Durability study of Pt–Pd/C as PEMFC cathode catalyst

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ABSTRACT

In this paper, Pt-Pd/C and Pt/C catalysts were evaluated and compared. The catalysts were evaluated as oxygen reduction reaction (ORR) catalysts in half cell test under potential cycling, and cathode catalysts in single cell test under dynamic loading simulating the vehicle operation. Physical and electrochemical techniques were applied to investigate the structure, performance and durability of those catalysts. The electrochemical active surface area (ECA) loss, particle size distribution, polarization behavior and electrochemistry impedance spectroscopy (EIS) suggested that the Pt-Pd/C showed a better durability than Pt/C.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered as promising alternative power sources for transportation due to the high energy efficiency and clean utilization. Within the last decades, much progress has been made for PEMFCs in materials, system design, manufacturing and application. Up to now, durability is thought to be one of the major problems hindering the commercialization of PEMFCs besides cost, hydrogen storage, etc. While the lifetime for stationary used PEMFCs has already exceeded 3 years, the lifetime for transportation used PEMFCs is still below 3000 h, which is nearly half of the 2010/2015 target lifetime 5000 h set by U.S. DOE [1]. It is known that PEMFCs will gradually degrade in performance due to many factors including operation, water-heat management, and materials deterioration, etc [2]. Membrane electrode assemble (MEA) is the most important component of PEMFCs. The deterioration of MEA directly leads to the degradation of PEMFCs. One of the most important causes for MEA deterioration is the degradation of catalyst in the cathode side due to the high voltage, low pH and oxidation environment [3]. For the most popular Pt/C catalyst, it is reported that the nano-sized platinum supported on carbon black will gradually grow larger during long-term operation, thus reduce the electrochemical active area (ECA) and resulted in an irreversible performance loss [4].

This degradation will be even severer when PEMFCs are operated under dynamic loadings. Borup investigated the degradation behavior of single cell under cycling dynamic loading and found that the growth extent of cathode catalyst
particles was greater than that observed during steady-state testing [5]. The half cell electrochemical potential cycling test also revealed that higher upper potential and scan frequency lead to a higher degradation rate [5]. Darling and Meyer calculated the Pt dissolution under potential cycling and found platinum will dissolve rapidly when transitioning from low to high potentials [6]. The proposed degradation mechanisms of Pt/C catalysts include coarsening of Pt particles, Pt dissolution, carbon corrosion [7,8] and loss of contact of ionomer and Pt [9].

Much work has tried to improve the performance and durability of the catalyst. One approach is using alloy or bimetallic catalysts [10]. However, if cheap transition metals are used, they may dissolve and move into the polymer phase. Zhang studied the Pt–Au/C catalyst and demonstrated that this bimetallic catalyst exhibited fairly high durability under half cell potential cycling test [11]. However, gold is still a very expensive metal. In the past a few years, much attention has been paid to Palladium and its alloys. Adzic and coauthors made a series of study on the ORR activity of Pt–monolayer on model Pd crystal surface substrate as well as Pd–monolayer on model Pt crystal surface substrate through experimental and computational methods [12–17]. They reported that when Pd is added to Pt, a change in the electronic structure may lead to a higher ORR activity in half cell evaluation. Li prepared Pt–Pd/C catalyst using ethylene glycol (EG) reflux reduction method and found that this kind of catalyst poses higher ORR activity than Pt/C catalyst in half cell test [18]. Lim synthesized Pd–Pt bimetallic nanodendrites consisting of a dense array of Pt branches on a Pd core and found that the Pd–Pt nanodendrites were two and half times more active on Pt mass for the ORR than the state-of-the-art Pt/C catalyst [19]. Peng and Yang using a sequential synthetic method prepared carbon supported Platinum-on-palladium bimetallic heterogeneous nanostructure, in which 3-nm Pt particles grew on the surfaces of 5-nm Pd nanoparticles. The electrochemical study showed not only enhancement in electrocatalytic activity for ORR but also improved stability in comparison to a commercial platinum catalyst [20]. Based on the summaries above, one can notice that Pt–Pd/C is a promising catalyst for PEMFCs. In order to meet the practical applications, more investigations should be taken on its durability, especially under full fuel cell test conditions under dynamic loading.

In this paper, the Pt–Pd/C and Pt/C catalyst was prepared by an ethylene glycol reduction process. The designed metal weight ratio is 50% which was preferred in practical PEMFC application. In order to get a highly dispersion of fine metal particles with such metal weight ratio, a high surface area carbon black was used as the support. The Pt–Pd/C catalyst was then compared with home-made Pt/C and commercial Pt/C catalysts in terms of durability in both half cell and single cell under dynamic loading simulating the vehicle operation.

2. Experimental

2.1. Catalyst preparation

The synthesis of the Pt–Pd/C catalyst was following the ethylene glycol (EG) reflux reduction method described in Ref. [18]. A high surface area carbon black was used as the support. The carbon black bought from Dalian Sunrise Power Co., Ltd. (P.R. China) has a high specific surface area of 770 m²·g⁻¹. Briefly, calculated amount of the carbon black was dispersed in an EG solution by adding H₂PtCl₆ and PdCl₂ under vigorous stirring. The pH of the solution was then adjusted to 12 with 2 M NaOH. The mixture was kept at 130 °C for 3 h under the protection of high purified nitrogen. After washing and drying the Pt–Pd/C catalyst was obtained. The designed atom ratio was Pt:Pd = 3:1. A Pt/C catalyst was prepared following the same way. A commercial Pt/C catalyst from Tanaka Kikinzoku Co., Ltd (Japan) was also used for comparison. For convenience, the catalysts were denoted as Pt₃Pd/S770, Pt/S770 and TKK 46.6%, respectively.

2.2. Half cell test

The half cell test was conducted on a thin film rotating disk electrode (TFRDE) in a three electrode electrochemical system. It is a simple and fast way widely used to investigate the activity and stability of fuel cell catalysts [21]. The TFRDE was prepared as following: 5 mg catalyst was dispersed in a mixture of 50 µL 5% Nafion solution and 4 ml ethanol. The mixture was agitated by ultrasonic for 30 min to form an ink. 10 µL of this ink was then dropped on a glassy carbon rotating disk electrode and dried to yield a thin film electrode. The geometric area of the TFRDE is 0.1256 cm² and the metal loading is ca. 45 µg cm⁻². During the durability test, the TFRDE was subjected to a potential cycling test. Specifically, the catalyst was repeatedly scanned from 0.6 V to 1.2 V versus SHE at a rate of 50 mV s⁻¹ in 0.5 M H₂SO₄ deaerated with high purified N₂. Cyclic voltammetry (CV) was recorded at the beginning and every 100 cycles of the potential sweep by a CHI 600C potentiostat from 0 to 1.2 V versus SHE at 50 mV s⁻¹. The ECA can be obtained by integrating the CV profile after subtracting the double layer from the hydrogen adsorption peak of each CV curve. The charge related to a monolayer H adsorption to the catalyst crystal was supposed to be 210 µC cm⁻².

The ORR curves were measured in an O₂ saturated 0.5 M H₂SO₄ from 1.0 V to 0.241 V versus SHE at 5 mV s⁻¹ with a rotating speed of 1600 rpm.

2.3. Single cell test

Based on the half cell test results, single cell test was conducted to the Pt₃Pd/S770 and TKK 46.6% catalysts on an Arbin FCTS BT2000 model. The metal loading of all the Gas Diffusion Electrode (GDE) was 0.5 mg cm⁻². The MEA was manufactured by hot pressing the GDE onto each side of a Nafion®-115 membrane. The single cell with an active area of 5 cm² was operated for 400 h under a cyclic dynamic loading. Within one single cycle the current was varying in the following sequence: 0 mA cm⁻² for 60 s, 200 mA cm⁻² for 60 s, 400 mA cm⁻² for 180 s, 300 mA cm⁻² for 60 s, 600 mA cm⁻² for 60 s and 200 mA cm⁻² for 60 s. The time of one cycle is 480 s, so each single cell experienced 3000 cycles during the test. The dynamic loading test was carried on an Arbin BT 2000 electric load. A schematic presenting the controlled currents and voltage reactions is given in Fig. 1. The cell temperature was 85 °C, which is between the typical 60–90 °C operation range.
and high to accelerate the degradation rate. The reactant gas was controlled as 35 ml min⁻¹/800 ml min⁻¹ for H₂/air at 0.2 MPa. Polarization curves were recorded periodically under the same operation parameters. After the I–V plot was recorded, the in-situ electrochemical impedance spectroscopy (EIS) was measured. The perturbation amplitude for the sine signal was 20 mV over a frequency range from 10 kHz to 100 mHz. CV was also periodically recorded to monitor the degradation of ECA after purging the cathode with N₂. The scan was from 0 to 1.0 V vs. SHE at 50 mV s⁻¹. All the electrochemical characterizations on single cell were carried on a potentiostat Model 2273 A from EG&G Princeton Applied Research.

2.4 Physical characterization

X-ray diffraction (XRD) measurements were performed on a PANalytical X’Pert Pro diffractometer with nickel-filtered CuKα radiation at 40 kV and 40 mA. The lattice parameter \( A_0 \) and the mean diameter of catalysts were calculated by Bragg and Scherrer formula [22].

Transmission electron microscopy investigations of all catalysts before and after the half cell test were carried on a JEOL JEM-2011 electron microscope operating at 120 kV. Particle size distribution diagrams were obtained by counting all particles on each TEM picture.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analyses were conducted for the element analysis on Leeman Plasma–Spec–I equipment.

3. Results and discussion

3.1 Physical characterization

The powder XRD patterns and TEM images are shown in Figs. 2 and 3, respectively. The lattice parameter \( A_0 \) and the

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**Table**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>lattice parameter</th>
<th>Mean diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Pd/S770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/S770</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TKK 46.6%</td>
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</tr>
</tbody>
</table>

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**Fig. 1 – Schematic of the dynamic loading in single cell dynamic loading test.**

**Fig. 2 – XRD patterns of Pt-Pd/C and Pt/C catalysts.**

**Fig. 3 – TEM images of fresh Pt-Pd/C and Pt/C catalysts: (a) Pt₃Pd/S770; (b) Pt/S770; (c) TKK 46.6.**
mean particle size derived from (220) peak are summarized in Table 1. All catalysts showed a face-centered cubic (FCC) structure. The (220) peak of Pt3Pd/S770 is positively shifted with a shortening of crystal parameter, indicating that Pd has an obvious effect on the Pt crystal size. The particle size of Pt3Pd/S770 increased by nearly 1.37 nm compared with Pt/S770 due to the high precipitation tendency of Pd when $\text{pH} > 7$. The atomic ratio of Pt/Pd is 3.3 close to the designed value. The particle morphology of fresh catalysts is shown in Fig. 3. Compared with Pt/S770, the metal particles for Pt3Pd/S770 are larger and more agglomerates can be found, thus resulted in a wider distribution of Pt3Pd/S770 than Pt/S770 presented in Fig. 4. The mean diameter of metal particles measured by TEM is little larger than the value measured by XRD, because particles smaller than 1 nm are hard to count in TEM [23].
3.2. **Electrochemistry test in half cell**

The CV and ORR curves of as-prepared Pt$_3$Pd/S770 and Pt/S770 catalysts are shown in Fig. 5. The hydrogen adsorption/desorption peak area of the Pt$_3$Pd/S770 declines as its particle is larger. Another difference in Fig. 5(a) is the Pt–O reduction peak of Pt$_3$Pd/S770 shifts by 0.024 V compared to Pt/S770. It is believed that a shift of the Pt–O reduction peak to higher potential reflects a decrease of the adsorption strength for the oxygen containing species on the surface, e.g. OH$_{ads}$ [24,25]. Although Pt weight and ECA of Pt$_3$Pd/S770 is less than Pt/S770, its ORR curve is very close to the latter, which means Pt$_3$Pd/S770 poses a high activity comparable to pure Pt/S770. However, the improvement of the ORR as Li[18] described was not found, which may result from different carbon supports and metal/carbon ratios.

Potential cycling is a widely used way to test the stability and durability of fuel cell catalysts [24,26,27]. The potential window chosen in this paper is 0.6–1.2 V vs. SHE, which is a typical operation region of H$_2$/O$_2$ PEMFC. Fig. 6 shows the normalized ECA variation of different catalyst during the half cell potential cycling test. The ECA was normalized to the initial ECA before potential cycling. As the results indicated, all catalysts gradually decrease in ECA as the potential scan proceeds. After the half cell test, nearly 55% of the initial ECA of Pt$_3$Pd/S770 has been lost, compared to 68% of Pt/S770 and 65% of TKK 46.6%. It can be clearly seen that Pt$_3$Pd/S770 has the lowest decreasing rate, while Pt/S770 has the highest one. The ECA degradation is listed in Table 2.

**Table 2 – Catalyst degradation in half cell.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ECA loss</th>
<th>Mean particle size by TEM (nm)</th>
<th>Before test</th>
<th>After test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_3$Pd/S770</td>
<td>55%</td>
<td>3.18</td>
<td>4.52</td>
<td></td>
</tr>
<tr>
<td>Pt/S770</td>
<td>68%</td>
<td>2.24</td>
<td>5.36</td>
<td></td>
</tr>
<tr>
<td>TKK 46.6%</td>
<td>65%</td>
<td>2.75</td>
<td>5.27</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 6 – Comparison of normalized ECA for various catalysts during potential cycling.**

![Normalized ECA graph](image)

**Fig. 7(a)–(c) presents the TEM images of all the catalysts after the potential cycling test. The size distribution derived from Fig. 7 is presented in Fig. 8. Particle sizes before and after the potential cycling are also listed in Table 2. After the potential cycling all particles grow larger and many agglomerates can be clearly observed. However, the metal particle of Pt$_3$Pd/S770 becomes the smallest one and the Pt/S770 becomes the largest one. After the potential cycling, the size distribution of Pt/S770 becomes much wider with a tail toward to large particle size. It is reported this shape of the particle size distribution may ascribe to the micrometer-scale platinum dissolution-diffusion-precipitation mechanism [23]. However, the same distribution behavior is not found on Pt$_3$Pd/S770, which suggests that**

![TEM images](image)

**Fig. 7 – TEM images of Pt–Pd/C and Pt/C catalysts after potential cycling: (a) Pt$_3$Pd/S770; (b) Pt/S770; (c) TKK 46.6%.**
the addition of Pd may change the degradation mechanism of the catalyst. Mayrhofer [28] observed that Pt particles detached from the carbon support under potential cycling. So ECA should depend on two terms: one is the number of particles survived on carbon support and the other is the size of those particles. Actually, one could see that the particles on carbon are much less in Fig. 8b than Fig. 8a. A further discussion will be conducted later.

3.3. Durability test in single cell

Based on the results of half cell test, Pt3Pd/S770 and TKK 46.6% were chosen to be evaluated under single cell condition, which is more similar to the real operation conditions of vehicles. Both cells experienced open circuit voltage, mediate current density and high current density in each cycle which was repeated 3000 times during the whole 400 h test. The polarization curves of cells with Pt3Pd/S770 and TKK 46.6% are shown in Fig. 9. As listed in Table 3, the initial performance of

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Voltage at 200 mA cm⁻² (V) Before test</th>
<th>Voltage at 200 mA cm⁻² (V) After test</th>
<th>ECA loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt3Pd/S770</td>
<td>0.758</td>
<td>0.749</td>
<td>37%</td>
</tr>
<tr>
<td>TKK 46.6%</td>
<td>0.748</td>
<td>0.703</td>
<td>58%</td>
</tr>
</tbody>
</table>
the two cells are close to each other, though the cell using Pt3Pd/S770 are slightly better. The voltage at 200 mA cm⁻² is 0.758 V for cell with Pt3Pd/S770 and 0.748 V for cell with TKK 46.6%. After 400 h operation, the performances of both cells are degraded. The voltage at 200 mA cm⁻² decreased to 0.749 V for cell with Pt3Pd/S770 and 0.703 V for cell with TKK 46.6%.

The Nyquist plots at 200 mA cm⁻² are shown in Fig. 10. All plots present a single arc indicating the electrode process is dominated by the interfacial kinetics of the ORR process [29]. It is believed that the high-frequency intercept of the impedance arc on the real axis, $R_\text{oc}$, represents the total ohmic resistance of the cell, while the diameter of the arc, $R_\text{ct}$, is a measure of the charge transfer resistance of the ORR. From Fig. 10, it can be seen that the $R_\text{oc}$ of both cells did not change much during the operation suggesting the 100% RH humidification was kept well. However, the $R_\text{ct}$ of both cells did increase obviously after the test. The $R_\text{ct}$ of cell using TKK 46.6% increased much larger than the $R_\text{ct}$ of cell using Pt3Pd/S770. This may be an explanation of higher performance in the latter cell after the long time test.

The ECA change of single cell with running time is also shown in Fig. 11 and Table 3. It is observed that the degradation phenomenon is similar to what found in half cell test. The ECA declines faster in the cell using TKK 46.6% than in the cell of Pt3Pd/S770. And the ECA loss may make a major contribution to the drop in ORR kinetics.

### 3.4. Proposed degradation mechanisms

The single cell test results along with the half cell test results demonstrated that addition of Pd may improve the durability of the Pt/C catalysts for PEMFC cathode. The direct evidences are the growth of particle size and ECA loss. As pointed out in the Introduction section, there are several mechanisms suggested to explain this degradation. Shao-Horn and coauthors discussed a few different mechanisms through experimental and theoretical computation, and conclude that the sub-monolayer dissolution of Pt nanoparticles may be the governing factor for the surface area loss [7]. In details, the Pt can be oxidized to Pt-O between ca. 0.9 and 1.2 V. The oxidized Pt then can be chemically dissolved into the solution, thus causing a Pt loss or precipitation by reduction. A mathematic model of this mechanism built by Darling [6] also demonstrated that the oxidation played an important role in the dissolution of Pt. Although this mechanism needs more investigations to be identified, it is acceptable to use it to explain the durability enhancement of Pt–Pd/C catalyst in this paper. Gasteiger studied the ORR activity at different Pt crystal surface and supposed that the specific ORR activity can be reflected by the position of Pt–O reduction peak [25]. When the peak position is more positive, it means the catalyst binds oxygen species more weakly and thus the specific ORR activity is higher. As observed in Section 3.2, the position of Pt–O reduction peak is shifted to more positive, which means the Pt–Pd binds oxygen species more weakly than pure Pt. It is reported that the addition of Pd may change the electronic structure and d-band center of the catalyst surface, thus weaken the adsorption of oxygen species [16]. So, here we proposed a possible mechanism as following: the introduction of Pd can alleviate the oxidation of catalyst, reduce its dissolution and finally improve the durability.

There are also other possible mechanisms. Holby and coauthors studied the impact of particle size distribution on related degradation rate by experiment and theoretic simulation [30]. They found that larger particles are more stable than smaller ones due to lower Gibbs–Thomson energy. Adding Pd made the catalyst size larger than pure Pt but without obvious deterioration of ORR activity. This may at the same time enhance the stability of the catalyst. Carbon corrosion also can cause coalescence of particles and detachment of Pt particles from the support, just like what the Fig. 8b of Pt/S770 reveals. Whether the addition of Pd could alleviate the carbon corrosion is not clear yet. And the degradation mechanisms still needs more work to be clarified.

### 4. Conclusions

The Pt–Pd/C catalyst was prepared and compared with homemade and commercial Pt/C catalysts. Both half cell test and single cell test demonstrated that this bimetal catalyst showed a comparable performance and better durability than...
conventional Pt/C catalyst. The possible reasons for the durability enhancement are discussed. Firstly, Pd may modify the electronic structure of catalyst surface and thus alleviate the dissolution of it; secondly, increased particle size may also improve the resistance to degradation; lastly, less detachment from carbon support has been observed for Pt–Pd catalyst. Further work is still needed to clarify the degradation mechanisms.

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