Article

Electrocatalytic Performance of Carbon Supported WO_3-Contained Pd-W Nanoalloys for Oxygen Reduction Reaction in Alkaline Media

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Abstract: In this paper, we first report that WO_x contained nanoalloys exhibit stable electrocatalytic performance in alkaline media, though bulk WO_3 are easy to be dissolved in NaOH solutions. Carbon supported oxide-rich Pd-W alloy nanoparticles (PdW/C) with different Pd:W atom ratios were prepared by reduction-oxidation method. Among the catalysts, the oxide-rich $Pd_{0.8}W_{0.2}$/C (Pd/W = 8:2, atom ratio) exhibits the highest catalytic activity for oxygen reduction reaction. The X-ray photoelectron spectroscopy data shows that ~40% of Pd atoms and ~ 60% of the W atoms are in their oxides form. The Pd $3d_{5/2}$ peaks in oxide-rich Pd-W nanoalloys are positive shift compared with that of Pd/C, which indicates the electronic structure of Pd is affected by the strong interaction between Pd and W/WO_3. Compare to Pd/C, the onset potential of oxygen reduction reaction at the oxide-rich $Pd_{0.8}W_{0.2}$/C is positive shifted. The current density (mA·mg Pd^{-1}) at the oxide-rich $Pd_{0.8}W_{0.2}$/C is ~1.6 times of that at Pd/C. The oxide-rich $Pd_{0.8}W_{0.2}$/C also exhibits higher catalytic stability than Pd/C, which demonstrate that it is a prospective candidate for the cathode of fuel cells operated with alkaline electrolyte.

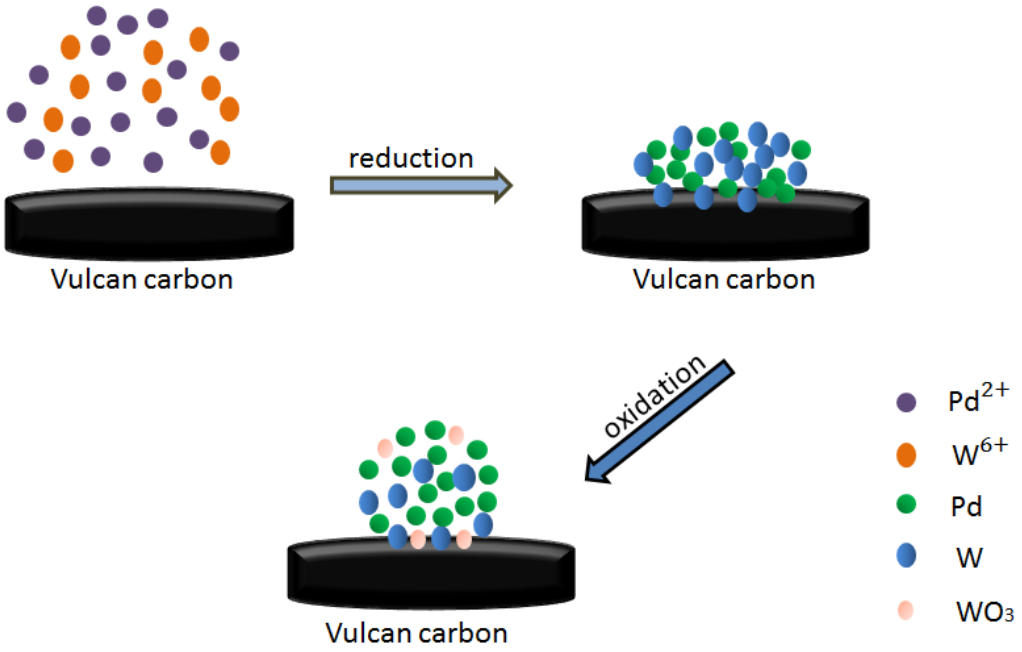
Keywords: WO_3; electrocatalysts; alkaline**;** Pd-W alloy; oxygen reduction reaction; reduction-oxidation method

1. Introduction

The study of oxygen reduction reaction (ORR) has a long history of more than one century since Grove fabricated the earliest hydrogen-oxygen fuel cell with Pt as the catalyst for ORR in 1839. In recent years, the research of ORR are promoted by the increasing demand of clean energy technology like fuel cells. The energy efficiency and battery voltage of the electrochemical cells are obviously limited by the slow kinetics of the ORR[1,2], thus there is a great need of high efficient catalysts for ORR. Various of electrocatalysts for ORR have been developed, include but not limit to Pt-based catalysts[3-5], Pd-based catalysts[6,7], catalysts based on non-precious metals[8,9], catalysts based on carbon nanostructure/nanocomposites[10-13], catalysts based on metal oxides[14,15], catalysts based on metal-organic frameworks[16,17], catalysts based on complexes[18,19], enzyme-based catalysts[20-24], metal carbides[25-28], and so on. Among the catalysts for ORR, Pt-based catalysts are regarded as the most active catalysts[29]. However, the scarcity of platinum limited the large scale application of Pt-based electrocatalysts. As one of the alternative candidates, palladium is about 200 times abundant on the earth than platinum[30]. There have been some reviews about Pd-based electrocatalysts[31-33]The ORR [34]can be

performed under both acid conditions and alkaline conditions in fuel cells. It is reported that the alkaline media is benefit for the kinetics of ORR[35-37]. In alkaline solutions, the oxygen can be reduced through four-electron pathway or two-electron pathway[38,39]. A lot of novel Pd-based electrocatalysts for ORR appears, include but not limit to carbon or metal supported Pd alloys [40-42], nitrogen and sulfur co-doped carbon supported PdNi catalyst (PdNi-NS/C)[43], Pd supported on TiO_2 with oxygen vacancy(Pd/TiO_2-Vo) [44], PdW nanoparticles supported on sulfur-doped graphene(PdW/SG)[45], PdNiCu/PdNiCo supported on nitrogen dope graphene[46], PdSnCo/nitrogen-doped -graphene [47], electrochemically reduced graphene-oxide supported Pd-Mn_2O_3 nanoparticles [48], AuPd@PdAu alloy nanocrystals [49],three-dimensional nitrogen-doped graphene supports for palladium nanoparticles (Pd-N/3D-GNS)[50]，and so on. Most of the latest reports about Pd-based electrocatalysts for ORR in alkaline media mentioned above are supported on graphene that had been specially treated (doping, modifying, and so on). Though carbon black is the mostly used support for noble metal electrocatalysts in fuel cells, Pd-based electrocatalysts supported on carbon black (C) for ORR in alkaline media is rarely reported in the recent two or three years. Besides the boom of novel support materials like doped graphene, one of the possible reasons is the high activity of Pd/C for ORR in alkaline media. It is reported that Pd/C exhibit significantly high activity that is close to Pt/C in alkaline solutions[51,52], so other electrocatalysts for ORR in alkaline media is difficult to exhibit much higher activity than Pd/C. The new reports about carbon-black supported Pd based catalysts for ORR in alkaline media have to face the awkward situation that compared with the ultra high active catalyst Pd/C.

After DFT calculations, Goddard et.al.[53]predict that Pd_3W is a prospective catalyst for ORR , which have been confirmed by our previous work $Pd_{0.7}W_{0.3}$ in acid media[54]. In this work, we attempt to fabricate high performance Pd-W/C systems for ORR in alkaline media. Most of the noble metal electrocatalysts used in fuel cells are in the form of naonoparticles supported on carbon. Since the surface of metal nanoparticles nanoalloy are easy to be oxidized by ambient air, the effect of oxides in the Pd-based catalysts for ORR in alkaline media should be discussed. The interaction of metal and metal oxides in catalysts has attracted research interests for decades[55-58].It is reported recently that metal and metal oxides interactions greatly affect with the catalytic consequence for the electrocatalysis reactions such as oxygen reduction reaction [59]and ethanol oxidation reaction[60,61]. Bulk WO_3 crystal can be dissolved in strong NaOH solutions, which limited its direct application in fuel cells operated in alkaline conditions. At the beginning of this work, we imagine that one of the possible solutions to solve this problem is to separate the W atoms with noble metals such as Pd in the atomic scale before their oxidation. Thus the chemical bonds attached to most of the W atoms are not the W-O-W bonds but Pd-W metallic bonds. The Pd-W bonds is more stable than W-O-W bonds in alkaline solutions. According to Monte Carlo simulation [62,63], alloy clusters at the surface of nano-materials sometimes exhibit higher stability. As mentioned above, we have studied the $Pd_{0.7}W_{0.3}$ catalyst for ORR in acid media[64]. Though some of the W dealloyed from the surface of $Pd_{0.7}W_{0.3}$ alloy during the ORR in acid media, the electrocatalytic performance of $Pd_{0.7}W_{0.3}$ catalyst kept stable. Thus we suppose that even if a part of W/WOx leak out, the catalytic activity of the catalyst will not decay rapidly. In this paper, we fabricate WO_x-contained Pd-W nanoalloys with the reduction-oxidation method (Scheme 1.). The onset potential of ORR at the as prepared oxide-rich $Pd_{0.8}W_{0.2}/C$ (Pd/W=8:2, metal atomic ratio) is close to the Pd/C and Pt/C fabricate with chemical reduction method[65]. The ORR stability and current density ($mA \cdot mg\ Pd^{-1}$) of the oxide-rich $Pd_{0.8}W_{0.2}/C$ is higher than that of Pd/C, which indicates that the oxide-rich $Pd_{0.8}W_{0.2}/C$ is a prospective candidate for the cathode of the fuel cells operated in alkaline conditions.

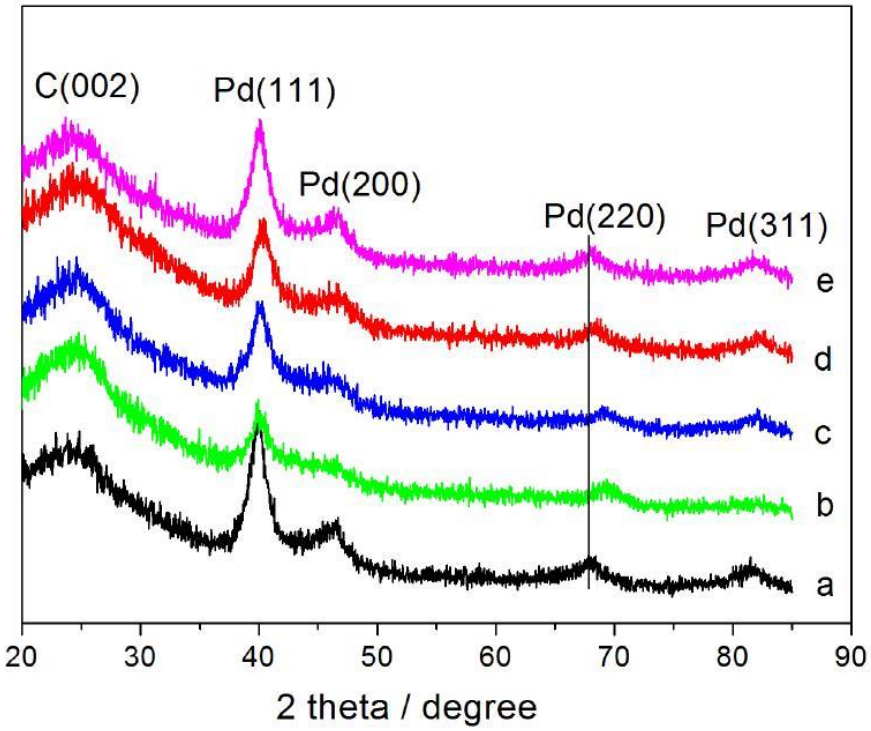


Scheme 1. Schematic illustration of the formation of catalyst. Dimensions are not in scales

2. Results and Discussion

2.1. Characterization of oxide-rich PdW/C catalysts

The X-ray diffraction (XRD) patterns of Pd/C (a), oxide-rich Pd0.6W0.4/C (b), Pd0.7W0.3/C (c), Pd0.8W0.2/C (d), Pd0.9W0.1/C (e) are shown in Figure 1. Five typical diffraction peaks of the catalyst were observed at about 24.8°, 40°, 46°, 68°, 82° in the diffractogram, which correspond to the Vulcan XC-72R carbon (002) crystal face, face centered cubic (FCC) metal Pd (111), (200), (220) and (311) crystal plane diffraction. The XRD patterns do not show any diffraction peaks corresponding to W (fcc) or WO3, this indicates that most of the W atoms do not exist as an individual phase, but entered into the lattice of Pd crystal. The absence of peaks for tungsten also appears in our previous reported $Pd_{0.7}W_{0.3}$ catalyst [64] used in acid conditions. The diffraction angle of crystal plane diffraction peak of the Pd element in all the PdW/C catalysts is higher than that of the corresponding Pd/C catalyst. The size of catalyst metal particles can be estimated with Scherrer's equation[66]. The estimated particle size of Pd/C, $Pd_{0.6}W_{0.4}$/C, $Pd_{0.7}W_{0.3}$/C, $Pd_{0.8}W_{0.2}$/C and $Pd_{0.9}W_{0.1}$/C were 5.6 nm, 4.8 nm, 4.5 nm, 4.3 nm and 5.2 nm. The particle size of the oxide-rich Pd-W/C nanoparticles is smaller than that of Pd/C



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108 **Figure 1.** XRD patterns of Pd/C (a), oxide-rich $Pd_{0.6}W_{0.4}$/C (b), oxide-rich $Pd_{0.7}W_{0.3}$/C (c), oxide
109 rich $Pd_{0.8}W_{0.2}$/C (d), and oxide rich $Pd_{0.9}W_{0.1}$/C (e).

110 The morphology and particle distribution (Figure 2) of Pd/C (a, b) and oxide-rich $Pd_{0.8}W_{0.2}$/C (c,
111 d) have been characterized by transmission electron microscope (TEM). The oxide-rich $Pd_{0.8}W_{0.2}$
112 nanoparticles are more uniformly dispersed on the carbon surface than Pd. The average diameter of
113 Pd nanoparticles is 5.6 nm while the average metal particle diameter of oxide-rich $Pd_{0.8}W_{0.2}$ is 4.3
114 nm. Which are consistent with the XRD results. Figure 3 (a, b, c) showes the HRTEM of oxide-rich
115 $Pd_{0.8}W_{0.2}$/C catalyst. The lattice spacing in Figure 3 (a, b, c) is 0.224 nm, 0.193 nm and 0.263 nm
116 which respectively correspond to the(111), (200) crystal planes of face-centered cubic Pd and (220)
117 plane of WO_3, respectively. The lattice fringes of WO_3 can be found in a few nanoparticles. Which
118 support the existence of WO_x in the $Pd_{0.8}W_{0.2}$/C catalysts. Though their is no diffraction peaks
119 corresponding to W in the XRD patterns mentioned avove, the energy dispertive spectrum (EDS) of
120 the as prepared oxide-rich (Figure 3d) shows the content of W in the Pd-W nanoalloys.

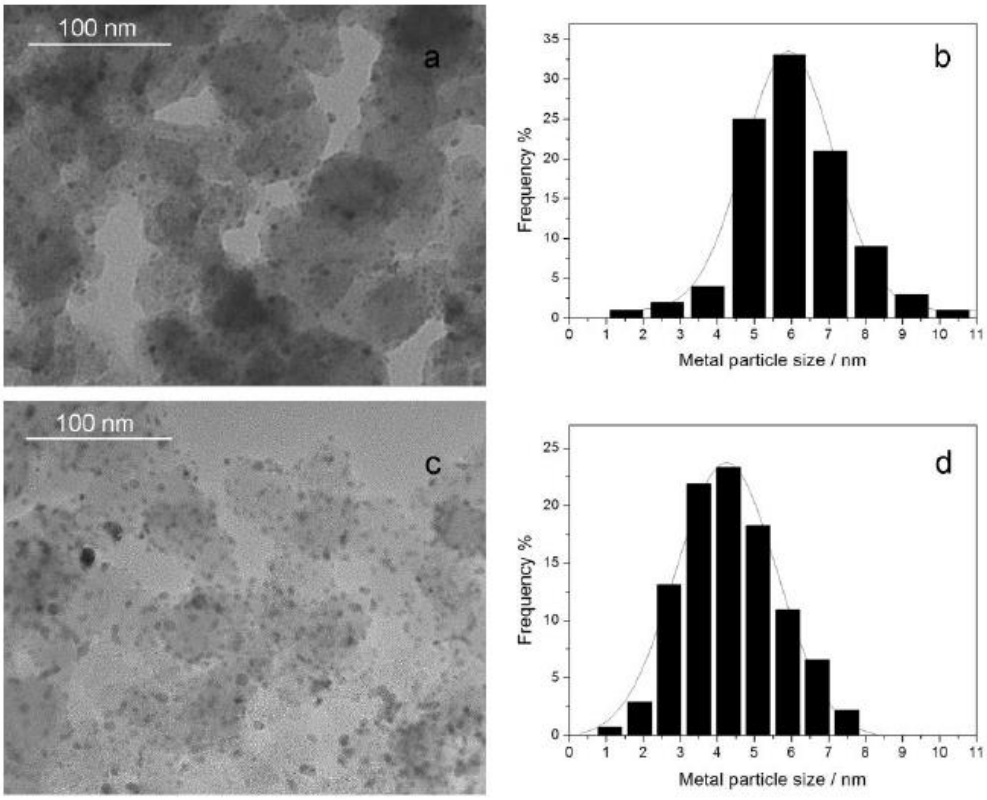


Figure 2. The morphology and particle distribution of Pd/C (a, b) and oxide-rich Pd0.8W0.2/C (c, d) .

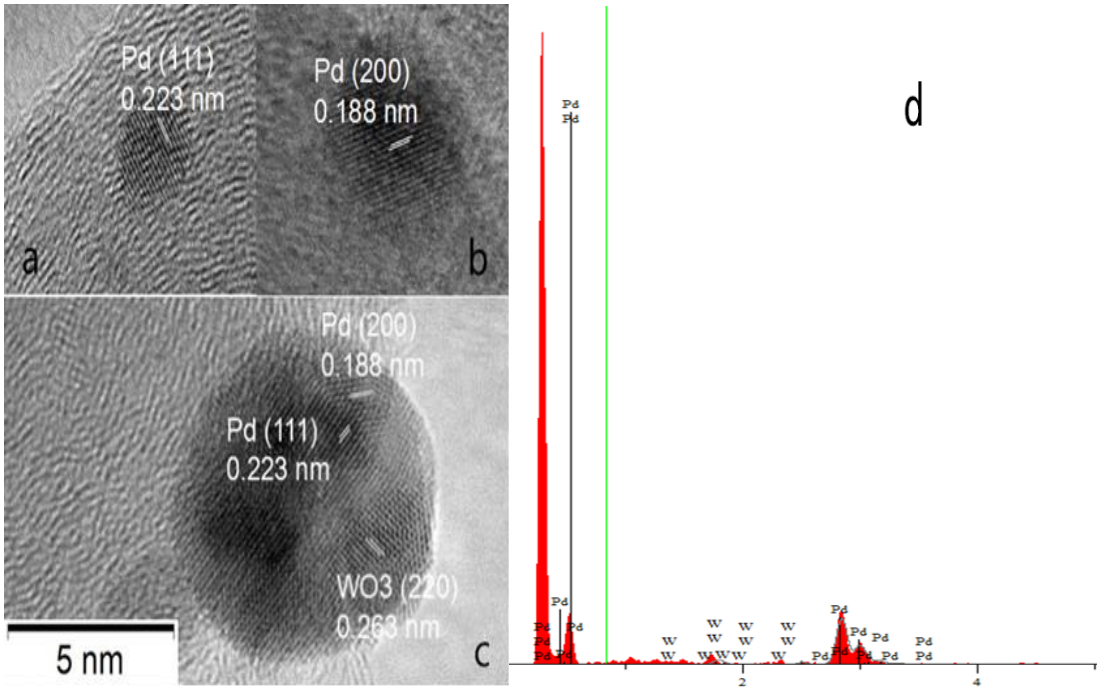


Figure 3. HR-TEM (a, b, c) and EDS (d) spectra of the oxide-rich $Pd_{0.8}W_{0.2}$ / C catalyst

Figures 4 shows the X-ray photoelectron spectroscopy (XPS) spectra of oxide-rich Pd0.6W0.4/C, Pd0.7W0.3/C, Pd0.8W0.2/C, Pd0.9W0.1/C. The XPS spectra of Pd/C has been published in our recent works [67-69].All XPS curves were fitted using the Gaussian-Lorentzian (20%) method after substracting the background with Shirley's method. The compositions obtained by XPS analysis is shown in Table 1. The surface composition ratios of the Pd: W elements in oxide-rich $Pd_{0.6}W_{0.4}/C$, $Pd_{0.7}W_{0.3}/C$, $Pd_{0.8}W_{0.2}/C$ and $Pd_{0.9}W_{0.1}/C$ are $Pd_{0.57}W_{0.43}$ 、 $Pd_{0.70}W_{0.20}$ 、 $Pd_{0.79}W_{0.21}$ 、 $Pd_{0.87}W_{0.23}$, respectively. In Figure 4 (a), the peaks of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ are corresponding to Pd and PdO_y (0<2<y), and the Pd element is present in all the samples as Pd metal and PdO_y. The binding energy of Pd 3d5/2 peak of PdW/C catalysts shift +0.21 eV, +0.28 eV, +0.36 eV, +0.52 eV respectively compared with that of Pd/C (335.6 eV, the solid line).The positive shifts of the Pd 3d binding energy indicate the decrease of Pd 3d electronic cloud densities. Which is due to the formation of high-valency oxides. Figure 4 (b) is the peak of W 4f.

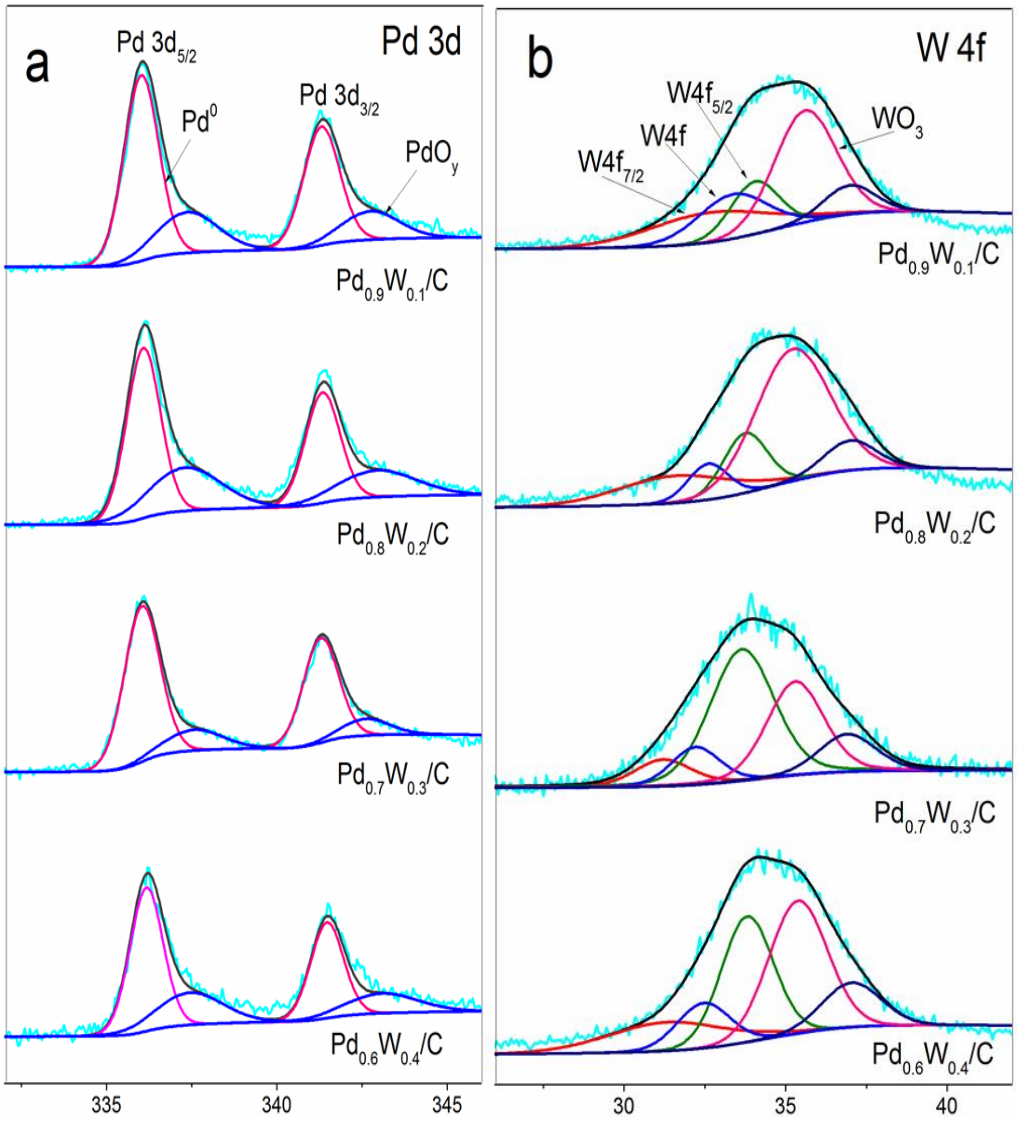
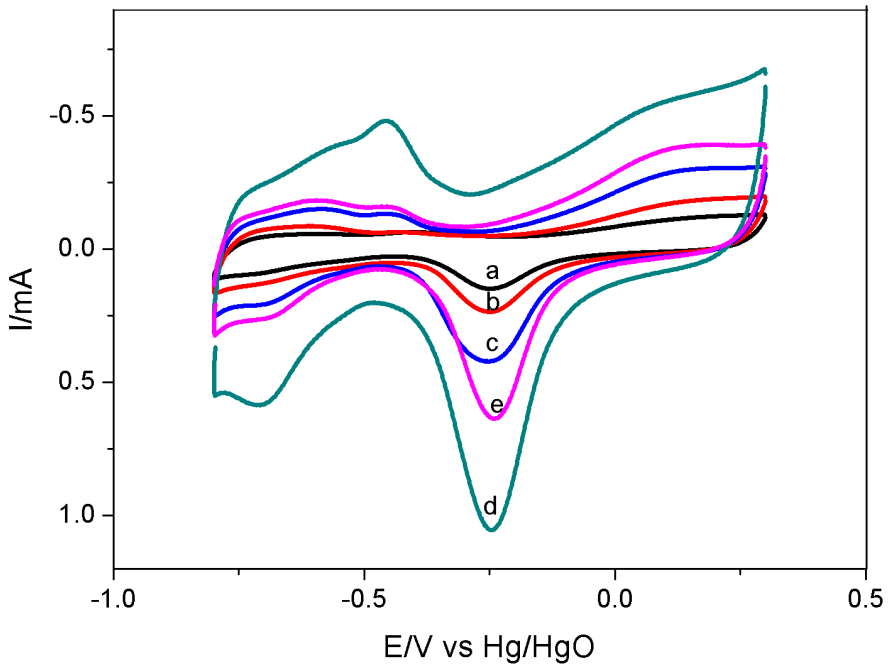


Figure 4. XPS spectra of oxide-rich PdW/C catalyst

2.2. Electrochemical performance

Figure 5 show the cyclic voltammograms (CV) of Pd/C (a), oxide-rich Pd0.6W0.4/C (b), Pd0.7W0.3/C(c), Pd0.8W0.2 /C (d),Pd0.9W0.1/C (e), all the CVs were measured in 1 M NaOH

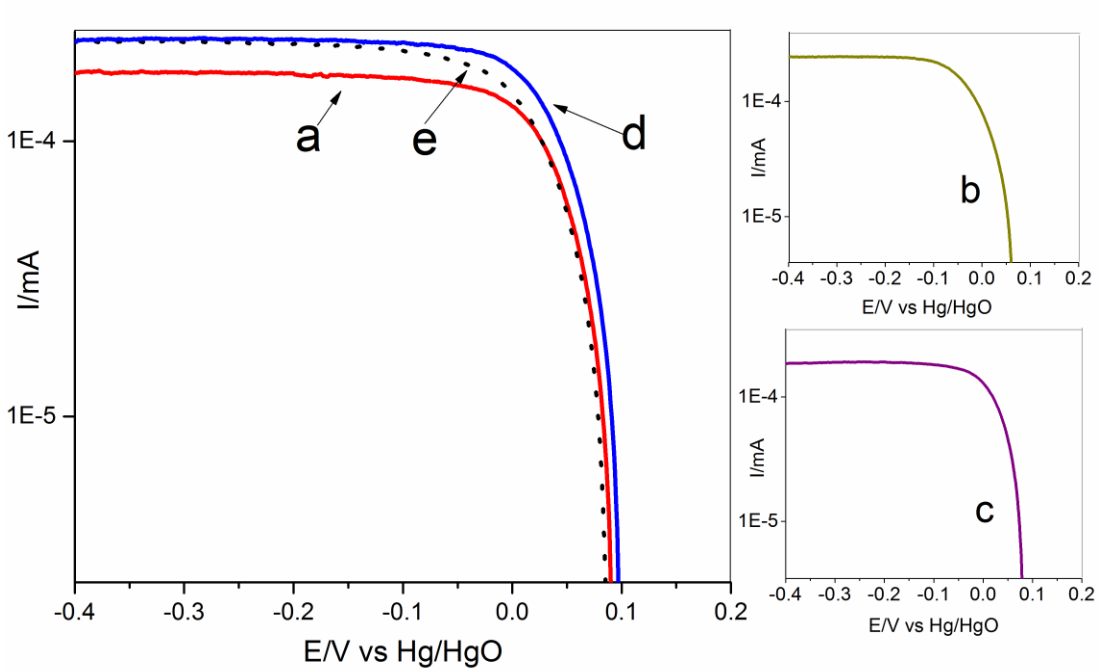
146 solution at a scan rate of 10 mV·s^{-1}. The peak of hydrogen adsorption / desorption is at about -0.7 V.
147 The peak of OH^- adsorbed on the surface of the electrocatalys is at is the range from -0.6 to -0.4 V,
148 while the oxidation of the surface metal and the resulting reduction of the oxide are at the range
149 from -0.4 V to 0.2 V.



150

151 **Figure 5.** Cyclic voltammograms (CV) of Pd/C (a), oxide-rich $Pd_{0.6}W_{0.4}$/C (b), oxide-rich
152 $Pd_{0.7}W_{0.3}$/C(c), oxide-rich $Pd_{0.8}W_{0.2}$/ C (d),oxide-rich $Pd_{0.9}W_{0.1}$ / C (e). In 0.1 M NaOH solution. Scan
153 rate 10 mV·s^{-1}

154 Figure 6 displays the linear sweep voltammetry (LSV) of Pd/C (a), oxide-rich $Pd_{0.6}W_{0.4}$/C (b),
155 $Pd_{0.7}W_{0.3}$/C (c), $Pd_{0.8}W_{0.2}$/C (d), $Pd_{0.9}W_{0.1}$/C (e) catalysts were measured in 0.1 M NaOH solution with
156 saturated O_2 at a speed of 2000 r/min and a scan rate of 1 mV·s^{-1}. Compare to Pd/C catalyst, the
157 onset potential of oxide-rich $Pd_{0.8}W_{0.2}$/C catalysts is positive shifted. Which is consistent to the
158 theoretic calculation results about the high activity of Pd_3W by Goddard[70] and his coworkers .



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160 **Figure 6.** LSV of Pd/C (a), oxide-rich $Pd_{0.6}W_{0.4}$ / C (b), oxide-rich $Pd_{0.7}W_{0.3}$ / C (c), oxide-rich
161 $Pd_{0.8}W_{0.2}$/C (d), oxide-rich $Pd_{0.9}W_{0.1}$/C (e) . In 0.1 M NaOH solution saturated with O_2 . Rotating
162 speed 2000 r/min. Scan rate 1 $mV \cdot s^{-1}$.

163 Electrocatalytic stability of Pd/C and oxide-rich Pd0.8W0.2C catalysts were characterized by
164 chronoamperometry (Figure 7) at -0.3 V vs Hg/HgO in 0.1 M NaOH solution.At the beginning both
165 current of Pd/C and oxide-rich Pd0.8W0.2/C catalyst decreased rapidly, then the current density of
166 each catalyst was relatively stable. Obviously the oxide-rich $Pd_{0.8}W_{0.2}$/C catalyst exhibits higher
167 electrocatalytic stability than Pd/C. Though the electrocatalytic stability is confirmed, it is still
168 difficulty for us to draw a conclusion that the composition of the WO_3 contained Pd-W nanoalloys is
169 unchanged during the ORR measurements. Some catalysts with unchanged compositions such as
170 pure Pd[71] or pure Pt[72] sometimes exhibit poor electrocatalytic stability. The catalysts $Pd_{0.7}W_{0.3}$
171 [64] for ORR in acid media exhibit high catalytic stability. However, its surface composition changed
172 during the ORR measurement. It can be seen from figure 6 that $Pd_{0.9}W_{0.1}$/C also exhibit high activity.
173 That means even if a half of the W/WO_3 dealloyed from the $Pd_{0.8}W_{0.2}$ nanoalloys, the Pd-W catalysts
174 still keep high activity. The current density ($mA \cdot mg\ Pd^{-1}$) at the oxide-rich $Pd_{0.8}W_{0.2}$/C is more than
175 1.6 times of that at Pd/C

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Peer-reviewed version available at Catalysts 2018, 8, 225; doi:10.3390/catal8060225

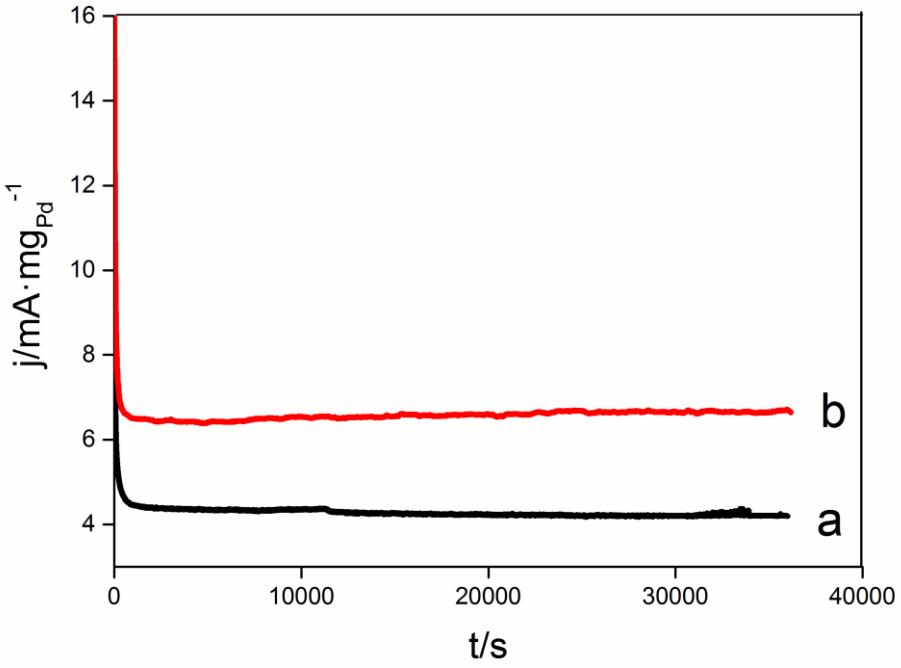

Figure 7. Electrocatalytic stability of Pd/C (a) and oxide-rich $Pd_{0.8}W_{0.2}/C$ (b) . In 0.1 mol/L NaOH solution saturated with oxygen. Potential -0.3 V vs Hg/HgO. Rotating speed 2000 r/min.

3. Materials and Methods

3.1 Preparation and characterization of the catalysts

$PdCl_2$ was purchased from Sinopharm Chemical Reagent Co.Ltd (Shanghai, China). The Vulcan carbon powder XC-72R was obtained from Cabot Corporation (Cabot Corp., Billerica, MA, USA). Nafion solution (5%) was obtained from DuPont (Delaware, DE, USA). All other chemicals were of analytical grade and used as acquired unless otherwise noted. Triple-distilled water was used through-out. The WO_3 contained Pd-W catalysts were prepared with the reduction-oxidation procedures, which is schematically illustrated in Scheme 1.

Pd/C and PdW/C catalysts with the metal loading of 20 wt% were prepared by the $NaBH_4$ chemical reduction method (Scheme 1, step 1) we have used before [73] . $PdCl_2$ and Na_2WO_4 were used as the precursors. Electrocatalysts with different atomic ratios are controlled by the molar ratio of metal precursors. The Pd-W nanoalloys are easy to be oxide in the ambient airs and formed the WO_3-contained Pd-W/C catalysts (Scheme 1, step 2).

The X-ray diffraction analysis (XRD) was carried out by a Bruker D8 advance X-ray diffractometer operating at 40 keV and 30 mA with Cu Kα radiation source, λ = 0.15406 nm. The TEM/HRTEM images were obtained on a JEOL JEM-2100 transmission electron microscopy . The content of metal elements on the surface of the samples was analyzed by EDS. The presence of the metal was excited by X-ray photoelectron spectroscopy (XPS) using Al Kα X-ray radiation on an ESCALAB 250 (Thermo Fisher SCIENTIFIC) spectrometer. Peak fitting using Gaussian / Lorentzian (20% Gaussian) method after background subtraction using Shirley's method[74].

3.2 Electrochemical Measurements

The electrochemical measurements were performed with a CHI832B electrochemical workstation (CHInstruments, Austin, TX, USA) and a conventional three-electrode electrochemical cell. A carbon-rod was used as the auxiliary electrode. Hg/HgO electrode was used as the reference electrode. The working electrode was prepared with the following procedures: The glassy carbon electrode (GCE, 3 mm in diameter) was carefully polished with 0.05 μm alumina (Al2O3) powder, and washed with the triple-distilled water before use. 10 mg of the catalyst powder in a mixture of 0.5 mL water and 0.5 mL ethanol was ultrasonicated for 15 min to prepare the ink of catalysts. 20 μL (2 μL× 10 times) of the ink was dropped on the GCE. 3μL of Nafion solution (5 wt%) was dropped on the surface after the ink was dried in air.

4. Conclusions

The WO_3 contained oxide-rich Pd-W/C catalysts were successful fabricated by reduction-oxidation procedures. The As prepared oxide-rich $Pd_{0.8}W_{0.2}$/C catalysts exhibit high electrocatalytic activity and stability. Which demonstrates that the as prepared oxide-rich $Pd_{0.8}W_{0.2}$/C is a prospective candidate for the cathode of the fuel cells operated with alkaline electrolyte..

Acknowledgments: This work was supported by the Natural Science Foundation of Shandong Province (ZR2016BM31)

Author Contributions: The corresponding author Wenpeng Li is the advisor/director of all other authors. Wenpeng Li and Nan Cui conceived and designed the experiments . Nan Cui and Zengfeng Guo performed the experiments; Xun Xu, Hongxia Zhao analyze the experiment data; Guang Dong，Xin Han, Haoquan Zhang,Shuzheng Xu, Peipei Yu repeated the experiments to make sure the results to be repeatable; Nan Cui wrote the paper

Conflicts of Interest: The authors declare no conflict of interest.

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