COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Novel Pt/CeO_2/C catalysts for electrooxidation of alcohols in alkaline media†

Changwei Xu and Pei Kang Shen*

State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China. E-mail: stdp32@zsu.edu.cn;
Fax: 86-20-84113369; Tel: 86-20-84036736

Received (in Cambridge, UK) 7th June 2004, Accepted 26th July 2004
First published as an Advance Article on the web 25th August 2004

Electrochemical oxidation of methanol, ethanol, glycerol and ethylene glycol (EG) on novel Pt–CeO_2/C catalysts in alkaline media has been studied and shows an improved performance in terms of the electrode activity and the poisoning resistance.

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.[1,2] PtRu/C is a prominent catalyst based on the bi-function mechanism.[3] Here, we report a ceria (CeO_2) based novel catalyst for the direct electrochemical oxidation of alcohols in alkaline solutions. Ceria based catalysts have been investigated extensively for water-gas-shift reactions.[4–6] The direct electrochemical oxidation of methane in solid oxide fuel cells (SOFCs) on ceria-based anode has been reported.[7] Pt-group metals/ceria catalysts have received considerable attention because of their use in the automobile catalytic converter.[8,9]

The Pt–CeO_2/C catalysts reported here are the first to be used for the direct oxidation of alcohols in low temperature fuel cells. Matsuoka and co-workers reported the results of electrochemical oxidation of polyhydric alcohols such as ethylene glycol (EG), glycerol on platinum electrode in alkaline solution.[10] All polyhydric alcohols showed higher reactivity in alkaline media than in acidic media. The critical problem with precious metals catalysts used in low temperature fuel cells is their prohibitive economics. This type of catalysts, if properly developed, would of course be much more economical.

Ceria can be prepared by homogeneous precipitation,[11,12] or hydrothermal synthesis.[13] Recently, Liao and co-workers used a microwave aided hydrothermal method to rapidly prepare ceria.[14] CeO_2/C used in this study was prepared by a solid-state reaction under microwave irradiation (see the ESI). The method used in this study has the advantages of being simple and fast compared with hydrothermal synthesis according to our experience.[15,16] However, we have found that the method used here has to be improved (see Fig. S2 in the ESI).

Fig. 1 shows the typical linear sweep curves of EG oxidation on Pt/C and Pt–CeO_2 (1 : 1 by weight)/C electrodes, respectively. It is clear that the involvement of CeO_2 significantly increased the electrode activity at the same Pt loadings. The performance of methanol, ethanol, glycerol and EG electrochemical oxidation on Pt–CeO_2/C electrodes is summarized in Table 1. The data were obtained under the conditions of 1 mol dm^{-3} alcohol/1 mol dm^{-3} KOH, 303 K and the scan rate of 50 mV s^{-1}. The results not only show that the peak current densities are much higher on Pt–CeO_2/C electrode, but also show that the peak potentials shift to a more negative direction, indicating all the alcohols studied are more active on Pt–CeO_2/C electrode than on Pt/C electrode.‡

We measured the surface areas of the two electrodes at 30 °C in 1 M KOH by cyclic voltammetry since the activity of an electrode is not only controlled by the catalytic properties but also by the surface area, hence the microstructure. According to Reference [17], the peaks in the potential region $-800 \text{ mV} < E < -500 \text{ mV}$ on the CV curve are associated with the hydrogen adsorption process in the anodic scan. The coulombic charge for hydrogen desorption (Q_H) is 2.43 mC cm^{-2} at Pt–CeO_2 (1.2 : 1 by weight)/C. The electrochemical active surface (EAS) is calculated according to the Eqn. (1)[18]

$$\text{EAS} = 4.76\, Q_H/[\text{Pt}] \qquad (1)$$

where [Pt] represents the platinum loading (mg cm^{-2}) in the electrode. EAS for Pt–CeO_2 (1.2 : 1 by weight)/C is 38 m^2 g^{-1}. The EAS for Pt/C is 34 m^2 g^{-1}. The results show that the electrochemical active surface areas are almost the same for both the electrodes, indicating that the alcohol electrochemical oxidation is more active on Pt–CeO_2/C electrode than on Pt/C electrode without increasing the EAS of the electrode.

Fig. 2 shows the effect of the content of the CeO_2 in Pt/C

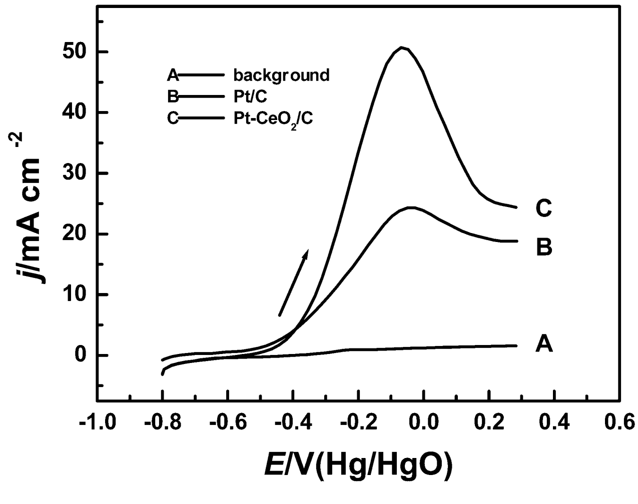

Fig. 1 Linear sweep curves for the electrooxidation of EG on Pt/C (B) and PtCeO_2/C (C) electrodes in 1 mol dm^{-3} EG/1 mol dm^{-3} KOH. 303 K, scan rate: 50 mV s^{-1}.

Table 1 Comparison of the peak current density and the peak potential of alcohols electrooxidation on Pt/C and Pt–CeO_2/C electrodes[a]

	Pt/C		Pt–CeO_2/C	
Alcohols	E_p/V	j_p/mA cm^{-2}	E_p/V	j_p/mA cm^{-2}
Methanol	−0.07	18.0	−0.09	36
Ethanol	−0.09	11.9	−0.14	17.0
Glycerol	−0.07	21.0	−0.09	30.6
EG	−0.05	24.3	−0.07	50.7

[a] Methanol, ethanol, glycerol and EG are of analytical grade. All the solutions were freshly prepared with distilled deionized water. The experiments were carried out at 303 K controlled by a water bath.

---

† Electronic supplementary information (ESI) available: catalyst preparation and characterization. See http://www.rsc.org/suppdata/cc/b4/b408589b/

DOI: 10.1039/b408589b

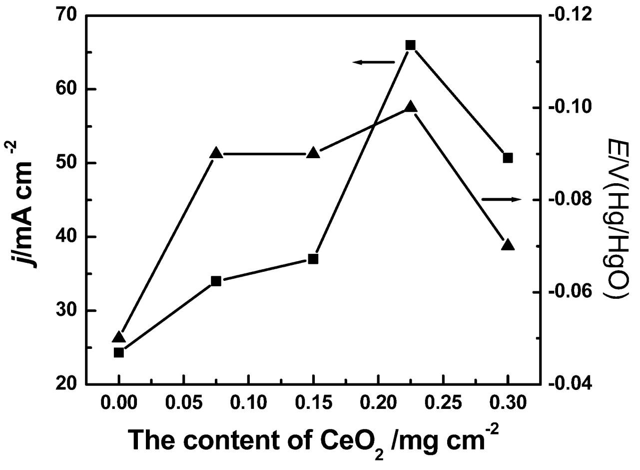

Fig. 2 Effect of the content of CeO_2 in Pt/C catalysts on the electrode performance at the Pt loading = 0.3 mg cm^{-2}. 303 K, scan rate: 50 mV s^{-1}.

catalysts on the electrode performance for the oxidation of EG. The figure presents the plots of peak current density and peak potential against the content of CeO_2 in the catalysts. It can be seen that the peak current density increases with an increase in the amount of CeO_2 and at the same time, the potential shifts toward the negative side with the same tendency. The best performance was found when the CeO_2 loading reached about 0.225 mg cm^{-2}, or the molar ratio of Pt and CeO_2 was 1.2 : 1, at 303 K. The performance declines with a further increase in the amount of CeO_2 as shown in the figure, probably due to decreases in the electrode conductivity.

As we know that the activity of alcohol oxidation on Pt is proportional to the Pt loading at a certain amount, in this study we focused on the study of the synergistic effect of the catalyst. In fact, the Pt percentage (wt%) in the catalyst is changeable even if we control the Pt loading at 0.3 mg cm^{-2} since the loading of the ceria is changeable. The fact that the maximum effect closes to Pt : CeO_2 = 1 : 1 could be explained by a one to one adsorption mechanism. That is, every Pt atom can afford one poisoning species (*e.g.* CO) and one oxygen-containing species adsorbs on each ceria. The rapid removal of the poisoning species by reaction with the oxygen-containing species leaves the active sites for alcohol adsorption and oxidation, resulting in a best performance.

The chronopotentiometric curves of EG oxidation on Pt–CeO_2/C electrodes with different CeO_2 contents are shown in Fig. 3. The same current density was supplied on the electrodes with the different CeO_2 loadings. The potential increases with the polarization time and finally shifts to a higher potential for oxygen evolution, indicating the poisoning of the catalysts. The sustained time is longer with the increase in the CeO_2 content. A maximum is found for the electrode with 0.225 mg cm^{-2} CeO_2 as seen in Fig. 2. Moreover, the polarization potentials are lower for the better ones. The spikes appearing on the curves C and D in Fig. 3 are caused by the formation and release of the poisoning species on the surface of the electrode. The poisoning species could be the small fragments formed by the breakdown and dehydrogenation of alcohol during the electrochemical oxidation. The formation of the poisoning species causes an increase in the overpotential until a certain value and at that potential the poisoning species are oxidized. The further oxidation of the poisoning species releases the active sites for the alcohol oxidation at a lower potential. This periodic process forms the spikes (or potential oscillation).

The preliminary results indicated that the addition of CeO_2 into Pt catalysts could significantly improve the electrode performance for alcohols oxidation, in terms of the reaction activity and the poisoning resistance. It is possible that CeO_2 functions as Ru does in PtRu/C catalysts because oxygen-containing species could easily form on the surface of the CeO_2. The formation of oxygen-containing species at lower potential can transform CO-like poisoning species on Pt to CO_2, leaving the active sites on Pt for further electrochemical reaction. As described above, the improved electrode response is more likely due to a synergistic effect. The mechanistic study is in progress.

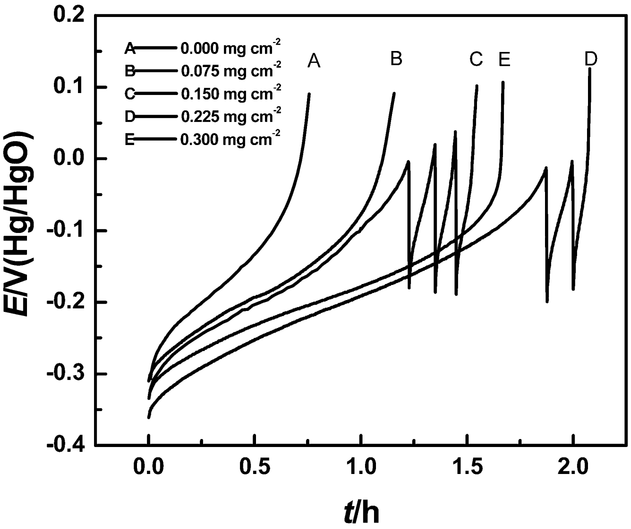

Fig. 3 Chronopotentiometric curves of EG oxidation on Pt–CeO_2/C electrodes with different CeO_2 contents at 5 mA cm^{-2} in 1 mol dm^{-3} KOH solution. Temperature = 303 K, Pt loading = 0.3 mg cm^{-2}.

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

Notes and references

‡ Electrochemical experiments were performed on an IM6e electrochemical workstation. A standard three-electrode cell was used. A platinum foil (3.0 cm^2) and Hg/HgO (1.0 mol dm^{-3} KOH) were used as counter and reference electrodes, respectively.

1 X. Ren, T. E. Springer, T. A. Zawodzmski and S. Gottesfeld, *J. Electrochem. Soc.*, 2000, **147**, 466.
2 K. Scott, W. M. Taama, P. Argyropoulos and K. Sundmacher, *J. Power Sources*, 1999, **83**, 204.
3 H. A. Gasteiger, N. Markovic, P. N. Ross, Jr. and E. J. Cairns, *J. Phys. Chem.*, 1993, **97**, 12020.
4 Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science*, 2003, **301**, 935.
5 J. M. Zalc, V. Sokolovskii and D. G. Loffler, *J. Catal.*, 2002, **206**, 169.
6 Q. Fu, S. Kudriavtseva, H. Saltsburg and M. Flytzani-Stephanopoulos, *Chem. Eng. J.*, 2003, **93**, 41.
7 E. P. Murray, T. Tsai and S. A. Barnett, *Nature*, 1999, **400**, 649.
8 H. S. Gandhi, G. W. Graham and R. W. McCabe, *J. Catal.*, 2003, **216**, 433.
9 M. Fernández-García, A. Martínez-Arias, L. N. Salamanca, J. M. Coronado, J. A. Anderson, J. C. Conesa and J. Soria, *J. Catal.*, 1999, **187**, 474.
10 K. Matsuoka, M. Inaba and Y. Iriyama, *Fuel Cells*, 2002, **2**, 35.
11 X. Chu, W. Chung and L. D. Schmidt, *J. Am. Ceram. Soc.*, 1993, **76**, 2115.
12 P. L. Chen and I. W. Chen, *J. Am. Ceram. Soc.*, 1993, **76**, 1577.
13 M. Hirano and E. Kato, *J. Am. Ceram. Soc.*, 1996, **79**, 777.
14 X. H. Liao, J. J. Zhu, J. Z. Xu and H. Y. Chen, *Chem. Commun.*, 2001, 937.
15 Z. Q. Tian, F. Y. Xie and P. K. Shen, *J. Mater. Sci.*, 2004, **391**, 509.
16 P. K. Shen and Z. Q. Tian, *Electrochim. Acta*, 2004, **49**, 3107.
17 H. Y. Eileen, K. Scott and R. W. Reeve, *J. Electroanal. Chem.*, 2003, **547**, 17.
18 S. J. Lee, S. Mukerjee, J. McBreen, Y. W. Rho, Y. T. Kho and T. H. Lee, *Electrochim. Acta*, 1998, **43**, 3693.