Improved Accelerated Stress Tests for ORR Catalysts Using a Rotating Disk Electrode

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RDE-based accelerated stress tests (ASTs) are often used for early-stage research of fuel cell catalysts, in which the electrochemical surface area (ECSA) and the mass activity (MA) are usually measured only at the beginning and the end of the testing procedure, although their intermediate values in the transitional period are very important to understand the degradation mechanisms. This is because the ECSA and the MA are measured in the O2-free and the O2-saturated electrolytes, respectively, and frequent gas switching introduces extra burden to the already lengthy AST. In this study, we developed a new method to measure the ECSA in the O2-saturated electrolyte, which leads to an improved AST that can acquire the intermediate ECSA and MA values without changing the purging gases. Then, we evaluated Pt/C and Pt3Ni/C model catalysts with the new AST. The results showed a clear difference in degradation behavior: while the MA of the Pt/C gradually reduced as a result of the ECSA loss, the MA of the Pt3Ni/C rapidly decreased owing to the decrease in the specific activity. This new AST protocol would enable us to accurately compare the durability of different catalysts and to deeply understand their degradation mechanism.

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Fuel cell electric vehicles (FCEVs), enabled with a hybrid of battery and polymer electrolyte membrane fuel cell (PEMFC) systems, have been expected to be one of the future “green” alternatives to internal combustion engine cars.1 Nearly 5,000 fuel cell cars have been already sold in the US since 2015.2 However, for larger scale of deployment of FCEVs, there are still many challenges to be solved including fuel efficiency, material durability, costs and so on. According to the cost analysis studies done by US Department of Energy (DOE), catalyst is the most expensive material component of the PEMFC system at a production scale of 500,000 units per year and significant reduction of platinum group metals (PGM) usage in catalysts are required, especially on the cathode for oxygen reduction reaction (ORR).3 To address this challenge, extensive studies have been conducted to develop various types of novel ORR catalysts such as Pt-alloy, core-shell, and shape-controlled catalysts.4-6 These catalysts have demonstrated much higher activity than the Pt/C catalysts, mostly due to carefully optimized reaction sites, which, on the other hand, also make them vulnerable to performance degradation as even subtle changes to the specific composition, shape or structure may lead to substantial activity loss.7

During the early-stage research on fuel cell catalysts, a rotating disk electrode (RDE) is often used for accelerated stress tests (ASTs)8-12 to assess catalyst durability, instead of a membrane-electrode-assembly (MEA). This is mainly because the RDE-based AST can be conducted with just a few milligrams of catalyst material that can be readily obtained from a small batch of synthesis. The electrochemical surface area (ECSA) and the mass-based ORR activity (MA) are usually acquired at the beginning and the end of the AST to quantify catalyst performance degradation. The ECSA is usually measured in the N2 or Ar purged, namely O2-free, electrolyte by estimating the amount of charge transfer from the hydrogen adsorption region of a cyclic voltammogram, while MA is typically evaluated by linear sweep voltammetry in the O2 saturated electrolyte. Such a practice worked well with the traditional Pt/C-type catalysts, however, for many of the newly developed catalysts that are more sensitive to degradation, it is of great importance to acquire the intermediate ECSA and MA values during ASTs for better understanding of their degradation behaviors. Unfortunately, obtaining these ECSA and MA information is quite time-consuming because the electrolyte has to be purged with different gases to prepare O2-free and the O2-saturated electrolytes for ECSA and MA measurement, respectively. Given the AST procedure itself is a long process already, adding these steps of switching purging gases would make it even more tedious and less efficient, which might be the reason that intermediate ECSA and MA values have been rarely reported in previous AST results.

In this study, we developed a new method to measure the ECSA in the O2-saturated electrolyte and applied it to an AST protocol, which enables us to acquire the intermediate ECSA and MA values efficiently without changing the purging gases. Then we further examined Pt/C and Pt3Ni/C model catalysts to validate the effectiveness of the new AST protocol.

Experimental

Commercial Pt/C (TEC10E50E, Tanaka Kikinzoku Kogyo) and Pt3Ni/C (40% Platinum Nickel (3:1) on Vulcan, Fuel Cell Store) were used as model catalysts for durability study. To prepare catalyst ink, the catalyst was first mixed with 25vol% 2-propanol aqueous solution and 5wt% Nafion solution (D520, Ion Power), and then sonicated in an ice bath for 60 min. Subsequently, 5 μL of the catalyst ink was pipetted on a polished glassy carbon disk electrode (GC, 5 mm in diameter) and dried in air at room temperature by using an inverted rotator at 700 rpm.13 The catalyst loadings on the electrodes were 10 μgPt/cm2, 8.8 μgPt/cm2, and 20 μgPt/cm2 for Pt/C and Pt3Ni/C, respectively. The ionomer (Nafion) (Nafton) to carbon ratio was 0.5.

A potentiostat (VSP, BioLogic), an electrode rotator and a standard three-electrode glass cell (Pine Research Instrumentation) were used for electrochemical measurements. The working electrode was the catalyst-applied GC disk. The counter electrode (CE) was an in-house built platinumized nickel electrode and the reference electrode (RE) was an in-house built reversible hydrogen electrode (RHE). The CE and the RE were isolated from the main cell compartment using a glass fritted tube. The glassware and other components were soaked in a mixed acid (H2SO4:HNO3 = 1:1) for more than 4 hours. Subsequently, they were thoroughly rinsed with ultrapure water from a Milli-Q system (Millipore Sigma) and boiled more than 2 times. The electrolyte was 0.1 M HClO4 prepared from 70% perchloric acid (VERITAS DOUBLE DISTILLED, GFS chemicals, Inc.).14

For the conditioning of the catalysts, cyclic voltammetry was conducted between 0.05 and 1.05 V at 100 mV/s in the O2-saturated
electrolyte at 400 rpm until the ORR current at 0.9 V reached the maximum value. For the ECSA measurement, cyclic voltammetry was conducted between 0.05 and 1.05 V at 50 mV/s in O₂-saturated electrolyte at 50 rpm. The ECSA was determined from the average of hydrogen adsorption and desorption charges approximately between 0.06 V and 0.4 V, assuming a specific charge of 210 μC/cm²·g. For the ORR activity measurement, linear sweep voltammogram (LSV) was obtained from 0.05 to 1.05 V at 10 mV/s in O₂-saturated electrolyte at 900 rpm. The mass activity (MA) and the specific activity (SA) were determined by normalizing the kinetic current in the O₂-free electrolyte to avoid influences of the ORR current. Figure 1

CVs measured in the O₂-free and O₂-saturated electrolytes at 50 rpm.

The ECSA was determined from the average of the hydrogen adsorption and desorption charges (H,ads and H,des) expressed by Eq. 2 and Eq. 3, respectively.

\[ i_\text{H,ads} = i_p - i_L,\text{p} + i_{\text{DLC},p} \]  

where \( i_p \) is the double-layer-charging current. Suffix p indicates negative-going and positive-going scans, respectively. Since \( i_{\text{H,ads}} \) and \( i_{\text{H,des}} \) are almost symmetric against the horizontal line, the hydrogen coverage at each potential for the negative-going scan seems to be the same as that for the positive-going scan. Supposing that the decrease in \( i_{\text{H,ads}} \) is determined by the hydrogen coverage, the \( i_{\text{H,ads}} \) and \( i_{\text{H,des}} \) can be regarded as the same. Therefore, integrating the difference between \( i_{\text{H,ads}} \) and \( i_{\text{H,des}} \), the ECSA can be further calculated as shown in Eq. 5.

\[ Q_{\text{H,ave}} = \frac{1}{2} \left( \sum (i_p - i_a) - \sum (i_{\text{DLC},p} - i_{\text{DLC},a}) \right) = \frac{1}{2} \sum (i_{\text{H,ads}} - i_{\text{H,des}}) \]  

Improved design of AST protocol.—We propose here an improved design of AST protocol as illustrated in Figure 4. In our new AST protocol, the ECSA and the ORR activity were both obtained in the

Results and Discussion

ECSA measurement in O₂-saturated electrolyte.—For ECSA measurements, cyclic voltamograms (CVs) are usually obtained in the O₂-free electrolyte to avoid influences of the ORR current. Figure 1 shows the CVs of the Pt/C and Pt₃Ni/C measured in the O₂-saturated electrolyte at different rotation speed, together with the CV measured in the O₂-free electrolyte for comparison. The hydrogen adsorption region of the CV was within the O₂-diffusion limiting potential range for ORR, therefore, it shifted to the negative current direction as the diffusion limiting current \( i_L \) increased with increasing the rotation speed. If \( i_L \) were constant regardless of the potential, hydrogen adsorption region would be just shifted to the negative current direction. However, the shape of the hydrogen adsorption region was actually deformed especially at the high rotation speed, because \( i_L \) decreased in the hydrogen adsorption region owing to the change in the ORR pathway from 4- to 2-electron reaction caused by the blocking of the O₂ dissociation with the adsorbed hydrogen. This makes it difficult to measure the ECSA in O₂-saturated electrolyte. To minimize the effect, it’s important to reduce \( i_L \) and to increase the hydrogen adsorption and desorption current (\( i_{\text{H,ads}} \) and \( i_{\text{H,des}} \)). Thus, we used the slowest rotation speed guaranteed for the rotator used in this study and the higher scan rate than 50 mV/s to increase the ratio of \( i_L \) to \( i_{\text{H,ads}} \). Figure 2 shows the CVs measured in the O₂-free and O₂-saturated electrolytes at 50 rpm. In order to compare the hydrogen adsorption region, a replicate of the CV in O₂-saturated electrolyte, which is represented with the broken line, is superimposed on the CV in the O₂-saturated electrolytes. The size and the shape of the hydrogen adsorption region in the O₂-saturated electrolyte were almost the same as that in the O₂-free electrolyte. It appears that the distortion effect by \( i_L \) can be mitigated if the electrode rotation speed and the CV scan rate are appropriate. It should be noted here that we chose the lowest electrode rotation speed even though \( i_L \) would be less when the electrode stayed stationary. This is because \( i_L \) is unstable and difficult to estimate without the rotation owing to the change in the O₂ diffusion layer thickness during CV measurement.

The currents in the hydrogen adsorption region for the negative-going and positive-going scans \( (i_{\text{H,ads}} \) and \( i_{\text{H,des}} \)) are expressed by Eq. 2 and Eq. 3, respectively.

\[ i_a = i_{\text{H,ads}} + i_{\text{H,des}} + i_{\text{DLC,ads}} \]  

\[ Q_{\text{H,ave}} = \frac{1}{2} \left( \sum (i_p - i_a) - \sum (i_{\text{DLC},p} - i_{\text{DLC},a}) \right) = \frac{1}{2} \sum (i_{\text{H,ads}} - i_{\text{H,des}}) \]  

Figure 1. CVs for (a) Pt/C and (b) Pt₃Ni/C measured in the O₂-saturated electrolyte at different rotation speed together with that measured in the O₂-free electrolyte. The scan rate: 50 mV/s.

Improved design of AST protocol.—We propose here an improved design of AST protocol as illustrated in Figure 4. In our new AST protocol, the ECSA and the ORR activity were both obtained in the

\[ i_{\text{H,ads}} = i_p + i_{\text{DLC},p} \]  

where \( i_{\text{DLC},p} \) is the double-layer-charging current. Suffix p indicates negative-going and positive-going scans, respectively. Since \( i_{\text{H,ads}} \) and \( i_{\text{H,des}} \) are almost symmetric against the horizontal line, the hydrogen coverage at each potential for the negative-going scan seems to be the same as that for the positive-going scan. Supposing that the decrease in \( i_{\text{H,ads}} \) is determined by the hydrogen coverage, the \( i_{\text{H,ads}} \) and \( i_{\text{H,des}} \) can be regarded as the same. Therefore, integrating the difference between \( i_{\text{H,ads}} \) and \( i_{\text{H,des}} \), the ECSA can be further calculated as shown in Eq. 5.

\[ \text{ECSA} = \frac{Q_{\text{H,ave}} [C]}{2.10 \left[C/m^2/g\right] \times \text{Pt amount [g]}} \]  

Improved design of AST protocol.—We propose here an improved design of AST protocol as illustrated in Figure 4. In our new AST protocol, the ECSA and the ORR activity were both obtained in the
Figure 2. Comparison of the CVs for (a) Pt/C and (b) Pt3Ni/C measured in the O2-free and O2-saturated electrolytes. The rotation speed: 50 rpm. The scan rate: 100 mV/s.

O2-saturated electrolyte by using the method mentioned above. Therefore, their intermediate values can be efficiently acquired without switching purging gases.

Figure 5 shows the changes in the CV and the LSV measured in the O2-saturated electrolyte during the AST for the Pt/C. The peak potentials in the hydrogen adsorption region of the CV did not shift during the AST. This result means that the reference potential of RHE is stable as long as it is properly separated from the O2-saturated electrolyte. Meanwhile, the diffusion limiting current for the ORR of the LSV did not change during the AST. This observation indicates that the electrolyte was always saturated with O2, although the O2 gas flew on the electrolyte (did not went through the electrolyte) to avoid the fluctuation of the diffusion limiting current.

Validation of the new AST using model catalysts.—In order to demonstrate the robustness and the effectiveness of the new AST
Figure 6. Change in (a) the CV and (b) the LSV for the Pt$_3$Ni/C during the AST. The rotation speed: 50 rpm for the CV, 900 rpm for the LSV; The scan rate: 50 mV/s for the CV, 10 mV/s for the LSV.

Figure 7. The intermediate values of (a) the MA, (b) the ECSA (c) the SA during the ASTs for the Pt/C and the Pt$_3$Ni/C.

Conclusions

In summary, we reported here a new AST protocol for evaluating the durability of ORR catalysts by using a rotating disk electrode. The key improvement in this study involves the enabling the ECSA measurement in O$_2$-saturated electrolyte by carefully selecting the electrode rotation speed and the CV scan rate to minimize the influence of O$_2$ diffusion limiting current on the calculation of the charge transfer during hydrogen adsorption/desorption processes. As a result, both the ECSA and the MA can be measured in O$_2$-saturated electrolyte and their intermediate values were readily acquired during the AST without changing the purging gas. We further applied the new AST protocol to evaluate the durability of Pt/C and Pt$_3$Ni/C catalysts. The difference of their degradation behavior was clearly revealed with the trends of ECSA and MA changes during the AST. This newly developed AST protocol is expected to be an effective tool that can be readily adopted to accurately compare the durability among different catalysts and to...
deeply understand catalyst degradation mechanisms in combination with other characterization methods and computer simulations.

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