

Electrochemical oxidation of ethanol on Pt-CeO₂/C catalysts

Changwei Xu, Pei Kang Shen*

*The State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering,
Sun Yat-Sen University, Guangzhou 510275, PR China*

Received 7 July 2004; accepted 1 October 2004

Available online 13 December 2004

Abstract

CeO₂/C used in this study was prepared by a solid-state reaction under the microwave irradiation. The activities of Pt/C, Pt-CeO₂/C for electrochemical oxidation of ethanol were studied in 1.0 M KOH solution by cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy (EIS). The results showed that the composite of Pt-CeO₂/C gave the better performance than Pt/C. The influence of the amount of the addition of CeO₂ on the catalytic activity of alcohols oxidation on platinum electrode in alkaline solution was tested. The electrode with the weight ratio of Pt to CeO₂ of 2:1 with a platinum loading of 0.30 mg cm⁻² showed the highest electro-catalytic activity.
© 2004 Published by Elsevier B.V.

Keywords: Microwave irradiation; Ethanol oxidation; Alkaline; CeO₂

1. Introduction

Direct methanol fuel cells (DMFCs) are recognised to be a promising power source for portable electronic devices and electric vehicles [1,2]. However, two major obstacles found that inhibit applications of DMFCs are (i) the relatively low dynamics of methanol electrooxidation and (ii) high methanol crossover through the membrane [3,4].

Therefore, other alcohols are considered as alternative fuels. As one of the alternative fuels, ethanol is safer and has more energy density compared to methanol (8.01 kWh kg⁻¹ versus 6.09 kWh kg⁻¹). Moreover, as a green fuel, ethanol can be easily produced in great quantity by fermentation of sugar-containing raw materials. It has been known for long that the anodic oxidation of methanol in alkaline media is more feasible than in acidic media [5–10]. The ethanol electrooxidation at Pt in alkaline solution has been reported [11,12].

The development of new catalysts is particularly important for direct alcohol fuel cells (DAFCs) due to their slow dynamics and the poisoning of catalyst by the intermediates produced during the oxidation processes [13,14]. PtRu/C is a prominent catalyst based on the bi-function mechanism [15]. Here we report a ceria (CeO₂) based novel catalyst for the direct electrochemical oxidation of ethanol in alkaline solutions. Ceria based catalysts have been investigated extensively for water-gas-shift reactions [16–18]. The direct electrochemical oxidation of methane in solid oxide fuel cells (SOFCs) on ceria-based anode has been reported [19]. Pt-group metals/ceria catalysts have received considerable attention because of their use in the automobile catalytic converter [20,21].

The Pt-CeO₂/C catalysts reported here is the first time to be used for the direct oxidation of ethanol. The critical problem with precious metal catalysts used in the low temperature fuel cells is their prohibitive economics. This type of catalysts, if properly developed, would of course be much more economical. Ceria could be prepared by homogeneous precipitation [22,23], hydrothermal synthesis [24]. Recently, Liao et al. used microwave aided hydrothermal method to rapid prepare ceria [25].

* Corresponding author. Tel.: +86 20 84036736; fax: +86 20 84113369.
E-mail address: stdp32@zsu.edu.cn (P.K. Shen).

2. Experimental

CeO₂/C used in this study was prepared by a solid-state reaction under the microwave irradiation. The aqueous solution of K₂CO₃ was added to the Ce(NO₃)₃ aqueous solution and mixed with dispersed carbon black (Vulcan XC-72R, Cabot Corp., USA). The precipitate was dried in an oven at 100 °C. The mixture was put into a microwave oven and then alternatively heated for 20 s and paused for 60 s for six times. Pt-CeO₂/C catalysts were prepared by the reduction of H₂PtCl₆ solution on CeO₂/C powder. The ratios of Pt and CeO₂ were controlled by stoichiometric calculation. The Pt/C or Pt-CeO₂/C powders were dispersed in 2-propanol with Nafion solution under ultrasonic stirring, then, the catalyst ink was deposited on the surface of a graphite rod with the geometric area of 0.50 cm² and dried at 80 °C for 30 min. The Pt loadings on the Pt/C and Pt-CeO₂/C electrodes were normally controlled at 0.3 mg cm⁻¹.

Ethanol was of analytical grade. All the solutions were freshly prepared with distilled-deionized water. The experiments were carried out at 30 °C controlled by water-bath thermostat.

Electrochemical measurements were carried out in a three-electrode cell by using IM6e electrochemical workstation (Zahner-Electrik, Germany). A platinum foil (3.0 cm²) and 1.0 M KOH/Hg/HgO were used as counter and reference electrodes, respectively. Power X-ray diffraction (XRD) was employed to obtain information about the surface and bulk structure of Pt and/or ceria supported on carbon and carried out on a D/MAX2200 diffractometer employing Cu K α radiation ($\lambda = 0.15418$ nm).

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of Pt-CeO₂ (1:1 by weight)/C comparing with the results of CeO₂/C and Pt/C. It is obvious that the XRD pattern of Pt-CeO₂/C combined the crystalline features of Pt and CeO₂, indicating the coexistence of both them.

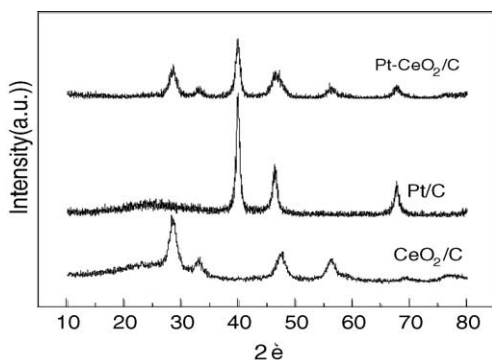


Fig. 1. XRD patterns of CeO₂/C, Pt/C and Pt-CeO₂/C.

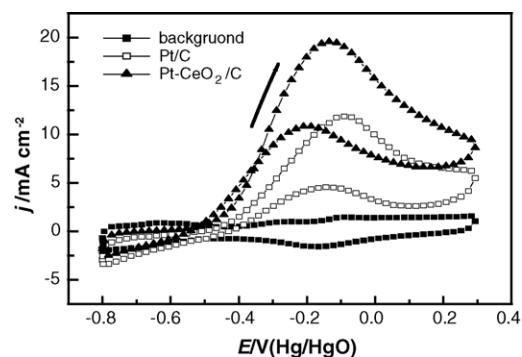


Fig. 2. Cyclic voltammograms of the electrochemical oxidation of ethanol in 1.0 M KOH containing 1 M ethanol with a sweep rate of 50 mV s⁻¹.

Fig. 2 shows the cyclic voltammograms of ethanol oxidation on Pt/C and Pt-CeO₂ (2:1 by weight)/C electrodes with a platinum loading of 0.30 mg cm⁻² at 30 °C in 1.0 M KOH solution containing 1.0 M ethanol, respectively. The peak potential of the ethanol oxidation locates at -0.09 V for Pt/C electrode and the peak potential negatively shifts to -0.14 V for Pt-CeO₂/C. It is clear that the involvement of CeO₂ significantly increased the electrode activity at the same Pt loadings. The results not only show that the peak current density is much higher on Pt-CeO₂ (2:1 by weight)/C electrode than that on Pt/C electrode, but also show that the starting potential for ethanol oxidation shifts to more negative direction, indicating ethanol electrooxidation is more active on Pt-CeO₂/C electrode than that on Pt/C electrode. The surface area of the electrode was calculated by counting the amount of hydrogen adsorption/desorption in alkaline background. According to the Ref. [10], the peaks in the potential region -800 mV < E < -500 mV are associated with the hydrogen adsorption process in the anodic scan. The coulombic charge for hydrogen desorption (Q_H) is 2.28 mC cm⁻² at Pt-CeO₂ (2:1 by weight)/C. The electrochemical active surface (EAS) was calculated according to the Eq. (1) [26].

$$\text{EAS} = \frac{4.76 Q_H}{[\text{Pt}]} \quad (1)$$

where [Pt] represents the platinum loading (mg cm⁻²) in the electrode. EAS for Pt-CeO₂ (2:1 by weight)/C is 36 m² g⁻¹. The EAS for Pt/C is 34 m² g⁻¹. The results further revealed that the electrochemical oxidation of ethanol is more active on Pt-CeO₂/C electrode than that on Pt/C electrode at almost the same EAS for hydrogen adsorption.

The content of CeO₂ in the Pt-CeO₂/C catalysts affects the catalytic activity for ethanol oxidation. The optimisation of the content of CeO₂ was conducted by changing the ratios of Pt and CeO₂ at fixed platinum loading of 0.30 mg cm⁻². Cyclic voltammetric studies were carried out to understand the variation of CeO₂ with fixed platinum loading. Fig. 3 shows the effect of the content of CeO₂ in Pt-CeO₂/C catalysts with platinum loading of 0.30 mg cm⁻² on the electrode performance for the oxidation of ethanol. The figure presents the plots of peak current density and peak potential against

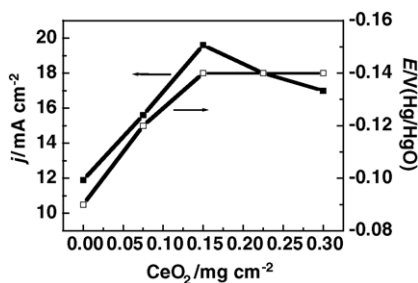


Fig. 3. Effect of the content of CeO₂ in Pt-CeO₂/C catalysts on the electrode performance at the Pt loading = 0.3 mg cm⁻² with a sweep rate of 50 mV s⁻¹.

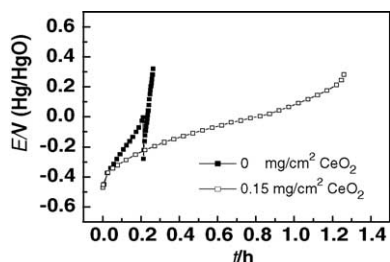


Fig. 4. Chronopotentiometric curves of ethanol oxidation on Pt-CeO₂/C electrodes with different CeO₂ contents at 3.0 mA cm⁻² in 1 M KOH containing 1 M ethanol solution, Pt loading = 0.3 mg cm⁻².

the content of CeO₂ in the catalysts. It can be seen that the peak current density increases with the increase in the amount of CeO₂ and at the same time, the potential shifts toward the negative side with the same tendency. The best performance was found when the CeO₂ loading is about 0.15 mg cm⁻², or the weight ratio of Pt and CeO₂ is 2:1. The performance declines with the further increase in the amount of CeO₂ as shown in the figure due to the decreases in the electrode conductivity.

The chronopotentiometric curves of ethanol oxidation on Pt/C and Pt-CeO₂ (2:1 by weight)/C electrodes with a platinum loading of 0.30 mg cm⁻² are shown in Fig. 4. The same current density was supplied on the electrodes. The potential increases with the lasting of the polarization time and finally shifts to a higher potential for oxygen evolution, indicating the poisoning of the catalysts. Oscillations occurred at Pt/C electrode at the current density less than 3 mA cm⁻². The sustained time is much longer for Pt-CeO₂/C at the same current density. Moreover, the polarization potential is lower on Pt-CeO₂/C. The results are important for a fuel cell operating at interested conditions. The better performance of the Pt-CeO₂/C in comparison to Pt/C is the result of electrode poisoning-resistance.

4. Conclusions

The preliminary results indicated that the addition of CeO₂ into Pt catalysts could significantly improve the electrode

performance for ethanol oxidation, in terms of the reaction activity and the poisoning resistance. It is possible that CeO₂ functions as Ru does in PtRu/C catalysts because oxygen-containing species could easier form on the surface of CeO₂. The formation of oxygen-containing species at lower potential can transform CO-like poisoning species on Pt to CO₂, releasing the active sites on Pt for further electrochemical reaction. The mechanistic study is in progress.

Acknowledgements

This work was supported by the China National 863 Program (2003AA517050) and Guangzhou Science and Technology key project (2003Z2-D0081).

References

- [1] J.C. Amphlett, B.A. Peppley, E. Halliop, A. Sadiq, J. Power Sources 96 (2001) 204.
- [2] V.M. Barragán, A. Heinzl, J. Power Sources 104 (2002) 66.
- [3] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466.
- [4] K. Scott, W.M. Taama, P. Argyropoulos, K. Sundmacher, J. Power Sources 83 (1999) 204.
- [5] R. Parsons, T. VanderNoot, J. Electroanal. Chem. 257 (1988) 9–45.
- [6] A.V. Tripkovic, K.D. Popovic, B.N. Grgur, B. Blizanac, P.N. Ross, N.M. Markovic, Electrochim. Acta 47 (2002) 3707.
- [7] C. Lamy, E. Belgsir, J. Appl. Electrochem. 3 (2001) 799.
- [8] R. Manoharan, J. Prabhuram, J. Power Sources 96 (2001) 220.
- [9] J. Prabhuram, R. Manoharan, J. Power Sources 74 (1998) 54.
- [10] H.Y. Eileen, K. Scott, R.W. Reeve, J. Electroanal. Chem. 547 (2003) 17.
- [11] S.L. Chen, M. Schell, Electrochim. Acta 45 (2000) 3069.
- [12] A.V. Tripkovic, K.D. Popovic, J.D. Lovic, Electrochim. Acta 46 (2001) 3163–3173.
- [13] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466.
- [14] K. Scott, W.M. Taama, P. Argyropoulos, K. Sundmacher, J. Power Sources 83 (1999) 204.
- [15] H.A. Gasteiger, N. Markovic, P.N. Ross Jr., E.J. Cairns, J. Phys. Chem. 97 (1993) 12020.
- [16] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, Science 301 (2003) 935.
- [17] J.M. Zalc, V. Sokolovskii, D.G. Loffler, J. Catal. 206 (2002) 169.
- [18] Q. Fu, S. Kudriavtseva, H. Saltsburg, M. Flytzani-Stephanopoulos, J. Chem. Eng. 93 (2003) 41.
- [19] E.P. Murray, T. Tsai, S.A. Barnett, Nature 400 (1999) 649.
- [20] H.S. Gandhi, G.W. Graham, R.W. McCabe, J. Catal. 216 (2003) 433.
- [21] M. Fernández-García, A. Martínez-Arias, L.N. Salamanca, J.M. Coronado, J.A. Anderson, J.C. Conesa, J. Soria, J. Catal. 187 (1999) 474.
- [22] X. Chu, W. Chung, L.D. Schmidt, J. Am. Ceram. Soc. 76 (1993) 2115.
- [23] P.L. Chen, I.W. Chen, J. Am. Ceram. Soc. 76 (1993) 1577.
- [24] M. Hirano, E. Kato, J. Am. Ceram. Soc. 79 (1996) 777.
- [25] X.H. Liao, J.J. Zhu, J.Z. Xu, H.Y. Chen, Chem. Commun. (2001) 937.
- [26] S.J. Lee, S. Mukerjee, J. McBreen, Y.W. Rho, Y.T. Kho, T.H. Lee, Electrochim. Acta 43 (1998) 3693.