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Short communication

Ethanol electrooxidation on Pt/C and Pd/C catalysts promoted with oxide

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Abstract

This research aims to investigate Pd-based catalysts as a replacement for Pt-based catalysts for ethanol electrooxidation in alkaline media. The results show that Pd/C has a higher catalytic activity and better steady-state behaviour for ethanol oxidation than that of Pt/C. The effect of the addition of CeO_2 and NiO to the Pt/C and Pd/C electrocatalysts on ethanol oxidation is also studied in alkaline media. The electrocatalysts with a weight ratio of noble metal (Pt, Pd) to CeO_2 of 2:1 and a noble metal to NiO ration 6:1 show the highest catalytic activity for ethanol oxidation. The oxide promoted Pt/C and Pd/C electrocatalysts show a higher activity than the commercial E-TEK PtRu/C electrocatalyst for ethanol oxidation in alkaline media.

Keywords: Ethanol; Fuel cells; Palladium; Oxide; Electrooxidation

1. Introduction

Direct alcohol fuel cells (DAFCs) generate electrical power by feeding a liquid fuel directly to an anode, which makes them easier to design as small and lightweight fuel cells. DAFCs are promising power sources for portable electronic devices and electric vehicles [1]. Direct ethanol fuel cells (DEFCs) have attracted attention since ethanol has no toxicity compared to methanol and can be easily produced in great quantities by fermentation of sugar-containing raw materials [2–5]. Pt-based catalysts are recognized as the best catalysts for low temperature fuel cells [6]. It has been accepted that PtRu/C is an effective anode catalyst for DAFCs. Here we report oxide-promoted (CeO_2, NiO) Pt/C and Pd/C catalysts for direct electrochemical oxidation of ethanol in alkaline media. The oxide has been used to promote Pt activity for ethanol electrooxidation in alkaline media [7,8]. CeO_2 and NiO promoted Pt for alcohol electrooxidation has been reported [9–12]. However, the limitation of the use of the Pt-based electrocatalysts also comes from the high cost and limited resources of Pt [13]. The authors' previous work on the development of Pt-free electrocatalysts for alcohol oxidation has focused on the preparation of oxide promoted Pd electrocatalysts [12,14]. It is significant since Pd is at least fifty times more available in the earth than Pt [15]. Pd-based electrocatalysts have also been used for oxygen reduction and formic acid electrooxidation in low temperature fuel cells [16–20].

2. Experimental

The preparation procedure of these oxides and oxide promoted catalysts was previously reported in the literature [9,12,14]. An aqueous solution of $Ce(NO_3)_2$ or $Ni(NO_3)_2$ was mixed with dispersed carbon black (Vulcan XC-72R, Cabot Corp., USA). The mixture was dried in oven at 80 °C, then, the dried mixture was put into a microwave oven and then was alternatively heated 20 s and paused 60 s for six times to control the temperature to produce CeO_2/C or NiO/C powders. The electrocatalysts were prepared by the reduction of H_2PtCl_6 or H_2PdCl_4 solution on oxide/C powder using 0.01 M $NaBH_4$ solution. The ratios of the noble metal and oxide were controlled by stoichiometric calculation. The electrocatalyst powders were dispersed in 2-propanol with 5 wt.% Nafion solution under ultrasonic stirring, then, the catalyst ink was deposited on the surface of a graphite rod with the geometric area of $0.50\,cm^2$ and dried at 80 °C for 30 min. The noble metal loadings on the electrodes were normally controlled at $0.3\,mg\,cm^{-2}$.

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Ethanol was of analytical grade. All the solutions were freshly prepared with doubly distilled water. The experiments were carried out at 30 °C controlled by water-bath thermostat. All electrochemical measurements were carried out in a three-electrode cell using IM6e electrochemical workstation (Zahner-Electrik, Germany). A platinum foil ($3.0\,\mathrm{cm}^2$) and Hg/HgO (1.0 M KOH) were used as counter and reference electrodes, respectively. X-ray diffraction (XRD) was employed to obtain the information of the surface and bulk structure of the electrocatalysts and was carried out on a D/MAX2200 diffractometer employing Cu Kα radiation ($k = 0.15418$ nm).

3. Results and discussions

The electrolysts of Pt/C, Pt–CeO_2 (1:1 by weight)/C, Pt–NiO (1:1 by weight)/C, Pd/C, Pd–CeO_2 (1:1 by weight)/C and Pd–NiO (1:1 by weight)/C all exhibited 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 39.76°, 46.24° and 67.45° correspond to the (1 1 1), (2 0 0) and (2 2 0) facets of Pt crystals. The strong diffraction peaks at the Bragg angles of 40.10°, 46.49° and 68.08° correspond to the (1 1 1), (2 0 0) and (2 2 0) facets of Pd crystals. For the patterns of Pt–CeO_2 (1:1 by weight)/C, Pt–NiO (1:1 by weight)/C, Pd–CeO_2 (1:1 by weight)/C and Pd–NiO (1:1 by weight)/C, all of the diffraction peaks of noble metal and oxide can be observed indicating their coexistence in the catalysts. There is no obvious shift in any of the diffraction peaks of noble metal in these catalysts indicating that the addition of oxide has no effect on the crystalline lattice of noble metal. The Pt(1 1 1) and Pd(1 1 1) peaks were used to calculate the particle size of Pt and Pd according to Scherrer's equation. The average Pt nanoparticle sizes of Pt/C, Pt–CeO_2 (1:1 by weight)/C and Pt–NiO (1:1 by weight)/C are 12 nm, 8 nm and 5 nm. The average Pd nanoparticle sizes of Pd/C, Pd–CeO_2 (1:1 by weight)/C and Pd–NiO (1:1 by weight)/C are 10 nm, 6 nm and 7 nm.

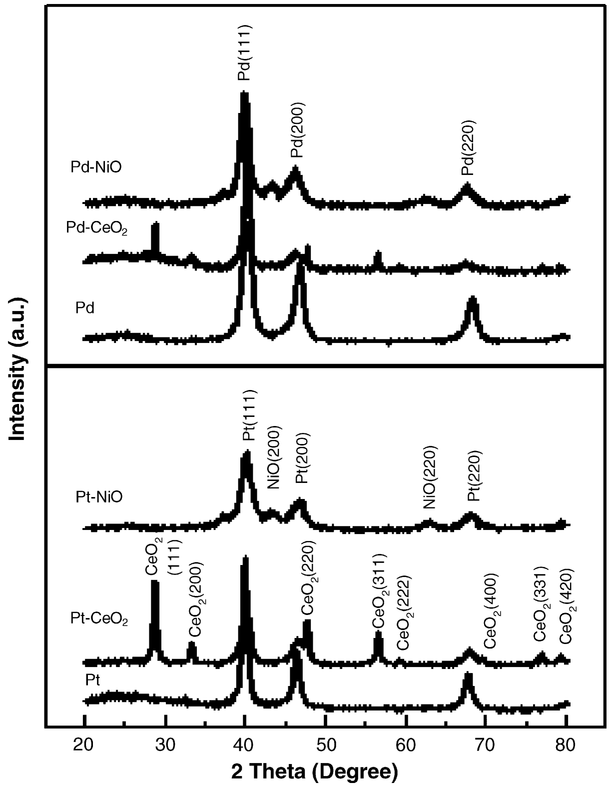

Fig. 1. XRD patterns of Pt/C, Pt–CeO_2 (1:1 by weight)/C, Pt–NiO (1:1 by weight)/C, Pd/C, Pd–CeO_2 (1:1 by weight)/C and Pd–NiO (1:1 by weight)/C.

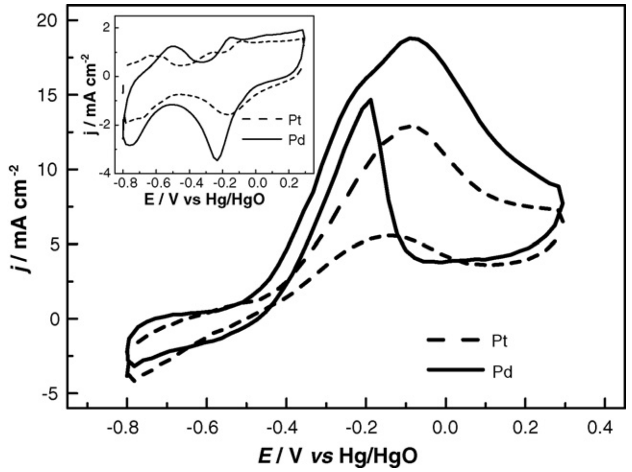

Fig. 2. Cyclic voltammetric curves for ethanol electrooxidation on Pt/C and Pd/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol with a sweep rate of $50\,\mathrm{mV\,s^{-1}}$, Pt or Pd loading: $0.3\,\mathrm{mg\,cm^{-2}}$. (The inset figure is the cyclic voltammograms of Pt/C and Pd/C in 1.0 M KOH with absence of ethanol.)

Fig. 2 shows the typical cyclic voltammograms of ethanol electrooxidation on Pt/C and Pd/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol. The scan rate is $50\,\mathrm{mV\,s^{-1}}$ in the potential range of −0.8 to 0.3 V. The cyclic voltammograms of Pt/C and Pd/C electrodes in 1.0 M KOH with absence of ethanol are shown in inset figure of Fig. 1. The humps in the potential region −800 to −500 mV on Pt/C [21] and −650 to −450 mV on Pd/C [22] are associated with hydrogen adsorption process in the anodic scan. The electrochemical active surfaces (EASs) of catalysts were calculated according to literature [23] and the results were listed in Table 1. The EASs of noble metal supported on oxide/C are almost the same as that of noble metal supported on carbon black. The results further reveal that the electrochemical oxidation of ethanol is more active on noble metal supported on oxide/C electrode without increasing the EAS of the electrodes.

By comparing with the cyclic voltammograms in the absence of ethanol, an ethanol oxidation peak can be clearly observed in the cyclic voltammograms on both electrodes in 1.0 M KOH solution containing 1.0 M ethanol. The current densities (j) at different potentials were compared and summarized in Table 1. It is clear that the current densities are higher at corresponding potentials on Pd/C than that on Pt/C. The most significant phenomenon is that the onset potential (E_s) for ethanol oxidation on Pd/C is more negative for 90 mV compared with that on Pt/C at the same condition. The peak current on Pd/C begins to rise much more sharply at more negative potential, which will directly improve fuel cell efficiency. The results show that Pd has higher catalytic activity for ethanol electrooxidation than Pt.

Table 1
Comparison of the electrochemical performance of catalysts for ethanol oxidation at a sweep rate of 50 mV s^{-1}, Pt or Pd loading: 0.3 mg cm^{-2}

Electrocatalyst	EAS (m^2 g^{-1})	E_s (V)	E_p (V)	j_p (mA cm^{-2})	j at −0.3 V (mA cm^{-2})
E-TEK PtRu/C	44	−0.52	−0.03	20	12.9
Pt/C	34	−0.47	−0.09	13	6.0
Pd/C	39	−0.55	−0.08	19	11.1
Pt–CeO_2 (2:1 by weight)/C	36	−0.52	−0.14	20	11.6
Pd–CeO_2 (2:1 by weight)/C	40	−0.60	−0.09	39	27.1
Pt–NiO (6:1 by weight)/C	42	−0.55	−0.11	50	21.5
Pd–NiO (6:1 by weight)/C	47	−0.62	−0.08	95	56.7

The long-term stabilities of electrocatalysts for ethanol oxidation have been investigated with chronopotentiometric curves in 1.0 M KOH solution containing 1.0 M ethanol with a current density of 3 mA cm^{-2} and the corresponding results are shown in Fig. 3. In this experiment, the same current density was supplied on the electrodes. The polarization potential increases with the lasting of polarization time, indicating the poisoning of the catalysts. The polarization potential on Pd/C electrode increases gradually with the polarization time. When the polarization potential on Pd/C electrode gets to −0.2 V, the polarization time is 1.8 h. However, when the polarization potential on Pt/C electrode gets to −0.2 V the potential time is 0.1 h. The sustained time is much longer on Pd/C electrode than that on Pt/C electrode at the same current density of 3 mA cm^{-2}. Pt is known to be easily poisoned by adsorbed species coming from the dissociative adsorption of ethanol and then to deactivate rapidly [24–26]. Here, Pd/C is not easily poisoned and shows better steady-state performance than Pt/C for ethanol electrooxidation.

Fig. 4 shows the performance of ethanol oxidization on commercial E-TEK PtRu (2:1 by weight)/C, Pt–CeO_2 (2:1 by weight)/C and Pd–CeO_2 (2:1 by weight)/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol, respectively. The onset potential of ethanol oxidation is −0.47 V on Pt/C and it negatively shifts to −0.52 V on Pt–CeO_2/C. The onset potential of ethanol oxidation is −0.55 V on Pd/C and it negatively shifts to −0.60 V on Pd–CeO_2/C. The change in the onset potential shows an improvement in the kinetics due to synergistic effect by the interaction between noble metal and CeO_2. Both CeO_2 promoted catalysts show higher activities than E-TEK PtRu/C catalysts. The current density on Pd–CeO_2/C is doubled than that on E-TEK PtRu/C and the onset potential is more negative 90 mV than that on E-TEK PtRu/C.

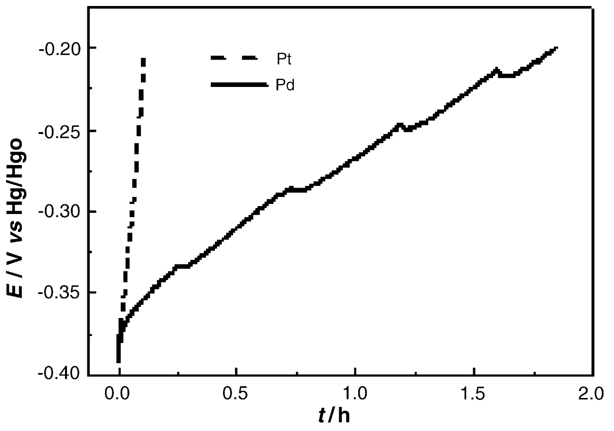

Fig. 3. Chronopotentiometric curves for ethanol electrooxidation on Pt/C and Pd/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol with 3 mA cm^{-2}, Pt or Pd loading: 0.3 mg cm^{-2}.

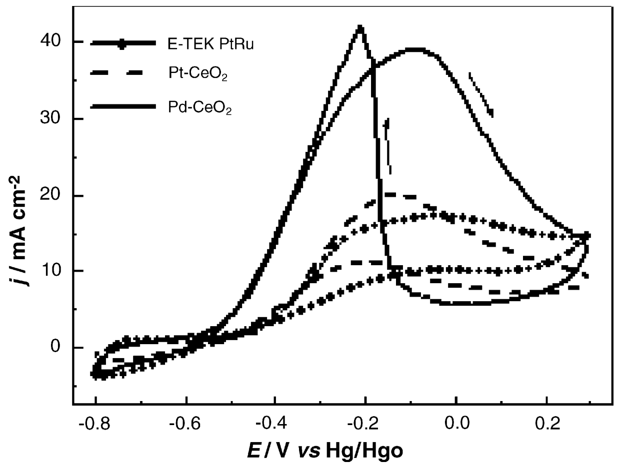

Fig. 4. Cyclic voltammetric curves for ethanol electrooxidation on E-TEK PtRu (2:1 by weight)/C, Pt–CeO_2 (2:1 by weight)/C and Pd–CeO_2 (2:1 by weight)/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol with a sweep rate of 50 mV s^{-1}, Pt or Pd loading: 0.3 mg cm^{-2}.

Fig. 5 shows the performances of ethanol oxidization on Pt–NiO (6:1 by weight)/C and Pd–NiO (6:1 by weight)/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol,

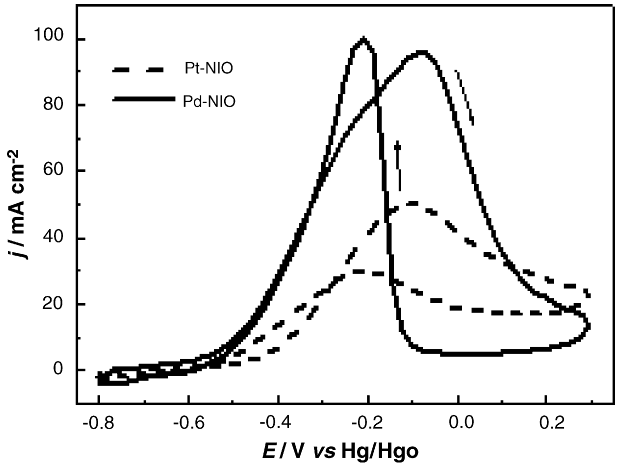

Fig. 5. Cyclic voltammetric curves for ethanol electrooxidation on Pt–NiO (6:1 by weight)/C and Pd–NiO (6:1 by weight)/C electrodes in 1.0 M KOH solution containing 1.0 M ethanol with a sweep rate of 50 mV s−1, Pt or Pd loading: 0.3 mg cm^{-2}.

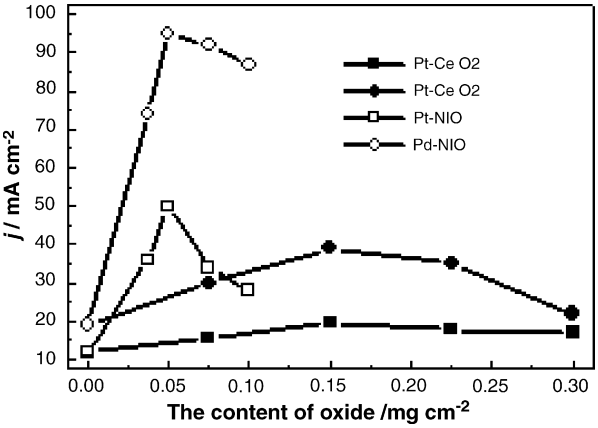

Fig. 6. Effect of the content of oxide in Pt/C and Pd/C catalysts for ethanol electrooxidation in 1.0 M KOH solution containing 1.0 M ethanol with a sweep rate of 50 mV s^{-1}, Pt or Pd loading: 0.3 mg cm^{-2}.

respectively. The onset potential of ethanol oxidation is −0.55 V on Pt–NiO/C and −0.62 V on Pd–NiO/C. The peak current density is 50 mA cm^2 on Pt–NiO/C and 95 mA cm^2 on Pd–NiO/C. The onset potentials for ethanol oxidation on Pt–NiO/C and Pd–NiO/C electrodes both negatively shift for 80 mV compared with that on Pt/C and Pd/C, respectively. Both NiO promoted catalysts show higher activities than commercial E-TEK PtRu/C catalysts. The peak current density on Pd–NiO/C is about five-times than that on E-TEK PtRu/C and the onset potential is more negative 100 mV than that on E-TEK PtRu/C.

The optimization of the ratios of oxide to noble metal in these electrocatalysts was conducted by changing the oxide content at a fixed noble metal loading of 0.30 mg cm^{-2} and recording the current densities at peak potential during ethanol electrooxidation. The activity for ethanol electrooxidation is significantly increased by addition of oxide and the results are shown in Fig. 6. It can be seen that current increases with the increasing in CeO_2 content in the catalysts. The best result was found on Pt–CeO_2/C and Pd–CeO_2/C electrocatalysts with noble metal to CeO_2 weight ratio of 2:1. The best result was found on Pt–NiO/C and Pd–NiO/C electrode with noble metal to NiO weight ratio of 6:1.

The alcohol electrooxidation on PtRu/C catalyst is explained as a bi-functional mechanism [27]. Pt acts as main catalyst for catalysing the dehydrogenation of alcohol during the oxidation reaction and oxygen-containing species (OH_{ad}) can form on the Ru surface at lower potentials. These oxygen-containing species react with CO-like intermediate species on the Pt surface to produce CO_2 and release the active sites [28]. Research revealed that hydrous RuO_2 is a more active catalyst for alcohol oxidation than do Ru^0 as part of bimetallic PtRu alloy [29–31]. The results can be interpreted as being associated with the presence of hydrous RuO_2 ($RuO_{2-\delta}(OH)_\delta$), which would play the role of donor of the oxygen-containing species that promote the CO to CO_2 oxidation. RuO_2 is rapidly and reversibly oxidized and reduced by electrochemical protonation [32]:

$$RuO_2 + \delta H^+ + \delta e^- \leftrightarrow RuO_{2-\delta}(OH)_\delta, \quad 0 \le \delta \le 2$$

Non-noble as well as their respective oxides was shown to be active sites for the formation of oxygen-containing species as Ru [33,34]. It is possible that oxide functions as Ru does in Pt–oxide/C and Pd–oxide/C catalysts because OH_{ad} species could easier form on the surface of oxide. The formation of OH_{ad} species at lower potential can transform CO-like poisoning species on the surface of noble metal to CO_2 or other products which could be dissolved in water, releasing the active sites on noble metal for further electrochemical reaction. At low oxide content, there are not enough oxide sites to effectively assist the releasing of adsorbed CO-like poisoning specie and the oxidation current remains almost at the level obtained from pure noble metal. When increasing the oxide content, the current density increases. The weight ratio of 2:1 for Pt(Pd):CeO_2 and 6:1 for Pt(Pd):NiO seems to present a site distribution close to the optimum for ethanol oxidation. The decrease in the oxidation current with the further increase in the oxide content can be rationalized in terms of an inhibition of ethanol adsorption, which is probably due to the diminution of noble metal sites. On the other hand, the performance declines with the further increasing in the amount of oxide may due to the decreases in the electrocatalysts conductivity since CeO_2 and NiO are semiconductor. The mechanistic study is in progress. The in situ FTIR and other methods are being used to further study the reaction mechanism.

4. Conclusions

These preliminary results show that Pd/C has a higher catalytic activity and better steady-state performance for ethanol electrooxidation than Pt/C in alkaline media. The addition of oxide (CeO_2, NiO) to Pt/C and Pd/C can significantly promote catalytic activity for ethanol electrooxidation. The electrocatalysts with the weight ratio of Pt or Pd to CeO_2 of 2:1 and Pt or Pd to NiO of 6:1 show the highest electrochemical catalytic activity for ethanol oxidation. The oxide promoted Pt/C and Pd/C electrocatalysts show higher activities for ethanol oxidation than a commercial E-TEK PtRu/C electrocatalyst. The activity of catalysts decreases in the order Pd–NiO (6:1 by weight)/C > Pd–CeO_2 (2:1 by weight)/C > Pt–NiO (6:1 by weight)/C > Pt–CeO_2 (2:1 by weight)/C > commercial E-TEK PtRu (2:1 by weight)/C ≈ Pd/C > Pt/C. The Pd-based catalysts show better electrocatalystic properties for ethanol oxidation than Pt-based catalysts and may be great potential in direct ethanol fuel cells.

It is possible that oxide functions as the Ru does in PtRu catalysts because OH_{ad} species could easier form on the surface of oxide. The formation of OH_{ad} species at lower potential can transform CO-like poisoning species on Pt and Pd to CO_2 or other products, which could be dissolved in water, releasing the active sites on Pt and Pd for further electrochemical reaction. A mechanistic study is in progress.

Acknowledgments

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