 hours to adsorb the complex cations into the hydrophilic cluster of ionomer; rinse process of the composite sheet by deionized water to remove the complex cations remained in the site besides the cluster; and reduction process of the complex cation into metallic platinum on the surface of carbon under the condition of hydrogen atmosphere at 180 °C for 6 hours.

## 2.2 Preparation of membrane electrode assembly and single test cell

The membrane electrode assembly (MEA) with 25 cm<sup>2</sup> was prepared by hot-pressing of cathode and anode ULPLE<sup>®</sup>s on the both side of polymer electrolyte membrane (DuPont, Nafion<sup>®</sup> 115) at 130 °C for 5 min.. The assembly was rinsed in 0.5 mol l<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 80 °C followed by in the deionized water at 80 °C. The single test cell was composed of the following serial constitution; anode gas flow plate / gas diffusion layer / catalyst layer / membrane / catalyst layer / gas diffusion layer / cathode gas flow plate. The gas diffusion layer was composed of macro and micro diffusion layers. The former one was the carbon paper (SGL, DGL10AA) treated with hydrophobic resin (DuPont-Mitusifluorochemical, PTFE 30-J<sup>®</sup> dispersion). The latter one was composed of carbon powders (Cabot, Vulcan<sup>®</sup> XC72) of 70 mass% and hydrophobic resin (DuPont-Mitusifluorochemical, FEP 120-J<sup>®</sup> dispersion) of 30 mass%. The gas diffusion layer was heated at 380 °C for 15 min. for hydrophobic property.

## 2.3 Catalytic mass activity and active surface area

The catalytic mass activity of catalyst was calcu-

lated from the data of IR-corrected cell voltage at 0.8 V under the condition of cell temperature of 80 °C and humidified temperature of 80 °C for hydrogen and oxygen gases. The catalytic mass activity was defined as the value of its current density divided by platinum loading level. The active surface area was investigated by cyclic voltammograms at room temperature under the condition of scan rate of 100 mV s<sup>-1</sup> and scan range from 0.04 V to 1.2 V. The value was calculated from its columbic charge for hydrogen desorption divided by 210 μC cm<sup>-2</sup>.

## 3 Results and discussion

### 3.1 Viscosity of ionomer solution

The effect of concentration of ionomer solution on its viscosity is shown in Fig. 1. The viscosity of ionomer solution decreased down to 10.4 mPa s from 73.4 mPa s with decreasing the concentration from 5.0 mass% to 1.0 mass%. The loading level of catalyst in ULPLE<sup>®</sup> using the diluted ionomer solution of concentration of 1.0 mass%, 2.5 mass%, and 5.0 mass% is shown in Table 1. The level of platinum loading of each electrode was 0.027 mg cm<sup>-2</sup> or lower. The level is considered to be proportional to the content of ionomer in electrode, namely, to the thickness of electrode, because the platinum is formed by the re-

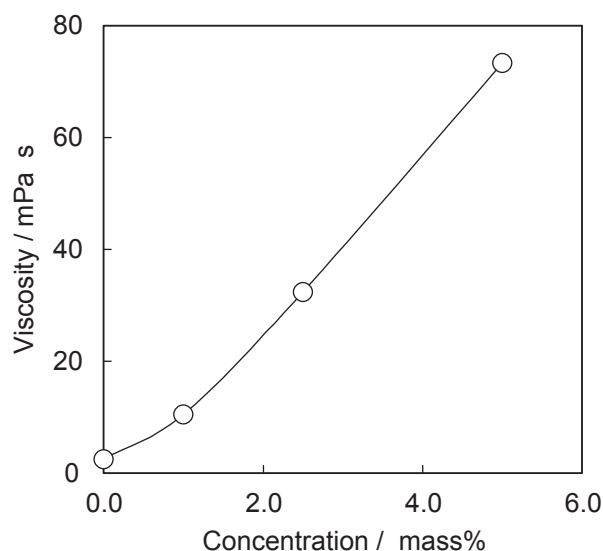


Fig. 1 Viscosity of the ionomer solution with its concentration. The dilution solvent is 2-propanol.

duction of adsorbed  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  complex cation in the cluster of it. Therefore, the loading level of ULPLE<sup>®</sup> using 5.0 mass% ionomer solution is higher than that of the other.

### 3.2 Catalytic mass activity and electrochemically active surface area

The effect of viscosity of ionomer solution for preparation of ULPLE<sup>®</sup> on the catalytic mass activity of platinum catalyst is shown in Fig. 2. The value of catalytic mass activity decreased with increasing the viscosity of ionomer solution. In other words, the catalytic mass activity of platinum catalyst in ULPLE<sup>®</sup> was enhanced by using ionomer solution with lower viscosity for the preparation processes of composite sheet comprising carbon and ionomer as the precursor of electrode. Furthermore, the electrochemically

Table 1 Loading level of catalyst of ultra-low platinum loading electrode prepared from different concentration of ionomer solution.

Ionomer solution		Pt loading	Thickness of
Content	Viscosity	level	catalyst layer
/ mass %	/ mPa s	/ mg cm <sup>-2</sup>	/ μm
1.0	10.4	0.021	15
2.5	32.4	0.021	15
5.0	73.4	0.027	17

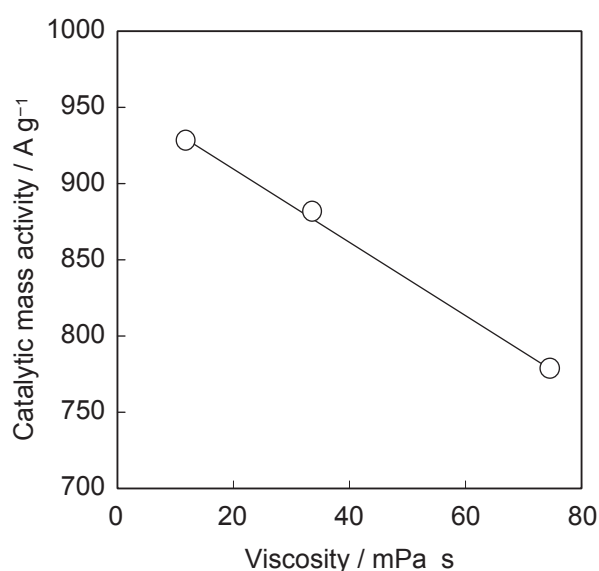


Fig. 2 Effect of viscosity of ionomer solution on catalytic mass activity of ULPLE<sup>®</sup> calculated at IR-corrected cell voltage of 0.8 V at cell temperature of 80 °C under the condition of humidified temperature of 80 °C for hydrogen and oxygen gases.

active surface area of platinum catalyst in ULPLE<sup>®</sup> was evaluated by cyclic voltammograms in order to investigate the enhancement of catalytic mass activity. The effect of viscosity of ionomer solution for preparation of ULPLE<sup>®</sup> on the electrochemically active surface area of platinum catalyst is shown in Fig. 3. The electrochemically active surface area is found out to decrease with increasing the viscosity of ionomer solution as the same dependence of catalytic mass activity in Fig. 2. The change in catalytic mass activity as a function of the electrochemically active surface area of platinum catalyst is shown in Fig. 4. It is found out that the catalytic mass activity is enhanced with increasing the electrochemically active surface area of platinum catalyst. Additionally, the increase of catalytic mass activity seems to be caused by the decrease of particle diameter of platinum catalyst judging from the loading level of platinum is same (See Table 1).

### 3.3 Particle diameter of platinum catalyst

The value of particle diameter of platinum catalyst in ULPLE<sup>®</sup> is shown in Table 2. The particle diameter was calculated from the X-ray diffraction (XRD) measurements, namely, the value of half width and

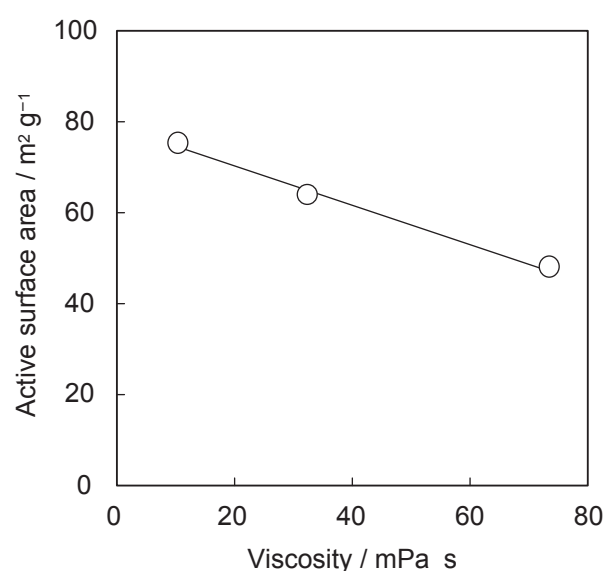


Fig. 3 Effect of viscosity of ionomer solution on specific active surface area of catalyst calculated from hydrogen desorption peak of cyclic voltammograms for ULPLE<sup>®</sup>.

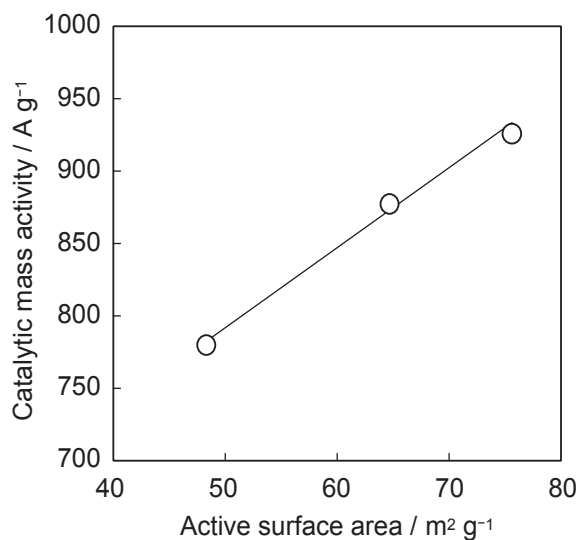


Fig. 4 Plots of catalytic mass activity as function of specific active surface area of catalyst calculated from hydrogen desorption peak of cyclic voltammograms of ULPLE<sup>®</sup>.

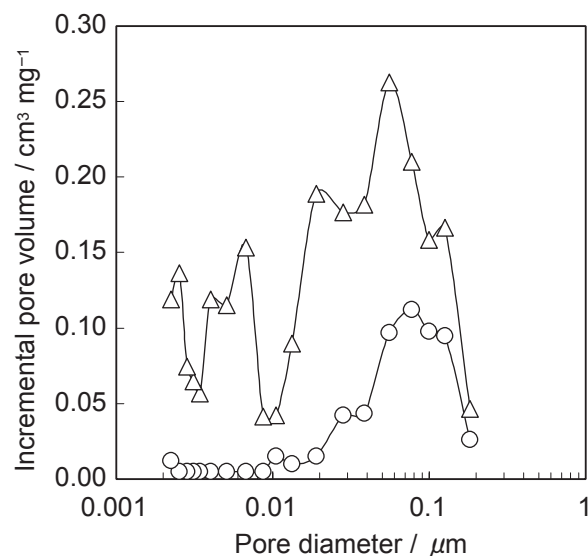


Fig. 5 Pore distribution of ultra-low platinum loading electrode using different ionomer solution of (○) 1.0 mass% and (△) 2.5 mass%.

Table 2 Electrochemically active surface area and calculated diameter for platinum particle of ultra-low platinum loading electrode.

Concentration of ionomer solution	Mass activity at 0.8 V	Active surface area	Platinum diameter	
			by XRD	by CV *
/ mass %	/ A g <sup>-1</sup>	/ m <sup>2</sup> g <sup>-1</sup>	/ nm	/ nm
1.0	922	75.1	2.03	2.26
2.5	875	64.2	2.55	2.62
5.0	772	47.6	3.30	3.52

\* Cyclic voltammogram

angle for diffraction peak assigned lattice (111) of platinum using Scherrer equation. The value of particle diameter increases with increasing the viscosity of ionomer solution. Namely, the particle diameter of platinum catalyst in ULPLE<sup>®</sup> was found out to be decreased by the use of ionomer solution with lower viscosity for the preparation processes of composite sheet. Furthermore, the value of particle diameter of platinum catalyst was also calculated from the value of electrochemically active surface area based on the assumption in which all platinum particles are spherical shape with even diameter. The calculation results are summarized in Table 2. It is found out that the calculated value from the data of cyclic voltammogram (CV) has a tendency to be larger than that of XRD. This tendency suggests that a part of ULPLE<sup>®</sup>

comprising carbon, ionomer, and platinum is electrically isolated from macro porous layer resulting in the larger value, because the coulombic charge for hydrogen desorption of platinum particles loaded on the isolated mixture is uncountable in the cyclic voltammogram measurement.

Judging from the fact that both calculated values of particle diameter of platinum catalyst are decreased with decreasing the viscosity of ionomer solution, the enhancement of catalytic mass activity of platinum is considered to be due to the increase of active surface area by the decrease of particle diameter of platinum in ULPLE<sup>®</sup> by using of ionomer solution with lower viscosity for the preparation process of composite sheet comprising carbon and ionomer as the precursor of electrode.

### 3.4 Pore distribution of ULPLE<sup>®</sup>

The pore distribution of ULPLE<sup>®</sup> using ionomer solution with different concentration of 1.0 mass% and 2.5 mass% is shown in Fig. 5. The pores with the diameter of less than 0.01 μm in ULPLE<sup>®</sup> using 1.0 mass% solution are found out to dramatically decrease than that of 2.5 mass% solution. The decrease is considered to be due to the penetration of ionomer solution with lower viscosity into the micro pores within the aggregate and the voids within the ag-

glomerate of carbon particles. The penetration leads to the widespread covering of ionomer solution on the carbon, consequently, the thin ionomer films are to be formed on the surface of carbon by using ionomer solution with lower viscosity for the preparation process of composite sheet. The thin ionomer film is thought to bring the decrease of particle diameter of platinum catalyst in ULPLE<sup>®</sup>. The particle diameter is considered to be proportional to the cubic root of thickness of the ionomer film on carbon as its support materials, because the electrode is prepared by unique process, namely, the platinum particles are formed at interface between surface of carbon and hydrophilic cluster of ionomer by the reduction of adsorbed  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  complex cations in the cluster to metallic platinum as already mentioned before. In other words, the thickness of ionomer film is to be estimated from the particle diameter of platinum catalyst in ULPLE<sup>®</sup>.

### 3.5 Thickness of ionomer film

The estimated value of thickness of ionomer film is shown in Table 3. The estimated value is obtained according to the equation (1) and the calculated particle diameter of platinum from XRD data. This estimation is based on the four assumptions: the thickness of ionomer film located on carbon is uniform; the size and shape of cluster in the ionomer film is uniform; the cluster shape is cylindrical with diameter of 3.8 nm; the volume of cluster in the film is 27%. It is found out from the estimation results that the thickness of ionomer film dramatically decreases by one-fourth according to the decreasing viscosity of ionomer solution from 73.4 mPa s to 10.4 mPa s. The decrease of film thickness is considered to be due to the penetration of ionomer solution with lower

Table 3 Estimated thickness value of ionomer film in ULPLE<sup>®</sup> with the different concentration of ionomer solution calculated from platinum diameter by XRD parameters.

Concentration of ionomer solution / mass%	Platinum diameter by XRD* / nm	Ionomer film thickness / nm
1.0	2.03	13.3
2.5	2.55	26.3
5.0	3.30	56.9

\* From the value of Table 2.

viscosity into the micro pores within the aggregate and the voids within the agglomerate of carbon at the mixing process of carbon and ionomer solution, resulting in the widespread formation of film on the surface of carbon.

$$d = \frac{2 \times EW \times V}{\pi \times N \times r_{\text{clus}}^2 \times \rho \times R_{\text{red}}} \times \left( \frac{r_{\text{part}}}{r_{\text{atom}}} \right)^3 \times R_{\text{pack}} \quad \dots \dots (1)$$

$d$  : Thickness of ionomer film

$EW$  : Inverse number of ion-exchange capacity =  $930 \text{ g mol}^{-1}$

$V$  : Volume rate of cluster = 27.0% (assumption value)

$N$  : Avogadro's number =  $6.02 \times 10^{23}$

$R_{\text{clus}}$  : Diameter of cluster = 3.8 nm (assumption value)

$\rho$  : Density of ionomer =  $2.0 \text{ g cm}^{-3}$

$R_{\text{red}}$  : Reduction rate of adsorbed  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  = 80%

$r_{\text{part}}$  : Radius of platinum diameter estimated from XRD

$r_{\text{atom}}$  : Radius of platinum atom = 1.39 nm

$R_{\text{pack}}$  : Packing rate of platinum atom = 74%

## 4 Conclusions

The catalytic mass activity in ULPLE<sup>®</sup> has been improved by 16.5% when using of ionomer solution with lower viscosity of 10.4 mPa s from 73.4 mPa s. The improvement is considered to be due to the increase of electrochemically active surface area according to the decrease of particle diameter for platinum. Furthermore, the decrease is estimated to be caused by the formation of thinner ionomer film on the surface of carbon in ULPLE<sup>®</sup> through the sufficient penetration of ionomer solution with lower viscosity into the micro pores within the aggregate and the voids within the agglomerate of carbon powders.

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