Is reduced graphene oxide favorable for nonprecious metal oxygen-reduction catalysts?

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Abstract

Reduced graphene oxide (rGO), as a newly emerged carbon material, has attracted great attention concerning its applications for electrocatalysts. Presently, there are mixed opinions regarding the advantages to using rGO as a support for preparing nonprecious metal catalysts for the oxygen reduction reaction (ORR). The primary goal of this work is to determine whether rGO would be favorable for nonprecious metal catalysis of oxygen reduction or not. In the case of Fe-free catalysts, when polyaniline (PANI) was used as nitrogen/carbon precursor, the PANI-rGO catalyst is superior to the PANI-Ketjenblack (KJ) carbon black catalyst in terms of ORR activity and H2O2 yield. When comparing the ORR activity of PANI-Fe-rGO to the traditional PANI-Fe-KJ, in more challenging acidic electrolyte, PANI-Fe-rGO performed no better than PANI-Fe-KJ. However, rGO does indeed enhance stability of the FeNxC catalyst in acidic media. In addition, in an alkaline electrolyte, ORR activity was significantly improved when using rGO in comparison to the KJ-supported FeNxC catalysts. Based on detailed comparisons of structures, morphologies, and reaction kinetics, the traditional KJ support with dominant microporous is able to accommodate more FeNxC moieties that are crucial for the ORR in acid. Oppositely, the richness of nitrogen-doped graphene edge sites provided by rGO facilitates the ORR in the alkaline electrolyte.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs), one of the most promising energy conservation systems today, are featured with the merits of environmental benignity, flexible applications, and high efficiency, when compared to conventional combustion engine systems [1–3]. Platinum and its alloys, supported on high-surface-area carbons, are routinely used as electrocatalysts in PEMFCs, for the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR), due to their high activity and stability [3–6]. However, the prohibitively high price and low abundance of Pt greatly limit the wide-spread commercialization of PEMFCs for transportation and other applications. For PEMFCs to become economically competitive, cost-effective alternatives to Pt-based electrocatalysts are desperately needed [7–9]. This demand has acted as a strong driving force behind a substantial number of studies concerning non-precious-metal-catalysts (NPMC) dispersed on various carbon supports [10–16]. Among the NPMC formulations studied, Fe–N–C catalysts derived from nitrogen-carbon and iron precursors well-dispersed onto high-surface-area carbon supports, are considered the most promising due to their high activity and good stability [5,17–19]. Carbon supports play an important role in governing catalyst performance, especially for Fe–N–C catalysts [20]. The catalyst activity and durability of various carbon materials, including high-surface-area carbon blacks (e.g. Ketjenblack, Vulcan XC-72, and Blackpearl) and highly graphitized carbon nanotube (CNTs) have been studied for catalyst development [21,22]. Relative to conventional carbon black supports, stability enhancement was observed with CNT-supported Fe–N–C catalysts [21,23]. Furthermore, recent studies suggest that divacant defective centers on carbon supports may serve as anchors for doped nitrogen atoms and transition metals allowing
for formation of a N–M (M: Fe or Co) coordination [24]. Thus, the number of active centers on Fe–N–C catalysts, which consists of metal centers stabilized by nitrogen-containing ligands, is limited by the total edges or defects, provided by carbon supports [7,25]. With this knowledge it was recognized that graphene oxide (GO) and reduced graphene oxide (rGO) and its derivatives, being edge- and defect-rich, are viable potential supporting materials for NPMCs [26–29].

Since 2009, interest in GO or rGO as a novel graphene-support for electrocatalysts in fuel cell applications has grown [26,30–33]. This includes both Pt-based catalysts and NPMCs [34]. In particular, the rGO with dominant nitrogens doped into carbon planes plays an important role as an active catalyst for the ORR, as evidenced by simple treatments or reduction using nitrogen-containing compounds such as hydrazine or NH3 [26,35–37]. It should be noted that improved catalyst activity for the ORR was usually observed in alkaline media and such highly active GO or rGO-derived catalysts even can be prepared without any detectable metal content [26,38].

On the other hand, the presence of transition metals, especially Fe, has been found indispensable for generating active sites with high intrinsic activity and four-electron selectivity in more challenging acidic environments. In the case of Fe participation, graphitized carbon nanostructures (e.g., onion like carbon, carbon nanotubes, graphene-sheets) derived from nitrogen-carbon precursors are typically dominant, which is likely a critical factor dictating active site generation [5,39,40]. In particular, compared to other carbon nanostructures, the formation of graphene-like morphology in catalysts is more closely associated with the enhancement of the catalyst activity and stability [21,41]. For example, it was found that the graphene-rich TiO2-supported catalyst had higher activity than the graphene-free KJ black-supported catalyst [41]. Furthermore, the graphene-containing catalysts exhibited significant enhancement of performance durability during the fuel cell long-term (up to 500 h) life test, when compared to other catalysts that do not contain such graphene-sheet-like morphologies [21]. Thus, the existence of graphene in catalysts seems to have a promotional role in improving Fe–N–C catalyst performance. This experimental observation provides motivation for us to directly concentrate on the use of high-surface-area graphene (i.e., rGO) as a support for designing and synthesizing advanced NPMCs.

In this work, we prepared a series of NPMCs derived from rGO both with and without the addition of Fe precursors. In addition, various nitrogen precursors were used for catalyst synthesis and their corresponding catalyst activities for the ORR were determined. Of the many studied reduction methods of GO, we prefer to use the microwave oven treatment to prepare rGO. This method removes the oxygen-containing functional groups from GO surfaces and recovers the π-conjugation of carbon structures, leading to a high-surface-area rGO with excellent electrical conductivity increased by a few orders of magnitude [42]. Furthermore, high-temperature treatments during the NPMC synthesis aid in the complete reduction of GO as well. It should be noted that we once used as-prepared GO, instead of rGO, as supports to prepare NPMCs, however, the obtained activity was far below that when used rGO as supports. Hence, we systematically compared the rGO and graphene oxide (Ketjenblack, KJ) based catalysts in the forms of N–C and Fe–N–C in terms of their catalytic activity and durability in both acidic and alkaline media. An important understanding from this work is that even the best performing rGO-derived Fe catalyst is still inferior to the KJ-based Fe catalyst in acidic electrolyte, but exhibits improved stability. It was determined, however, that rGO enhances the ORR activity in alkaline media, relative to the conventional KJ-based catalyst. The possible promotional mechanisms, based on extensive materials characterization, are discussed in detail. Compared to KJ, rGO has less overall surface area due to the lack of micropores, but it is able to provide more edge sites and defects, which are especially favorable for the ORR in alkaline media. In addition, less significant loading (thickness) dependence for the rGO-based catalysts was observed in alkaline media, relative to acid. These findings suggest that optimal active site and catalyst morphologies are different for the ORR in alkaline vs. acid media. The unique morphology resulting from rGO is particularly favorable for the ORR in alkaline media.

2. Experimental details

2.1. Catalyst synthesis

Reduced graphene oxide (rGO) and Ketjenblack EC 300J (KJ-300J) were used as the support in the catalyst synthesis. GO aqueous solution was prepared using the Hummers’ method by using several strong oxidants such as potassium permanganate, sodium nitrate, and sulfuric acid to treat natural graphite powder [43,44]. After filtration, solid GO samples were obtained via filtration of the GO aqueous solution, followed by drying in a vacuum oven. Microwave treatment was then used (30 s) in order for the GO samples to generate high-surface-area rGO powders. Using our previously reported catalyst synthesis procedure [11,45], rGO and KJ-derived PANI-Fe catalysts were then prepared and labeled as PANI-Fe-rGO and PANI-Fe-KJ, respectively. Typically, 2.0 mL aniline was then reacted with the 5.0 g oxidant (ammonium peroxydisulfate (APS), (NH4)2S2O8) and transition metal precursors (10 g FeCl3) in 2.0 M HCl solution. The suspension was kept below 10 ºC for 5 h, then 0.4 g carbon supports were added. After constant mixing for 48 h, the suspension consisting of carbon, PANI, and iron species was freeze-dried. Subsequent heat treatments were performed at an optimal temperature of 900–1000 ºC in an inert atmosphere of nitrogen gas for one hour. The heat-treated sample was acid-leached in 0.5 M H2SO4 at 80 ºC for 8 h to remove unstable and inactive species from the catalyst, and then thoroughly washed in de-ionized water. In the final step, the catalyst was heat-treated again at 900 ºC for three hours to remove oxidized/damaged carbon layers from the catalysts with obvious enhancement of activity. The “Fe-free” samples were prepared under identical conditions in the absence of metal precursors. They were labeled as PANI-rGO or PANI-KJ. In order to universally study the feasibility of rGO as a support in NPMC synthesis, three nitrogen-carbon precursors including PANI, ethylene diamine (EDA), and melamine (Me) were used to prepare the rGO-supported Fe catalysts. These were labeled as PANI-Fe-rGO, EAD-Fe-rGO, and Me-Fe-rGO, respectively.

2.2. RDE/RRDE tests

Rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) tests were performed at room temperature using a CHI Electrochemical Station (Model 760e) in a conventional three-electrode cell at a rotating disk speed of 900 rpm. Unless otherwise stated, the catalyst loading on the RDE was controlled at 0.6 mg cm–2. A graphite-rod was used as the counter electrode. Hg/HgSO4 (0.5 M H2SO4) and an Ag/AgCl (3 M NaCl) were used as the reference electrodes for 0.5 M H2SO4 and 0.1 M NaOH solutions, respectively. ORR steady-state polarization plots with a potential step of 0.03 V and a period of 30 s, corrected to background capacitance current, were recorded in O2-saturated electrolytes.

The ring potential, for the RRDE testing, was set to 11 V. Before performing the experiments the Pt ring was activated by potential cycling, for 10 min, in 0.5 M H2SO4, from 0.0 V to 1.4 V, at a scan rate of 50 mV s–1. Four-electron selectivity of catalysts was evaluated...
based on H₂O₂ yields calculated from the equation [46].

2.3. Physical characterization

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra spectrometer using a Mg Kα source operating at 150 W, monochromatic Al Kα source operating at 300 W, and charge compensation using low energy electrons. The base pressure was about 2 × 10⁻¹⁰ torr, and operating pressure was around 2 × 10⁻⁹ torr. Survey and high-resolution spectra were acquired at pass energies of 80 eV and 20 eV respectively. Sample morphology was characterized by scanning electron microscopy (SEM) on a Hitachi S-5400 instrument. High-resolution transmission electron microscopy (HR-TEM) images were acquired using a Hitachi HF3300 TEM operated at 300 kV.

The surface areas of the catalysts were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2010 instrument. Each sample was degassed by heating at 150 °C under vacuum prior to measuring the surface area.

3. Results and discussion

3.1. rGO supported Fe-free N–C catalysts

Using microwave oven treatment, the oxygenated functional groups on GO can be effectively removed. In our previous study, after reduction, well-defined sheet-like morphology was observed and electrical conductivity was raised up to four orders of magnitude for rGO [42]. In this work, we systematically studied the synthesis and eletrocatalytic performance of both the Fe-free N–C and Fe–N–C catalysts using the well-defined rGO supports. In the synthesis of Fe-free N–C catalysts, the heating temperature plays an important role in prompting electrocatalytic activity for the ORR. RRDE measurements were performed in aqueous H₂SO₄ (0.5 M) at room temperature to study the effect of temperature on ORR activity and four electron selectivity of these N–C catalysts from rGO and KJ supports. Herein, the activity and selectivity of the Fe-free PANI-rGO catalysts were measured in 0.5 M H₂SO₄ as a function of reaction temperature, ranging from 800 to 1100 °C. As shown in Fig. 1, the catalytic activity of PANI-rGO increases when raising the reaction temperature up to 1000 °C (black) and then drops for 1100 °C (blue). The best activity was measured with a 1000 °C-treated sample, evidenced by the highest ORR onset potential (~0.80 V) and half-wave potential E₁/₂ (~0.58 V) in the RDE polarization plots. In addition, the sample synthesized at 1000 °C (black curve) gives the lowest H₂O₂ yield. The best performing PANI-GO is superior to the well-studied ketjenblack (KJ)-derived catalysts (PANI-KJ) in terms of improved E₁/₂ (Fig. 1c) and H₂O₂ yield (Fig. 1d), in more challenging acidic electrolyte (0.5 M H₂SO₄). It should be noted that, unlike the PANI-GO sample, PANI-KJ shows no mass-transfer controlled potential region. XPS analysis doesn’t detect any metals especially Mn from the as-prepared GO and heat treated PANI-rGO samples (Fig. 51). However, there is still no concrete evidence that GO-derived catalysts are truly “metal-free”, considering the involvement of KMnO₄ in preparation of GO when using Hummers’ methods. Thus, the observed promotional role of rGO in Fe-free PANI-rGO samples may be due to possible contamination of Mn [47] or the unique defect/edge-rich morphologies of rGO. Utilization of real metal-free GO as the support to prepare samples is required to verify the possible benefit from rGO itself. However, the challenge for synthesis of GO via a “metal-free” approach, such as solvent exfoliation, is hard to scale up for catalyst applications at this point [48]. In addition, the possible existence of Mn in GO will not affect our research, because, instead of “metal-free”, we specially focus on the most promising Fe-based catalysts prepared from rGO, which is described below.

Doped nitrogen is believed to be important for ORR activity, therefore XPS analysis was carried out to study nitrogen doping position and content in these PANI-rGO samples. The results of this analysis were used to correlate measured electrocatalytic performance with structural and chemical properties of catalyst samples. At first, the best performing PANI-rGO and PANI-KJ samples were compared in terms of their elemental qualification (Fig. 2a). There is no any detectable metals in these Fe-free samples, suggesting possible metal content is below the detection level. As shown in Fig. 2b, N 1s XPS spectra indicate that two dominant nitrogen atoms, graphitic and pyridinic nitrogen, were doped into the carbon planes. Graphitic nitrogen is doped inside carbon planes with binding energy around 401 eV, while pyridinic nitrogen is located at the edge of the graphene sheets showing a binding energy at 398.6 eV [49,50]. When the heating temperature was raised from 800 to 1100 °C, the nitrogen doping structure of PANI-rGO changed significantly. In particular, ratios of graphitic to pyridinic nitrogen increase from 1.7 to 2.6 and the total nitrogen content decreases from 7.5 to 4.5% (Table 1). These results suggest that the ratio of graphitic to pyridinic nitrogen, rather than the total nitrogen content, governs electrocatalytic activity for the ORR. It has been suggested that pyrolysis, such as solvent exfoliation, is hard to scale up for catalyst samples. However, graphitic nitrogen sites are also important for the ORR in modifying electronic structures of the carbon planes, making them favorable for O₂ adsorption and subsequent electron transfer [39]. DFT modeling further indicated that adsorption of intermediates such as *OO and *OOH on graphitic sites is much stronger than at the edge sites [51,52]. It was believed that graphitic N doping leads to positive shifts of onset potentials for the ORR when compared to nitrogen-free graphene. This is in good agreement with the ORR activity measured with these PANI-rGO samples. When the heating temperature is increased from 800 to 1000 °C, greater positive onset potentials were measured in the samples containing higher ratios of graphitic nitrogen. In addition, the PANI-rGO sample with higher graphitic N, presented a greater positive onset potential compared to the PANI-KJ sample. Meanwhile, the nearly identical C 1s XPS spectra suggest that the degree of graphitization of carbon structures is independent of the heating temperature above 800 °C (Fig. 2c). Therefore, the effect of changes of electrical conductivity on catalyst activity should be negligible. Thus, the reduced ORR activity measured with 1100 °C treated sample is likely due to two reasons. Firstly, the significantly decreased surface area was observed with the samples treated at higher temperatures (>1000 °C), which is partially responsible for the low ORR activity. Secondly, decreases of total nitrogen content and pyridinic N would compromise the overall ORR activity, given the fact that doped nitrogen atoms are considered as active sites. Therefore, a balance among nitrogen doping position and total content along with resulting morphology (e.g., surface areas and porosity) eventually requires an optimal heating temperature with maximum activity.

High-resolution transmission electron microscopy (TEM) images of as-prepared rGO, Fe-free PANI-rGO, and PANI-KJ samples were compared in Fig. 3. Compared to as-received sheet-like structures (Fig. 3a and b), the structure in PANI-rGO exhibit abundant and, apparently, exposed edges (Fig. 3c and d) probably due to nitron doping. Nitrogen, as a heteroatom relative to carbon, leads to geometrical changes of carbon planes by disordering the carbon atom arrangement and creating edge site defects. According to our previous Raman analysis [45,53], compared to undoped carbon materials (e.g., Ketjenblack or nanotubes), an increased full-width-half-maximum (FWHM) of the D-band was observed with nitrogen-doped carbon. In addition, the presence of heteroatoms within the graphene planes reflected by a peak in Raman spectra
around 1510 cm\(^{-1}\) becomes dominant with an increase of nitrogen doping content. This is consistent with the results of the XPS analysis concerning nitrogen doping, i.e., more nitrogen doping, more disordered structures in carbon planes. In PANI-KJ samples, obvious KJ nanoparticles were surrounded by amorphous carbon derived from PANI (Fig. 3e and f). The dominant edge planes observed with the rGO-derived catalysts are the most distinct feature when compared to the PANI-KJ sample. This unique morphology may provide more appropriate locations for \(\text{O}_2\) and intermediate adsorption and subsequent reduction, leading to significantly reduced \(\text{H}_2\text{O}_2\) yields.

3.2. rGO supported Fe–N–C catalysts

According to elemental analysis by using XPS, there is no detectable Mn in the GO samples that were employed in this work. Although we could not absolutely exclude the existence of Mn in the GO, the possible effect of Mn on overall ORR activity of Fe–N–rGO catalysts can be considered negligible due to the profound role of Fe in enhancing activity. To study the universal feasibility of using rGO for various NPMCs, ORR activity of the rGO-derived Fe–N–C catalyst was studied to be a function of types of nitrogen-carbon precursors including EDA, PANI, and melamine. Significant increases in activity for PANI-Fe-rGO and Me–Fe-rGO were evidenced (Fig. 4) in 0.5 M \(\text{H}_2\text{SO}_4\) electrolyte, in relation to an EDA-Fe-rGO catalyst. This can be seen by the greater positive onset and half-wave potentials. In particular, the significant shifts of onset potentials suggest the nature of active sites in these aromatic nitrogen-carbon precursor-derived Fe–N–C catalysts, such as PANI and Me, is not likely the same as that in amine (e.g., EDA)-derived Fe-based catalysts. This is in agreement with our previous studies that PANI is a more effective nitrogen precursor than EDA [54]. Our speculation is that the possible Fe-N\(_x\) moieties, with improved intrinsic ORR activity, are more favorably incorporated into the carbon planes during the heat treatments of PANI and Me, when compared to EDA. Compared to acidic electrolyte, although significant enhancement of ORR activity for the EDA-Fe-rGO catalyst was obtained in 0.1 M \(\text{NaOH}\) electrolyte, its activity was still much lower than those of PANI-Fe-rGO and Me–Fe-rGO catalysts. As with the acidic media, the PANI-Fe-rGO catalyst exhibits higher ORR activity relative to the Me–Fe-rGO catalyst, showing an onset potential of 1.05 V and an \(E_{1/2}\) of 0.89 V. The studied various Fe–N–C catalysts based on rGO and traditional KJ supports were carefully compared using their electrochemical parameters including onset potential, half-wave potential, limiting current density, and peroxide yields. The comparison was summarized in Table S1. Thus, to determine the potential advantage of using rGO to prepare Fe–N–C catalysts, we still focus on the best performing PANI system.

During the synthesis of PANI-Fe-rGO catalysts, the influence of heating temperature for nitrogen doping was also studied. Similar to Fe-free PANI-rGO systems, with an increase in heating temperature for nitrogen doping, more nitrogen doping, more disordered structures in carbon planes. In PANI-KJ samples, obvious KJ nanoparticles were surrounded by amorphous carbon derived from PANI (Fig. 3e and f). The dominant edge planes observed with the rGO-derived catalysts are the most distinct feature when compared to the PANI-KJ sample. This unique morphology may provide more appropriate locations for \(\text{O}_2\) and intermediate adsorption and subsequent reduction, leading to significantly reduced \(\text{H}_2\text{O}_2\) yields.

![Image](https://example.com/image.png)
for the PANI-Fe-KJ catalyst [45], which doesn’t happen for the PANI-Fe-rGO catalyst. Thus, rGO is superior to KJ in terms of its thermal stability, capable of sustaining high surface areas at the elevated temperature during the catalyst synthesis.

To study the possible promotional role of rGO in Fe–N–C catalysts in terms of ORR activity in both acidic and alkaline media, the best performing PANI-Fe-rGO catalyst was compared with well-studied PANI-Fe-KJ catalysts, and other control samples (e.g., rGO and PANI-rGO) (Fig. 5). In acidic electrolyte, ORR activity of rGO was very poor, despite of its excellent electrical conductivity. However, integration of rGO and PANI, followed by heat treatment, significantly improved ORR activity. Furthermore, addition of Fe into the PANI-rGO resulted in significant performance enhancement, but the half-wave potential of PANI-Fe-rGO catalyst is still inferior to the well-studied PANI-Fe-KJ (0.78 vs 0.80 V) (Fig. 5a). Regarding the \( \text{H}_2\text{O}_2 \) yield for these Fe catalysts, as shown in Fig. 5b, both PANI-Fe-KJ and PANI-Fe-rGO catalysts achieved high selectivity of 4-electron reduction with negligible \( \text{H}_2\text{O}_2 \) yield (less than 1%). Theoretically, electron transfer number during the ORR can be determined by calculating the slopes of the Koutecky–Levich plots. Alternatively, this also can be calculated by directly measuring \( \text{H}_2\text{O}_2 \) yield. Here, the electron transfer number is 3.98 for both catalysts in the whole potential region, indicating a direct 4-electron reduction mechanism. Therefore, there is no additional benefit in gaining ORR activity by using rGO in acidic electrolyte. However, cycling tests on PANI-Fe-rGO were performed from 0.6 to 1.0 V in \( \text{O}_2 \) saturated 0.5 M H\( _2\text{SO}_4 \) solution (Fig. 5). Enhancement of PANI-Fe-rGO cycling stability was evident from these tests. In our previous study, PANI-Fe-KJ was not stable during the identical cycling tests, showing 80 mV loss in \( E_{1/2} \) after 5000 cycles [25]. However, only a 25 mV loss, of \( E_{1/2} \), was observed with the PANI-N-rGO catalyst after 5000 potential cycles. Therefore, relative to conventional KJ, utilization of rGO is able to improve stability of Fe–N–C in more challenging acidic electrolytes.

On the other hand, in alkaline media, the PANI-Fe-rGO catalyst indeed exhibits enhanced ORR activity in terms of increased half-

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**Table 1**

Elemental qualifications of iron-free PANI-rGO and PANI-KJ catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>N (at%)</th>
<th>C (at%)</th>
<th>O (at%)</th>
<th>S (at%)</th>
<th>Graphitic/pyridinic N ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI-rGO-800 °C</td>
<td>7.52</td>
<td>87.64</td>
<td>4.31</td>
<td>0.53</td>
<td>1.7</td>
</tr>
<tr>
<td>PANI-rGO-900 °C</td>
<td>6.41</td>
<td>92.45</td>
<td>0.92</td>
<td>0.22</td>
<td>1.8</td>
</tr>
<tr>
<td>PANI-rGO-1000 °C</td>
<td>5.70</td>
<td>92.82</td>
<td>1.13</td>
<td>0.35</td>
<td>2.2</td>
</tr>
<tr>
<td>PANI-rGO-1100 °C</td>
<td>4.45</td>
<td>94.11</td>
<td>1.19</td>
<td>0.25</td>
<td>2.6</td>
</tr>
<tr>
<td>PANI-KJ-900 °C</td>
<td>6.40</td>
<td>92.18</td>
<td>1.16</td>
<td>0.26</td>
<td>1.8</td>
</tr>
</tbody>
</table>
wave potential (0.89 vs 0.87 V) determined from measured polarization plots (Fig. 5b), relative to the conventional PANI-Fe-KJ catalyst. The improved behavior of the rGO supported Fe catalyst in NaOH electrolyte compared with in H2SO4 suggests that the reaction mechanisms and the optimal active sites for ORR in both electrolytes are different. Meanwhile, the relatively poor performance of Fe-free PANI-GO and rGO attest to the importance of nitrogen doping and transition metals in inducing high ORR activity observed in the Fe–N–C catalysts in both electrolytes.

Furthermore, according to the Koutechky–Levich equation, the kinetic current density can be calculated from the steady-state polarization and used to prepare Tafel plots for PANI-rGO, PANI-Fe-rGO, and PANI-Fe-KJ catalysts in both acidic and alkaline electrolytes (Fig. 6). In the case of 0.5 M H2SO4 electrolyte, the Tafel slope of Fe-free PANI-rGO (−146 mV/deg) is notably different than that of PANI-Fe-rGO (−94 mV/dec). This suggests that the addition of Fe greatly affects the overall reaction mechanism. Generally, oxygen reduction in aqueous electrolyte involves multiple steps due to many possible intermediate species. In theory, the rate-determining step (RDS) associated with the first-electron transfer yields a Tafel slope of −118 mV/dec. Oppositely, a Tafel slope of −59 mV/dec is attributed to a migration of adsorbed oxygen intermediates on catalysts, resulting from a coverage-dependent activation barrier for the ORR [14]. Thus, the Tafel slope of −94 mV/dec is between −118 and −59 mV/dec, suggesting that oxygen reduction on PANI-Fe-rGO catalysts is controlled simultaneously by charge transfer and intermediate migration. However, a high Tafel slope value determined with the Fe-free PANI-rGO indicates that O2 adsorption onto catalytic sites becomes the RDS [33]. Interestingly, the difference of Tafel slopes between PANI-rGO
(−82 mV/dec) and PANI-Fe-rGO (−86 mV/dec) become more insignificant in alkaline media, indicative of similar reaction mechanisms for the ORR on both types of catalysts. Therefore, while Fe-free PANI-rGO and PANI-Fe-rGO catalysts behave differently in acid, they may follow the similar reaction mechanism in alkaline media.

We also studied thickness dependence (catalyst loading) on ORR activity of the studied PANI-Fe-rGO catalyst in both acidic and alkaline electrolytes. The results are shown in Fig. 7. More dominant loading dependence (thickness) was observed in acidic electrolyte, when compared to the alkaline electrolyte. This suggests that the active sites for the ORR in acid and base are likely different. Furthermore, the catalysts seem to contain different types of active sites. The number of active sites for alkaline media is larger than
that for acid, showing less dependence of the ORR activity on loading or thickness in alkaline media. In other words, the rGO-based catalysts are more suitable for the ORR in alkaline, relative to acid.

To gain insight concerning the different performance of rGO- and KJ-derived Fe catalysts, in acidic and alkaline electrolytes, we used TEM images to compare the nanostructures of these two catalysts (Fig. 8). Compared to the spherical hollow nanoshell morphology observed in the PANI-Fe-KJ catalyst, a defect- and edge-rich rGO morphology is dominant in the PANI-Fe-rGO catalyst. However, conventional Ketjenblack has a greater surface area relative to rGO, leading to a higher surface area for PANI-Fe-KJ (845 m²/g) than that of PANI-Fe-rGO (610 m²/g). It should be noted that there are two types of carbon materials in these Fe-based catalysts. One is directly from supports such as KJ carbon black and rGO. The other is derived from PANI via graphitization process. These two types of carbon usually mixed together. Actually, the associated catalyst morphology of Fe–N–C catalysts is more greatly dependent on the use of supports.

As shown in the SEM images (Fig. 9), in the absence of supports, it is likely that high-temperature treatment during the synthesis would yield less porous morphology for the Fe-based catalysts. Relative to the support-free Fe catalyst, the high-surface area KJ facilitates to obtain more uniform and porous morphology for the Fe–N–C catalyst, exhibiting markedly enhanced activity for the ORR as evidenced by both RDE and fuel cell tests (Fig. S6).
Meanwhile, the rGO-derived catalyst presents totally different morphology, but is highly porous with dominant rGO sheet-like structures. Therefore, addition of proper support is crucial for preventing serious agglomeration of nitrogen-carbon precursors such as PANI during the high-temperature treatment. In addition, close integration of Fe and N species adsorbed into porous supports appears imperative for subsequent thermal treatment and the generation of active sites related to FeNₓ moieties [55]. Higher activity in acidic electrolyte measured with the PANI-Fe-KJ catalyst suggests the highly porous carbon black support is able to accommodate more active FeNₓ moieties for the ORR [56].

Furthermore, doped nitrogen functionalities as function of supports (KJ vs rGO) were also studied using XPS (Fig. 10). These results show higher nitrogen content and less graphitic nitrogen are in PANI-Fe-rGO relative to PANI-Fe-KJ. This may explain the relatively lower activity in acidic electrolyte for the PANI-Fe-rGO catalyst, which is a result of the lower surface area and less graphitic nitrogen doping. Oppositely, an increase in pyridinic N of the PANI-Fe-rGO catalyst may be one of factors that lead to enhanced ORR activity in alkaline media when compared to the PANI-Fe-KJ catalyst. Meanwhile, as shown in Table S1, the Fe content determined by using XPS for the best performing PANI-Fe-rGO sample is around 0.60 at%. This value is comparable to the Fe content found in PANI-Fe-KJ catalyst (0.48 at%) [11]. Due to the very low Fe content in both catalysts, the Fe 2p XPS spectra are very noisy, incapable of providing informative structural and chemical properties. The iron precursor, FeCl₃ was used during the synthesis with a nominal content of 10 wt%. The fact that final catalysts have very low Fe content is due to the formation of FeS that acts as an effective sacrificial pore forming agent and can be removed during subsequent acid leaching treatment. The residual Fe in both rGO and KJ-based catalysts could be either in the form of FeS that was fully encapsulated within carbon agglomerates [57], or in the form of active FeNₓ moieties [58]. The discussion about the Fe-associated active sites in the field is still ongoing. It is not yet clear if Fe acts directly as an active site for O₂ adsorption or just affects surrounding C or N sites.

4. Conclusions

In summary, reduced graphene oxide (rGO) is a good support for incorporating nitrogen and transition metal species during non-precious metal catalyst synthesis, using a high-temperature approach. Using our well-studied polyaniline (PANI) system, both iron-free PANI-rGO and PANI-Fe-rGO catalysts were prepared to study the possible promotional role of rGO in terms of activity and durability enhancement for the ORR. Higher ORR activity and significantly reduced H₂O₂ were measured with Fe-free PANI-rGO compared to PANI-KJ. However, there is no concrete evidence that GO-derived catalysts are “metal-free”, considering the involvement of KMnO₄ in preparation of GO when using Hummers’ methods. In the Fe-based catalysts, due to the overwhelming role of Fe in enhancing ORR activity, the contamination of Mn could be negligible. Although there is no additional benefit in using rGO for the ORR in acidic electrolyte, relative to KJ carbon black supports, the PANI-Fe-rGO catalyst demonstrated enhancement of stability relative to the conventional PANI-Fe-KJ catalyst. More importantly, in alkaline media, rGO is able to yield improved ORR activity for the
PANI-Fe-rGO catalyst when compared to PANI-Fe-KJ. The edge-rich morphology and high ratio of pyridinic nitrogen in the PANI-Fe-GO may contribute to the enhanced ORR activity in alkaline media.

We believe that the ORR activity of rGO can still be improved by optimizing reduction procedures of GO and morphology of rGO (e.g., surface areas, porosity, and nanostructures). Reduction procedures and morphology are considered critical aspects of templating nitrogen and transition metal species during heat treatments. Extensive electrochemical and physical characterization were employed in this work to explain why rGO catalysts behave differently in acidic and alkaline media. It is very likely that FeNx is more critical for the ORR in acidic media, and the nitrogen-doped graphene edge sites are more relevant in the alkaline media.

Advanced physical characterizations and theoretical calculations could further provide insights as to the optimal active site structure and catalyst morphology for the ORR in each electrolyte.

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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.2016.02.054.

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