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Short communication

The Influence of Potential Sweep Cycle Number on the Electrocatalytic Activity of the Boiled PdO/Graphene for Ethanol Oxidation Reaction (EOR)

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A suspension solution consisting of PdO and graphene was boiled at 200 ^{o}C for 2 h, and the filtered and dried samples were denoted as materials of PdO/G. Subsequently, the obtained samples were immobilized on a glassy carbon (GC) electrode, producing a PdO/G modified GC electrode. Lastly, the prepared electrodes were swept by a potentiostatic method at the scan rate of 10 mV s^{-1} in a solution having $PdCl_2$ and Na_2SO_4 for various cycles (0, 20, 50 and 80 cycles), yielding four kinds of PdO/G electrodes, being denoted as potential sweep cycle (PSC)-treated PdO/G electrodes. The morphologies of the scraped samples were mainly characterized by using Transmission electron microscopy (TEM). And the electrocatalytic abilities of the PSC-treated catalysts towards ethanol oxidation reaction (EOR) were basically examined by using cyclic voltammetry (CV) and chronoamperometry (CA). The electrochemical consequences indicated that the catalyst of PdO/G treated by 50 cycles (catalyst **c**) delivered the best electrocatalytic activity among all as-prepared catalysts. The smaller particle size and higher percentage of Pd were regarded as the main reasons for the excellent electrocatalytic activity of catalyst **c** towards EOR as compared to other catalysts. Showing the fact that the potential sweep cycle could be employed as a method to enhance the electrocatalytic activity of PdO/G materials was the main contribution of this short communication.

Keywords: PdO; graphene; boiling treatment; potential sweep cycle number; ethanol oxidation reaction; electrocatalysis

1. INTRODUCTION

Recently, the research work on direct ethanol fuel cells (DEFCs) has attracted much interest mainly due to the advantages of using DEFCs as the power sources for some portable applications [1]. Except for the higher energy density compared to direct methanol fuel cells (DMFCs), relatively easy large-scale production from biomass and the facile storage and transportation, the lower toxicity is regarded as the most important property of DEFCs as compared to other alcohol-based fuel cells [2]. It is well-known that platinum (Pt) is the most widely used electrocatalyst in ethanol oxidation reaction (EOR), one anodic electrode reaction in DEFCs. However, recent works have also indicated that the limited supply and higher cost as well as the slow kinetics of EOR on Pt have remarkably impeded the wide utilization of Pt in DEFCs, further restricting the commercialization of DEFCs [3]. Therefore, developing novel electrocatalysts for EOR has become into a main task for DEFCs-related researcher. Of late, many kinds of Pt-free electrocatalysts for EOR were generated. Among these Pt-free electrocatalysts, palladium (Pd), mainly due to its lower cost and more abundant reserves [4], has been proven to have electrocatalytic activity towards EOR particularly in alkaline solution. Meanwhile, the role of PdO in enhancing the electrocatalysis of Pt has been demonstrated in the previous report [5]. For example, Pan's group [5] examined the electrocatalytic behavior of Pt/PdO electrode (Pt nanoparticles electrodeposited on the PdO thin film) in methanol oxidation reaction (MOR) in acidic media, and they thought that the good electrocatalytic performance of the Pt/PdO electrode should be due to a high CO tolerance and the large ESA. Our previous works [6, 7] have also indicated that the catalysts of PdO supported on multi-walled carbon nanotubes (MWCNTs) could show unexpected electrocatalytic activity towards EOR.

As we know, cyclic voltammetry (CV) is common technique which is generally accompanied by the electro-oxidation or electro-reduction reactions. Can the electrocatalysis of the system that contained PdO and graphene be modified by CV? Can we use the potential sweep cycle number as a parameter to alter the electrocatalytic activity of the system having PdO and graphene? To the best of our knowledge, the report of using potential sweep cycle as a technique to modify the electrocatalytic ability of the system that contained metal oxides and carbon, not to mention the materials having PdO and graphene, was not published so far.

In this work, a suspension solution consisting of PdO and graphene was boiled for a period. And then, the filtered and dried products were anchored on the surface of a glassy carbon (GC) electrode. Finally, the obtained electrodes were potentially swept at a scan rate of 10 mV s^{-1} for various cycles, generating four kinds of PdO/G modified GC electrodes. It was found that the PSC-treated PdO/G modified GC electrodes with different potential sweep cycles delivered rather different electrocatalytic activities towards EOR. The results effectively indicated that PSC-treated PdO/G materials could be utilized as electrocatalysts for EOR, and the potential sweep cycle number is a sensitive parameter which could modify the electrocatalysis of the materials having PdO and graphene. It is expected that the developed method of PSC could be employed as a useful technique to change the properties of the materials having other metal oxides and carbon.

2. EXPERIMENTAL

2.1 Materials

Graphene was supported by the Fengfan Co., Ltd. **(**China). All the electrodes were bought from Tianjin Aida Co., Ltd (China). All the analytical grade chemicals were used as-received without further treatment. Doubly distilled water was utilized to prepare the aqueous solutions.

2.2 Preparation of PdO/G samples

Firstly, 4.0 mg PdO and 10.0 mg graphene were mixed in a proper amount of doubly distilled water to fabricate a suspension solution. And then, the suspension solution sealed in a home-made autoclave was boiled at 200 ºC for 2 hours. After being cooled down to the room temperature, the resultant samples were filtered and washed several times by distilled water till the pH value of filtrate was equal to 7. Lastly, the resulting samples were dried in air, leading to the formation of a composite material that contained PdO and graphene.

2.3 Preparation of PSC-treated PdO/G modified GC electrode

Prior to the production of the PSC-treated PdO/G modified GC electrode, PdO/G-modified GC electrodes were prepared first. Briefly, a GC electrode with a diameter of 3 mm was polished using alumina powder suspensions carefully, and then the burnished GC electrode was washed by distilled water for several times to create a clean substrate. And then, the catalyst ink having PdO/G and Nafion solution was dropped onto the well-polished GC electrodes, generating a PdO/G modified GC electrode. It should be emphasized that the catalyst ink used above was prepared by dispersing 1 mg of PdO/G samples into 1 mL Nafion ethanol solution (The Nafion content was equal to 0.1 wt.%).

A conventional three-electrode cell was used to create the PSC-treated PdO/G modified GC electrode. In this cell, a PdO/G-modified GC electrode, a saturated calomel electrode (SCE) and a platinum wire were used as the working electrode, reference electrode and counter electrode, respectively. And then the working electrode was potentiostatically cycled at the scan rate of 10 mV s^{-1} for various cycles in a solution that contained 10^{-3} M $PdCl_2$ and 0.5 M Na_2SO_4, generating PSC-treated PdO/G modified GC electrodes. The electrodes potentially cycled for 0, 20, 50 and 80 cycles, were nominated as catalyst **a**, **b**, **c** and **d**, respectively. Correspondingly, the electrodes, being subjected to above cycles, were called electrode **a**, **b**, **c** and **d**, respectively.

2.4 Characterizations

The morphologies of samples were studied by transmission electron microscopy (TEM, HITACHI, H-7650). Electrochemical measurements, mainly including Cyclic voltammetry (CV), Chronoamperometry (CA), Electrochemical impedance spectroscopy (EIS), were performed on a CHI 660B electrochemical working station (Shanghai Chenhua Apparatus, China) which was connected to a personal computer.

A solution of 1 M KOH having 1 M C_2H_5OH was used to probe the electrocatalytic activity of the prepared catalysts for EOR. As prepared PSC-treated PdO/G modified GC electrode, a platinum wire and a saturated calomel electrode (SCE) were, respectively, employed as the working electrode, auxiliary electrode and reference electrode. All the experiments were accomplished at room temperature.

3. RESULTS AND DISCUSSION

3.1 Morphology characterization

Fig. 1 shows the TEM images of all prepared materials. Obviously, in all images, the sheet-shaped graphene is displayed clearly, which indicated that the main morphology of graphene was not damaged by the boiling process and potential sweep cycle treatment. For catalyst **a**, a sample that was not subjected to the treatment of potential sweep cycling, almost no particles were observed. While, for catalyst **b**, **c** and **d**, numerous small particles were observed on the surface of graphene. It appeared that several huge aggregates, that contained many small nanoparticles, were formed in the case of catalyst **b**.

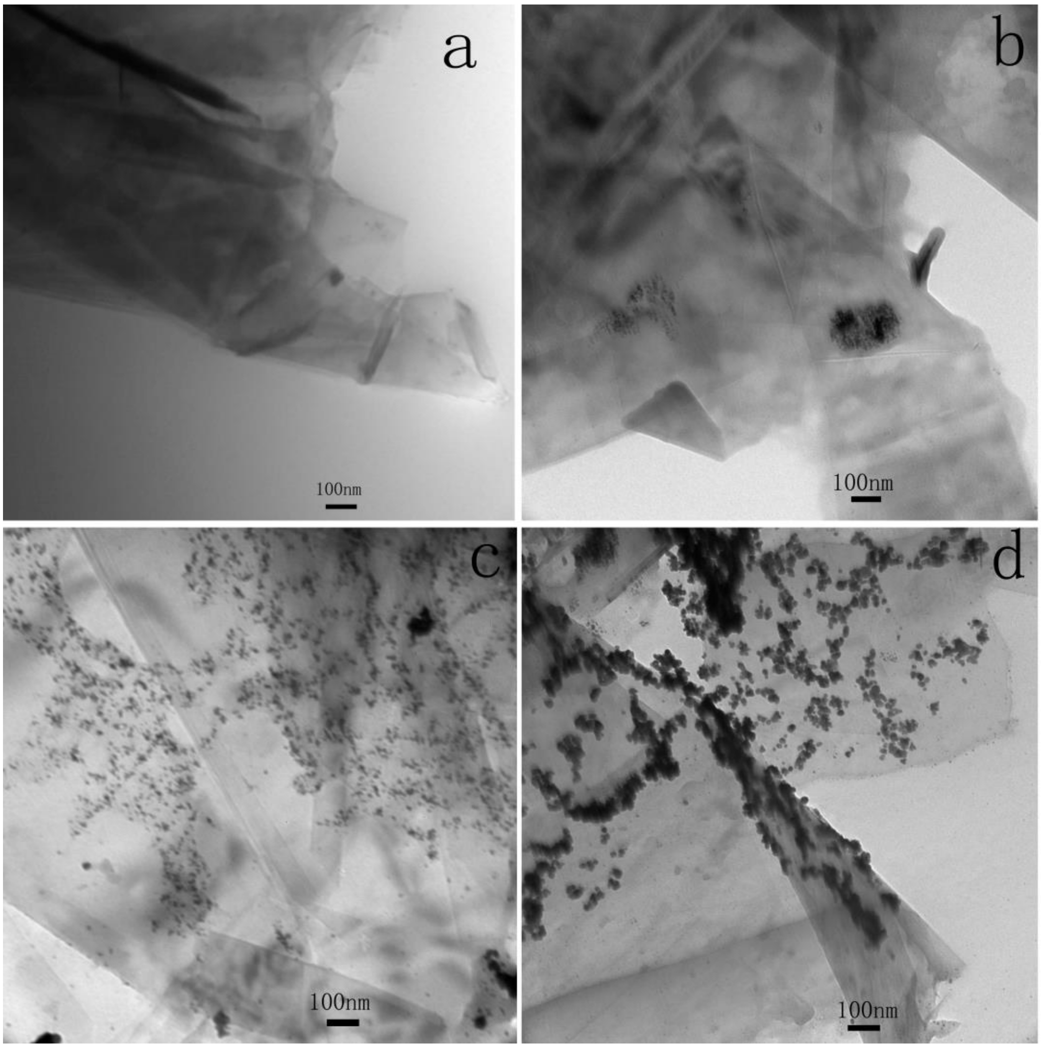

Figure 1. TEM images for all prepared PSC-treated PdO/G catalysts. Image **a**, **b**, **c** and **d** represented catalyst **a** (0 cycle), **b** (20 cycles), **c** (50 cycles) and **d** (80 cycles).

The particle sizes for catalyst **c** and **d** were estimated to be 11 nm and 15 nm, respectively. Evidently, the particle size distribution of catalyst **c** was superior to that of catalyst **d**. This result substantially indicated that potential sweep cycle was a powerful tool which could alter the particle size of the catalyst that contained PdO and graphene. Also, it was reported previously that the material of carbon had no electrocatalytic activity for EOR [6], thus, the catalysis of catalysts, prepared here, for EOR should be originated from the presence of small nanoparticles on the surface of graphene. That is to say, PSC-treated PdO/G may present various electrocatalytic abilities towards EOR due to the rather different particle size as shown in Fig.1. As far as we know, this is the first time to report the synthesis of potential sweep cycle-treated PdO/G materials.

3.2. Electrocatalytic performance of PSC-treated PdO/G towards EOR

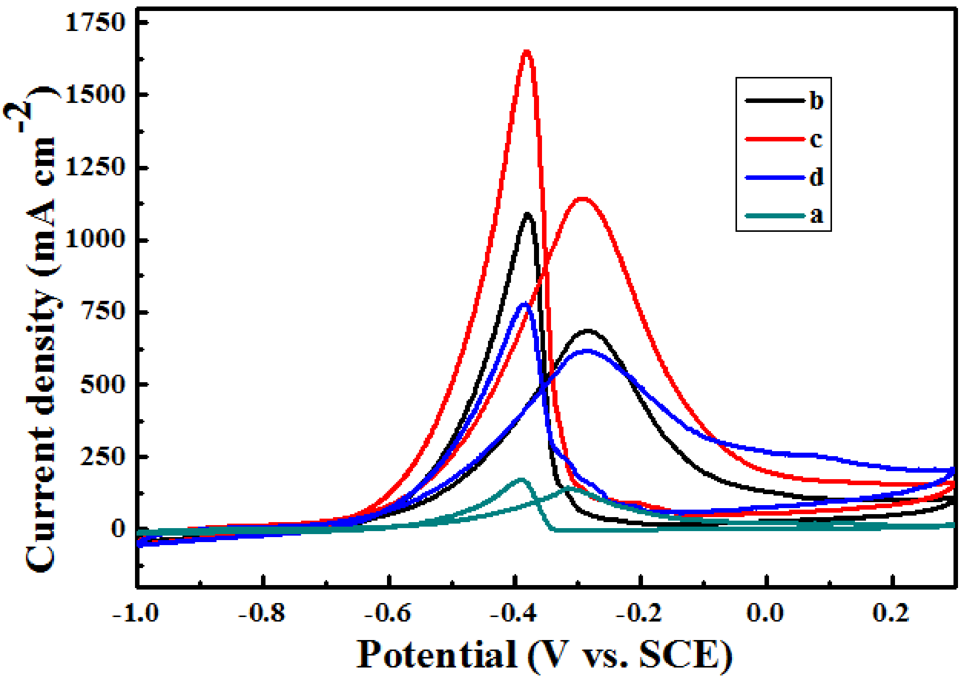

Figure 2. Cyclic voltammograms (CVs) measured on the PSC-treated PdO/G catalysts modified GC electrodes in 1M KOH +1M C_2H_5OH solution at 50 mV s^{-1}. The green, black, red and blue curves were recorded on the catalyst **a**, **b**, **c** and **d** modified GC electrode.

The cyclic voltammograms (CVs) of EOR on the synthetic GC electrodes, as displayed in Fig.2, were all recorded at the scan rate of 50 mV s^{-1} in a solution having 1 M KOH and 1M C_2H_5OH. Apparently, in above four kinds of CVs, one electro-oxidation peak positioned at ~-0.31V was observed in the positive direction potential sweep, and one electro-oxidation peak centered at ~-0.38 V, generally called abnormal oxidation peak, was displayed in the negative direction potential sweep. These results strongly proved that all fabricated PSC-treated PdO/G catalysts had electrocatalytic activities towards EOR. The shapes of above CV curves were very similar to those measured on the Pd-coated GC electrode [8]. The peak current and the onset potential are commonly thought as the most important parameters which can be used to evaluate the electrocatalytic activity of a new catalyst towards EOR. For the positive direction oxidation peaks, the peak currents were roughly measured as

150, 686, 1153 and 614 mA cm^{-2} for catalyst **a**, **b,** **c** and **d**, respectively. Thus, catalyst **c** delivered the largest peak current among all the prepared materials, indicating that catalyst **c** had the best electro-catalytic activity towards EOR among all prepared catalysts. And the onset potential for EOR on the catalyst **a** was about -0.50V, which was significantly larger than those of other catalysts (the onset potential of EOR on catalyst **b**, **c** and **d** was close to -0.66V). That is to say, EOR could proceed easier on the PSC-treated PdO/G catalyst when compared to that occurring on the untreated PdO/G catalyst. In other words, potential sweep cycle could be employed as a powerful tool to enhance the electrocatalytic activity of PdO/G catalyst for EOR.

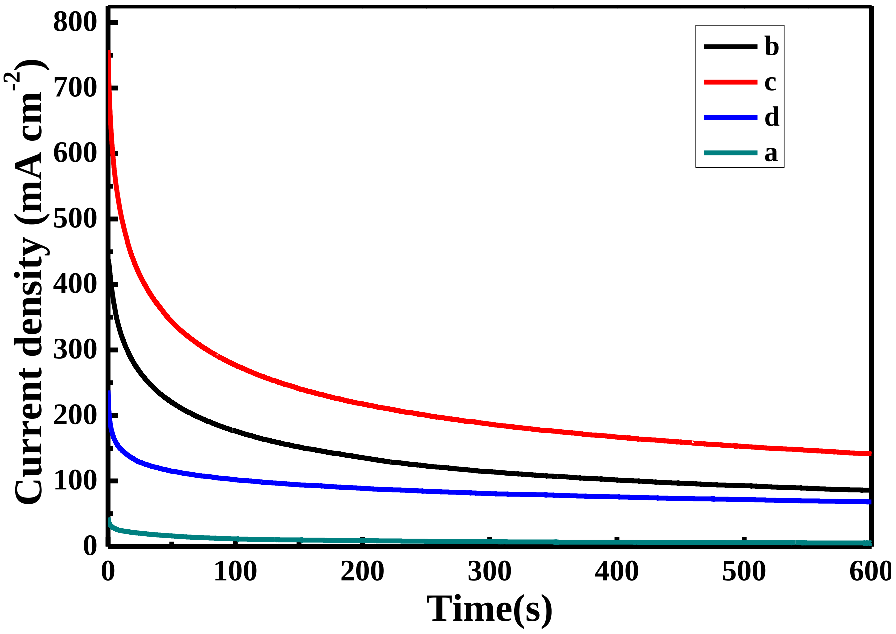

Figure 3. Chronoamperometry curves noted on the PSC-treated PdO/G catalysts modified GC electrodes in 1M KOH +1M C_2H_5OH at -0.24 V. The green, black, red and blue curves were measured on the catalyst **a**, **b**, **c** and **d**-modified GC electrodes.

The durability of an electrocatalyst in an electrocatalytic reaction is a key parameter which could directly determine the service life of an electrocatalyst in a practical fuel cell. To evaluate the durability of the prepared electrocatalysts, the technique of chronoamperometry was utilized and the results are shown in Fig.3. For all curves, the sharp drop of current density in the starting step was generally resulted from the electric double layer of the electrodes. And the relatively stable current density in the left period was from the direct electro-oxidation of ethanol [9]. Obviously, the catalyst **c** showed the largest current density in the total measuring period. For instance, the current densities were approximately evaluated to be 2.7, 86.5, 142.4 and 67.5 mA cm^{-2} at 600 s on the catalyst **a**, **b**, **c** and **d**, respectively. For the untreated catalyst **a**, almost no polarized current density was found when the testing time was up to 600 s. While, for other three PSC-treated samples, the polarized currents, that were from the electrooxidation of ethanol, could be observed in whole testing period. This result strongly indicated that PSC was a feasible method for enhancing the electrocatalytic activity of the system containing PdO and graphene.

3.3. Discussion of the electrocatalytic mechanism

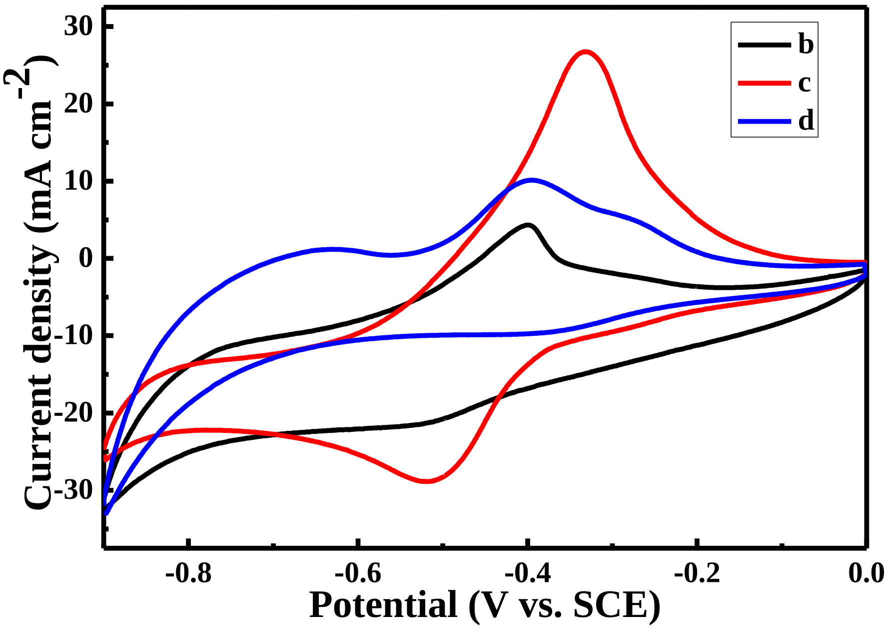

Figure 4. The last CV curves for all PSC-treated PdO/G modified GC electrodes, which were measured in 0.5M Na_2SO_4 + 10^{-3} M $PdCl_2$ at the scan rate of 10 mV s^{-1}. The black, red and blue curves corresponded to catalyst **b**, **c** and **d**.

Why did the catalyst **c**, which was treated by potential sweep for 50 cycles, exhibit the best electrocatalytic performance for EOR among all the samples? To uncover the possible reasons, the last CV curves of three PSC-treated PdO/G modified GC electrodes in 0.5 M Na_2SO_4 containing 10^{-3} M $PdCl_2$ are illustrated in Fig. 4. Evidently, for all catalysts, there is an oxidation peak in the positive direction potential sweep. Commonly, the oxidation peaks should correspond to an electrooxidation reaction, probably, ions of Pd^{2+} were formed via the following electrochemical reaction, i.e., $Pd-2e\rightarrow Pd^{2+}$. As for the electro-reduction reaction, only catalyst **c** (red curve) showed an evident reduction peak at around -0.5V. Generally speaking, the presence of the reduction peak was resulted from an electrochemical reduction reaction. In this case, probably, the following reduction reactions occurred, namely, $Pd^{2+}+2e\rightarrow Pd$, or $PdO+2e+H_2O\rightarrow Pd+2OH^-$ [9]. That is to say, the reduction peak should correspond to the formation of metallic Pd. While for catalyst **b** and **d**, almost no reduction peaks were displayed. The results of EDS analysis (data not shown) also revealed that the Pd atomic contents in catalyst **b**, **c** and **d** were about 6.4%, 14.2% and 5.1%, respectively. Therefore, it can be concluded that the components of the boiled PdO/G material were varied after the potential sweep cycling treatment. Commonly, the higher content of Pd in the final samples was favorable to the electrooxidation reaction of ethanol on Pd, since EOR could proceed well on the surface of metallic Pd [8].

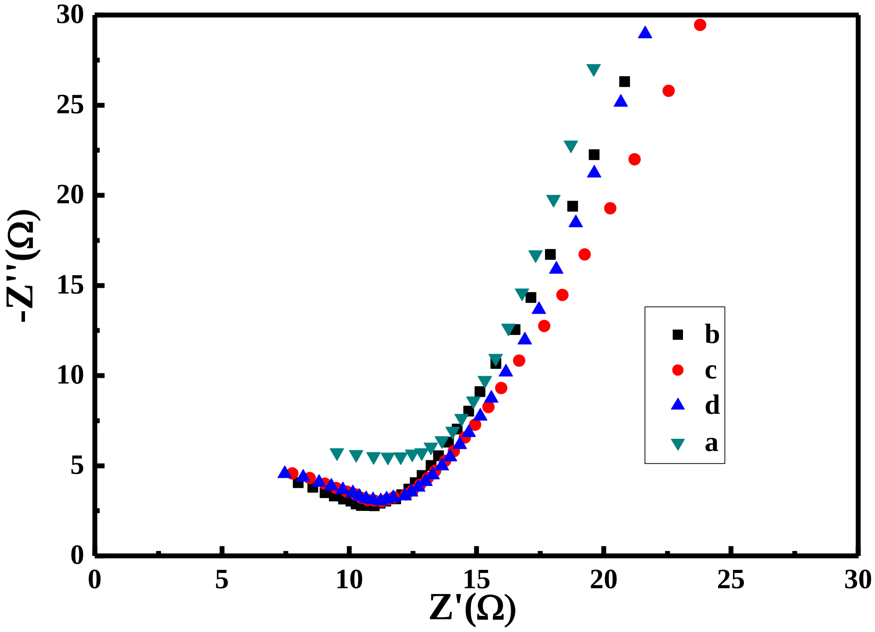

Figure 5. Nyquist plots for all PSC-treated PdO/G modified GC electrodes, which were measured in 1M KOH +1M C_2H_5OH under their open circuit potentials. The green, black, red and blue curves corresponded to catalyst **a**, **b**, **c** and **d**.

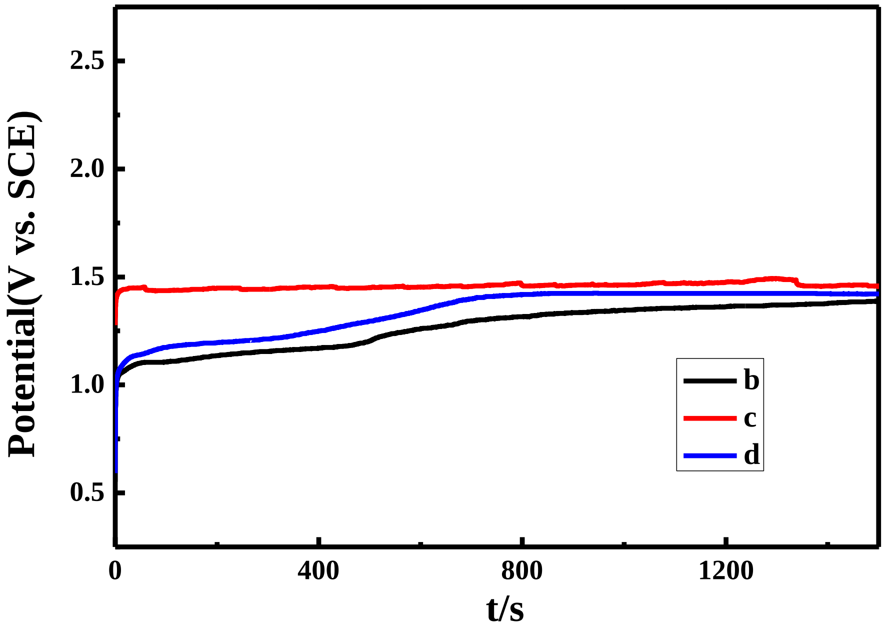

Figure 6. Chronopotentiometric curves of all PSC-treated PdO/G modified GC electrodes in 1M KOH +1M C_2H_5OH at 1.4 mA. Curve b, c and d corresponded to catalyst **b**, **c** and **d**.

Electrochemical impedance spectroscopy (EIS), due to its simple analysis and intuitiveness, has been widely used in the investigation field of electrochemical reaction. Nyquist plots, one typical kind of curves in EIS, are presented in Fig.5. Evidently, all Nyquist plots contained two parts, namely, depressed semicircles in the high frequency region and the inclined lines in the low frequency region.

According to the previous report [6], the presence of semicircle was due to the formation of a parallel circuit that contained a resistance element and a capacitance element. For an electrochemical reaction, commonly, the diameter of the semicircle approximately corresponded to the value of charge transfer resistance (R_{ct}). Thus, it is clear that after the PSC treatment, the value of R_{ct} decreased remarkably, yielding an increased kinetics of EOR. This result also suggested that potential sweep cycle could be used as a tool to enhance the electrocatalytic activity of the system having PdO and graphene.

The chronopotentiometric (CP) curves for all PSC-treated PdO/G modified GC electrodes at a constant current of 1.4 mA are given in Fig.6. On the basis of the electrochemical theory, the electrode potential will enhance when being applied by a positive current [10]. Really, for all three electrodes, the electrode potentials increased with applying time. For the catalyst **c** modified GC electrode (red curve), its electrode potential promptly was increased to be about 1.45V. And then, this potential value was maintained in the whole testing period. While, for catalyst **b** and **d** modified GC electrodes, it almost took 1000 s for these two electrodes to reach a relatively stable electrode potential. This result demonstrated that compared to other two catalysts modified GC electrode, catalyst **c** modified GC electrode was easier to be polarized by the applied current. Or in other words, the over-potential of EOR on the catalyst **c** modified GC electrode was rather lower than that of catalyst **b** and catalyst **d** modified GC electrodes. This consequence was consistent with the result shown in Fig. 2. Additionally, in the total measuring time, the electrode potential of electrode **c** was the highest value among the three electrodes. For example, at the testing time of 1500 s, the electrode potentials for electrode **b**, **c** and **d** were reckoned as 1.38V, 1.46V and 1.42V, respectively. According to the Nernst equation [11], the electrode with a higher electrode potential was advantageous to an electro-oxidation reaction. As a result, the best electrocatalytic performance was displayed by catalyst **c**, compared to catalyst **b** and **d**.

4. CONCLUSION

For the first time, potential sweep cycle was employed as a tool to adjust the electrocatalytic activity of PdO/G towards EOR, and the result indicated that 50 cycle-treated PdO/G catalyst showed the best electrocatalytic ability for EOR among all prepared catalysts. Results of TEM images demonstrated that the potential sweep cycle number remarkably influenced the particle sizes of prepared samples, and the 50 cycle-treated PdO/G materials had the smallest particle size among all prepared samples. The electrocatalytic activities of the PSC-treated PdO/G catalysts towards EOR were majorly examined by CV and CA, and the results indicated that catalyst **c** showed the best electrocatalytic activity for EOR. It was thought that in an electrolyte that contained ions of Pd^{2+}, potential sweep cycle number could alter the composition of the PdO/G material, thus, affecting the electrocatalysis of the resultant PdO/G towards EOR. Also, it was found from the chronopotentiometric curves that the electrode potential was increased when being applied by an anodic current, and catalyst **c** showed the highest electrode potential among the selected three PSC-treated PdO/G electrodes. Showing the fact that the potential sweep cycle could be employed as a tool to enhance the electrocatalytic activity of PdO/G material for EOR was the main contribution of this work. And also, the work described in this short communication is expected to be used as a new method to enhance the property of electrocatalysts that contained metal oxides and carbon support.

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