

Zirconia Modified Pd Electrocatalysts for DFAFCs

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Abstract

In order to enhance the Pd based anodic catalysts for direct formic acid fuel cells (DFAFCs), the research work includes increasing catalyst activity and preventing CO poison. In this study, various zirconium oxides-modified multi-walled carbon nanotubes (MWCNTs) were prepared as the supports of Pd catalysts for DFAFCs by adjusting the preparation parameters: metal adding, sintering temperature and atmospheres. The prepared pure zirconia has both monoclinic and tetragonal phases. The addition of MWCNTs depresses the growth of monoclinic phase. A small amount of Pd adding allows both monoclinic and tetragonal zirconia structures to appear again. Pd nanoparticles of 20 wt% synthesized on MWCNTs and tetragonal ZrO₂/MWCNTs have similar particle size, while Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] have more nanoparticles aggregation. The electrochemical surface area can be improved by adding zirconia which implies those zirconia modified Pd catalysts better electrocatalytic performance. By analyzing the maximum current density and the corresponding potential, Pd/AO-MWCNTs are inferred to undergo the formic acid direct oxidation initially. The Pd catalysts modified by tetragonal ZrO₂ have higher current density. Those having both tetragonal and monoclinic ZrO₂ modified Pd catalysts have lower potential of formic acid oxidation. All the Pd based catalysts with zirconia modification possess better CO resist ability and electrocatalytic activity.

Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar] and

Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] which catalyze formic acid in direct oxidation path are the two best catalysts.

Keywords

DFAFCs, Dual Path, Zirconia, Pd, MWCNTs

1. Introduction

For the topic of clean and renewable energy, fuel cell is an expectable choice: no noise, no charge need, and not depending on weather. People research different types of fuel cells for transportation, stationary power and small electric devices. The basic physical structure of fuel cell consists of an electrolyte layer in contact with an anode (negative electrode) and a cathode (positive electrode). The fuel is fed to anode and oxidized, and oxygen is fed to cathode and reduced. Depending on the electrolyte, fuel cells can be divided into: alkaline fuel cells (AFCs), proton exchange membrane fuel cells (PEMFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs). Direct methanol fuel cells (DMFCs) have high volumetric energy density ($4900 \text{ Wh}\cdot\text{L}^{-1}$) but high fuel crossover through Nafion® membrane. Methanol has the well-known inherent toxicity at vapor phase. Formic acid is nontoxic, nonflammable, with high theoretical open circuit voltage (OCV) at room temperature (25°C), and low fuel crossover through PEM due to the electrostatic repulsion between HCOO^- of formic acid and SO_3^- ions of the membrane. Although direct formic acid fuel cells (DFAFCs) have the lower volumetric energy density ($2104 \text{ Wh}\cdot\text{L}^{-1}$) than DMFCs, it can be overcome via using higher formic acid concentration [1] [2] [3] [4]. It had been studied that the oxidation of formic acid had two reaction pathways at the anode: the direct dehydrogenation and the indirect dehydration in 0.25 - 0.4 V and 0.5 - 0.6 V, respectively [2] [3]. The direct dehydrogenation pathway directly converts formic acid into carbon dioxide (CO_2). The indirect dehydration pathway has partial oxidation of formic acid to form CO intermediate adsorbing on the catalysts surface. The adsorbed CO may poison the catalyst or conduct further oxidation to CO_2 .

The anodic catalyst research work is to increase the formic acid oxidation current, which may promise the higher electric power, and to prevent Pd poisoned by CO. Many literatures show that Pd performance can be enhanced by depositing on carbon nanotubes (CNTs) for the well dispersion and CNTs as good chemical promoter [5] [6] [7] [8] [9]. Some studies prepared graphite and carbon nanotubes as expanded surface to deposit Pd [7], developed a shorter-time process to oxidize MWCNTs as the support which increased Pd activity [8], or prepared CNT supported Pd with various metals: Co, V, Mn and Zn by using NaBH_4 reduction method [9]. Our group had investigated different modifications to enhance the catalyst performance, such as coating CNTs with conductive polymer to enhance the electro conductance [10] or metal oxide for CO resistance [11] [12] [13] [14]. For transition metal oxide modification, our works include tungsten oxide which has hydrogen spillover effect [12], cerium oxide with metal doping which decrease the CO oxidation temperature and enhance the Pd performance [13], and nitrogen doped titanium oxide which improved the electric conductivity [14]. So the electrocatalytic performance is improved by the modifications.

Zirconia has several advantages such as excellent thermal stability, nontoxicity, and low cost. Zirconia is known to have three low-pressure structural phases:

monoclinic (<1440°C), tetragonal (1440°C - 2640°C) and cubic (>2640°C) [15] [16] [17]. Tetragonal zirconia is promised to have better oxygen supporting ability under high temperature. Lesiak *et al.* studied ZrO₂ modified MWCNTs as the supports of AuPd catalysts for DFAFCs [18]. They found that ZrO₂ adding can enhance the catalyst activity while the AuPd solid solution contributes the stability. Zirconia in monoclinic phase may be oxygen deficient [19]. As CO adsorbing, CO and zirconia can form a linear structure [20]. This study is to develop optimal prepared zirconia to modify CNTs supports and find the effect for Pd electrocatalytical performance.

2. Experiment Procedures

2.1. Sample Preparation

The supporters were prepared as following. The pristine multiwalled carbon nanotubes (MWCNTs, Yong-Zhen Techno material CO., LTD, China. Purity 98% - 99%) were first acidized by nitric acid to remove the impurity and to form some functional group to benefit the nanoparticles deposition. Then 20 wt% zirconia were synthesized on the acid oxidized MWCNTs (AO-MWCNTs) via solgel method and followed by different sinter atmosphere (air or Ar) and temperature (700°C or 900°C). Some zirconia was added by 1 wt% Pd to change the structure of zirconia.

Pd electrocatalysts were deposited on the prepared supporters via x-ray photosynthesis about 8 minutes. The X-ray irradiation experiments were performed at the beamline 01A in National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The parameters of storage ring were 1.5 GeV and 200 mA. Un-monochromatic “white” X-ray beam was utilized throughout the exposure. After the Pd based products centrifuged and dried at 85°C, the nanoparticles were sintered in 5 mol% H₂/Ar at 200°C for 1 hour. Finally, Pd/AO-MWCNTs, Pd/ZrO₂/AO-MWCNTs, and Pd/(Pd:ZrO₂/AO-MWCNTs) were obtained in the process above.

2.2. Characterization and Electrocatalytical Performance

The structure and morphology of the prepared samples were determined by XRD, FESEM and TEM. The metal contents of the samples were confirmed by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin Elmer Optima-2000 DV). Electrochemical activities of catalysts were characterized by cyclic voltammetry (C-V) measurement by adopting a three-electrode system and CHI Instrument Model 6081C potentiostat/galvanostat instrument. Three-electrode cell system is composed by a working electrode (SE100-Carbon Single Electrode SPE, Zensor R&D Co., Ltd., working diameter 0.5 cm, area 0.196 cm²), a Pt net counter electrode and a Ag/AgCl reference electrode. The measured current was normalized by the Pd weight loaded on the working electrode. During each C-V experiment, the dissolved gas, oxygen, CO or CO₂, was removed from the solution by purging Ar before and during the experiment. In order to observe the resistance of CO, the prepared Pd catalysts working elec-

trode were purged by CO gas for 5 minutes at a flow rate of 10 ml/min, and then kept in CO atmosphere for 30 minutes. The procedure served enough CO to poison Pd/AO-MWCNTs. The poisoned working electrodes were then conducted the CV test.

3. Results and Discussion

The results of characterization and electrocatalytic performance of the prepared Pd based catalysts are discussed below. In **Figure 1**, the structure of the prepared different zirconia can be first compared in (a). The zirconia has both tetragonal and monoclinic phases as treated under Ar at 700°C. As the heat treatment temperature increase, tetragonal phase can be depressed and there only exists monoclinic zirconia. However, as carbon nanotubes adding, zirconia only has tetragonal phase. As 1 wt% Pd adding in the ZrO₂/MWCNTs process, the second pattern in (b), there are both monoclinic and tetragonal zirconia phases. The synthesis of 20 wt% Pd on the Pd:ZrO₂/MWCNTs supporter, the first pattern in (b), causes less monoclinic zirconia with tetragonal phase. Even Pd:ZrO₂/MWCNTs supporter after high temperature treatment, monoclinic zirconia on MWCNTs is unstable during the Pd synthesis process. The 20 wt% Pd on the tetragonal zirconia modified MWCNTs supporters, the lower three patterns in (b), doesn't change zirconia structure. The prepared Pd catalysts on different supporters, MWCNTs, three tetragonal zirconia/MWCNTs in different heat treatment conditions, and Pd:ZrO₂/MWCNTs with tetragonal and monoclinic zirconia phases, will be studied below.

Figure 2 shows the FESEM morphology of the prepared Pd catalysts. AO-MWCNTs has average diameter about 17 nm which can be kept constant as Pd or ZrO₂ synthesized on the surface. The images of (b) to (f) show Pd synthesized on different supporters. Grey and black particles can be observed dispersing on the carbon nanotubes surface and recognized as ZrO₂ and Pd nanoparticles, respectively. For Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] in (f), more aggregation is observed. As the morphology observing in high resolution TEM

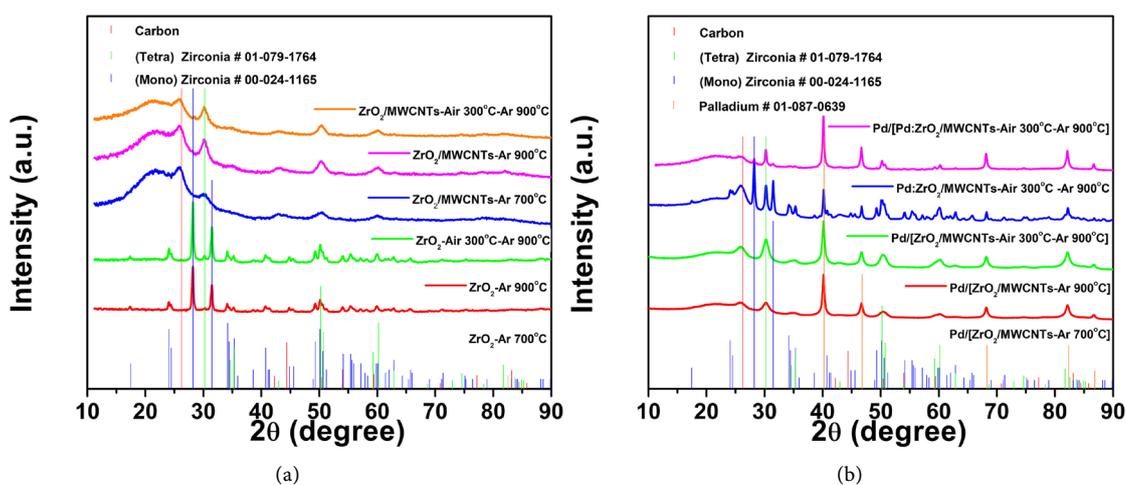


Figure 1. XRD patterns of (a) the prepared zirconia, (b) the prepared Pd catalysts.

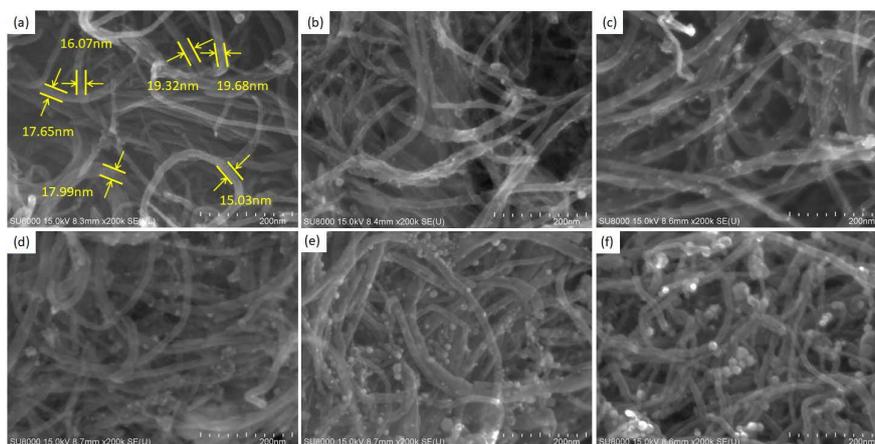


Figure 2. FESEM images of (a) AO-MWCNTs, (b) Pd/AO-MWCNTs, (c) Pd/[ZrO₂/AO-MWCNTs-700Ar], (d) Pd/[ZrO₂/AO-MWCNTs-900Ar], (e) Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar], (f) Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar].

and analyzing the particle size distribution, all the Pd based nanocomposites look similar. **Figure 3**, the TEM image and particle size distribution of Pd/[ZrO₂/AO-MWCNTs-Air300-Ar900], is a typical image. The smaller grey particles as zirconium oxide and the larger black ones as Pd metal can be recognized. The particle size distribution shows two peaks as smaller zirconia (~3 nm) and larger Pd (~8 nm). As recalling the XRD patterns and estimating the particle size via Sherrer's formula, the results are ZrO₂ as 6.8 nm, Pd as 14.3, 17.6, 19.0, 15.3 and 27.6 nm for Pd/AO-MWCNTs, Pd/[ZrO₂/AO-MWCNTs-700Ar], Pd/[ZrO₂/AO-MWCNTs-900Ar], Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar], and Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar], respectively. The trend is consistent to the observation of microscope. Though the nanoparticle size in TEM seems similar in nano scale, Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] may have more nanoparticles combination.

For the electrocatalytical performance, the catalysts were prepared as a working electrode, and conducted the CV test in sulfuric acid to measure the electrochemical surface area (ECSA) of the Pd catalysts as shown the results in **Figure 4(a)**. Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] (45.2 m²/gPd) which has both monoclinic and tetragonal phases, has a little improved ECSA value from Pd/AO-MWCNTs (43.6 m²/gPd). The larger Pd particle size can decrease the specific surface area, but zirconia modification may compensate via preventing Pd poisoned. The three Pd/[ZrO₂/AO-MWCNTs]'s with tetragonal zirconia modified Pd catalysts have enhanced the hydrogen adsorption ability more. Their ECSA values are 61.9, 64.4 and 58.1 m²/gPd for Pd/[ZrO₂/AO-MWCNTs-700Ar], Pd/[ZrO₂/AO-MWCNTs-900Ar], and Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar], respectively. The adding of zirconia does enhance the acid adsorption ability of Pd.

Figures 4(b)-(f) show the CV results of the prepared catalysts oxidizing formic acid in various cycles. Pd/AO-MWCNTs in (b) initially has a big peak at 0.4 V and a minor peak at 0.75 V for direct and indirect formic acid oxidation.

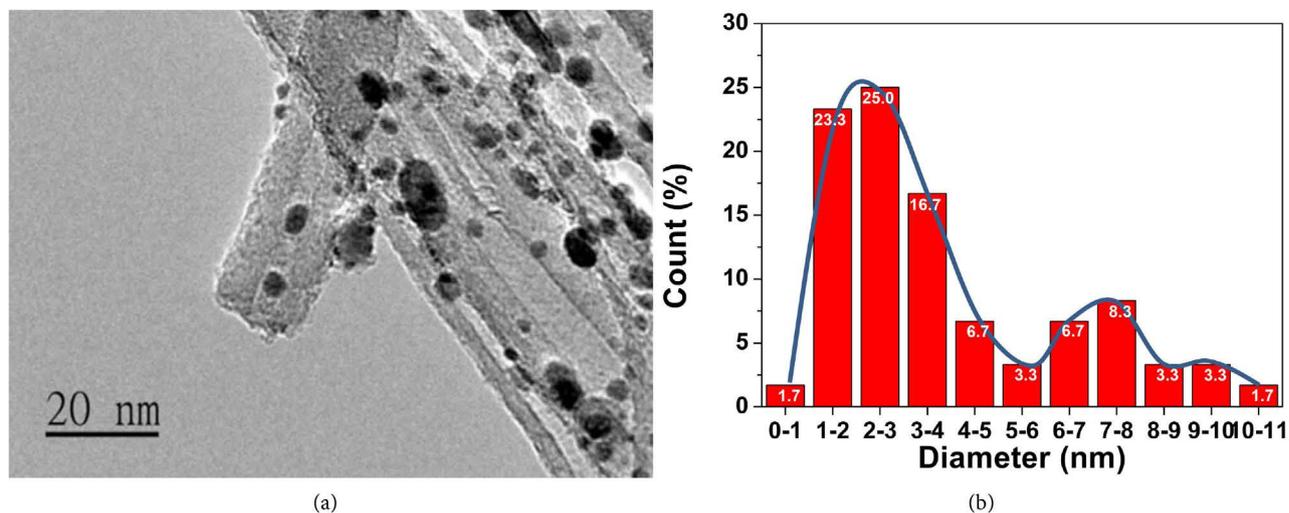
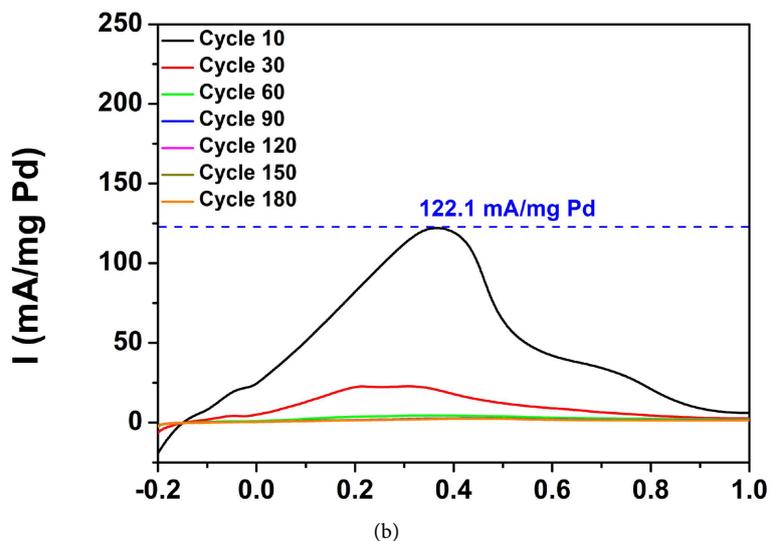
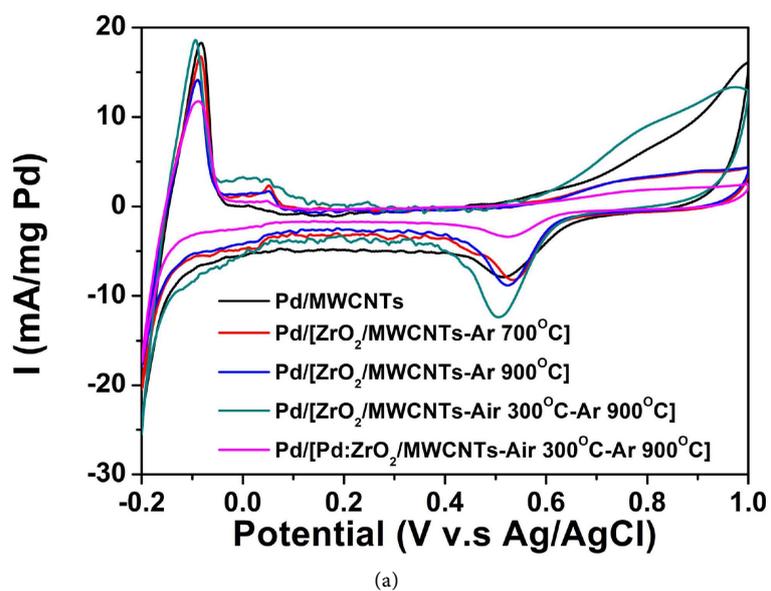
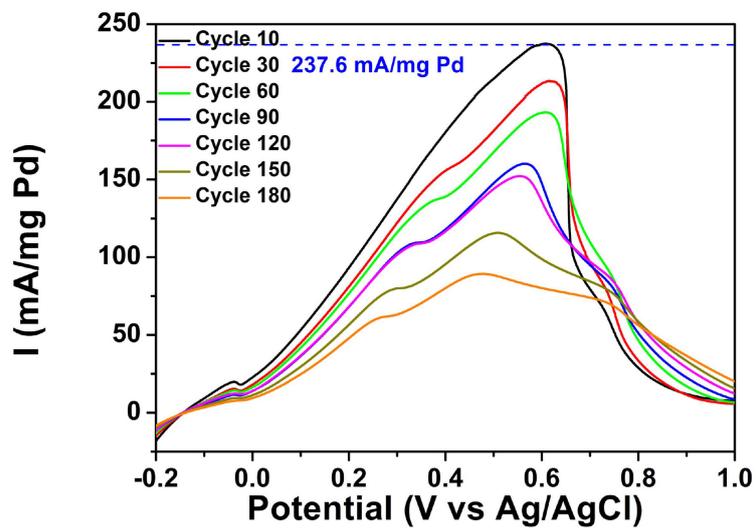
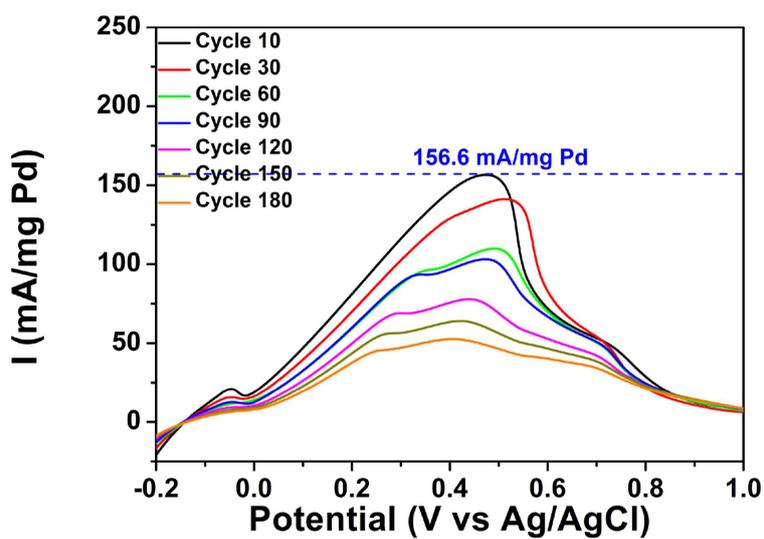


Figure 3. TEM image and particle size distribution of Pd/[ZrO₂/AO-MWCNTs-Air300-Ar900].

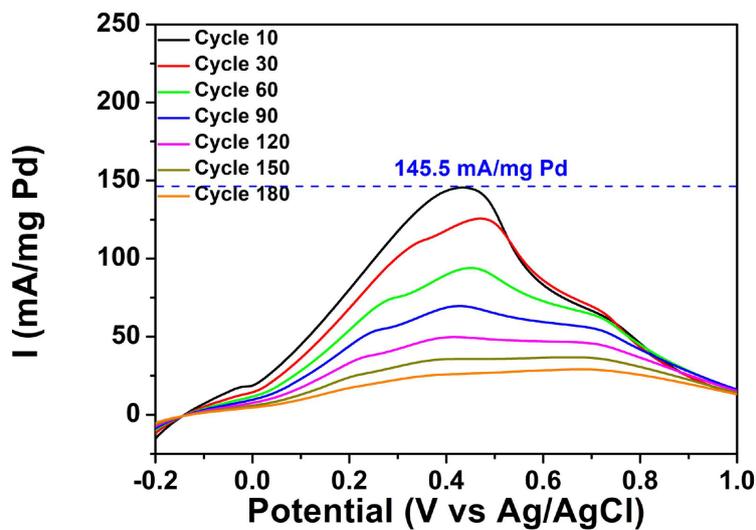




(c)



(d)



(e)

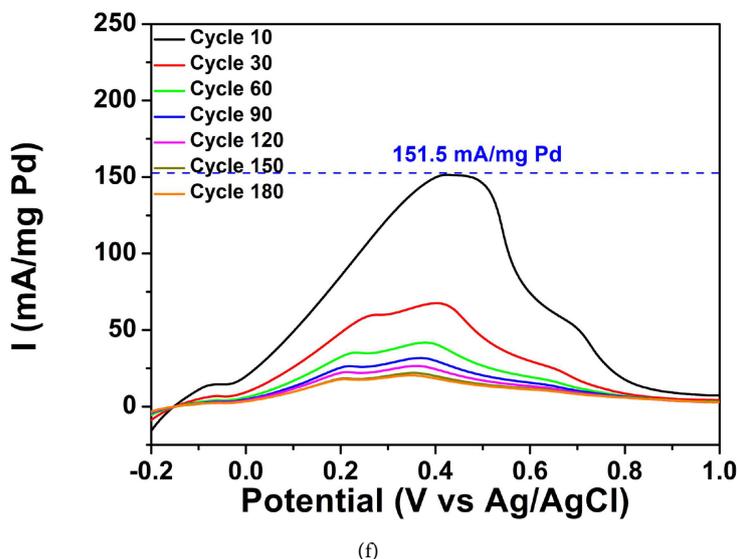
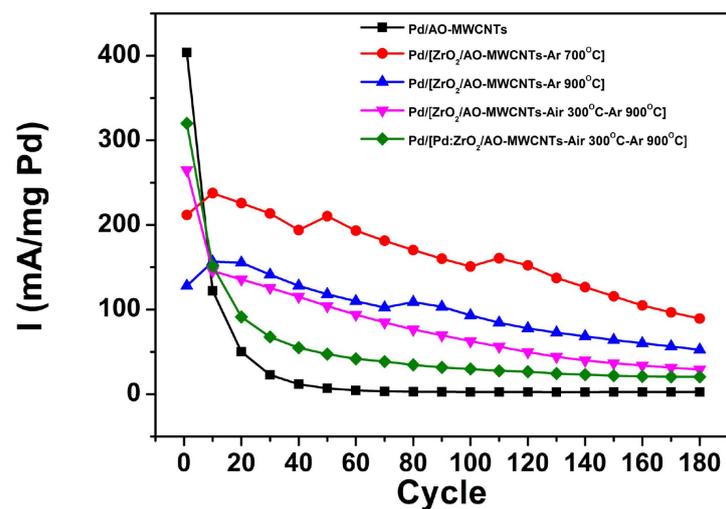


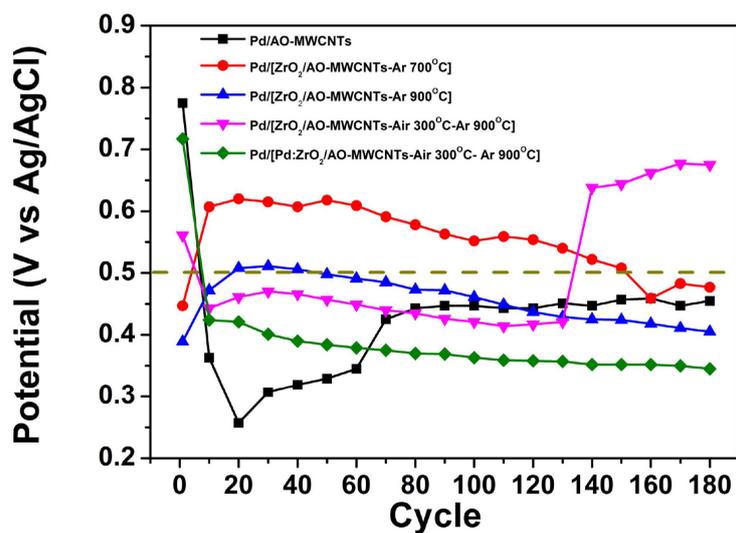
Figure 4. (a) ECSA plots of Pd catalysts in 1M H₂SO₄, and CV plots of (b) Pd/AO-MWCNTs, (c) Pd/[ZrO₂/AO-MWCNTs-700Ar], (d) Pd/[ZrO₂/AO-MWCNTs-900Ar], (e) Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar], (f) Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] in 3M HCOOH and 1M H₂SO₄. Scan rate 10 mV/s.

The activity decays fast. As AO-MWCNTs modified by zirconia, no matter what the preparing parameters are, the activity and stability of formic acid oxidized by the Pd based electrocatalysts are improved. Pd/[ZrO₂/AO-MWCNTs-700Ar] in (c) has high current density even after 180 cycles. For Pd/[ZrO₂/AO-MWCNTs-900Ar] and Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar], in (d) and (e), the latter has lower oxidation potential. In (f), Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] initially has good current density, but it decays fast.

In order to analyze the behavior of the Pd catalysts in CV test, the maximum current density and the corresponding potential of every 10 cycles were replotted in **Figure 5(a)** and **Figure 5(b)**, respectively. The (a) plot shows the three tetragonal zirconia modified Pd catalysts (red, blue and pink) have the best current density than the others. It is similar to the ECSA results. In (b), Pd/AO-MWCNTs has low potentials 0.3 V in the first 60 cycles, then it changes to higher potential about 0.45 V. It shows Pd/AO-MWCNT conducts a formic acid direct oxidation initially. Pd/[ZrO₂/AO-MWCNTs-700Ar] and Pd/[ZrO₂/AO-MWCNTs-900Ar] have higher but stable corresponding potential about 0.6 V and 0.5 V. Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar] has corresponding potential about 0.45 V before 130 cycles then high potential about 0.7 V. The higher temperature treatment of zirconia may decrease the oxidation potential of formic acid. For the tetragonal zirconia modified Pd catalysts, their relative higher corresponding potential indicates formic acid undergoing an indirect path. The produced CO intermediate in the indirect path may be oxidized by tetragonal zirconia. It promises the slower decay in current density of the Pd catalysts. The green curve



(a)

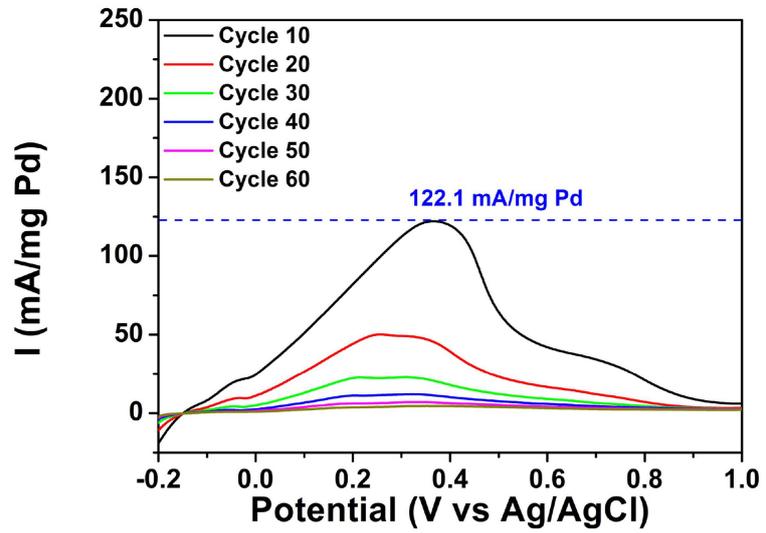


(b)

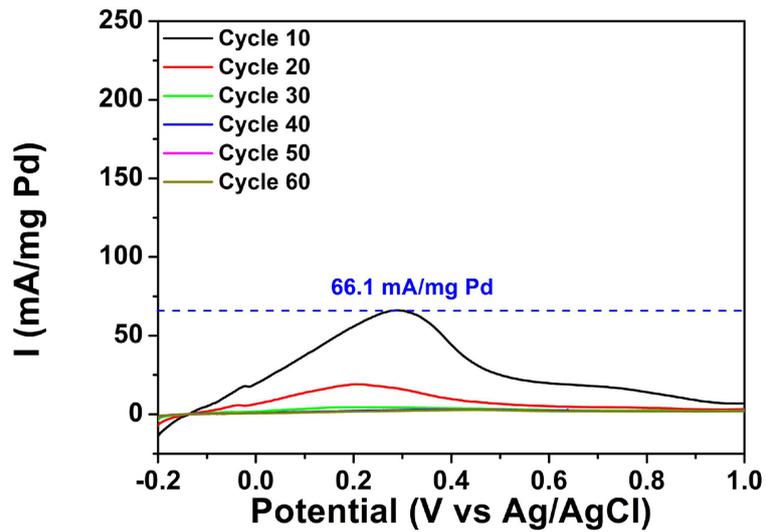
Figure 5. CV analysis: (a) the maximum current density vs cycle, (b) the corresponding potential vs cycle.

of Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar], with monoclinic and tetragonal zirconia modification, can be recognized as Pd direct oxidation behavior for the potential about 0.35 V. While the aggregation of Pd nanoparticles offsets most zirconia effect in CV test.

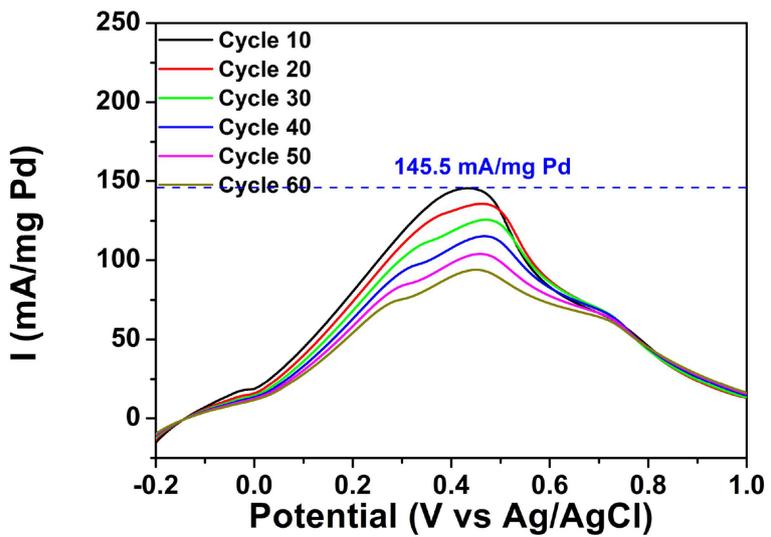
The two Pd catalysts, Pd/AO-MWCNTs and Pd/[ZrO₂/AO-MWCNTs(C)-300Air-900Ar], were compared their 60-cycle CV performance of not poisoned and CO poisoned. In **Figure 6**, the poisoned Pd/AO-MWCNTs catalyst (b) decays faster than not poisoned (a). For Pd/[ZrO₂/AO-MWCNTs(C)-300Air-900Ar] in (c) and (d), the 10th cycle maximum current densities are 145.5 mA/mgPd (not poisoned) > 82.4 mA/mgPd (CO poisoned). While for the poisoned Pd/[ZrO₂/AO-MWCNTs(C)-300Air-900Ar], the maximum current density of the 30th and 40th cycles are larger than 150



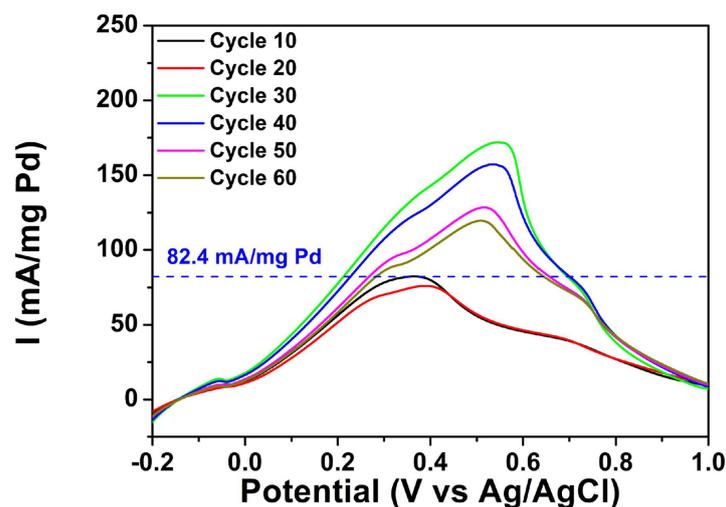
(a)



(b)



(c)



(d)

Figure 6. 60-cycle CV results of (a) Pd/AO-MWCNTs, (b) CO poisoned Pd/AO-MWCNTs, (c) Pd/[ZrO₂/AO-MWCNTs(C)-300Air-900Ar], and (d) CO poisoned Pd/[ZrO₂/AO-MWCNTs(C)-300Air-900Ar].

mA/mgPd. The Pd/[ZrO₂/AO-MWCNTs(C)-300Air-900Ar] seems to be activated by CO reduction and the potential shift to higher voltage. As more cycles, the catalyst still decay due to CO poison. The result reveals the addition of ZrO₂ can improve the resistance of CO poison.

Figure 7 shows the current-time (I-t) behavior of the Pd catalysts in formic acid and sulfuric acid under constant potential of 0.3 V.

Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar] and

Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] are the two best. The two catalysts have the relatively lower and stable corresponding potential in CV indicating direct dehydrogenation path of formic acid. If the catalysts undergo a direct oxidation of formic acid, it will be more stable. Though

Pd/[ZrO₂/AO-MWCNTs-700Ar] and Pd/[ZrO₂/AO-MWCNTs-900Ar] have tetragonal zirconia to prevent CO poison, their higher potential formic acid oxidation may not benefit this 0.3 V I-t test.

4. Conclusion

This study prepared different ZrO₂ by adjusting preparation parameters: carbon nanotubes, 1% Pd adding, sintering temperature and atmospheres. The prepared zirconias are: pure ZrO₂ (tetragonal + monoclinic), ZrO₂/AO-MWCNTs (tetragonal) and Pd:ZrO₂/AO-MWCNTs (tetragonal + monoclinic). The synthesized Pd has more aggregation on the surfaces of Pd:ZrO₂/AO-MWCNTs. The effect of different zirconia for Pd electrocatalytic performance is studied via the CV tests. Tetragonal zirconia modified Pd/ZrO₂/AO-MWCNTs have larger ECSA area values than those others. The more electrochemical active surface may promise better performance in electrocatalytic performance. Through the analysis of maximum current density and the corresponding potential of the

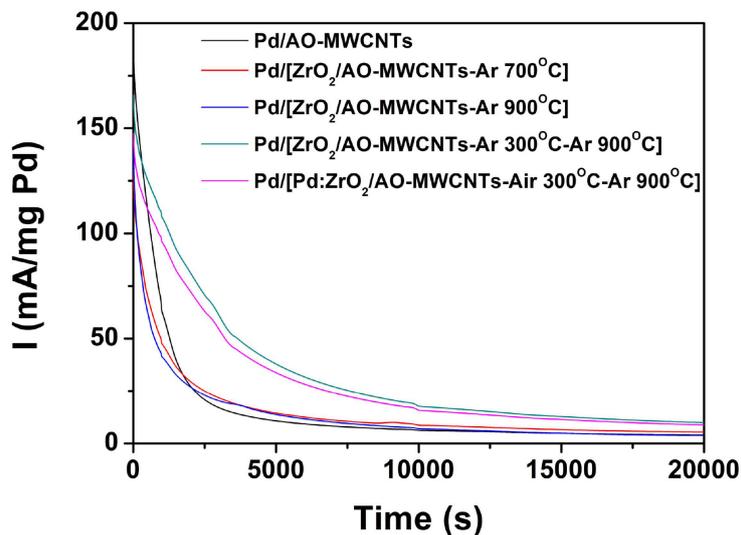


Figure 7. Chronoamperometric measurements (I-t) of the prepared catalysts in 3M HCOOH and 1M H₂SO₄, 0.3 V.

prepared Pd catalysts catalyzed formic acid, Pd/AO-MWCNTs undergo the direct oxidation (lower potential) initially and change to indirect path for CO poisoning Pd. For those three Pd catalysts modified by tetragonal ZrO₂, they have higher current density and higher oxidation potential. It reveals that though the catalysts oxidize formic acid in the indirect path, tetragonal zirconia may release oxygen easier to benefit the CO oxidation and enhance the Pd activity. For Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] with tetragonal and monoclinic ZrO₂ modified, monoclinic ZrO₂ may keep more CO than Pd does, and the oxygen deficient monoclinic ZrO₂ may have pseudo metal behavior that helps Pd obtains electron supply as Pd catalyzes formic acid. These cause the lower potential for monoclinic zirconia modified Pd catalysts. In constant potential 0.3 V I-t test, Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar] and Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] are the two best catalysts. The former, Pd/[ZrO₂/AO-MWCNTs-300Air-900Ar] with tetragonal zirconia, and the latter, Pd/[Pd:ZrO₂/AO-MWCNTs-300Air-900Ar] with monoclinic zirconia, both directly oxidize formic acid in a lower potential. The two prepared Pd catalysts can be candidates for anodic catalysts in DFAFCs.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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