



CeO₂ promoted Au/C catalyst for glycerol electro-oxidation in alkaline medium



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ABSTRACT

Glycerol has a very high value of onset potential on the Au/C, so it is difficult to be electrochemically oxidized on pure Au electrocatalyst. When CeO₂ is added to the Au/C, the value of onset potential is more 190 mV shifted negatively and close to that on the E-TEK Pt/C. The results demonstrate that CO remarkably poisons the Pt/C catalyst and CO is a promoter for glycerol oxidation on the Au/C and Au–CeO₂/C electrodes. In presence of CO, a current promotion from 7.5 mA cm⁻² to 15.0 mA cm⁻² on the Au–CeO₂/C electrode, then the current slow decays to the same current without CO. The results show that Au–CeO₂/C has great anti-poisoning effect on CO and is more stable catalyst than the E-TEK Pt/C for glycerol oxidation in presence of CO.

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1. Introduction

Fuel cells are of tremendous interest from both energy and environmental considerations [1]. Much effort has been devoted to the development of direct alcohol fuel cells (DAFCs) with methanol as fuel [2,3]. However, the development of DAFCs based on methanol fuel is facing serious difficulties: (i) slow electro-kinetic of methanol oxidation, (ii) high methanol crossover and (iii) high toxicity of methanol. Therefore, other alcohols have been considered as alternative fuels. Glycerol has been investigated as fuel for DAFCs because it has high boiling point and it is non-toxic compared with methanol. Pt-based catalysts have been extensively investigated and proved as good electrocatalysts for glycerol oxidation [4–7]. However, high price and limited supply of Pt are major barriers to the development of DAFCs using Pt-based catalysts. Our previous work and other groups on the development of Pt-free electrocatalysts for alcohol oxidation has focused on Pd-based electrocatalysts and the results revealed that Pd is a good electrocatalyst for glycerol oxidation in alkaline medium [8–13]. However, the price of Pd also is expensive. Scientists pay more attention to Au because it is much more abundant and more available than Pt and Pd on the earth. Our group and Habibi et al. have studied the activity and stability of glycerol oxidation on the Au electrode in alkaline medium [14,15]. Glycerol shows a remarkable stability on the Au electrode. Glycerol has higher theoretical energy density than methanol and can be electrochemically oxidized [16–18]. The application of glycerol electro-oxidation on DAFCs has attracted increasing interest and the DAFCs with glycerol as fuel show certain advantages such as low fuel cross-over and high power density [19–22]. A few of studies have reported the electrocatalytic property of glycerol oxidation on the Au electrode [23–31]. Oxides such as RuO₂ [32], MnO₂ [33] have used to enhance Au activity for glycerol oxidation. We have reported firstly CeO₂ enhanced Pt and Pd for alcohol electro-oxidation in 2004 and 2006 [8,34]. Then many groups have also reported the same results [35–44]. Here we firstly report the CeO₂ enhanced Au catalyst for glycerol electro-oxidation in alkaline medium.

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2. Material and methods

The CeO₂/C powders were synthesized by intermittence microwave irradiation method in a microwave oven with infrared measuring temperature (Nan jing, Jie quan, NJL07-3) with a weight ratio of 1:2 of CeO₂ to C. The Au–CeO₂/C electrocatalyst was prepared by reduction HAuCl₄ solution on the CeO₂/C powders using an excess 0.01 mol L⁻¹ NaBH₄ solution. The weight ratio of Au to CeO₂ is 1.3:1 with the previous results of Pt or Pd to CeO₂ [8]. The electrocatalyst powders were dispersed in 2-propanol with 5 wt% PTFE (polytetrafluoroethylene) on the surface of a graphite rod with a geometric area of 0.33 cm². The loading of PTFE and Au on the electrodes was accurately controlled at 0.1 mg cm⁻². All electrochemical measurements were tested in a three-electrode cell using the EG&GPAR283 electrochemical workstation (Princeton, U.S.A) in a temperature-controlled water-bath (Polyscience 9106, U.S.A.). Solutions were freshly prepared before each experiment. A platinum foil (3.0 cm²) was used as counter electrode. All the potentials were measured versus a saturated calomel electrode (SCE, 0.241 V versus RHE) electrode. A salt bridge was used between the cell and the reference electrode. CO beams were expanded in the solution with a pressure less than 500 Pa to control 4–5 beams per second. X-ray diffraction (XRD) was carried out with a D/MAX2200 diffractometer employing Cu K α radiation ($k = 0.15418$ nm). Transmission electron microscopy (TEM) was performed with a Philips CM-300 high resolution system operating at 200 keV.

3. Results and discussion

XRD patterns for the CeO₂/C, Au/C and Au–CeO₂/C all exhibit an XRD pattern of a typical face-centered-cubic (fcc) lattice structure as shown in Fig. 1. The strong diffraction peaks at the Bragg angles of 38.1°, 44.3°, 64.6°, 77.5° and 81.7° correspond to the (111), (200), (220), (311) and (222) diffraction peaks of gold and the strong diffraction peaks at the Bragg angles of 28.4°, 33.0°, 47.3° and 56.1° correspond to the (111), (200), (220), (311) and (222) diffraction peaks of ceria. All the diffraction peaks indicate coexistence of Au and CeO₂ in the Au–CeO₂/C electrocatalyst. Fig. 2a is TEM image of the Au–CeO₂/C and shows that the particles are well dispersed with a diameter of less than 7 nm. Fig. 2b is high-resolution TEM (HRTEM) image. The parallel fringe with the spacing of 0.31 nm is correspond to the (111) plane of the cubic CeO₂.

Fig. 3 shows cyclic voltammograms (CVs) for glycerol oxidation on the Au/C (Au loading: 0.10 mg cm⁻²), Au–CeO₂/C (Au loading: 0.10 mg cm⁻²) and commercial E-TEK 30% Pt/C (Pt loading: 0.10 mg cm⁻²) electrodes in 1.0 mol L⁻¹ KOH + 1.0 mol L⁻¹ glycerol with a sweep rate of 10 mV s⁻¹. The background is the CV on the Au–CeO₂/C electrode in 1.0 mol L⁻¹ KOH absence of glycerol. The magnitude of oxidation current on the forward scan indicates the activity of electrocatalyst for alcohol oxidation [45]. The values of onset potential (E_s) for glycerol electro-oxidation are -0.326, -0.516 and -0.570 V on the Au/C, Au–CeO₂/C and E-TEK Pt/C electrodes. The lower value of E_s shows more easily electrochemically oxidized for alcohol. Glycerol has a very high value of E_s on the Au/C and the value of E_s is more 244 mV positively than E-TEK Pt/C electrode, so it is difficult to be electrochemically oxidized on pure Au electrocatalyst. When CeO₂ is added to the Au/C, the value of E_s is more 190 mV shifted negatively and close to that on the E-TEK Pt/C. The peak current densities (j_p) are 20.4 mA cm⁻² (at the peak potential of 0.09 V) on the Au/C electrode, 75.4 mA cm⁻² (-0.08 V) on the Au–CeO₂/C electrode, 20.4 mA cm⁻² (-0.25 V) on the E-TEK Pt/C electrode. The current densities at -0.3 V ($j_{-0.3V}$) are 1.8, 7.1 and 18.1 mA cm⁻² on the Au/C, Au–CeO₂/C and E-TEK Pt/C electrodes. The values of j_p and $j_{-0.3V}$ on the Au–CeO₂/C are 3.7 and 4.0 times higher than that on the Au/C.

The chronoamperometric curves from -0.6 V to -0.3 V for glycerol oxidation on the Au/C, Au–CeO₂/C and E-TEK Pt/C electrodes in 1.0 mol L⁻¹ KOH solution containing 1.0 mol L⁻¹ glycerol are shown as Lines 1, 3 and 5 in Fig. 4. It is well-known that the intermediate species such as CO-like species during alcohol oxidation will block the electrode surface to poison the catalyst, then the current of alcohol oxidation will decrease. Nevertheless, at the end of the test, the oxidation current density is 2.8 mA cm⁻² on the Au–CeO₂/C electrode which is larger

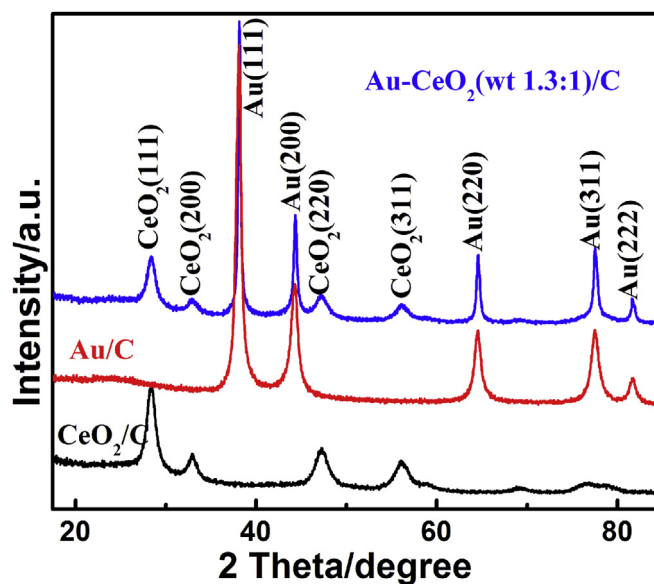


Fig. 1. XRD patterns of CeO₂/C, Au/C and Au–CeO₂(wt 1.3:1)/C catalysts.

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