PdFeCo Supported on N-rGO as a Bifunctional Catalyst for Methanol Oxidation and High Stability Oxygen Reduction Reaction

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Abstract

The oxygen reduction reaction (ORR) is one of the most important reactions in fuel cell system. A high performance cathode catalyst may participate to reduce a high overpotential during ORR. In this study, we have synthesized nitrogen doped reduced graphene oxide (N-rGO) supported ternary PdFeCo nanoparticle by three methods. A hydrothermal method to synthesize N-rGO, an emulsion method to synthesize PdFeCo nanoparticle, and a rotative evaporation to synthesize PdFeCo/N-rGO composite. A bifunctional PdFeCo/N-rGO exhibited excellent electrocatalytic activity towards both methanol oxidation and stability in ORR. During methanol oxidation reaction, PdFeCo/N-rGO exhibited stronger methanol tolerance than Pt/C. In stability ORR, PdFeCo/N-rGO exhibited 2.85 times greater than Pt/C in ORR stability. The high performance of PdFeCo/N-rGO was attributed by strong bonding of structure. A strong bonding of transition metals in Pd based catalyst can serve as methanol tolerance and stability during ORR activity.

Keywords: PdFeCo/N-rGO; methanol oxidation; oxygen reduction reaction

1. INTRODUCTION

Alkaline electrode membrane fuel cell (AEMFC) is an electrochemical device that can convert chemical energy of H\textsubscript{2} directly through a membrane into electrical current. AEMFC offer some advantages over other fuel cells, they can enhance oxygen reduction catalysis, extend range of cell and stack materials stable in environment, a wider choice of fuels in addition to pure hydrogen [1].

One of the primary interested for electrocatalyst in fuel cell is a high performance cathode catalyst to reduce a high overpotential during oxygen reduction reaction (ORR). Based on fuel cell operation, carbon-supported platinum (Pt/C) catalyst has well known as the best fuel cell catalyst due to high ORR performance. In another case, platinum are limited reserve, high cost, and instability during operation in fuel cell [2]. Therefore, some strategies have been developed such as some non-Pt based catalysts.

Palladium (Pd) based catalyst has exhibited higher activity due to decrease anion poisoning effect in alkaline solution [3]. Transition metals serve as a promising alternative due to their intrinsic activity and stability in oxidative electrochemical environments. Ferrous (Fe) and Cobalt (Co) are transition metals have been explored as bifunctional catalyst that capable increasing ORR activity and well known high dispersion [4]. Graphene has been studied as alternative support to enhance nanoparticle catalyst activity and durability due to high surface area, high conductivity, high stability, and strong
interaction [5-6]. Doping graphene with heteroatoms such as nitrogen also has promised significantly enhance ORR performance due to facilitate charge transfer between electrode-electrolyte interaction [7].

Although many researchers have observed Fe and Co as Pd based alloyed on carbon matrix, but none of them have reported about ternary PdFeCo supported on nitrogen doped reduced graphene oxide (N-rGO). To the best of our knowledge, this is a ternary PdFeCo catalyst supported on N-rGO as a bifunctional methanol oxidation and high stability oxygen reduction reaction (ORR) catalyst.

2. METHODS
2.1 Materials
Palladium (II) acetylacetonate with a purity of 35%, Iron (III) acetylacetonate with a purity of 99+%, and Cobalt (II) acetylacetonate with a purity of 99% as metal precursors of catalyst. Benzyl alcohol was used as a reducing agent in presence of oleic acid and oleylamine. Graphene oxide (GO) and urea with a purity 99.5% as material precursors of carbon matrix.

2.2 Synthesis of Nitrogen doped Reduced Graphene Oxide
Hydrothermal method was used to synthesize nitrogen doped reduced graphene oxide (N-rGO) in Figure 1. 50 mg of GO was dissolved in 35 ml of deionized (DI) water and 15,000 mg of urea was subsequently added. To homogeneous dispersion, the suspension was ultrasonicated for 2 hours. Then the suspension was poured into 100 mL Teflon-lined autoclave and heated at 180°C for 30 minutes in microwave hydrothermal to complete reduction reaction. Finally, the product was filtered and washed with DI water for several times to remove some impurities, then freeze dried for overnight.

![Figure 1. Schematic of synthesize nitrogen doped reduced graphene oxide](image)

2.3 Synthesis of PdFeCo Nanoparticles
An emulsion method was applied to synthesize PdFeCo nanoparticles in Figure 2. The amount of molar ratio nanoparticles, metal precursors were maintained at 3:1:1. The amount ratio of metal precursors were dropped into benzyl alcohol as reducing agent in presence of oleic acid and oleylamine. The suspension was purged in nitrogen and heated at 150°C for 30 minutes to reduce metal precursors, then continue heated at 200°C for 40 minutes to form alloy. After cooling down to room temperature, the black suspension was washed by toluene one time and ethanol three times. Finally, the product was centrifuged to remove solvent, then freeze dried overnight.
2.4 Synthesis of PdFeCo/N-rGO

The amount 40%wt of PdFeCo nanoparticles and 60%wt of N-rGO were dropped into 10 mL N-hexane solution in Figure 3. The suspension was sonicated for 10 minutes and stirred for 2 hours to homogeneous dispersion. Then the suspension was evaporated by rotary evaporator machine at 40°C and 90 hPa.

3. RESULT AND DISCUSSION

3.1 X-ray Photoelectron Microscopy

X-ray photoelectron microscopy (XPS) is used to investigate some reduction level of PdFeCo nanoparticles. XPS spectra of catalyst elements are shown by Figure 4. Two characteristic peaks with binding energies at 335.2 and 341.2 eV corresponding to Pd⁰ 3d⁵/₂ and Pd⁰ 3d⁷/₂, respectively. Compared to standard spectra of metal Pd⁰, Pd binding energies increase greatly (from 335 eV to 335.2 eV and 340 eV to 341.2 eV) due to presence transition metals on N-rGO matrix [8]. Furthermore, two characteristic peaks with binding energies at 336.4 and 345.2 eV are attributed Pd⁰ 3d⁵/₂ and Pd⁰ 3d⁷/₂.
respectively. The existence of Pd$^{2+}$ due to some reasons: (a) Pd-N bond formed at Pd/N-rGO interface, (b) a reduction of Pd$^{2+}$ is not completed, and (c) an external metal Pd$^0$ is likely oxidized to Pd$^{2+}$ at ambient conditions [9-11].

Figure 4. The XPS spectra of PdFeCo/N-rGO (a) Pd-3d spectra, (b) Fe-2p spectra, (c) Co-2p spectra, (d) C-1s spectra, and (e) N-1s spectra

The XPS spectra of transition metals are observed in Figure 4 (b and c). Two main peaks observed with binding energies at 711.7 and 723.9 eV (Figure 4b) corresponding to Fe 2p$^3/2$ and Fe 2p$^1/2$, respectively. These peaks increase slightly compared to Fe standard spectra (from 707 eV to 711.7 eV and 720 eV to 723.9 eV), indicating oxidation of Fe due to catalyst is highly sensitive to air so easily oxidized [12]. The dominant Co 2p$^3/2$ and Co 2p$^1/2$ are observed with binding energies at 778.57 and 793.06 eV, respectively (Figure 4c). These peaks also increase slightly compared to Co standard spectra (778 eV to 778.57 eV and 793 eV to 793.06 eV). In addition, two shake-up
satellite (sat.) peaks at 784.7 and 800.28 eV corresponding to Co 2p$_{3/2}$ sat. and Co 2p$_{1/2}$ sat., respectively, indicating a presence of Co$^{2+}$ due to surface oxidation or chemisorption of enviromental oxygen during synthesis [13-14].

The XPS spectra of N-rGO matrix components are shown in Figure 4 (d and e). The C-C/C=C, C=N/C=O, C=O/O=C=O, and C=O formation are observed with binding energies at 284.6, 286.3, 287.97, and 289.3 eV, respectively, indicating C 1s peaks (Figure 4d) [15]. Three types of N 1s peak are pyridinic-N (398.32 eV), pyrrolic-N (399.48 eV), and graphitic-N (400.48 eV) (Figure 4e) [16]. Both of planar pyridinic-N and pyrrolic-N have known as low electrical resistance and high electrocatalytic activity on N-rGO since the nitrogens with planar sp$^2$ hybridization would not interrupt π-π conjugation and avoid an intrinsic barrier impairing a continuos pathway for electron transport [17].

Table 1. The percentages of N-types in PdFeCo/N-rGO

<table>
<thead>
<tr>
<th>Pyridinic-N (%)</th>
<th>Pyrrolic-N (%)</th>
<th>Graphitic-N (%)</th>
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<tbody>
<tr>
<td>23.78%</td>
<td>37.39%</td>
<td>38.83%</td>
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3.2 Methanol Oxidation

The formation of CO$_2$ and carbonate during methanol (MeOH) oxidation could play a problem when Pt/C catalyst applied in liquid alkaline electrolyte. A commercial 40% Pt/C (Figure 5) exhibits a marked change in ORR polarization curve after addition of 0.1 M MeOH, the half-wave potential shifted negatively, indicating both of methanol and oxygen simultaneously reacted at particle surfaces [18]. In another, PdFeCo/N-rGO exhibits higher methanol oxidation potential and leads to lower current density peak value than Pt/C. A narrow shape peak oxidation of PdFeCo/N-rGO which is resulted due to a strong electrolyte of methanol [19].

![Figure 5. Methanol oxidation of PdFeCo/N-rGO and Pt/C in 0.1 M KOH + 0.1 M MeOH solution under O$_2$-saturated](image)

3.3 Stabilization

In fuel cell operation, the long-term stability of catalyst is the most important thing. The stability of PdFeCo/N-rGO catalyst has been compared to commercial 40% Pt/C using LSV scanning in O$_2$-saturated 0.1 M KOH solution (Figure 6). A commercial 40% Pt/C loses significant activity about 14.76% from initial value after 30,000 cycles in kinetic and diffusion-limiting regions (Table 2). This phenomenon would result from Pt
dissolution, redeposition on catalyst surfaces and Pt migration through surfaces [20]. Dissolving Pt$^{2+}$ ions can be redeposited on Pt surfaces, resulting large Pt nanoparticles dispersed, known as Ostwald ripening [21]. In contrast with PdFeCo/N-rGO, it only loses activity about 5.25% from initial value after 30,000 cycles in diffusion-limiting regions, but smooth degradation in kinetic region due to strong bonding of nanoparticles catalysts on carbon sheets [22].

**Table 2. The stability parameters of PdFeCo/N-rGO and Pt/C**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Initial half-wave (mV)</th>
<th>1000 cycles (mV)</th>
<th>2000 cycles (mV)</th>
<th>3000 cycles (mV)</th>
<th>$\Delta E_{1/2}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PdFeCo/N-rGO</td>
<td>799</td>
<td>773</td>
<td>765</td>
<td>757</td>
<td>42</td>
</tr>
<tr>
<td>40% Pt/C</td>
<td>813</td>
<td>707</td>
<td>695</td>
<td>693</td>
<td>120</td>
</tr>
</tbody>
</table>

**Figure 6. The stability performance of (a) PdFeCo/N-rGO and (b) Pt/C in 0.1 M KOH solution under O$_2$-saturated**

4. **CONCLUSION**

A bifunctional PdFeCo/N-rGO exhibited excellent electrocatalytic activity towards both methanol oxidation and stability in oxygen reduction reaction (ORR). During methanol oxidation reaction, PdFeCo/N-rGO exhibited stronger methanol tolerance than Pt/C. In stability ORR, PdFeCo/N-rGO exhibited 2.85 times greater than Pt/C in ORR stability. The high performance of PdFeCo/N-rGO was attributed by strong bonding of structure. A strong bonding of transition metals in Pd based catalyst can serve methanol tolerance and stability during ORR activity.

**REFERENCES**


