Electrochimica Acta 158 (2015) 18–23

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Ethanol oxidation on Pd/C promoted with $CaSiO_3$ in alkaline medium

Hui Chen [a], Yiyin Huang [b], Dian Tang [a], Teng Zhang [a,*], Yaobing Wang [b,**]

[a] *College of Materials Science and Engineering, Fuzhou University, Fuzhou, Fujian, 350108, China*
[b] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, YangQiao West Road 155#, Fuzhou, 35002, PR China*

ARTICLE INFO

Article history:
Received 30 October 2014
Received in revised form 13 January 2015
Accepted 22 January 2015
Available online 24 January 2015

Keywords:
Palladium
Calcium Silicate
Ethanol Oxidation
Alkaline Solution

ABSTRACT

In this paper, $CaSiO_3$ was prepared using a thermal decomposition approach and added to Vulcan XC-72 carbon black as support material. The X-ray diffraction and Transmission electron microscopy results show that the addition of $CaSiO_3$ does not significantly change the particle size and distribution of Pd nanoparticles. The X-ray photoelectron spectroscopy reveals the interaction between Pd and $CaSiO_3$. In addition, the electrochemical CO-striping measurement reveals that the Pd/50$CaSiO_3$/C catalyst exhibits the largest electrochemical active surface and best CO tolerance. Moreover, cyclic voltammetry and chronoamperometry tests demonstrate that the Pd supported by $CaSiO_3$ and C (50:50 in wt.%) possesses a much higher current density (1408 $mA\,mg^{-1}$) than that of the Pd/C catalyst (743 $mA\,mg^{-1}$) towards ethanol oxidation in alkaline media, and better stability as well. These results support the suitability of Pd/50$CaSiO_3$/C catalyst developed in this work as a promising candidate for direct ethanol fuel cells application

1. Introduction

With a high theory energy density, direct alcohols fuel cells (DAFCs) with methanol as fuel are recognized as promising power sources for portable electronic devices and electric vehicles [1,2]. However, the development of DAFCs based on methanol fuel (DMFCs) is facing serious difficulties such as innate toxicity, sluggish anodic oxidation kinetics, and the fuel crossover problem in Nafion based membranes [3–5]. Therefore, other alcohols have been considered as alternative fuels. In particular, direct ethanol fuel cells (DEFCs) attract increasing attentions in recent years, due to their low operating temperature and high energy density [6,7]. In addition, DEFCs have many advantages including abundant availability, much less toxicity and crossover effects [8,9], compared with the DMFCs.

Pt-based catalysts are recognized as the best catalysts for low temperature fuel cells, because of their excellent acidic-resistance [10]. However, the poor earth reserves of Pt causes the expensive price and thus limits the commercial application of Pt-based catalyst [11]. It is well known that the oxidation of alcohols in alkaline media proceeds much easier than in an acidic environment [12]. This contributes to increasing interests in the development of Pt-free catalysts in recent years. In particular, Pd has been regarded as one of the most promising catalysts in fuel cells [5,13], considering its high electrocatalytic activity and relatively abundant reserves compared with Pt [14–16].

In addition, oxide-modified Pd has been proved to be superior to Pd/C catalyst for alcohol oxidation [10,17–19]. For example, Shen et al. reported that the reaction activity and the poisoning resistance for ethanol oxidation can be significantly improved by addition of MgO into Pd/C catalysts, due to the synergistic effect between Pd and MgO [20]. Yang et al. also reported the promoted ethanol oxidation on Pd/Fe_2O_3 hybrid catalyst [21]. The results showed that Fe_2O_3 promotes the oxidation and removal of adsorbed CO-like intermediate species during oxidation of ethanol.

On the other hand, Sakata *et al.* reported that the adsorption sites of CO on Pt/$CaSiO_3$ is homogeneous, while different kinds of CO adsorption sites present on Pt/r-Al_2O_3 and Pt/MgO [22]. Considering the different bond energie of Pd-O and Pd-C (2.46 vs. 4.92 eV) [23], one can expect that $CaSiO_3$ might be beneficial for the CO tolerance and consequently the stability of catalysts toward the ethanol oxidation.

However, to the best of our knowledge, there are no reports on $CaSiO_3$ as support for DEFC in literature, which might be due to its dielectric nature [24]. In this paper, $CaSiO_3$ was added into Vulcan XC-72 carbon black, from 0 to 75 wt.%, to obtain composite support for Pd based catalysts. The possible bifunctional mechanism in composite support lies in that carbon provides the necessary conductivity and $CaSiO_3$ enhances the CO tolerance of Pd. Attention has been focused on the effect of $CaSiO_3$/C ratio on the structure,

---

[*] Corresponding author. Tel.: +86 591 22866540; fax: +86 591 22866537.
[**] Corresponding author. Tel.: +86 591 83714517; fax: +86 591 83714946.
E-mail addresses: wangyb@fjirsm.ac.cn (D. Tang), teng_zhang@fzu.edu.cn (T. Zhang).

http://dx.doi.org/10.1016/j.electacta.2015.01.103

morphology and electrocatalytic performance of Pd-based catalysts.

2. Experimental

2.1. Sample Preparation

$Ca(NO_3)_2 \cdot 4H_2O$ (Sinopharm Chemical Reagent Co., Ltd AR), tetraethyl orthosilicate (TEOS, Sinopharm Chemical Reagent Co., Ltd AR) and hexadecyl trimethyl ammonium bromide (CTAB, Sinopharm Chemical Reagent Co., Ltd AR) were dissolved in 3 mL distilled water (Ca:Si:TEOS = 1:1:1, in mol.%) and stirred for 30 min. The resulting transparent solution was dried in an electric oven for 5 h and then heat treated at 600 °C for 2 h to obtain $CaSiO_3$.

The supported Pd catalysts were synthesized using a borohydride reduction method [25]. Briefly, 10 mg of $PdCl_2$ (Shanghai Jiuyue Chemical Reagent Co., Ltd AR) and 20 mg pretreated Vulcan XC-72 carbon black were mixed in ultrapure water and sonicated for 1 h to obtain a uniform solution. The pH of the resulting solution, with a nominal Pd-loading of 20 wt.%, was then adjusted to 8.0 by the dropwise addition of 28% $NH_3 \cdot H_2O$ under vigorous stirring. Subsequently, 20 mg of prepared $CaSiO_3$ was added, and the solution was ultrasonicated and stirred for 4 h to obtain a homogeneous suspension. For the reduction of the Pd precursor, $NaBH_4$ (Pd:$NaBH_4$ = 1:8, in mol.%) was dissolved in ice-cooled ultrapure water and added to the solution, which was then stirred vigorous for 4 h. The resulting precipitate was filtered and washed several times with ultrapure water and ethanol before being dried at 60 °C. The resulting catalyst was designated as Pd/50$CaSiO_3$/C. The catalysts with different weight ratios of $CaSiO_3$ and XC-72, 0:100, 25:75 and 75:25, were also prepared and referred to as Pd/C, Pd/25$CaSiO_3$/C and Pd/75$CaSiO_3$/C, respectively.

2.2. Materials Characterizations

The crystalline structure of the catalysts was measured using an X-ray diffractometer (XRD, Rigaku D/max-IIIC), with a copper Kα source ($\lambda = 1.5406$ Å) at an accelerating voltage of 40 kV and a current of 30 mA. The scanning rate of 2 degrees per minute with the step length of 0.02 degrees was used.

High resolution transmission electron microscopy (HRTEM) was performed in a Tecnai G2 F20 S-TWIN Electron Microscope system at 200 kV. For TEM, samples were prepared by placing a drop of the catalyst suspension with ethanol on a carbon-coated copper grid.

The chemical valence of Pd in catalysts was analyzed by X-ray photoelectron spectroscopy (ESCALAB 250, Thermo Scientific, Inc.) using a monochromatic Al Kα source (10 mA, 15 kV).

2.3. Electrochemical measurements

3 mg of the catalysts was suspended in 0.6 mL of 0.5 wt.% Nafion solution and the slurry was ultrasonically stirred for 30 min to prepare homogeneous catalyst ink. Then 4 μL of the catalyst ink was transferred using a micropipette onto the prepared glassy carbon disk electrode surface (3 mm in diameter), followed by drying in an oven at 70 °C for 10 min.

The electrochemical measurements were performed using CHI660D electrochemical workstation (Chenhua Inc. , Shanghai, China) in a conventional sealed three-electrode system. The counter electrode was Pt plate (1 cm^2) and a Hg/HgO electrode was served as the reference electrode. The glassy carbon disk electrode was employed as the working electrode. All electrochemical measurements were carried out in the water bath of 30 ± 1 °C. The Pd loading in the catalysts was determined to be 0.057 mg cm^{-2}, using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

For the electrochemical CO-stripping measurements, CO was bubbled into the solution of 1 M KOH for 15 min when the catalyst potential was fixed at 0 V vs. Hg/HgO. Then, N_2 (99.9%) was bubbled into the solution for 20 min to remove CO in the solution. The Cyclic voltammograms (CVs) were recorded in a potential range of −0.9 V∼0.4 V at a sweep rate of 50 mV s^{-1} (1 M KOH and 1 M KOH contained 1 M ethanol, respectively). The chronoamperometry was carried out at a potential of −0.25 V (1 M KOH contained 1 M ethanol). Electrochemical impedance measurements were performed with amplitude of 5 mV in the frequency range 100 kHz to 0.05 Hz at −0.25 V.

3. Results and discussion

3.1. XRD, TEM and XPS analyses

Fig. 1 shows the XRD patterns of different catalysts. The peaks at the 2θ of 39.4°, 45.9°, 66.5° and 80.7° can be ascribed to the (111), (200), (220) and (311) planes of Pd, respectively. The peaks at the 2θ of 23.1°, 29.4°, 36.0°, 43.2° and 47.5° correspond for the (012), (104), (110), (202) and (018) planes of $CaSiO_3$, respectively. In addition, the Pd (111) peak was used to calculate the particle size of Pd based on the Sherrer's equation [26]. The average palladium particle sizes in Pd/C and Pd/50$CaSiO_3$/C are 3.2 and 3.6 nm, respectively.

Shown in Fig. 2 are the TEM images of different catalysts. It is clear that the catalysts consist of uniform and monodisperse Pd nanoparticles. The average sizes of Pd nanoparticles in Pd/C and Pd/50$CaSiO_3$/C are 4.2 and 4.1 nm, respectively, consistent with those calculated according to the XRD data. In addition, some grains with a d-spacing of 0.232 nm can be observed in the High-resolution TEM images of all catalysts (in Fig. 2B and 2E), which can be assigned for the (111) plane of Pd. Therefore, the addition of $CaSiO_3$ does not significantly change the particle size and distribution of Pd nanoparticles in present work.

Fig. 3 shows the Pd 3d XPS spectra of different catalysts. It is known that the peaks corresponding to Pd $3d_{5/2}$ (∼335.8 eV) and Pd $3d_{3/2}$ (∼341.0 eV) core levels can be deconvoluted into Pd and PdO_y ($0 < y < 2$) [27]. It is clear that the PdO content decreases from 25% for Pd/C to 9% for Pd/50$CaSiO_3$/C. This indicates that the addition of $CaSiO_3$ significantly reduces the PdO content in

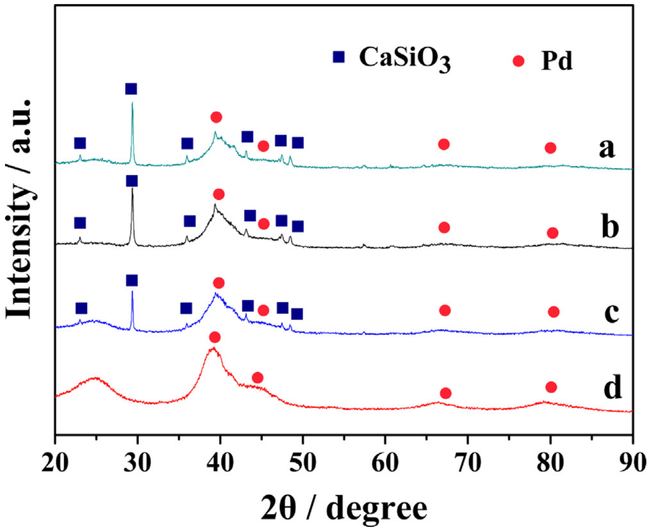

Fig. 1. XRD patterns of Pd/75$CaSiO_3$/C (curve a); Pd/50$CaSiO_3$/C (curve b); Pd/25$CaSiO_3$/C (curve c) and Pd/C (curve d), respectively.