Effect of surface oxygen functionalization of carbon support on the activity and durability of Pt/C catalysts for the oxygen reduction reaction

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ABSTRACT

Oxygen functionalization of carbon supports has been a widely used strategy to enhance catalytic performance of carbon supported Pt (Pt/C) catalysts. However, the effect of oxidative functionalization on the catalytic performance of Pt/C catalysts for the oxygen reduction reaction (ORR) has rarely been investigated. We report the impact of oxygen functionalization of carbon black (CB) supports on the activity and durability of CB supported Pt catalysts for the ORR. Pristine and mildly oxygen-functionalized CB supported Pt catalysts (Pt/CB and Pt/CB_O, respectively) show nearly identical structural parameters, including surface areas and pore volumes of the CB support, and supported Pt particle sizes. The Pt/CB_O catalyst shows higher electrochemically active surface area and ORR activity than Pt/CB catalyst, which is likely caused by differing interfacial structure between the carbon support and Pt nanoparticles in the two catalysts. In ORR durability tests, Pt/CB exhibits significantly higher stability than Pt/CB_O. Spectroscopic characterizations reveal that oxygen functionalization in the Pt/CB_O catalyst partially oxidizes the Pt nanoparticles, triggering facile dissolution and Ostwald ripening of Pt nanoparticles, which accelerates the decline of the ORR activity of Pt/CB_O.

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1. Introduction

Carbon supported metal catalysts constitute an important class of heterogeneous catalysts [1–3]. Particularly, carbon supported Pt or Pt-based alloy (Pt/C and PtM/C; M = other metal) catalysts have often been used in fuel cells, since carbon supports have a range of desirable properties including high conductivity, large surface area, and chemical stability [4–11]. During the preparation of Pt/C catalysts, the carbon supports are commonly functionalized with oxygen-containing groups by acid treatment in order to activate chemically inert carbon surfaces. Such oxygen functionalization can enable the formation of small, uniform Pt nanoparticles via homogeneous distribution of Pt precursors, resulting in the enhanced performance of the Pt/C catalysts. Hence, the impact of oxygen functionalization of carbon supports on the catalytic activity and stability of Pt/C catalysts have attracted continuous interest [1–3]. However, there is still an ongoing debate as to whether oxygen functionalization is beneficial [12–14] on the catalytic properties or not [15–18].

This ambiguity originates mainly from the concomitant changes in structural parameters of carbon supports during the oxygen functionalization process. Oxygen functionalization is mainly accomplished by acid treatment of the carbon support, leading to the functionalization of oxygen-containing groups, such as carboxylic acid and ketone, on the carbon surface [19]. Unfortunately, unwanted changes in surface area [20], morphology [21] and the formation of defects [22] can also occur as a result of acid treatment. Moreover, the size of the Pt nanoparticles, which is a crucial factor in their catalytic performance [23], is also subject to change.
upon acid treatment of the carbon support [24,25]. Therefore, these undesirable changes in structural parameters have so far made it difficult to conclusively establish the impact of oxygen functionalization on the catalytic properties.

Since the early 2000s, the influence of oxygen functionalization of Pt/C catalysts on electrocatalytic reactions has also been of significant interest [18,26–38]. Among various electrocatalytic reactions, the oxygen reduction reaction (ORR) is a key component in many important energy conversion and storage devices such as fuel cells and metal-air batteries [39,40]. Particularly, in proton exchange membrane fuel cells (PEMFCs), the development of highly active and stable ORR catalysts has been of tremendous interest, as they can dictate the overall performance of the PEMFCs [41]. Nevertheless, the effects of oxygen functionalization have been predominantly investigated for oxidation reactions [18,27–34] and only sporadic works have been reported for the ORR [35–38]. Furthermore, the effects of oxygen functionalization on durability have rarely been previously investigated, even though durability is as important as activity for the performance of an ORR catalyst [42–44].

Herein, we report the impact of oxygen functionalization of the carbon support on the activity and durability of Pt/C catalysts. For this purpose, commercial carbon black (CB, Vulcan XC–72R) was functionalized with a mild acid, yielding an oxygen group functionalized carbon black support with minimal changes in other structural parameters. Similar sized Pt nanoparticles were supported on pristine and oxygen-functionalized CB to yield Pt/CB and Pt/CB_O catalysts. The Pt/CB_O catalyst showed higher electrochemically active surface area (ECSA) and ORR activity, which could originate from more exposed surface of Pt nanoparticles in the Pt/CB_O catalyst than Pt/CB. In contrast, the Pt/CB exhibited significantly better durability for the ORR than Pt/CB_O. Spectroscopic characterization revealed that the surface of Pt nanoparticles in the Pt/CB_O was partially oxidized, which facilitated the dissolution and ripening of Pt nanoparticles and resulted in the rapid decrease in the ORR activity.

2. Experimental section

2.1. Preparation of carbon black supported Pt catalysts

Vulcan XC–72R (Cabot) was used as the carbon black support. For oxygen group functionalization of the carbon black surface, 126 mL of deionized (DI) water, 82 mL of HNO_3 (Samchun), and 42 mL (0.5 mol) of HCl (Samchun) were mixed to make an acidic solution. 0.6 g of CB support was added to the solution, and the mixture was stirred for 12 h at 80 °C. The slurry was then filtrated and washed with copious amounts of DI water until the filtrate became neutral. The resulting oxygen functionalized CB was denoted as CB_O. Pt nanoparticle catalysts were supported on pristine and oxygen-functionalized CB supports via incipient-wetness impregnation of Pt precursor, followed by hydrogen reduction [45]. 0.45 g of the carbon support was mixed with 1.0 mL of acetone containing 0.13 g of hexachloroplatinic acid (H_2PtCl_6, Aldrich). After being dried overnight at 60 °C in an oven, the H_2PtCl_6–6H_2O-impregnated carbon support was heated to 200 °C in H_2 flow at a ramping rate of 0.6 °C min⁻¹; the support was maintained at this temperature for 2 h to reduce H_2PtCl_6–6H_2O to Pt nanoparticles. Hydrogen adsorbed on the Pt particles was removed by heating the sample to 350 °C and keeping it at this temperature for 2 h under N_2 flow. Final catalysts prepared from pristine and functionalized CB supports were designated as Pt/CB and Pt/CB_O, respectively.

2.2. Characterization methods

All characterization was carried out at the Ulsan National Institute of Science and Technology Central Research Facilities (UCRF) Center. Fourier transform infrared spectroscopy (FT-IR) was conducted using a 620-IR spectrophotometer (Agilent). The porous structure of the samples was analyzed by a nitrogen adsorption experiment at 77 K using a BELSORP-Max system (BEL). X-ray photoelectron spectroscopy (XPS) was performed using a K-alpha instrument (Thermo Fisher). The morphology of the catalysts was observed using a Hitachi S-4800 scanning electron microscope (SEM) operating at 10 kV. The size and distribution of Pt nanoparticles in the catalysts were determined using a JEOL JEM-2100 transmission electron microscope (TEM). X-ray diffraction (XRD) patterns of the samples were obtained with an X-ray diffractometer (Rigaku D/Max 2500/PC) equipped with a Cu Kα source at 40 kV and 200 mA. Raman spectra were taken using an alpha300R instrument (WITec). Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was carried out using 720-ES instrument (Varian).

2.3. X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) data of the catalysts were collected on the Beamline 6D at the Pohang Accelerator Laboratory (PAL) with a beam energy and current of 3 GeV and 300 mA, respectively. A monochromatic X-ray beam could be obtained from the high intensity X-ray photons of a multi-pole wiggler source using a liquid N_2-cooled Si (111) double crystal monochromator (Bruker ASC) with an energy resolution (ΔE/E) of 2 × 10⁻⁴. Higher order harmonic contaminations were eliminated by detuning to reduce the incident X-ray intensity by ~15%. Energy calibration was simultaneously carried out for each measurement with a reference metal foil placed in front of the third ion chamber. Data reductions of the experimental spectra to normalized X-ray absorption near edge structure (XANES) were performed through the standard X-ray absorption fine structure procedure.

2.4. Electrochemical characterization

Electrochemical experiments were performed using an Ivium-Stat electrochemical analyzer (Ivium Technologies) at room temperature (25 °C) under atmospheric pressure using a three electrode system. Graphite and Ag/AgCl were used as the counter and reference electrodes, respectively. All data were reported with respect to the reversible hydrogen electrode (RHE) potential scale. Calibration of the Ag/AgCl reference electrode with respect to the RHE was carried out as follows: Ag/AgCl and RHE (HydroFlex) were used as the reference and working electrodes, respectively, and immersed in N_2-saturated 0.1 M HClO_4 (70%, Veritas, double distilled) for at least 30 min. Then, the constant open circuit potential (calibration value) was obtained. The potential difference was E (RHE) = E (Ag/AgCl) + 0.273 V. A rotating ring-disc electrode (RRDE) with a glassy carbon disk (4 mm diameter) and a Pt ring was used as the working electrode. The RRDE was polished with a 1.0 μm alumina suspension and then with a 0.3 μm suspension to produce a mirror finish.

The catalyst ink was prepared by mixing 10 mg of the Pt/CB catalysts, 0.1 mL of DI water, 1.06 mL of ethanol and 0.04 mL of 5 wt % Nafion (in isopropanol, Aldrich), and was dispersed homogeneously by sonication the mixture for 30 min. 3.0 μL of the ink was drop cast and dried to form a thin film on a glassy carbon disk electrode with a geometric surface area of 0.1257 cm². Before electrochemical measurement, electrochemical cleaning was performed by sweeping the potential between 0.05 V and 1.2 V at a scan rate of 500 mV s⁻¹ for 200 cycles in N_2-saturated 0.1 M HClO_4.
Cyclic voltammetry (CV) was performed in the 0.05 V–1.2 V potential range at a scan rate of 50 mV s\(^{-1}\) in N\(_2\)-saturated 0.1 M HClO\(_4\). After saturating CO gas with chronoamperometry at 0.05 V, CO-stripping was done on N\(_2\)-saturated condition by linear sweep voltammetry (LSV) with 50 mV s\(^{-1}\) between 0.05 V and 1.5 V. The ORR activity was evaluated by LSV in the anodic direction from −0.01 V to 1.1 V in O\(_2\)-saturated 0.1 M HClO\(_4\) at a rotating speed of 1600 rpm with a scan rate of 20 mV s\(^{-1}\). Currents were collected after iR-drop correction. The long-term durability of the catalyst s was evaluated by the accelerated degradation test (ADT). The ORR were obtained after 1500 cycles. Fresh electrolyte solution voltammetry (LSV) with 50 mV s\(^{-1}\)/C0\(_r\) collected after 3.1. Characterization of carbon supports

(Fig. S1) showed a new peak at 1740 cm\(^{-1}\) indicating the functionalization of the carbon surface with a carbonyl group. Oxygen group functionalization of the carbon support was further verified by XPS analysis of the C 1s spectra (Fig. S2). The C 1s XPS spectra of the two samples could be deconvoluted into three peaks. The peaks at ca. 284.6 eV, 286 eV, and 289 eV are ascribed to the presence of graphitized carbon, C−O, and C=O species, respectively [47]. The integrated area of the peaks corresponding to C−O and C=O species for CB_O is much higher than that for CB, which is consistent with the FT-IR results. The FT-IR and XPS results clearly demonstrate that oxygen containing functional groups were well functionalized on the carbon black surfaces via acid treatment.

Further structural characterizations of carbon supports were carried out with SEM, N\(_2\) physisorption, and Raman spectroscopy. SEM images of the CB and CB_O supports (Fig. S3) revealed that both samples are spherical in shape with sizes ranging from 30 nm to 200 nm, indicating that the morphology was preserved after acid treatment. The textural properties of the CB and CB_O, determined by N\(_2\) physisorption analysis (Table S1 and Fig. S4), indicated that the CB_O sample underwent a slight reduction in surface area from 294 m\(^2\) g\(^{-1}\) (for CB) to 258 m\(^2\) g\(^{-1}\). The graphic character of the carbon supports was probed by Raman spectroscopy, wherein the intensity ratio \(I_D/I_G\) of the D and G bands is commonly used as a fingerprint for the amount of graphitic carbon [48]. The calculated \(I_D/I_G\) values for the CB (1.01) and CB_O (1.02) samples were almost identical, indicating that the graphic character was maintained after oxygen functionalization (Fig. S5).

The above characterization data reveal that oxygen-containing functional groups were successfully functionalized on the carbon black supports by acid treatment, while most of the structural parameters remained unchanged. Such structural preservation is possible due to the mild conditions of the oxidative reaction. The preservation of structural parameters allowed us to investigate the effects of oxygen functionalization exclusively in the carbon supported Pt catalysts.

3.2. Preparation and characterization of Pt/carbon supports

The Pt/CB and Pt/CB_O catalysts were prepared via impregnation of a Pt precursor on the carbon support followed by hydrogen reduction. Since the ORR activity is strongly dependent on Pt particle size, the formation of Pt nanoparticles having similar size on different supports is crucial for studying the oxygen functionalization effect. In addition, if neighboring Pt nanoparticles are placed too close to each other, they may easily undergo agglomeration during long-term durability tests. Considering this, we controlled the loading of Pt nanoparticles to a relatively low value of around 15 wt%, which was confirmed by ICP-MS (Table S2). TEM images of the Pt/CB and Pt/CB_O (Fig. 1a,b,d,e) revealed that Pt nanoparticles were uniformly distributed on both carbon supports and the particles had similar Pt size. The histograms showing Pt particle size distribution clearly indicated that the Pt sizes in the two catalysts are almost identical with value of 1.7 and 1.8 nm for Pt/CB and Pt/CB_O, respectively (Fig. 1c,f). The nearly identical XRD patterns of the two catalysts corroborate the similar sizes of the Pt nanoparticles (Fig. S6). Both catalysts showed three broad peaks, around 40°, 66°, and 81°, respectively, which can be indexed to the (111), (200), and (222) facets of the face-centered-cubic (fcc) structure of Pt. The widths of the three peaks for Pt/CB were almost identical to those for Pt/CB_O, which indicates that the crystallite sizes of Pt nanoparticles in both catalysts are very similar, further confirming the TEM results. In summary, small Pt nanoparticles of very similar size were uniformly deposited on both CB and CB_O supports, and the resulting catalysts were used as model systems to study the role of oxygen functionalization of the carbon support on ORR performance.

3.3. Effect of oxygen functional group on the electrocatalytic activity and durability

The electrochemical properties of the Pt/CB and Pt/CB_O catalysts were investigated by CV (Fig. 2a,b), CO stripping (Fig. 2c,d), and LSV (Fig. 2e,f) techniques. The ECSAs of the Pt nanoparticles were calculated from the charge to desorb a layer of hydrogen in the so-called Hupd region in a CV, or to oxidize a pre-adsorbed monolayer of CO in a stripping mode, after correcting for the double layer charging current by using the following equation:

\[
\text{ECSA} = \frac{Q_H}{L} \times \frac{Q_{CO}}{Q_{H}}
\]

where \(Q_H\) is the charge for the hydrogen desorption and \(Q_{CO}\) is the charge for the oxidation of CO (\(\mu\)C cm\(^{-2}\)); \(L\) is the mass of Pt loaded on the working electrode (g m\(^{-1}\); \(q_H\) is the charge associated with the desorption of a monolayer of hydrogen on Pt (210 \(\mu\)C cm\(^{-2}\)) and \(q_{CO}\) is the charge associated with two electron transfer for the oxidation of CO to CO\(_2\) per Pt atom (420 \(\mu\)C cm\(^{-2}\)) [49]. The ECSA values were calculated every 100 cycles, and the changes in ECSA_Hupd and ECSA_CO are plotted in Fig. 2b and d, respectively. The mass activity and specific activity for the ORR were estimated from mass transport-corrected kinetic currents at 0.9 V (Table 1).

Comparison of the CVs of the two catalysts clearly revealed that a new peak at ca. 0.6 V (vs. RHE), corresponding to the redox couple of quinone/hydroquinone [50], appeared for the Pt/CB_O catalyst due to oxygen functionalization on the carbon support (Fig. 2a), which is consistent with FT-IR and C 1s XPS results for CB and CB_O. Interestingly, despite the similar loading and size of Pt nanoparticles for both catalysts, Pt/CB_O showed a larger hydrogen desorption peak area than Pt/CB, which translated into Pt/CB_O having a higher initial ECSA_Hupd (77.0 m\(^2\) gPt\(^{-1}\)) than Pt/CB (63.0 m\(^2\) gPt\(^{-1}\)). This trend between the two catalysts was also confirmed with CO-stripping method, which revealed that initial ECSA_CO of Pt/CB_O (117.8 m\(^2\) gPt\(^{-1}\)) is greater than that of Pt/CB (79.2 m\(^2\) gPt\(^{-1}\)). The initial ORR activity of Pt/CB_O was also slightly higher than Pt/CB (Fig. 2e), with half-wave potentials of Pt/CB_O and Pt/CB being 0.912 V (vs. RHE) and 0.904 V, respectively. At 0.9 V, the Pt/CB_O catalyst
exhibited higher initial kinetic current densities (10.47 mA cm$^{-2}$) than the Pt/CB catalyst (6.91 mA cm$^{-2}$). The mass activities of the two catalysts also showed a similar trend, with Pt/CB_O and Pt/CB exhibiting activities of 0.356 and 0.243 A mg Pt$^{-1}$, respectively. Detailed electrochemical data are summarized in Table 1. The difference in the initial activity of the two catalysts could be attributed to differing interfacial structure between the carbon support and Pt nanoparticles. The pristine CB supports are composed of highly graphitic layers, on which Pt precursors are adsorbed via interactions between $\pi$-electrons of graphitic layers and Pt cations [1]. Hence, the resulting Pt nanoparticles in Pt/CB are likely to have strong interaction with CB, and may have larger contact area between Pt and CB surfaces. On the other hand, such interactions would be relatively weaker for oxygen-functionalized Pt/CB_O, and the Pt nanoparticles may expose a higher portion of crystalline surfaces, compared to Pt/CB. These speculations can, in part, be substantiated by the shapes of the hydrogen desorption peaks in the CVs at 0.14 V and 0.20 V, which arise from the desorption of adsorbed protons from (110) and (100) facets of fcc Pt crystals [51]. Particularly for the peak at 0.20 V, the Pt/CB_O showed a more distinctive peak shape than Pt/CB, suggesting more exposed crystalline surfaces in the former, which can in turn explain its enhanced ORR activity.

The durability of the catalysts was evaluated by ADTs, which were carried out by cycling the potential from 0.05 V to 1.2 V up to 1500 times. The ADT results clearly indicated the better durability of the Pt/CB sample compared to Pt/CB_O, in contrast to their initial activity results. After the ADTs, the ECSA$_{\text{Hupd}}$ of Pt/CB and Pt/CB_O decreased from 63.0 m$^2$ g$_{\text{Pt}}^{-1}$ to 36.0 m$^2$ g$_{\text{Pt}}^{-1}$ and from 77.0 m$^2$ g$_{\text{Pt}}^{-1}$ to 34.9 m$^2$ g$_{\text{Pt}}^{-1}$, retaining 57% and 45% of their initial ECSAs.
Fig. 2. (a) CV of Pt/CB and Pt/CB_O before and after the ADTs; (b) Changes in ECSA values calculated from Hupd of Pt/CB and Pt/CB_O before and after the ADTs; (c) CO-stripping of Pt/CB and Pt/CB_O before and after the ADTs; (d) Changes in ECSA values calculated from CO-stripping of Pt/CB and Pt/CB_O; (e) ORR polarization curves of Pt/CB and Pt/CB_O before and after the ADTs (inset: enlarged polarization curves between 0.8 and 1.0 V); (f) Changes in mass activities of Pt/CB and Pt/CB_O. (A colour version of this figure can be viewed online.)

Table 1
Comparison of ECSA and ORR kinetic parameters of the catalysts before and after the ADTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{ECSA}_{\text{Hupd}}$ (m² g⁻¹ Pt)</th>
<th>$\text{ECSA}/\text{ECSA}_i$ (%)</th>
<th>$\text{ECSA}_{\text{CO}}$ (m² g⁻¹ Pt)</th>
<th>$\text{ECSA}/\text{ECSA}_i$ (%)</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_{1/2}$ (mV)</th>
<th>$\text{MA@0.9 V (A mg}\text{-Pt}^{-1})$</th>
<th>$\text{SA@0.9 V (mA cm}^2\text{-Pt}^{-2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CB</td>
<td>63.0</td>
<td>79.8</td>
<td>79.8</td>
<td>71.5%</td>
<td>0.904</td>
<td>12</td>
<td>0.243</td>
<td>0.386</td>
</tr>
<tr>
<td>Pt/CB after ADT</td>
<td>36.0</td>
<td>57.1%</td>
<td>57.1</td>
<td>45.3%</td>
<td>0.892</td>
<td>12</td>
<td>0.163</td>
<td>0.455</td>
</tr>
<tr>
<td>Pt/CB_O</td>
<td>77.0</td>
<td>117.8</td>
<td>117.8</td>
<td>71.5%</td>
<td>0.912</td>
<td>23</td>
<td>0.356</td>
<td>0.462</td>
</tr>
<tr>
<td>Pt/CB_O after ADT</td>
<td>34.9</td>
<td>45.3%</td>
<td>53.4</td>
<td>45.3%</td>
<td>0.889</td>
<td>23</td>
<td>0.138</td>
<td>0.394</td>
</tr>
</tbody>
</table>

$^a$ Electrochemically active surface area (ECSA) calculated from Hupd.
$^b$ ECSAi is initial ECSA calculated from Hupd and ECSA is ECSA calculated from $\text{Hupd}$ after ADT. The values are multiplied by 100 for expressing in percentage unit.
$^c$ Electrochemically active surface area (ECSA) calculated from CO-stripping.
$^d$ ECSAi is initial ECSA calculated from CO-stripping and ECSA is ECSA calculated from CO-stripping after ADT. The values are multiplied by 100 for expressing in percentage unit.
$^e$ Half-wave potential obtained at which the measured current is equal to one-half of the diffusion-limited current value.
$^f$ Changes of half-wave potential after ADT.
$^g$ Mass activity (MA) is estimated from kinetic current at 0.9 V normalized to the Pt loading of the disk electrode.
$^h$ Specific activity (SA) is estimated from kinetic current at 0.9 V normalized to the $\text{ECSA}_{\text{Hupd}}$ of the catalyst.
respectively (Fig. 2a,b and Table 1). With CO-stripping, consistent results were obtained. The ECSA of Pt/CB and Pt/CB_O decreased from 79.8 m² g⁻¹ to 57.1 m² g⁻¹ and from 117.8 m² g⁻¹ to 53.4 m² g⁻¹, retaining 71.5% and 45.3% of their initial ECSAs, respectively (Fig. 2c,d and Table 1). The better durability of the Pt/CB was more clearly evidenced by the kinetic data obtained after the ADTs (Fig. 2e,f and Table 1). While the half-wave potential of Pt/CB was decreased by 12 mV (from 0.904 V to 0.892 V) after the ADT, Pt/CB_O underwent a more significant decrease of 23 mV (from 0.912 V to 0.889 V). In addition, the Pt/CB preserved 67.4% of the initial kinetic current density and mass activity after the ADT, which is substantially higher than that of Pt/CB_O (39.4%). The clear difference in the durability between Pt/CB and Pt/CB_O appears to arise from the different degrees of agglomeration of Pt nanoparticles. TEM images of the two catalysts after the ADTs (Fig. 3) clearly revealed that the Pt/CB_O underwent more severe agglomeration during the durability tests; the size of Pt nanoparticles in Pt/CB_O (3.5 nm) was larger than that in Pt/CB (2.7 nm).

To identify molecular-level factors responsible for the ADT results, the two catalysts were studied by XPS, in situ XANES, and ICP-MS. The Pt 4f XPS spectra of the two catalysts (Fig. 4) showed doublet peaks at 71.8 eV and 75.2 eV, which can be deconvoluted into three peaks. The deconvoluted doublet peaks at 71.5 eV and 75.0 eV, 72.8 eV and 76.3 eV, and 74 eV and 77.5 eV can be ascribed to the Pt⁰, PtO, and PtO₂ phases, respectively [52]. We quantified the integrated areas of deconvoluted peaks in Pt 4f XPS spectra, and the results are presented in Table 2. The area corresponding to PtO₂ phase in the Pt/CB is 17.5%, and that in the Pt/CB_O is increased to 21.7%. On the other hand, the peak area for Pt is reduced from 53.2% in the Pt/CB to 50.3% in the Pt/CB_O. The trend becomes more
evident when the ratio of PtO2/Pt is compared. The PtO2/Pt ratio for Pt/CB is 0.32, whereas that for Pt/CB_O is 0.43. Therefore, XPS results indicate that the Pt/CB_O has higher oxidation state than Pt/CB. In situ Pt LIII-edge XANES data were used to corroborate the XPS results. In situ XANES spectra of Pt/CB and Pt/CB_O were obtained at open circuit voltage (OCV) and 0.3 V (vs. RHE) in fluorescence mode. At each potential, the electrode was stabilized for 5 min, and subsequently the XANES spectrum was recorded. Usually, the oxidation state of Pt is determined based on whiteline intensity in Pt LIII-edge XANES [53]. Under OCV (Fig. 5a) and 0.3 V (Fig. 5b) the whiteline intensities of Pt/CB_O are clearly higher than those of Pt/CB. Oxygen functionalization of the carbon support creates an oxygen-rich environment for Pt nanoparticles, whereby Pt electrons are withdrawn by the highly electronegative oxygen. Therefore, the Pt/CB_O sample has higher Pt oxidation states and sustains the oxidized form of Pt even at a reducing potential of 0.3 V. The oxidation state of Pt nanoparticles is closely related to their degradation, and in particular their dissolution and Ostwald ripening. Thermodynamically, highly oxidized Pt can be dissolved cathodically below 0.837 V via the following reaction [54],

$$\text{PtO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Pt}^{2+} + 2\text{H}_2\text{O}$$

$$E = 0.837 \text{ V} + 0.0295\log[\text{Pt}^{2+}] \text{ vs. SHE}$$

Moreover, it has been shown by DFT calculations that the electrochemical dissolution of higher order oxides is more favorable [55]. Topalov et al. also demonstrated that the electrochemical dissolution of Pt is usually related to the sub-surface oxide [56]. The presence of surface oxide weakens the Pt–Pt bonds and the outermost Pt atoms can easily be detached from the nanoparticles. In our system, oxygen groups introduced on the carbon support increase the oxidation state of the Pt nanoparticle surfaces, which lead to facile dissolution. Highly oxidized Pt nanoparticles in Pt/CB_O are more susceptible to dissolution in an electrolyte [57] and consequently undergo an Ostwald ripening process whereby smaller particle dissolve and re-deposit on larger particles resulting in an increase in average size. Matsumoto et al., also showed that when Pt surfaces were oxidized at least at the subsurface level, the extent of the dissolution was more significant at lower potentials [54]. In our case, the XANES data revealed that even at lower potentials (0.3 V), the Pt/CB_O sample remained in a more oxidized state, compared to Pt/CB. Thus, at lower potential, the dissolution of small Pt nanoparticles significantly occurs on Pt/CB_O, accelerating Ostwald ripening. To further substantiate the faster dissolution of Pt on Pt/CB_O, the electrolyte solutions after the ADTs were analyzed by ICP-MS. The analyses revealed that the concentrations of dissolved Pt ions were 33.8 µg/L for Pt/CB and 73.2 µg/L for Pt/CB_O (Table S3), clearly indicating more severe dissolution of Pt and subsequent Ostwald ripening on Pt/CB_O. Graphical illustrations of Pt dissolution processes over Pt/CB and Pt/CB_O are shown in Fig. 6. When oxygen groups were functionalized on carbon support, the electrons in Pt NPs nearby oxygen groups could be withdrawn by highly electronegative oxygen. As a result, Pt NPs could be oxidized, which may facilitate their dissolution into electrolyte as Pt ions. With dissolved Pt ions, the Oswald ripening takes place easily, and finally the ripening of Pt NPs were accelerated.
4. Conclusions

This study clarified the role of oxygen functionalization of the carbon support on the catalytic activity and durability of Pt/C catalysts for the ORR. To extract the impact of only oxygen functional groups, we used a mild acid treatment to preserve the other structural parameters of CB support. While the oxygen-functionalized Pt/CB_O catalyst with more exposed crystalline facets of Pt nanoparticles showed higher ECSA and ORR activity than pristine Pt/CB, it underwent more severe agglomeration upon degradation testing resulting in lower ORR activity compared to the Pt/CB catalyst. XPS and in situ XANES revealed that oxygen functionalization of the carbon support promotes enhanced surface oxidation of Pt nanoparticles facilitating the dissolution of Pt ions and subsequent Ostwald ripening in the Pt/CB_O catalyst. Our results indicate that oxygen functionalization of Pt/C catalysts can have a positive impact on the initial activity for the ORR, but can exert an adverse effect on its long-term durability.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.02.014.

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