Durability study of Pt$_3$Ni$_1$ catalysts as cathode in PEM fuel cells

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**Abstract**

The catalytic, corrosion and sintering properties of Pt/C and Pt$_3$Ni$_1$/C catalysts are evaluated using an accelerated durability test (ADT). The catalytic activity and dissolution rate of Ni from a Pt$_3$Ni$_1$/C alloy catalyst are estimated in the same time domain. A strong correlation exists between the amount of Ni dissolved and the oxygen reduction activity of the catalyst. To compare the sintering resistance of both the Pt/C and Pt$_3$Ni$_1$/C catalyst, the particle size of the catalysts before and after the ADT is measured by using transmission electron microscopy. The Pt$_3$Ni$_1$/C alloy, due to anchor effects in its structure, shows high sintering resistance.

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1. Introduction

The search for oxygen reduction reaction (ORR) catalysts more active, less expensive and with greater stability than Pt has resulted in the development of Pt alloys. It has been reported that alloying platinum with transition metals such as Co, Cr, V, Ni, Fe, etc., enhances the electrocatalytic activity for ORR [1–3]. The improvement in the ORR of Pt alloys has been attributed to various structural changes caused by alloying. Jalan and Taylor [4] claim that the enhancement of activity results from the shortening of the Pt–Pt interatomic distance after alloying. Beard and Ross [5] attribute the increase in activity to the exposure of a more active vicinal plane on dispersed platinum particles. The exposure of the more active plane is believed to take place during the heat treatments to induce alloy formation in the particles. Mukerjee et al. [6] explain the enhanced ORR activity on the basis of the interplay between the electronic Pt d-vacancy and Pt coordination number. Toda et al. [7] suggest an enhancing mechanism of the ORR based on an increased d-electron vacancy of the thin Pt surface layer caused by underlying alloy. Regardless of the reasons ascribed to the improvement of the catalytic activity toward ORR, there is evidence of dissolution of the transition metal from the Pt alloy. The observed decay in the performance of Pt alloy catalysts has been explained by the loss in active surface area caused by particle agglomeration [8–12] or by the leaching of the alloying non-precious metal to the electrolyte [13–15]. The operating environment of the PEM fuel cell is not sufficiently benign to prevent the corrosion of the Pt alloy. However, this process is not nearly as severe as in phosphoric acid fuel cells. As a consequence, evaluating durability in PEM fuel cells requires much time. In this study, an accelerated durability test (ADT) is developed to evaluate the long-term performance of the Pt alloys. This procedure provides an inexpensive and time-effective tool for screening the catalysts in terms of stability and performance.

2. Experimental

2.1. Electrode preparation

The commercial catalyst Pt$_3$Ni$_1$ supported by Vulcan XC-72 (20 wt% metal loading) was purchased from
E-TEK. The electrodes were prepared by ultrasonically blending for 1 h a mixture of carbon catalyst, Nafion solution (5 wt% from Aldrich) and isopropyl alcohol. The catalyst solution was then sprayed onto the surface of a single-sided uncatalyzed gas diffusion layer (GDL) obtained from E-TEK. The area of the electrode was fixed at 10 cm². After the catalyst was sprayed, the electrode was dried at 80 °C for 30 min. The process was repeated until a total metal loading of 0.4 mg/cm² was obtained.

2.2. Accelerated durability test

The ADT cell consists of a three-electrode system, which includes a reference electrode, a platinum mesh counter electrode and the catalyst-coated GDL as a working electrode. To avoid any chloride contamination, a Hg/Hg2SO4 reference electrode was used. For the ADT, the electrodes were immersed in a 0.3 M H2SO4 solution, which mimics the environment of the electrode-membrane interface on the cathode side. Unlike the case of an electrode-membrane assembly (MEA) interface, in which only the catalyst in contact with the membrane is active, in the case of the ADT the entire active surface area of the catalyst is exposed to proton, since the electrode is completely immersed in the electrolyte. Under this specific condition, the deterioration of the catalysts is accelerated. A fixed potential between 0.9 and 0.4 V vs. standard hydrogen electrode (SHE) was applied to the working electrode (the catalyst-coated GDL), and the responding current was recorded by using an Arbin instrument BT-2043. During the ADT analysis, the solution samples were extracted periodically and analyzed by using atomic absorption spectroscopy (AAS, Perkin–Elmer 3300). Using this procedure, it was possible to estimate the dissolution rate of the non-noble catalyst in the solution as a function of time and applied potential. The experiment was terminated when the ORR current reached steady state. Transmission electron microscopy (TEM, Hitachi H-8000) was used to determine the change in particle size of catalyst before and after the ADT. X-ray diffraction analysis (XRD, Rigaku 405S5 with Cu Kα as the radiation source) was carried out on the samples to examine the change of structure after the ADT.

3. Results and discussion

Fig. 1 shows the amount of Ni dissolved from the 20 wt% Pt3Ni1 alloy on Vulcan XC-72, estimated using AAS. The observed change in oxygen reduction current as a function of time at various potentials (0.9, 0.68 and 0.4 V) is also presented in this figure. As the results indicate, the oxygen reduction current decreases as the ADT proceeds. The oxygen reduction current profile matches the dissolution profile of Ni in the Pt alloy. Since the studies were done in the same time domain, the results indicate a strong correlation between the amount of Ni dissolved and the value of the oxygen reduction current. At the beginning of the ADT, the current initially increases until reaches a maximum value. This initial increase is believed to occur as part of the initial wetting and saturation of the thin Nafion
layer covering the catalyst particles. Once the current reaches the maximum, it starts to decrease and stabilizes within 200 h.

The dissolution rate of Ni from the alloy is high at the beginning of the ADT. The time necessary for the dissolution rate to reach steady state depends on the applied potential. To estimate the effect of the applied potential on the Ni dissolution rate, the loss of Ni and the oxygen reduction current were calculated by using the following equations:

\[
\text{ORR}_{\text{Loss}}\% = 100 - \frac{I_s}{I_{\text{max}}} \times 100, \tag{1}
\]

\[
\text{Ni}_{\text{Loss}}\% = \frac{N_{\text{is}}}{N_{\text{IT}}} \times 100. \tag{2}
\]

In the above equations, \(I_s\) is the steady state current, \(I_{\text{max}}\) is the maximum oxygen reduction current measured, \(N_{\text{is}}\) is the measured concentration of Ni dissolved in solution, and \(N_{\text{IT}}\) is the total concentration of Ni contained initially in the electrode. The results presented in Fig. 2 indicate that the total amount of Ni dissolved increases from 8.3% to 12% when the potential is increased from 0.4 to 0.9 V vs. SHE. The results can be explained by taking into account the overpotential for Ni dissolution reaction. According to mixed potential theory, the corrosion potential of Ni should be between the standard hydrogen reduction potential (0 V vs. SHE) and the Ni reversible potential (−0.25 V vs. SHE). If the applied potential in the ADT is more positive than the corrosion potential, the oxidation overpotential of Ni increases, thereby increasing the driving force for the Ni dissolution reaction.

The catalyst particle sizes were estimated using TEM. For purposes of comparison, a commercial Pt/C catalyst (20 wt% on Vulcan XC-72, E-TEK) was tested using the ADT; the change in particle size is shown in Fig. 3. As the results indicate, the particle size of platinum estimated at 0.8 V vs. SHE increases from 2.86 to 4.00 nm after 250 h of ADT analysis. The observed increase in Pt particle size is probably due to crystallite migration mechanism. Platinum particles migrate on the carbon surface and aggregate to form larger particle sizes. Wilson et al. [16] have reported that Pt/C catalyst loses 32% of its surface area, i.e. average particle size calculated from the particle size population distribution plot increases from 1.7 to 2.5 nm, after 1300 h of continuous operation in a PEM fuel cell. Based on the assumption that platinum on carbon is spherical, this loss in active surface area corresponds to the observation of particle size increase about after 250 h of ADT.

Fig. 4 shows the TEM images of Pt\(_{3}\)Ni\(_{1}\) catalyst when fresh and after the ADT analysis at various potentials. No agglomerates of metal particles are observed in this figure, and the morphology does not appear to be affected by the applied potential. The average particle size diameter for the fresh sample is calculated to be 4.18

\[
\begin{array}{c|c|c|c}
\text{Potential} & 0.9V & 0.68V & 0.4V \\
\hline
\text{Ratio (%)} & 30 & 40 & 50
\end{array}
\]

Fig. 2. Bar plot comparing loss in activity with loss in alloying material under steady state conditions.

Fig. 3. TEM images of Pt/C (20 wt% Vulcan XC-72, E-TEK): (a) before ADT; (b) after ADT at 0.8 V vs. SHE for 250 h.
nm, which is larger than that of Pt/C. For the samples polarized at 0.4 and 0.68 V vs. SHE, the particle size is measured to be approximately 4.19 nm. The particle size of the sample polarized at 0.9 V vs. SHE is 4.23 nm. Overall, the increase in the particle size is almost negligible despite the fact that a greater decrease in oxygen reduction current was observed at high potential. These results can be explained by taking into account the increased sintering resistance of Pt$_3$Ni$_1$/carbon (the anchor effects of Ni to platinum on carbon substrates) when compared with Pt/C. The mobility of platinum on a carbon surface is hindered when Ni is present; thus, the sintering effect of platinum atoms is suppressed. Similar results have been observed by Wei et al. [17] for Pt/Fe alloy on a carbon substrate.

The powder XRD patterns of the Pt/C and Pt$_3$Ni$_1$/C catalysts are given in Fig. 5. The characteristic diffraction peaks of the face centered cubic structure are detected in the platinum supported on the carbon catalyst sample. The diffraction peak at 20 of 25° shown in all the catalysts are associated with the (002) plane of the hexagonal structure of Vulcan XC-72 carbon. Among the diffraction peaks of Pt$_3$Ni$_1$/C catalysts, the typical peaks corresponding to Ni were not detected. However, the diffraction peak (1 1 1) of Pt shifts slightly to higher Bragg angles in the Pt$_3$Ni$_1$/C catalysts, which indicates a decrease in the lattice constant in the presence of Ni. Such evidence accounts for the formation of Pt–Ni alloy in the catalyst. After the ADT analysis at 0.68 V vs. SHE, despite a 10% loss of Ni, the sample diffraction pattern shows negligible change when compared with fresh Pt$_3$Ni$_1$/C.
Based on the ADT analysis, the stability of the catalyst can be considered in two regards: loss in active surface area due to sintering and dissolution loss in transition metal under the operating conditions. When platinum is alloyed with Ni, there is evidence that the resistance to sintering is enhanced while the corrosion of non-noble material accounts for the lessening of the oxygen reduction capability.

4. Conclusion

An ADT has been used to evaluate the durability of Pt$_3$Ni$_1$/C. This procedure usually allows degradation in the catalyst activity to be observed within several days, rather than the several weeks otherwise required before any significant decrease in fuel cell performance is noticed. According to the ADT results, the decrease in Pt$_3$Ni$_1$/C catalytic activity is correlated directly to Ni dissolution in the electrolyte. Pt$_3$Ni$_1$ alloy loaded on a carbon has shown better resistance to sintering than a platinum alone catalyst. The anchor effect of Ni to Pt is considered to be responsible for impeding the sintering during the ADT.

References