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# Cyclic Voltammetric Preparation of Palladium Nanoparticles for Ethanol Oxidation Reaction

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By simple cyclic voltammetry of a PdO-coated glassy carbon (GC) electrode for a few cycles with the potential swept from  $-1.0$  to  $-1.2$  V versus saturated calomel electrode in an alkaline solution containing ethanol, a Pd particle modified GC electrode was fabricated. It showed satisfactory catalysis toward the ethanol oxidation reaction.

## 1. Introduction

In the research field of fuel cells, the preparation of metal catalysts at the nanoscale, for example, platinum (Pt) nanoparticles, is regarded as the main strategy to reduce the manufacturing cost of fuel cells. Various synthetic methods to synthesize pure Pt nanoparticles have been reported.<sup>1,2</sup> However, due to the limited resources of Pt,<sup>3</sup> non-Pt-based catalysts used in the oxidation of small organic molecules, such as the methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR), have also been widely investigated.<sup>4,5</sup> Among those developed non-Pt-based catalysts, palladium (Pd) is thought to be the main Pt-free catalyst for EOR especially in an alkaline solution due to its unique tolerance surface against CO poisoning.<sup>6</sup> Therefore, developing a novel method to fabricate Pd particles (or nanoparticles) becomes a hot topic especially for electrochemistry researchers.

There are three typical methods to generate Pd nanoparticles: The first method is chemical reduction. For example, Huang et al.<sup>7</sup> prepared Pd nanoparticles on Vulcan XC-72 carbon black through a chemical reduction of  $\text{PdCl}_2$  using  $\text{NaBH}_4$  as the reducing agent. Lin and co-workers fabricated Pd nanoparticles on carbon nanotubes (CNTs) using a chemical reduction, in which  $\text{Pd}(\text{hfa})_2$  (hfa = hexafluoroacetonate) and hydrogen gas were employed as the Pd precursor and the reducing agent, respectively.<sup>8</sup> The second method is thermal decomposition. For instance, Hwang et al.<sup>9</sup> introduced a method to synthesize Pd aerosol nanoparticles via a spark, in which Pd nanoparticles were thermophoretically (a physical phenomenon in which the objects, subjected to a temperature gradient, move from high-temperature zone to low-temperature zone) deposited onto a flexible polyimide substrate. The third method is electrochemical reduction. Cheng et al.<sup>10</sup> reported the preparation of highly ordered Pd nanowire arrays (NWAs) using a porous aluminum oxide template via pulsed electrodeposition. Osaka et al.<sup>11</sup> have electrodeposited two types of Pd–Co films onto Au substrates by applying different current densities, and their application in the oxygen reduction reaction (ORR) has been thoroughly investigated.

The preparation of Pd nanoparticles on a glassy carbon (GC) electrode has also been reported. For example, Zhang et al.<sup>12</sup>

immobilized Pd particles on a base plane of a GC rod in a conventional evaporation chamber by electric heating. Casella and Contursi<sup>13</sup> immobilized Pd particles on a GC electrode by voltage cycling between  $0.0$  and  $-0.4$  V versus saturated calomel electrode (SCE) in a solution containing  $0.5$  mM  $\text{Na}_2\text{PdCl}_6$ . PdO is normally formed due to the easy oxidation of the Pd nanoparticles. Also, the way to minimize PdO on the powder surface is to physically remove it by polishing with  $\alpha$ -alumina powder.<sup>13</sup> An easy to transform PdO to Pd is demanding both technically and scientifically. However, there is no report on the preparation of Pd nanoparticles by cyclic voltammetry (CV) from PdO particles that are generated by a hydrolysis process of  $\text{PdCl}_2$  in an alkaline solution.

In this work, PdO particles are prepared by a facile hydrolysis process of  $\text{PdCl}_2$  in  $\text{NaOH}$  aqueous solution, and then the obtained PdO particle suspended solution is deposited on the surface of a GC electrode to yield a PdO-coated GC electrode. The metallic Pd coated GC electrode is prepared by subjecting the PdO-coated GC electrode to a voltage cycling from  $-1.0$  to  $-1.2$  V versus SCE. CV investigation has revealed that the as-prepared Pd particles have catalysis toward the ethanol oxidation reaction (EOR).

## 2. Experimental Section

**2.1. Pyrolysis Preparation of PdO Particles.** The pyrolysis method has been successfully utilized in our previous work, in which Pd particles and Pt nanoparticles have been successfully prepared.<sup>14,15</sup> In this experiment, the pyrolysis method is also used to prepare PdO particles. Briefly,  $2.0$  mL of  $\text{PdCl}_2$  ( $5.0$  mM) is added to  $2.0$  mL of  $\text{NaOH}$  solution ( $2.0$  or  $0.5$  M), then the resultant solution is placed in a homemade autoclave at room temperature, and the well-sealed autoclave is transferred to a SRJX-8-13 box-type furnace equipped with a KSY 12-16 furnace temperature controller. The temperature of the furnace is increased to  $200$  °C within  $20$  min and maintained at  $200$  °C for  $3$  h to fulfill the pyrolysis process. The resultant products are filtered, washed with deionized water, and dried at ambient conditions to generate PdO particles for further testing and characterization.

**2.2. Preparation of Pd-Coated Glassy Carbon (GC) Electrode by CV.** Prior to each experiment, a GC working electrode with a diameter of  $3$  mm is successively polished with  $1\ \mu\text{m}$  and  $60\ \text{nm}$  alumina powders on a microcloth wetted with deionized water, leading to a mirrorlike surface. The as-prepared PdO particles are mixed with deionized water to generate a

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suspended solution, which is subjected to ultrasonication for 30 min to form a uniform colloid (the content of PdO is about 1.0 mg/mL). Then the PdO particle suspended aqueous solution (5  $\mu$ L) is dropped onto the well-treated GC electrode to produce a PdO particle modified GC electrode. Interestingly, due to the excellent adhesion of the PdO particles to the GC electrode, it is unnecessary to use Nafion or other binders to prepare PdO-coated GC electrode.

The Pd-coated GC electrode is directly prepared by in situ electrochemical reduction of the PdO-coated GC electrode in a solution (1.0 M KOH and 1.0 M  $C_2H_5OH$ ). In the electrochemical reduction process, CV is employed; i.e., the potential is swept from -1.0 to -1.2 V versus SCE for several cycles at a sweeping rate of 50 mV/s.

**2.3. Electrochemical Measurements.** Electrochemical experiments are conducted on a Model CHI660B electrochemical workstation (Shanghai Chenhua Apparatus, China). A conventional three-electrode system is employed, in which a PdO particle modified GC electrode and a platinum wire ( $1\text{ cm}^2$ ) are used as the working electrode and counter electrode, respectively. The reference electrode is a saturated calomel electrode (SCE). All potentials in this work are reported with respect to SCE. All the experiments are carried out at room temperature. Electrochemical impedance spectroscopy (EIS) is performed in the frequency range from 1 to  $10^5$  Hz with an applied amplitude of 5 mV.

**2.4. Characterization.** Scanning electron microscopy (SEM) is performed on a Hitachi S-570 microscope (Japan). Electron dispersive X-ray analysis (EDX, PV-9900, USA) is performed by the WD-8X software established by Wuhan University.

X-ray diffraction (XRD) analysis of the catalyst is carried out on a Bruker D8 ADVANCE X-ray diffractometer equipped with a Cu K $\alpha$  source ( $\lambda = 0.154\text{ nm}$ ) at 40 kV and 30 mA. The  $2\theta$  angular region between 10 and  $90^\circ$  is recorded at a scan rate of  $1^\circ/\text{step}$ .

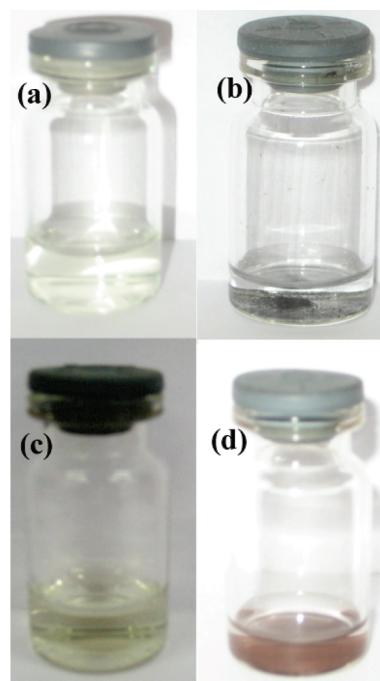
### 3. Results and Discussion

**3.1. Characterization of PdO Particles.** Figure 1 shows digital photos of the obtained samples. Figure 1a,b corresponds to the samples before and after the pyrolysis of  $PdCl_2$  (5 mM) in a 2.0 M NaOH aqueous solution, while Figure 1c,d corresponds to the samples before and after the pyrolysis processing of  $PdCl_2$  (5 mM) in a 0.5 M NaOH aqueous solution. After the pyrolysis process, black particles (Figure 1b) and red particles, (Figure 1d) are observed. These observations strongly indicate the formation of nanoparticles by this simple pyrolysis process, and the concentration of NaOH is a key factor in this simple pyrolysis process.

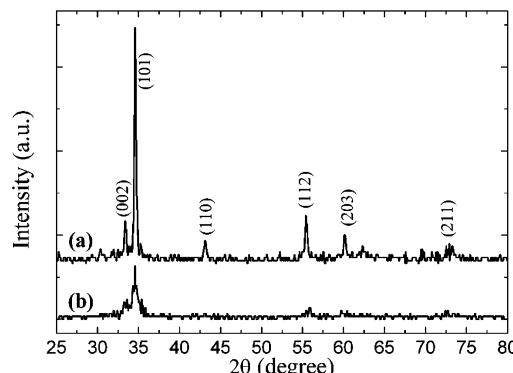
Figure 2 shows the typical XRD patterns of the obtained samples. Figure 2a corresponds to the black particles; the diffraction peaks at  $2\theta$  of  $33.44^\circ$  and  $34.60^\circ$  are indexed to the (002) and (101) planes of palladium oxide (PdO, JCPDS card, 01-088-2434), respectively. For the red particles (Figure 2b), a similar pattern is observed, suggesting that even in 0.5 M NaOH solution PdO can be generated by this simple pyrolysis process. More peaks are observed in Figure 2a, indicating a higher crystallization than that of the red particles. The average particle size ( $d$ ) is estimated using the Debye–Scherrer formula, eq 1:

$$d = 0.89\lambda/(\beta \cos \theta_B) \quad (1)$$

where  $\lambda$  is the X-ray wavelength ( $1.5406\text{ \AA}$ ),  $\theta_B$  is the Bragg diffraction angle, and  $\beta$  is the peak full width at half-maximum. For the black and red PdO particles, the average size is 61.0



**Figure 1.** Digital photos of (a) before and (b) after pyrolysis in 2.0 M NaOH solution and (c) before and (d) after pyrolysis in 0.5 M NaOH solution.

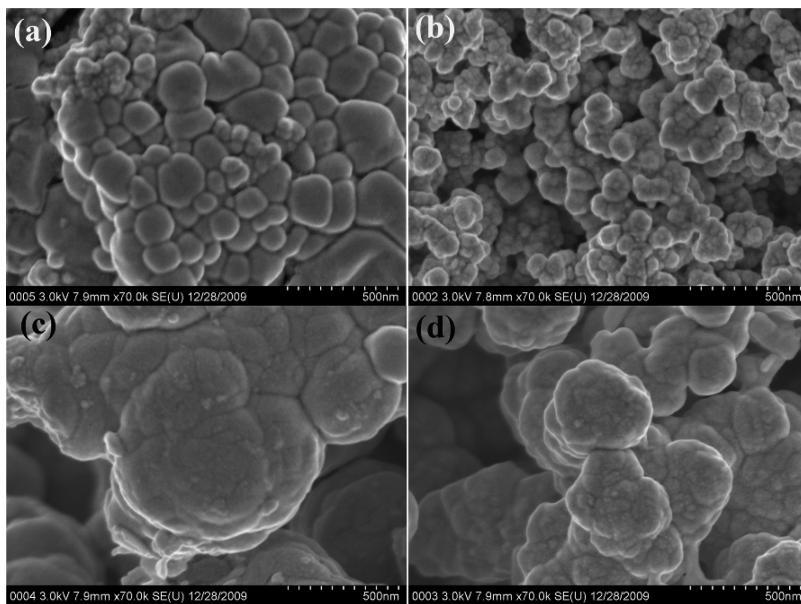


**Figure 2.** XRD patterns of (a) black and (b) red particles.

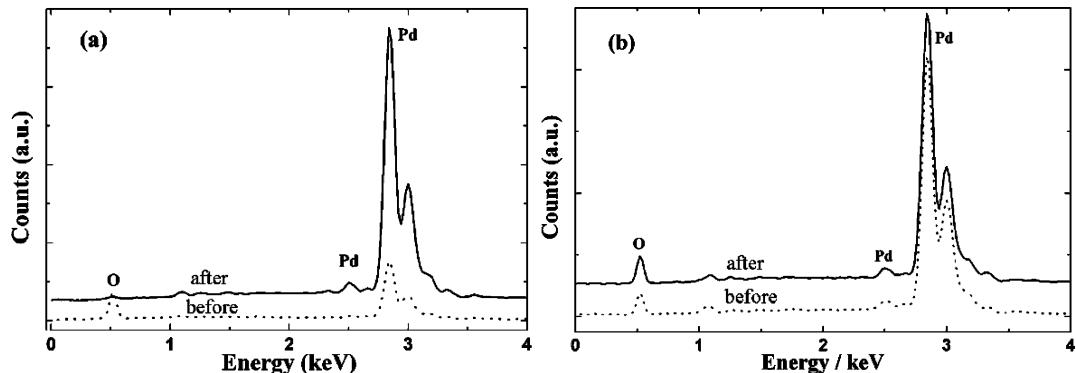
and  $25.9\text{ nm}$ , respectively, as calculated from the Debye–Scherrer formula on the major (101) peak of Figure 2.<sup>16</sup> However, the estimated particle size of the black and red particles from the SEM images, parts c and a of Figure 3, is about 300 and  $70\text{ nm}$ , respectively. The size difference is due to the aggregation occurring in the SEM sample preparation.

Figure 4 shows the EDX spectra of the obtained (Figure 4a) red and (Figure 4b) black PdO particles, respectively. Only elements of O and Pd are observed, which further testifies that a simple pyrolysis process of  $PdCl_2$  in NaOH aqueous solution can yield PdO nanoparticles.

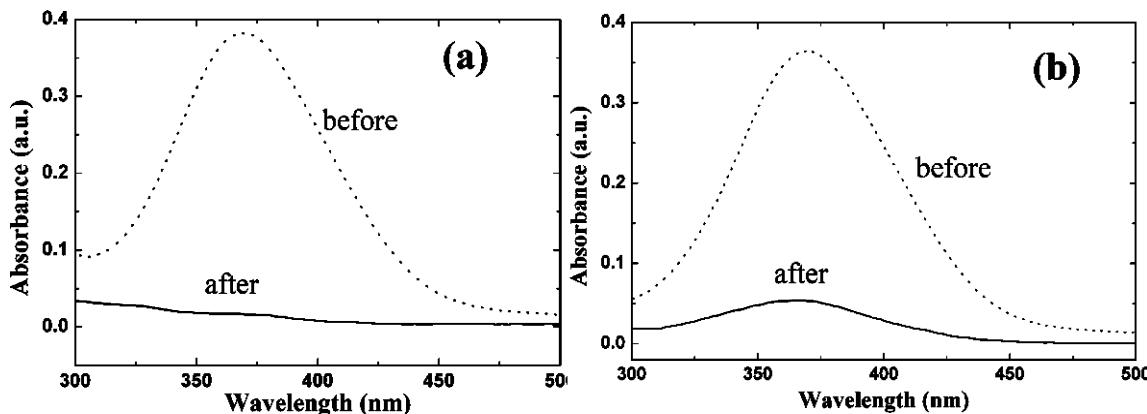
To interpret the mechanism of this facile pyrolysis process, a UV–vis absorption test is performed. A UV–vis absorption peak around  $370\text{ nm}$  is observed in the solution containing 0.5 M NaOH and 5.0 mM  $PdCl_2$  (Figure 5a) and in the solution containing 2.0 M NaOH and 5.0 mM  $PdCl_2$  (Figure 5b). It was reported that, in the presence of  $Cl^-$ , some complexes containing  $Pd^{2+}$  can form easily.<sup>17</sup> Thus, some  $Pd^{2+}$  complexes such as  $[Pd(OH)_4]^{2-}$  may have formed in an alkaline solution, resulting in an absorption peak at  $370\text{ nm}$ . However, after the pyrolysis process (Figure 5), the absorption peaks are totally attenuated, suggesting that the complexes having  $Pd^{2+}$  are almost destroyed entirely owing to the formation of palladium oxides.



**Figure 3.** SEM microstructures before (a, c) and after (b, d) in situ electrochemical reduction. (a, b) Red PdO particles; (c, d) black PdO particles.



**Figure 4.** EDX spectra before and after 10-cycle CV treatment for the obtained (a) red and (b) black PdO particles, respectively.

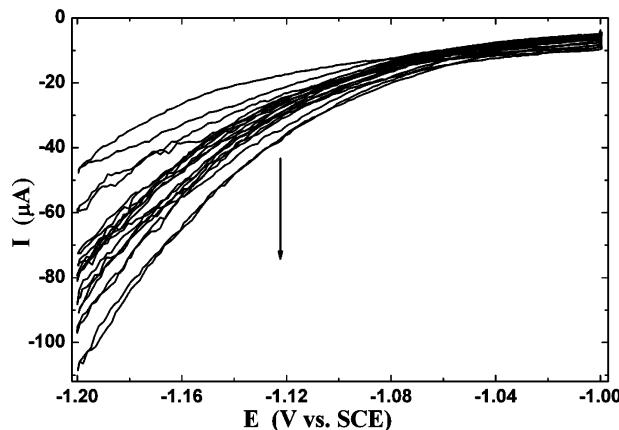


**Figure 5.** UV-vis absorption spectra of the samples in (a) 0.5 and (b) 2 M NaOH before and after pyrolysis process.

**3.2. Preparation of Pd Particles by CV.** For the black PdO-coated GC electrode, the potential sweeps from  $-1.0$  to  $-1.2$  V versus SCE for 10 cycles (Figure 6). The absolute reduction peak current values are observed to increase significantly with increasing potential cycling number. In this potential range, only  $\text{H}^+$  can be electrochemically reduced; thus, these reduction current peaks can only be attributed to the evolution of  $\text{H}_2$  rather than the electrochemical reductions of other substances. In addition, due to the evolution of  $\text{H}_2$ , “zigzag” curves are displayed. Under the same conditions, similar CVs are also

obtained on the red PdO particle coated GC electrode (data not shown here). To our surprise, after this simple potential cycling treatment, CVs of EOR can be observed clearly on the resultant electrode, which will be discussed in the following section.

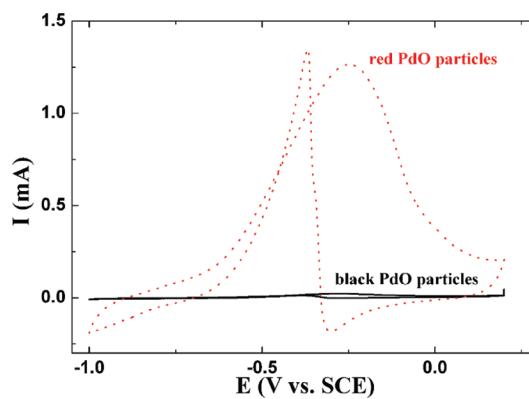
After the potential cycling, the samples are scraped from the electrode and characterized by SEM (Figure 3). Compared to the PdO particles (Figure 3a,c), smaller and more uniform particles are observed (Figure 3b,d). This indicates that PdO particles have reacted with the evolved hydrogen gas or



**Figure 6.** CVs obtained on a black PdO-coated GC electrode in a 1 M KOH solution containing 1 M  $\text{C}_2\text{H}_5\text{OH}$  for successive 10 cycles. The scan rate is 50 mV/s, and the arrow indicates cycle changing from 1 to 10.

hydrogen atom prepared by CV, leading to the particles with smaller sizes.

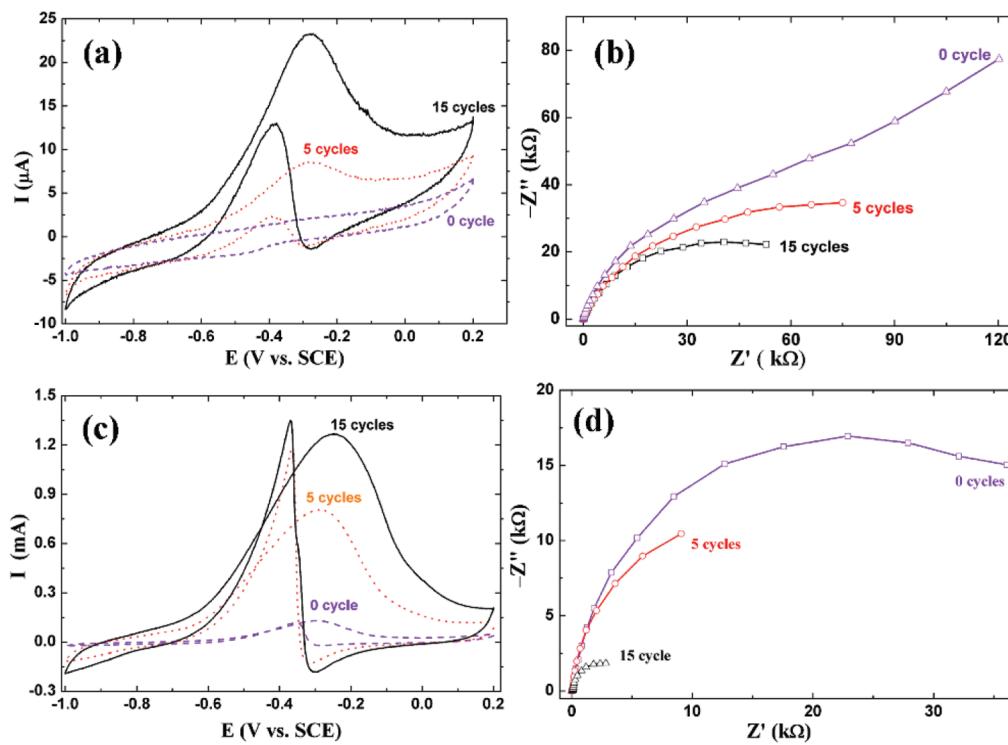
After the CV treatment, EDX is also performed (Figure 4). For the red particles, the peak corresponding to oxygen element can no longer be detected; only the peak of Pd element is displayed (Figure 4a), strongly indicating that Pd particles instead of other substances are fabricated by this simple CV treatment. However, for the black particles (Figure 4b), no obvious variation is found in the EDX curves, implying that only a small part of black particles are reduced by the evolved  $\text{H}_2$  gas with a possibility to form a core–shell nanoparticles. That is, compared to the red particles of PdO, the black particles of PdO are not easily reduced by  $\text{H}_2$ . Probably this is due to the higher crystallization of black particles than that of the red PdO particles. Also, the potential cycling number (data not shown here) is found to have a significant impact on the preparation of Pd particles; for example, as the potential cycling



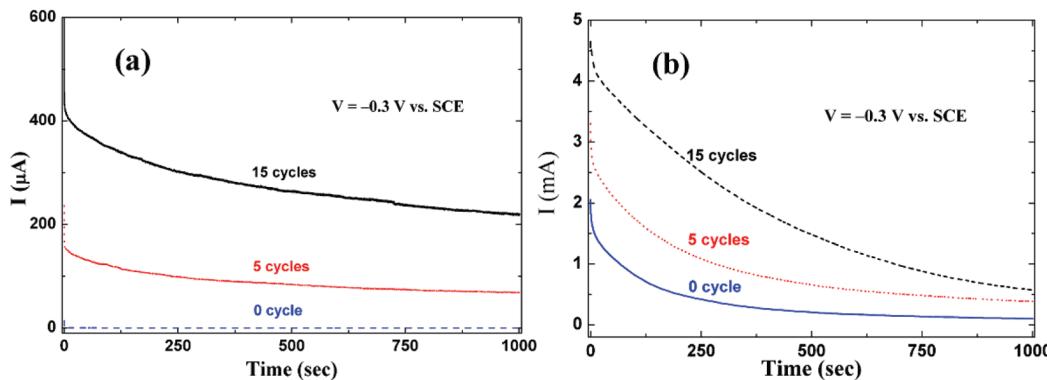
**Figure 8.** CVs of EOR in 1.0 M KOH solution containing 1.0 M ethanol on red and black PdO particle coated GC electrode in which the particles were treated by CV for 15 cycles. Scan rate 50 mV/s.

number is less than 5, Pd particles cannot be formed by this CV treatment, while when the potential cycling number exceeds 30, no variations of morphologies can be found in the SEM images and similar EDX spectra are observed. More detailed work should be done to elucidate the influence of CV treatment on the resultant samples. Here, our work has at least indicated that Pd particles can be prepared by this simple CV treatment, as is reported for the first time.

**3.3. Electrocatalysis of Pd Particles toward EOR.** The catalysis of the as-prepared PdO and Pd particles toward EOR is performed by cyclic voltammetry (Figure 7). Without prior CV experiment, the black PdO particle coated GC electrode exhibits no ethanol oxidation peak (Figure 7a), which indicates that PdO particles have no catalysis toward EOR at all and is consistent with the previous report.<sup>4</sup> However, after the CV treatment, evident EOR peaks are displayed (Figure 7a), which is consistent with the previous investigation.<sup>18</sup> Based on the curves with CVs of 15 and 5 cycles, one can infer that the



**Figure 7.** CVs of EOR in 1 M KOH solution containing 1 M ethanol on a (a) black and (c) red PdO particle coated GC electrode in which PdO particles were treated by CV for different potential cycling numbers; scan rate 50 mV/s. Nyquist plots with the electrodes from (b) black and (d) red PdO particles.



**Figure 9.** Chronoamperograms obtained at  $-0.3\text{ V}$  (vs SCE) in  $1.0\text{ M}$   $\text{C}_2\text{H}_5\text{OH}$  solution containing  $1.0\text{ M}$   $\text{KOH}$  for (a) black and (b) red  $\text{PdO}$  particle coated GC electrode treated by CV for different potential cycling numbers.

catalysis of Pd particles prepared by CV treatment toward EOR is closely related to the potential cycling number, and it seems that more potential sweeping cycles favor the process of EOR.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to characterize the electrode surface. Generally, a semicircle appearing in the intermediate frequency region corresponds to the charge transfer resistance ( $R_{ct}$ ), and a semicircle with a bigger diameter corresponds to a larger  $R_{ct}$ .<sup>19</sup> Thus, one can conclude from Figure 7b that the Pd particles prepared by 15-cycle CV show a better catalysis toward EOR than that of the Pd particles prepared by five-cycle CV. The results from Nyquist plots (Figure 7b) are consistent with the CVs of EOR very well (Figure 7a). Similar results are obtained for the red particles of  $\text{PdO}$ -coated GC electrode (Figure 7c,d). That is, after the CV treatment, CVs of EOR can be clearly observed on the as-prepared Pd-coated GC electrode.

Figure 8 shows the CVs of EOR in a solution ( $1.0\text{ M}$  KOH and  $1.0\text{ M}$  ethanol) on the red and black  $\text{PdO}$  particle coated GC electrodes with 15 cycles, respectively. To our surprise, under the same operational conditions, the current of EOR displayed on the Pd-coated GC electrode, in which Pd particles were prepared from the red  $\text{PdO}$  particles, is much higher than that on the Pd-coated GC electrode where Pd particles were prepared from the black  $\text{PdO}$  particles. Compared with the black  $\text{PdO}$  particles after the CV treatment, smaller Pd particles are fabricated from the CV-treated red  $\text{PdO}$  particles as evidenced by SEM observations (Figure 3). For the black  $\text{PdO}$  particles, only larger Pd particles are generated by the CV treatment.

Chronoamperometry is a powerful technique to compare the electrocatalysis of various catalysts.<sup>20</sup> The black  $\text{PdO}$ -coated GC electrode treated with 15-cycle CV exhibits the largest current among the same type of electrodes treated with different cycles (Figure 9a). This result is well consistent with the CV curves (Figure 7). For the red  $\text{PdO}$  particle coated electrode (Figure 9b), similar results are obtained. These current–time curves strongly demonstrate that the catalysis of the as-prepared Pd particles toward EOR is closely related to the potential cycling number. In addition, the red  $\text{PdO}$ -coated GC electrodes treated with CV show 10 times higher current than those from the black  $\text{PdO}$ -coated GC electrodes treated with CV.

According to the zigzag curves shown in Figure 6, one can conclude that  $\text{H}_2$  or H atoms are electrochemically produced. Thus,  $\text{PdO}$  is directly reduced by  $\text{H}_2$  or H atoms, i.e.,  $\text{PdO} + \text{H}_2$  (or H)  $\rightarrow$   $\text{Pd} + \text{H}_2\text{O}$ , leading to a Pd-coated GC electrode. As a result, CVs of EOR are observed on the as-prepared Pd-coated GC electrode. It was reported that the deterioration of Pd catalyst mainly resulted from the formation of  $\text{PdO}$ .<sup>21</sup> Therefore, based on the results shown in this work, one can

believe that the deteriorated Pd substrate could be partially repaired in situ by this simple CV method.

#### 4. Conclusion

In this work,  $\text{PdO}$  particles with different sizes were prepared by a facile pyrolysis process of  $\text{PdCl}_2$  dissolved in  $\text{NaOH}$ . The concentration of  $\text{NaOH}$  is determined to be a key parameter affecting the sizes of the obtained particles.  $\text{PdO}$ -coated GC electrodes were successfully fabricated by immobilizing the resultant  $\text{PdO}$  particles onto GC electrode. In a certain potential range, potential cycling was conducted. Interestingly, a Pd-coated GC electrode was fabricated by this simple CV method. More importantly, the as-prepared Pd-coated GC electrode showed satisfactory electrocatalysis toward EOR. In this experiment, SEM images, XRD, and EDX were all utilized to characterize the obtained  $\text{PdO}$  particles and Pd particles. To the best of our knowledge, this is the first time for reporting the preparation of  $\text{PdO}$  particles by a pyrolysis process containing alkaline and the preparation of Pd particles by CV from  $\text{PdO}$  particles.

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