Enhanced Pt/C catalyst stability using p-benzensulfonic acid functionalized carbon blacks as catalyst supports

Fan Xu  
*Indiana University - Purdue University Indianapolis, fxu@purdue.edu*

Mei-xian Wang  
*Indiana University - Purdue University Indianapolis*

Lili Sun  
*Indiana University - Purdue University Indianapolis, sun292@purdue.edu*

Qi Liu  
*Indiana University - Purdue University Indianapolis, qliu@purdue.edu*

Hong-fang Sun  
*Birck Nanotechnology Center, Purdue University*

See next page for additional authors

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Authors
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Fan Xu\textsuperscript{a}, Mei-xian Wang\textsuperscript{a}, Lili Sun\textsuperscript{a}, Qi Liu\textsuperscript{a}, Hong-fang Sun\textsuperscript{b}, Eric A. Stach\textsuperscript{c}, Jian Xie\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Department of Mechanical Engineering, Purdue School of Engineering and Technology, Indiana University-Purdue University, Indianapolis, IN 46202, USA
\textsuperscript{b} School of Materials Engineering and Birck Nanotechnology Center, Purdue University, West Lafayette, IN 47907, USA
\textsuperscript{c} Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY 11973, USA

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A B S T R A C T

The functional group p-benzensulfonic acid (pb-SO\textsubscript{3}H) was chemically attached to the surfaces of two different carbon supports, XC72 and BP2000, to improve carbon support corrosion resistance. An accelerated durability test (ADT) utilizing a rotating disk electrode (RDE) system was used to study the corrosion of Pt catalysts using these two carbon supports, Pt/XC72-SO\textsubscript{3}H and Pt/BP2000-SO\textsubscript{3}H, under simulated fuel cell conditions. The results showed that the functional group pb-SO\textsubscript{3}H can effectively reduce the performance decay of these catalysts by enhancing the corrosion resistance of the carbon support and promoting the stability of the Pt nanoparticles. The ECASA and ORR current measurements of these catalysts indicate that the effects of the functional group (pb-SO\textsubscript{3}H) on improving carbon corrosion resistance were more significant for the BP2000 than for the XC72. TME imaging revealed that the size of the Pt nanoparticles was significantly reduced and the particle distribution was improved in a polymer electrolyte fuel cell (PEFC).

1. Introduction

Polymer electrolyte fuel cells (PEFCs) are the most promising candidates as propulsion systems for transportation applications such as powertrains for electric vehicles because of their high efficiency, high energy density, low operating temperature (<100 °C) and zero emissions, making them clean energy conversion devices. Hence, PEFCs have attracted a lot of attention in recent years. However, PEFCs are still too expensive to be commercialized as propulsion systems for vehicles. The durability of the PEFCs is essential for their application in automobiles as the propulsion systems. The performance loss of the PEFCs during long-term operations under steady and dynamic conditions has been attributed to the deterioration of Pt and Pt alloy catalyst nanoparticles [1–5], the corrosion of carbon supports, and the degradation of the Nafion ionomer network inside the catalyst layer and the Nafion membrane [6–13].

Several publications have discussed the corrosion of carbon supports in PEFCs [14–18]. When the cell potential is greater than 0.8 V, carbon oxidation occurs on the surface of commercial carbon black supports [19,20]. This corrosion is accelerated when Pt nanoparticles exist on the carbon surface, as is the case in a catalyst layer of PEFCs. Carbon corrosion leads to the degradation of the catalyst layer, which not only results in an increase of the total resistance due to the loss of structural integrity [5] and a decrease of the electrochemically active surface area (ECASA) [21], but also affects Pt particle growth [22] by weakening or breaking the interaction (bond) between the Pt nanoparticles and the surface of the carbon support. Furthermore, this corrosion causes an increased mass transport loss due to the increased hydrophilicity within the catalyst layer [23–25].

We have demonstrated that the higher the degree of graphitization in the carbon support, the stronger the carbon corrosion resistance is in the carbon support in our previous work [26,27]. In order to improve corrosion resistance, carbon supports with more graphitic components have been explored [28], such as graphite carbon nanofibers [29], carbon nanotubes [30], ordered uniform porous carbon networks [31], nanographite [32], and graphene [33]. These carbon materials have been shown to be more corrosion-resistant than carbon blacks; however, the cost of manufacturing is still a significant concern.

The surface modification method is one of the approaches to change the morphology and chemical composition of the carbon support surface, which could have a significant effect on corrosion resistance. Charged functional groups like sulfonate, carboxylate, and tertiary amine groups can be chemically attached to the carbon surface by the reduction of diazonium cations [34–37], and oxidation by nitric acid [38]. The chemical attachment of functional groups to the carbon surface can make the surface pseudo-chemically homogeneous and can make the surface energy
uniform. Urichaga et al. [39] found a lower electrochemically active surface area loss for Pt particles deposited on functionalized XC72 carbon black after a long term Pt stability test, compared to particles deposited on bare XC72 carbon black. This lower electrochemically active surface area loss can be attributed to a better interaction (bond) between the Pt particles and the carbon substrate due to the thiophenol molecular bridge.

Our previous study showed that the corrosion mechanism of different carbon supports depends on the structure of those carbon supports [27]. Two major carbon blacks, XC72 and BP2000 were studied in the current work. XC72 is a low structure carbon black with a primary particle size in the range of 30 nm (primary particle) and interparticle pores ranging from 8 nm to 120 nm [45] and has been used for many years as a Pt catalyst support because of its high surface area (250 m²/g), high electronic conductivity, and easy dispersion. BP2000 is a high-structure carbon black with many intraparticle pores, a small particle size (i.e. dia.12 nm for primary particles), and a higher surface area (1500 m²/g) (a lower structure carbon black refers to a carbon black in which the inter-particle pores dominate the pore structure while a high structure carbon black refers to a carbon black in which the intra-particle pores are majority of the pores). In this study, we used these two different carbon supports as catalyst supports and hoped that the BP2000 would have better corrosion resistance. The different carbon support corrosion processes were shown in a previous publication [27,46], where it was found that in the case of XC72, major corrosion occurred at the center of the XC72 particle (with some minor corrosion on the surface of the carbon particle), removing some amorphous structured carbon black filaments; in the case of BP2000, the corrosion started on the surface. Based on this corrosion mechanism, for the current study, the charged functional group (pb-SO₃H) was chosen to attach to the surface of XC72 and BP2000. Catalysts using these two functional carbon blacks (FCB) as supports were made. The efforts in the current study concentrated on examining the durability of two Pt/FCB-SO₃H catalysts under potential cycling from 0.85 V to 1.4 V (vs. NHE), where the major damage was expected to occur during fuel cell operation. This paper presents an investigation of the functionalized carbon blacks as a Pt catalyst support using an accelerated degradation test under the conditions similar to those in fuel cells using a rotating disk electrode (RDE).

2. Experimental

2.1. Modification of carbon black supports

Two catalyst supports were used: a low-surface-area (254 m²/g) carbon black Vulcan XC72 (XC72) and a high-surface-area (1500 m²/g) Black Pearl BP2000 (BP2000), both from Cabot (Billerica, MA). The modification of Vulcan XC72 was performed by the reduction of a diazonium cation [39–44] p-aminobenzenesulfonic acid as a diazonium reaction reagent, to introduce charging functional groups (pb-SO₃H) onto the carbon surface (Y = sulfonate, SO₃⁻ · M⁺; carboxylate, COO⁻ · M⁺; tertiary amine, NR₃⁺ · X⁻; acrylic, polystereene, PEO, PPO, etc., X = NO₃⁻, SO₄²⁻ etc.).

\[
\text{NH}_2\text{C} = \text{N} - \text{Y} + 2 \text{HX} + \text{NaNO}_2 \rightarrow \text{XN=NR}_3 - \text{Y} + 2 \text{H}_2\text{O} + \text{NaX}
\]

The amount of sulfanilic acid was calculated based on the surface of the different carbon blacks, and a typically excessive amount, 2–3 X stoichiometric ratio or even higher, was used to ensure the maximum pb-SO₃H surface coverage. 3.5 g of sulfanilic acid was mixed with hydrochloric acid (50%) first and then mixed with dissolved sodium nitrate (2.6 g) in DI water. A specified amount of carbon black (i.e. 0.2 g BP2000 or 1.0 g XC72), which was based on a theoretical calculation, was put in a flask and DI water was also added into the flask. Then, the mixture of sulfanilic acid and hydrochloric acid was poured into the flask containing the carbon blacks; the sodium nitrate was added drop-wise to the flask while stirring. To ensure the reaction was complete, the mixture was stirred for 4 h and then heated up to 70 °C for another 3 h. The mixture was filtrated, fully washed with water, and re-filtrated three times.

2.2. Synthesis of the catalyst

Two functional carbon blacks (FCB-SO₃H), made via the steps described in Section 2.1, were used as catalyst supports: both of the functional carbon blacks were immersed in a 10 g L⁻¹ platinum precursor [Pt(NH₃)₄(OH)₂] salt solution. The mixture of the carbon blacks and the platinum precursor was dried in the oven at 110 °C. Reduction of the formed platinum clusters (on the carbon surface) to a metallic form was carried out by treatment with hydrogen gas at elevated temperatures. Generally, the preferable temperature of the reducing reaction is in the approximate range of <200 °C. For the exact amount of Pt nanoparticles on the carbon surface, the TGA (TA instrument, USA) was used to determine the exact Pt loading for 20% Pt/XC72-SO₃H and 20% Pt/FBP2000-SO₃H.

2.3. Accelerated degradation test (ADT)

2.3.1. Materials

All chemicals were used as received: 5 wt. % Nafion solution (Ion Power Inc., New Castle, DE), 60% perchloric acid (99.999% purity, Fisher Scientific), 70% isopropanol alcohol (IPA) (Fisher Scientific), and high purity water (resistance ~18.2 MΩ). Oxygen (research grade, 99.999% purity) and nitrogen gases (research grade, 99.999% purity) were obtained from Praxair.

2.3.1.2. Electrochemical apparatus

A glassy carbon rotating disk electrode (GCRDE) was used as the working electrode (0.196 cm², Pine Instruments, Inc., Raleigh, NC). The GCRDE was polished with a 0.3 μm followed by a 0.05 μm alumina suspension to give it a mirrored finish. Sonication was used to suspend 35 mg of the Pt/XC72 (or the Pt/FPB2000) catalyst in a solution of 200 μL 5 wt.% Nafion, 3 mL isopropyl, and 2 mL DI water for 5 min. A total of 10 μL aliquot of the Pt catalyst suspension (loading: 0.35 mgPt/cm²) was pipetted onto the glassy carbon and was dried at room temperature overnight to form a thin film catalyst layer over the GCRDE, referred hereafter as TFRDE. Electrochemical measurements were carried out using a three-compartment cell, a thin film catalyst layer over GCRDE (TFRDE) was used as the working electrode, a Pt wire and an
Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. Electrochemical measurements were recorded using a PARSTAT 2273 advanced electrochemical system (Princeton Applied Research, Oak Ridge, TN). All potentials cited in this article were normalized with respect to normal hydrogen electrode potential (NHE).

2.3.1.3. Electrochemical measurements

All experiments were performed at room temperature. After preparation of the thin film catalyst layer on the glassy carbon RDE, the catalyst was electrochemically cleaned by potential cycling between 0.05 and 1.2 V at 1 V/s for 200 cycles in a N2 saturated 0.1 M HClO4 electrolyte to achieve a full saturation of the active material with the electrolyte, similar to the “Break-in” of an MEA. The area under the absorption and desorption peaks of underpotentially deposited hydrogen in a cyclic voltammogram (CV) (scan rate of 20 mV/s between 0.05 and 1.2 V) was used to evaluate the ECASA of the Pt catalyst on the electrode. Polarization curves for the oxygen reduction reaction (ORR) on the RDE were recorded by scanning the potential from 0.05 V to 1.00 V at 20 mV/s in the oxygen saturated 0.1 M HClO4 solution and rotating the RDE at 1600 rpm. To perform the ADT, a cyclic voltammogram was used with a scan rate of 20 mV/s between 0.85 and 1.40 V. The procedure of the ADT was carried out by (1) running 1800 consecutive ADT cycles and measuring the ECASA and the polarization curve before and after the ADT; (2) taking the ECASA and polarization curve measurements every 300 cycles during the ADT until 1500 cycles were finished. All mass and specific activities were calculated at a voltage of 0.75 V (vs. NHE), given the known mass and area of the Pt. All experiments were repeated for 3 times.

2.4. Characterization of functional carbon blacks and catalyst supported on functional carbon blacks

Before and after the 1800 consecutive ADT cycles, the catalysts were collected for the morphology examination using a Philip Tecnai 20 transmission electron microscope (TEM). Image J 1.42 software was used to determine the average particle size and the size distribution; about 150 particles were analyzed. The surface chemistry of the carbons and corresponding Pt catalysts using these carbons were analyzed using a Kratos AXIS Ultra X-ray photoelectron spectrometer (XPS). XPS measurements were performed on a Kratos Axis Ultra spectrometer using a Al Kα X-ray source. An electron flood gun for charge neutralization and hemispherical analyzer with 8 multichannel photomultiplier detector was employed for analysis. Area of analysis is 700 μm x 300 μm in size. 3 areas per sample were analyzed for 90° take-off angle (TOA) – 8–10 nm depth. Survey (low resolution wide scan) was acquired at 80 eV pass energy for 4 min. High resolution spectra were acquired at 20 eV pass energy. The surface coverage of pb-SO3H group was determined using ICP analysis of the sulfur content in the functionalized carbon black. Then the coverage of pb-SO3H (θ) is calculated using the following equation:

$$\theta_A = \frac{f_{A_{pb-SO_3H}}}{S_0}$$

f-Packing factor, $A_{pb-SO_3H}$ is the cross-section area of a pb-SO3H molecule along the benzene plane, and $S_0$ is the specific surface area of carbon black. For ICP analysis, samples (i.e. carbons and corresponding Pt/C catalysts) were dissolved in 25 mL acid solution (HNO3:HCl = 1:3 volume ratio) and stirred for 24 h. Then, the obtained solution was diluted to 1:50 with using ultra-pure DI water (MQ-filtered) and analyzed using inductively coupled plasma atomic emission spectroscopy (ICP–AES, Leeman Labs, Hudson, NH) to determine the S content in the obtained solutions.

Fig. 1. Voltammograms and polarization curves (on a rotating disk electrode) for different Pt-based carbon supports before and after 1800 ADT cycling in 0.1 M HClO4 purged with N2 at room temperature at a sweep rate of 20 mV/s. The catalyst layer consisted of a total metal loading of 70 μg and 3 μL of a mixture of Nafion solution (5 wt.% from Ion Power, U.S.) and isopropl alcohol (1:20). (a) and (b) Pt/XC72; (c) and (d) Pt/XC72-SO3H.

3. Results and discussion

3.1. Electrochemical measurement of the activity degradation for the ORR

The objective of this work was to study the effects of the functional group pb-SO3H, which was chemically attached to the surfaces of the carbon supports, on carbon corrosion resistance for PEFCs using an RDE approach under simulated PEFC conditions. To verify whether the functional group pb-SO3H was chemically grafted onto the surface of carbon black, the surface chemical composition of the carbon black, the functionalized carbon black and the corresponding Pt catalysts using these carbons as supports was analyzed using XPS and the results were summarized in Table 1. Clearly, the pb-SO3H group was chemically grafted onto carbon black surface indicated by the existence of the S in the functionalized carbon black and the corresponding Pt catalyst. The surface coverage of pb-SO3H group on the functionalized carbon is almost full coverage (90 ± 0.5%) and slightly reduced (84 ± 0.75%) when Pt nanoparticles were loaded on the surface of the functionalized carbon (Table 2).
Fig. 2. Voltammograms and polarization curves (on a rotating disk electrode) for different Pt-based carbon supports before and after 1800 ADT cycling in 0.1 M HClO₄ purged with N₂ at room temperature at a sweep rate of 20 mV/s. The catalyst layer consisted of a total metal loading of 70 μg and 3 μL of a mixture of Nafion solution (5 wt.% from Ion Power, U.S.) and isopropyl alcohol (1:20). (a) and (b) Pt/BF2000; (c) and (d) Pt/FBC2000-SO₃H.

Table 1
Summary of ICP results for carbon supports and corresponding catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>S content (Hg/ml)</th>
<th>SO₃H content (nmol/m2)</th>
<th>SO₃H coverage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XC-72</td>
<td>8.65 ± 0.05</td>
<td>0.120 ± 0.001</td>
<td>3.00 ± 0.03</td>
</tr>
<tr>
<td>Functional XC-72</td>
<td>259.41 ± 1.54</td>
<td>3.60 ± 0.02</td>
<td>90.00 ± 0.50</td>
</tr>
<tr>
<td>Pt/XC-72</td>
<td>6.50 ± 0.05</td>
<td>0.090 ± 0.001</td>
<td>2.25 ± 0.03</td>
</tr>
<tr>
<td>Pt/functional XC-72</td>
<td>244.57 ± 2.17</td>
<td>3.39 ± 0.03</td>
<td>84.75 ± 0.75</td>
</tr>
</tbody>
</table>

Note: list is atomic ratio of elements in samples.

The typical CV and polarization curves, before and after consecutive ADT cycles (1800 cycles), respectively, are shown in Figs. 1(a) and 2(b) for Pt/XC72, and in Figs. 1(c) and 2(d) for Pt/FXC72-SO₃H. The ECASA was determined by averaging the integration of the H_{up} and H_{down} peaks with the assumption that the hydrogen desorption–adsorption process was on a polycrystalline Pt surface. The pair of peaks at 0.05 V and 0.3 V (vs. NHE) corresponded to the hydrogen desorption–adsorption on the Pt surface, respectively. The ECASA of Pt/FXC72-SO₃H (96.23 m² Pt/gPt) was higher than that of Pt/XC72 (87.34 m² Pt/gPt), which was caused by the smaller Pt particle size on FXC72-SO₃H than that on XC72. Based on the particle size distribution in the TEM image (Fig. 5(c)) of Pt/FXC72-SO₃H, using a weighted average calculation, the mean Pt particle size was about 2.92 nm for Pt/FXC72-SO₃H (about 3.32 nm for Pt/XC72 [46]). The reason for this size difference might be that the functional group (ph-SO₃H) could have guided the Pt precursors ([(NH₃)₂Pt(NO₃)₂]) to anchor on the carbon surface forming smaller Pt particles and a more uniform distribution, which can also be observed in the TEM images (Fig. 5). Compared with the Pt/XC72 TEM image [46], the Pt particles dispersed more uniformly on the FXC72-SO₃H.

With ADT cycling, a reduction of the H_{up} and H_{down} peaks was observed for both catalysts because of the Pt particle size increase, which was caused by Pt nanoparticle agglomeration [48]. After 1800 consecutive cycles, the ECASA loss of the Pt/FXC72-SO₃H was 59.52%, which was less than that of the Pt/XC72, 68.57% (Table 3), suggesting that the functional group (ph-SO₃H) could have prevented the Pt particle from aggregating. Urchaga et al. [39] reported that the ECASA loss was 10% lower for thiophenol-modified substrates than for bare Vulcan XC72 after 2000 consecutive ADT cycles (from 0.05 V to 1.2 V vs. RHE in a 0.1 M HClO₄ electrolyte purged.

Table 2
Summary of XPS results for catalyst supports and corresponding catalysts.

<table>
<thead>
<tr>
<th>Sample identifier</th>
<th>C 1s (%)</th>
<th>O 1s (%)</th>
<th>Pt 4f (%)</th>
<th>N 1s (%)</th>
<th>Na 1s (%)</th>
<th>S 2p (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XC72</td>
<td>90.7</td>
<td>7.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/XC72</td>
<td>90.5</td>
<td>8.4</td>
<td>1.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FXC72-SO₃H</td>
<td>88.3</td>
<td>9.2</td>
<td></td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Pt/FXC72-SO₃H</td>
<td>85.3</td>
<td>9.1</td>
<td>0.84</td>
<td>3.44</td>
<td>1.3</td>
<td>1.3</td>
</tr>
</tbody>
</table>
with N₂ at room temperature at a sweep rate of 50 mV/s), which is concordant with our results. The improvement of the substrate particle interaction (bond) might lead to the improved stability of the Pt catalyst.

The polarization curves before and after 1800 consecutive ADT cycles are shown in Fig. 1(b) for Pt/XC72, and in Fig. 1(d) for Pt/FXC72-SO₃H, respectively, at room temperature in 0.1 M HClO₄ saturated with O₂ using a GCRDE at 1600 rpm. As can be seen in Fig. 1, the polarization curves of each catalyst before and after cycling were parallel to each other. The difference between the Tafel slopes before and after 1800 ADT cycles for both the Pt/XC72 (83 mV/dec and 75.4 mV/dec) and the Pt/FXC72-SO₃H (86.3 mV/dec and 82.9 mV/dec) was very small, especially for the Pt/FXC72-SO₃H. This small difference is consistent with the ECASA results. At high potentials (between 0.96 and 0.80 V versus NHE), the ORR was under the kinetic control. These Tafel slope results indicate that the change in catalytic activity of both catalysts was minimal. Thus, the degradation of catalyst Pt nanoparticles during the ADT cycling was not the dominating process. The potential downshifts of the polarization curves before and after 1800 consecutive ADT cycles (Figs. 1(b) and 2(b) and (d)) were caused mainly by the increased electron resistance between the carbon particles due to the loss of physical contact between the carbon particles, a consequence of the carbon corrosion [46,49,50]. It can also be seen that the mass activity [51] of both catalysts after cycling significantly decreased. The mass activity loss (current density at 0.75 V versus NHE) of Pt/XC72 and Pt/FXC72-SO₃H was 73.6% and 65.1%, respectively. It can be concluded that Pt/FXC72-SO₃H showed higher stability than Pt/XC72 under equivalent conditions (the corrosion resistance of Pt/FXC72-SO₃H was about 1.3 times as much as that of Pt/XC72), which could be due to the effects of the functional group. The FCB surface can be fully covered by functional groups (e.g. p-benzene sulfonic acid, pb-SO₃H⁺), which can result in having a much stronger oxidation resistance than the surface of pure carbon because, in contrast with conventional Pt/C, where Pt electron donation to carbon increases the electron density on the carbon and makes the carbon more prone to oxidation, the electron withdrawing effect of these functional groups makes the carbon less prone to oxidation. In addition, the bond between the aromatic ring of p-benzene sulfonic acid (pb-SO₃H) and C atom on graphite stabilizes the carbon atoms.

The CV and polarization curves for Pt/BP2000 and Pt/FBP2000-SO₃H are shown in Fig. 2. The differences of CV and ORR between Pt/BP2000 and Pt/FBP2000-SO₃H are much larger than those between Pt/XC72 and Pt/FXC72-SO₃H. As can be seen from Table 3, the ECASA of Pt/FBP2000-SO₃H (84.6 m²/gPt) in Fig. 2(c)) is higher than the ECASA of Pt/BP2000 (63.45 m²/gPt) in Fig. 2(a)), which can be attributed to the effects of the pbSO₃H functional groups on forming smaller-sized Pt nanoparticles and more uniform Pt particle dispersion on the FBP2000-SO₃H carbon support than those on the bare BP2000. The average Pt particle sizes on FBP2000-SO₃H and BP2000 were 2.96 nm (Fig. 6(c)) and 3.7 nm [46]. There is an obvious reduction of Pt size when the carbon support was changed from BP2000 to FBP2000-SO₃H. As for the carbon corrosion resistance, after 1800 consecutive cycles, the ECASA loss of Pt/FBP2000-SO₃H was only 58.1%, which was much less than that of the Pt/BP2000, 76.7% (Table 3). This again confirms the speculation that functional groups (~SO₃H) could increase the interaction (bond) between the Pt and the carbon substrate, which could prevent the Pt particles from aggregating during cycling [39]. A pair of redox peaks, which corresponds to the reduction/oxidation of quinone/hydroquinone [41], at 0.55 V and 0.60 V appeared in the voltammogram of the Pt/BP2000 after 1800 consecutive ADT cycles (Fig. 2(a)). While, as seen in Fig. 2(c), this redox couple was not as strong in the voltammogram of the Pt/FBP2000-SO₃H as that in the Pt/BP2000 after the ADT cycles. This suggests that enhanced carbon corrosion resistance was obtained from the FBP2000-SO₃H.

Table 3
Summary of the electrochemically active surface area (ECASA), kinetically controlled oxygen reduction reaction (ORR) currents at 0.75 V vs. NHE, Pt nanoparticle size change and Tafel slope change for the Pt-based different carbon supports before and after 1800 consecutive ADT cycling.

<table>
<thead>
<tr>
<th></th>
<th>t₀ (Å⁻¹)</th>
<th>ECASA (m²/gPt)</th>
<th>Tafel slope</th>
<th>Pt average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/XC72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0th</td>
<td>95.85</td>
<td>87.34</td>
<td>86.3</td>
<td>3.32</td>
</tr>
<tr>
<td>1800th</td>
<td>26.24</td>
<td>27.45</td>
<td>82.9</td>
<td>4.27</td>
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<tr>
<td>Loss</td>
<td>73.6%</td>
<td>68.57%</td>
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<td></td>
</tr>
<tr>
<td>Pt/FXC72-SO₃H</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0th</td>
<td>103.5</td>
<td>96.23</td>
<td>73</td>
<td>2.92</td>
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<tr>
<td>1800th</td>
<td>36.1</td>
<td>38.95</td>
<td>69.3</td>
<td>3.66</td>
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<tr>
<td>Loss</td>
<td>65.1%</td>
<td>59.52%</td>
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<tr>
<td>Corrosion resistance increase</td>
<td>30%</td>
<td>30%</td>
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<tr>
<td>Pt/BP2000</td>
<td></td>
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<td>0th</td>
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<td>1800th</td>
<td>9.9</td>
<td>14.8</td>
<td>56.3</td>
<td>5.26</td>
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<tr>
<td>Loss</td>
<td>85.1%</td>
<td>76.7%</td>
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<td></td>
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<tr>
<td>Pt/FBP2000-SO₃H</td>
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<td></td>
</tr>
<tr>
<td>0th</td>
<td>86.6</td>
<td>84.60</td>
<td>69.3</td>
<td>2.96</td>
</tr>
<tr>
<td>1800th</td>
<td>31.75</td>
<td>35.36</td>
<td>68.7</td>
<td>4.03</td>
</tr>
<tr>
<td>Loss</td>
<td>64.1%</td>
<td>58.1%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion resistance increase</td>
<td>140%</td>
<td>70%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the stability of Pt nanoparticles by enhancing the interaction (bond) between Pt and carbon black [39], but they also could increase the corrosion resistance of carbon by shifting the electron density from the carbon atoms to the benzene ring (which is linked to –SO3H) through the electron withdrawing effects. It has been found that the corrosion process for the different catalysts started from the center of the particle for the Pt/XC72 and started on the surface of the particle for the Pt/BP2000 [43]. This is the reason why, after the BP2000 was functionalized by the functional group pb-SO3H, the corrosion resistance increased much more than it did for the XC72.

3.2. Electrochemical and physical characterization of the electrode surface area as a function of time

In order to further study the corrosion resistance of Pt/FXC72-SO3H and Pt/FBP2000-SO3H, CV and polarization curve testing were carried out every 300th cycle during a 1500 ADT cycle (0.85–1.4 V, scan rate 20 mV/s). All the data from Pt/XC72 and Pt/BP2000 in this part were obtained from our previous work [43] with the same experiment conditions. The CV curves as a function of the cycle number obtained are shown in Fig. 3(a) for Pt/FXC72-SO3H, and in Fig. 3(c) for Pt/FBP2000-SO3H, during the ADT cycles. In both the Pt/FXC72-SO3H and the Pt/FBP2000-SO3H, it was observed that the ECASA decreased with the cycling number (Fig. 3(d)), according to the hydrogen adsorption–desorption potential, in the region between 0.05 and 0.30 V (vs. NHE), which was caused by the increase of Pt nanoparticle size and carbon corrosion. For further analysis, the ECASA change trend as a function of the cycling number of Pt/FXC72-SO3H and Pt/FBP2000-SO3H is presented in Fig. 3(b) and (d). It was found that the decreasing rates of the ECASA for the Pt/FXC72-SO3H and the Pt/FBP2000-SO3H were different from those of the Pt/XC72 and the Pt/BP2000, especially for the Pt/FBP2000-SO3H. In the case of the Pt/FXC72-SO3H, the ECASA decrease rate was only 0.0076 m2/(gPt cycle) for the first 600 cycles, which was a little smaller than that of the Pt/XC72 (0.0125 m2/(gPt cycle)). In the case of the Pt/FBP2000-SO3H, the ECASA decrease rates were 0.0021 m2/(gPt cycle) for the first 600 cycles, which were much smaller than that of the Pt/BP2000 (0.0325 m2/(gPt cycle)). This indicates that the functional group could greatly increase the corrosion resistance of BP2000 in the initial period (the amorphous components of the carbon was mainly corroded within the first 600 cycles) because the outer layers of the BP2000 contain amorphous components, while the functional group could increase the corrosion resistance of the XC72 only a little because the most amorphous structured components of the XC72 are in the center.

The double layer capacity (DLC) was also obtained by integrating the CV curves from 0.32 V to 0.38 V (vs. NHE) for both the Pt/FXC72-SO3H and the Pt/FBP2000-SO3H. Double layer capacity is directly proportional to carbon surface area. In order to compare the exact changes of the DLC of the catalyst layer and the electrolyte, the CV curve was also measured on a fresh glassy carbon electrode (without any catalysts) after it went through the exact same ADT process. All the values shown in the right axis of Fig. 3(b), Pt/FXC72-SO3H, and Fig. 3(d), Pt/FBP2000-SO3H, have had the DLC values subtracted from those of the fresh glassy carbon electrode, which
served as the background. The DLC of the Pt/FXC72-SO$_3$H increased initially, then maintained the same level from the 300th to the 900th cycle, and then decreased after the 900th cycle. The behavior of DLC as a function of time is similar to the change trends of the DLC of Pt/XC72 [43]. The same trends of DLC for both Pt/XC72 and Pt/FXC72 suggest that the functional group attached to the XC72 did not protect the amorphous components in the center of the carbon particles. The initial increase of the DLC in Pt/FXC72-SO$_3$H suggests that the carbon corrosion still started from the center of the XC72 carbon particles, which increased some surface area; then further corrosion caused the loss of the carbon particles from the catalyst layer. However, in the case of the Pt/FBP2000-SO$_3$H (Fig. 3(d)), the DLC showed a different trend with an increase in the number of cycles from that of the Pt/BP2000 [43]. The DLC of the Pt/FBP2000-SO$_3$H decreased slowly, 0.061 mC/cm$^2$ cycle, compared with that of the Pt/BP2000, 0.23 mC/cm$^2$ cycle [43]. Between the 300th and the 900th cycles, the difference was even bigger. The decrease rate of the DLC for the Pt/FBP2000-SO$_3$H was 0.02 mC/cm$^2$ cycle, while the rate of the Pt/BP2000 was 0.26 mC/cm$^2$ cycle. The functional group appeared to prevent the BP2000 carbon surface from being corroded, as indicated by the smaller decrease rate of the DLC of the Pt/FBP2000-SO$_3$H compared with that of the Pt/BP2000. Therefore, the different effects of the functional group on the corrosion resistance of the XC72 and the BP2000 could have been caused by the different carbon corrosion processes, as is suggested by the different trends of the DLC (carbon surface area) of the Pt/FXC72-SO$_3$H and the Pt/FBP2000-SO$_3$H with regard to cycle number.

The polarization curves as a function of time (Fig. 4) were also analyzed to further illustrate the effects of the functional group (pb-SO$_3$H) on the carbon corrosion resistance of the two catalysts. There are three different control steps in the different regions of the polarization curves. From OCV to 0.85 V, it is the kinetic control region. The ORR mass activity current density at 0.85 V (kinetic performance), 0.75 V (ohmic performance), 0.65 V (mass transport performance) vs. NHE as a function of cycle number, respectively, are plotted in Fig. 4. The mass activity losses with the cycle number are shown in Fig. 4(a) and (b) for Pt/FXC72-SO$_3$H, and in Fig. 4(c) and (d) for Pt/FBP2000-SO$_3$H, and were obtained at room temperature in a 0.1 M HClO$_4$ solution saturated with O$_2$ using a TFRDE at 1600 rpm. As for Pt/FXC72-SO$_3$H, the current density decay rates at 0.85, 0.75, and 0.6 V were 0.0092 (0.02 for Pt/XC72), 0.065 (0.08 for Pt/XC72), and 0.11 (0.13 for Pt/XC72) (A g$^{-1}$ cycle$^{-1}$). As for Pt/FBP2000-SO$_3$H, the decrease rates were 0.0082 (0.018 for Pt/BP2000), 0.043 (0.07 for Pt/BP2000), and 0.07 (0.125 for Pt/BP2000) (A g$^{-1}$ cycle$^{-1}$), respectively. All the mass activity current density decay rates of functional carbon supported catalysts were lower than those of un-functional carbon supported catalysts, suggesting that the functional group can increase the corrosion resistance of both the XC72 and the BP2000. The differences on the mass activity, current density, and decay rate improvement for Pt/FXC72-SO$_3$H vs. Pt/XC72 and Pt/FBP2000-SO$_3$H vs. Pt/BP2000 suggest a strong effect of the functional group on both Pt stability and carbon corrosion resistance. At 0.85 V, the current density decay rate, reflecting the performance of the Pt catalysts supported on both carbons, XC72 and BP2000, increased, which confirmed the conclusion that functional groups can increase the stability of Pt. The mass transport performance.
was obtained by using a weighted average based on the distribution data. It was found that the Pt particle size increased from 2.92 nm to 3.66 nm (mean particles size) after 1800 continuous ADT cycles, accounting for a 25% loss in Pt surface area, which is a little smaller than the 28% from that of the Pt/XC72. The observed increase in the Pt particle size is probably due to the particle migration mechanism [44], which is explained by the migration and aggregation of platinum particles to form larger particles.

The TEM micrographs of the Pt/FBP2000-SO\textsubscript{3}H are shown in Fig. 6(a) and (b). It can be clearly seen that the corrosion feature of the Pt/FBP2000-SO\textsubscript{3}H was different from that of the Pt/BP2000 samples. Compared with the fresh Pt/FBP2000-SO\textsubscript{3}H (Fig. 6(a)), it can be seen that the boundary of the FBP2000-SO\textsubscript{3}H still could be seen after 1800 cycles. Compared with the Pt/BP2000, it can be concluded that the carbon corrosion on the Pt/FBP2000-SO\textsubscript{3}H has been greatly improved because the corrosion prefers to occur on the surface of the BP2000, which can be protected by the functional group; therefore, the functional group will decrease the aggregation of the Pt particles (a 1.07 nm increase for Pt/FBP2000, but a 1.56 nm increase for Pt/BP2000). The particle size distribution of the Pt/FBP2000-SO\textsubscript{3}H catalyst (Fig. 6(c)) showed an increase in mean particle size from 2.96 nm to 4.03 nm, accounting for
about a 35% Pt loss. This is consistent with the improvement in the decay of the ECSA and the mass activity results from the Pt/FBP2000-SO3H.

4. Conclusions

The functional group $p$-SO$_3$H was attached to the surface of two catalyst carbon supports, XC72 and BP2000, to improve carbon corrosion resistance. An ADT utilizing an RDE system was used to study the corrosion of Pt/FXC72-SO$_3$H and Pt/FBP2000-SO$_3$H. The results showed that SO$_3$H can reduce performance decay by increasing the corrosion resistance of the carbon support and the stability of the Pt particles. The results of the ECASA and ORR current measurements indicate that the effects of the functional group on carbon corrosion improvement are more significant for BP2000 than for XC72. The corrosion resistance of Pt/FBP2000-SO$_3$H increased the ECSA by 1.7 times and the mass activity by 2.4 times after 1800 ADT consecutive cycles, while the corrosion resistance of Pt/FXC72-SO$_3$H increased only 1.3 times for both ECSA and mass activity. This difference might have been caused by different corrosion processes.

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References


