



# Ethanol electrooxidation on Pd/C nanoparticles in alkaline media

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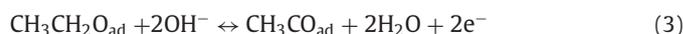
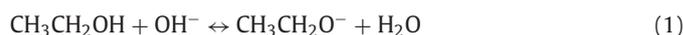
## ABSTRACT

Carbon-supported Pd nanoparticles were prepared by microwave heating-glycol reduction method, and characterized by a wide array of experimental techniques including X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM). The electrooxidation behaviors of ethanol on the Pd/C electrode in alkaline media were investigated using cyclic voltammetry (CV), chronoamperometry (CA), electrochemical impedance spectroscopy (EIS) and single cell performance methods. Pd/C electrode for ethanol oxidation showed high electro-catalytic activity and long term stability. However, it is observed that the current density decreases with the increasing of the potential and negative impedance presents in the potential from  $-0.1$  to  $0.1$  V. The decreasing current density and the negative impedance could be due to the adsorbed intermediates species that inhibited the further oxidation of ethanol. Based on the chemical reaction analysis and EIS spectra, equivalent circuits relating to various potential zones have been obtained. These results reveal the dynamic adsorption of intermediates species on Pd surfaces. Significantly, it is clarified that the adsorption behavior begins from the maximum catalysis of electro-catalysis and ends in the formation of the palladium (II) oxide layer on the electrode surface.

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## 1. Introduction

The direct alcohol fuel cell (DAFC) is considered as a promising technology for transportation and portable electronic devices [1], and a lot of progress has been made [2]. However, its performance is still limited by the poor kinetics of the anode reaction. Pt and Pt-based catalysts have been extensively investigated as the electro-catalysts for oxidation of methanol and ethanol [3–7]. However, the high price and limited supply of Pt constitute a major barrier to the development of DAFCs. Pd is a suitable low-cost transition metal, about 50 times more abundant in earth than Pt and possesses high catalytic activity towards methanol and ethanol oxidation in alkaline media [8]. Recently, Pd-based catalysts including Pd-oxide composite catalysts [9] and Pd-based binary [10–13] and ternary catalysts [14] have been investigated. For example, Pd-Co (8:1)/C catalyst synthesized by Shen et al. [12] exhibited higher electro-catalytic activity and better stability for formic acid oxidation than those of Pd/C catalyst. It was also found that the ball-milled CNTs-supported Pd-Co (8:1) catalyst was synthesized with better catalytic activity. However, the mechanism study on the ethanol electro-oxidation reaction on Pd is still quite limited, especially for nanoparticle Pd catalysts. The C<sub>2</sub> mechanism for ethanol oxidation on Pd/C in alkaline media was proposed by Liang [15] and the ethanol oxidation went through the following steps:



It has been confirmed that acetate is the main product of ethanol electro-oxidation on Pd. The ethanol electro-oxidation is believed to be an incomplete and complex multi-step reaction [16]. The active intermediate such as  $\text{CH}_3\text{CH}_2\text{O}_{\text{ad}}$ ,  $\text{CH}_3\text{CO}_{\text{ad}}$  would block the Pd/C electrode surface and lead to poison [17].

Our literature review reveals that although Pd catalysts can be alternatives to Pt catalysts for the electro-oxidation reaction in alkaline media, the catalytic activity and stability of Pd/C catalyst needs to be improved for better performance. It is essential to gain a better understanding of the adsorption behaviors and oxidation mechanisms of ethanol on the Pd catalyst in alkaline media. EIS is a powerful electrochemical technique to analyze heterogeneous electrode kinetics. Its ability to unravel complex reactive steps involving adsorbed species in different frequency domains provides advantages for getting kinetics information [18]. To develop a better anode electro-catalyst, attempts utilizing EIS to study anodic oxidation process were reported [19–21]. For example, the impedance data largely support the findings that methanol oxidation on Pt/C involves both adsorbed CO and

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adsorbed OH species [21]. The objective of this work was to study the adsorption behaviors on Pd/C catalyst using the EIS method. Based on the above chemical reactions and complex impedance spectra, individual equivalent circuits relating to various potential zones which can be highly fitted with the EIS spectra have been obtained. Nyquist plots in EIS present negative differential resistance in the second quadrant for intermediate potential zones. The phenomenon of negative differential resistance has been found in the past [22–28]. For example, Grauel et al. [23] found that in the region between  $-1.1$  and  $-1.2$  V the cyclic voltammogram displays a negative differential resistance. Mukoyama et al. [24] found that the  $\text{H}_2\text{O}_2$  reduction on Pt has two-type negative differential resistance. One arises from a decrease in the coverage of adsorbed OH with a negative potential shift, and the other arises from suppression of the  $\text{H}_2\text{O}_2$  reduction by formation of under-potential deposited hydrogen in further negative potentials. Negative resistance behaviors were also observed in the electrooxidation of methanol and formic acid on Pt and other Pt-based alloy electrodes, and were usually attributed to the adsorption of reaction intermediates on the catalyst surface [21,29–31].

## 2. Experimental

### 2.1. Synthesis of Pd/C catalyst

A carbon black (C) from Cabot (Vulcan XC72) was used as carbon support, and the palladium precursor used was  $\text{PdCl}_2 \cdot x\text{H}_2\text{O}$  (59.75% of Pd). Pd/C catalyst was synthesized by the microwave heating-glycol reduction method. Firstly, 2.5 mL  $\text{PdCl}_2 \cdot x\text{H}_2\text{O}$  (0.05 mol/L) was placed in a 100 mL reactor containing 50 mL glycol (China, 99.9%), 2 mL KOH solution (1.0 mol/L), and 0.24 g Vulcan XC-72 carbon powder (Cabot Corp. USA). Then, the reaction mixture was changed into carbon paste by ultrasonic concussion and moderately heated in a microwave oven (900 W, 2.45 GHz, Galanz, WD900ASL23-2, China) with a heating procedure of 120 s on 15 min pause, 60 s on 10 min pause, and 30 s, and so on. The reaction product was filtered and washed extensively with water and ethanol for three times. Finally, the product was dried at 333 K in an oven for 12 h.

### 2.2. Material characterization

The catalyst was investigated using X-ray diffraction spectroscopy, operated generated by the  $2\theta$  scan with the scanning rate of  $8^\circ/\text{min}$  and the angular resolution of  $10^\circ$ – $80^\circ$ . TEM analyses were conducted on a JEOL-1230 apparatus operated at 200 kV to observe the morphology and crystal size of the catalyst.

### 2.3. Electrochemical measurements

All the tests were conducted on a CHI 760D (Chen Hua, Shanghai, China) electrochemistry station in a three-electrode cell at room temperature. The prepared Pd/C electrode was used as a working electrode, while an Hg/HgO in 1.0 mol/L KOH and a platinum foil electrode were acted as a reference electrode and a counter electrode, respectively. CV was performed in aqueous solutions of 1.0 mol/L KOH in both the absence and presence of ethanol solutions. The CA and EIS curves were plotted in the mixed solution of 1.0 mol/L KOH and 1.0 mol/L  $\text{C}_2\text{H}_5\text{OH}$ . CV tests were performed within a potential range of  $-0.8$  to  $0.4$  V at a scanning rate of 10 mV/s. The impedance spectra were recorded in a constant potential mode with amplitude of 10 mV and a scanning frequency ranging from  $10^4$  to  $10^{-2}$  Hz.

### 2.4. Single cell discharge testing

The discharge testing of single cell was carried out to further elucidate the performance of Pd/C (Pd loading of  $0.1 \text{ mg}/\text{cm}^2$ ) on the ethanol oxidation in an anion exchange membrane DEFC, using

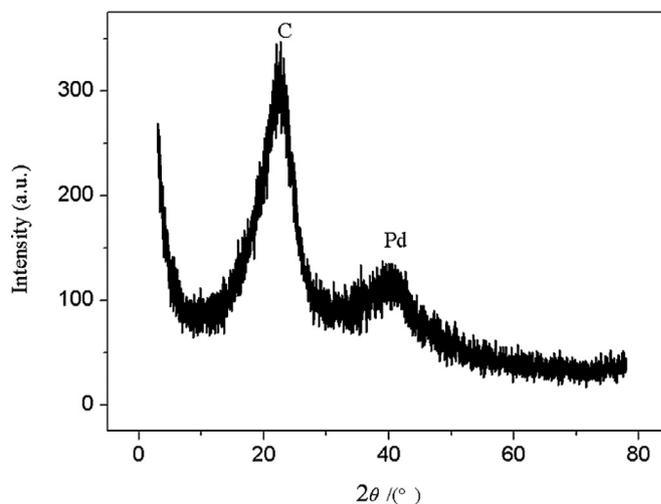


Fig. 1. XRD pattern of Pd/C.

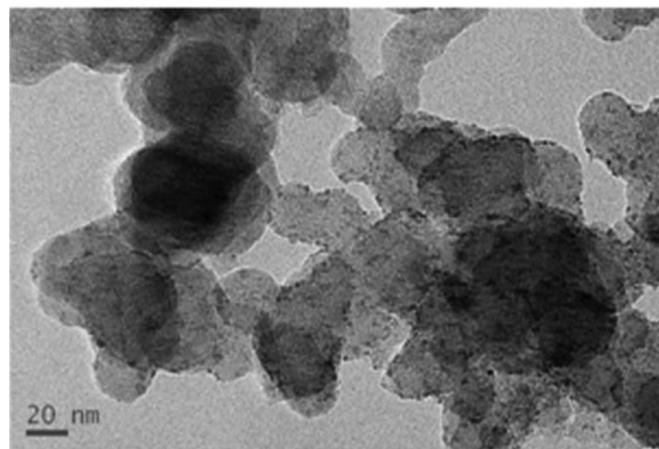


Fig. 2. TEM image of Pd/C.

a Neware charge–discharge device (Shenzhen Neware Corporation, China) at room temperature. The anode is Pd/C electrode, while the cathode is the gas diffusion electrode which involves diffusion layer (acetylene black) and activation layer ( $\text{MnO}_2/\text{C}$ ). The redox reaction area on both electrodes is  $2 \times 2 \text{ cm}^2$ , the current density of discharge is 15, 20, and  $30 \text{ mA}/\text{cm}^2$ . The anodic electrolyte is the mixed solution of 3.0 mol/L  $\text{C}_2\text{H}_5\text{OH}$  and 6.0 mol/L KOH, and accordingly, the cathodic electrolyte is 6.0 mol/L KOH.

## 3. Results and discussion

### 3.1. XRD and TEM

XRD pattern of the Pd/C is shown in Fig. 1. The broad diffraction peak at about  $24^\circ$  is ascribed to Vulcan XC-72 carbon. A single diffraction peak besides the diffraction peak from carbon at  $40^\circ$  is Pd. The average crystal size of Pd is about 3.8 nm, which is calculated using the Scherrer equation from XRD pattern, indicating that Pd nanoparticles dispersed on Vulcan XC-72 could be very small. The sample size is so small that there are not enough planes to produce complete destructive interference. TEM image was obtained to provide more information on particle size and distribution. Fig. 2 shows the TEM image of Pd/C particle. As seen clearly in Fig. 2, the Pd/C particles are uniform and well distributed on the carbon support, while the average particle size of Pd/C from TEM image is 2–4 nm, which is consistent with the XRD results.

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