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Short communication

Novel palladium–lead (Pd–Pb/C) bimetallic catalysts for electrooxidation of ethanol in alkaline media

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ABSTRACT

Carbon-supported bimetallic palladium–lead (Pd–Pb/C) catalysts with different amounts of lead are prepared using a co-reduction method. The catalysts are characterized by various techniques, which reveal the formation of an alloy nanoparticle structure. The electrochemical activities of the catalysts towards ethanol oxidation in alkaline media are examined by cyclic voltammetry, linear sweep voltammetry and chronoamperometry methods. The results show that the Pd–Pb(4:1)/C catalyst exhibits a better catalytic activity than the Pd/C catalyst. From carbon monoxide (CO) stripping results, the addition of lead also facilitates the oxidative removal of adsorbed CO. The promoting effect of lead is explained by a bi-functional mechanism and d-band theory.

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1. Introduction

Electrooxidation of ethanol has attracted increasing interest recently due to the potential of ethanol as a fuel for direct alcohol fuel cells [1–3]. The kinetics of ethanol electrooxidation are, however, quite slow even with a Pt-based catalyst, which is the best catalyst known to date [4]. Moreover, the high cost and limited reserves of Pt further restrict its potential application [5]. Recently, Pd has been found as a good catalyst for the oxidation of ethanol in alkaline solutions and its natural abundance is at least fifty times more than that of Pt [6]. Nevertheless, the activity of Pd for ethanol oxidation in alkaline media also needs to be enhanced before achieving practical application in direct ethanol fuel cells.

A number of studies have shown that Pb has a promoting effect on the electrooxidation of alcohols and other organic fuels [3,7–10]. For instance, Li and Pickup [3] reported that after addition of Pb, the catalytic activity of carbon-supported Pt and Pt/Ru catalysts for ethanol oxidation in acidic media increased greatly, especially at high potentials. Liu et al. [9] found that a PtPb/C catalyst displayed enhanced electrocatalytic activity towards both formic acid and methanol oxidation compared with Pt/C and commercially available PtRu/C catalysts. To the authors' knowledge, however, the catalytic performance of Pd–Pb/C bimetallic catalysts towards ethanol electrooxidation has not been reported. In this study, Pd/C electrocatalysts containing different amounts of Pb have been pre-

pared, and their activities towards the electrooxidation of ethanol in alkaline media have been evaluated.

2. Experimental

The materials, used in this work were deionized water, sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) (Sigma–Aldrich), PdCl_2 (Sigma–Aldrich), $\text{Pb}(\text{NO}_3)_2$ (Sigma–Aldrich), NaBH_4 (Sigma–Aldrich), $\text{C}_2\text{H}_5\text{OH}$ (Fluka), Nafion solution (5 wt.% in isopropanol and water), and carbon black (XC-72, Gashub, Singapore). All chemicals were of analytical grade.

To synthesize the electrocatalysts, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ and an appropriate amount of metal precursors were dissolved in water. Then excess amounts of 0.01 M NaBH_4 (freshly prepared) were added dropwise into the solution. The mixtures were stirred for 2 h. After that, carbon black was added to the mixtures followed by stirring overnight at room temperature. The resulting suspensions were filtered and washed several times with suitable amounts of hot deionized water to remove completely all excess of reducing agent. The remaining solids were dried in a vacuum oven for 24 h at ambient temperature. The final catalysts were Pd/C, Pd–Pb(8:1)/C, Pd–Pb(4:1)/C and Pd–Pb(2:1)/C, and the weight percentage of Pd was 16 wt.% in these catalysts.

The structure and morphology of the catalysts were investigated using X-ray diffraction (XRD, Rigaku D/max-2500) and transmission electron microscopy (TEM, JEOL 1400, 120 kV). Elemental analyses were performed by means of energy dispersive X-ray spectroscopy (EDX, 6390 (LA)).

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Cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronoamperometry (CA) were collected in 1 M KOH + 1 M C₂H₅OH solution. The working electrode was prepared by dropping 5 μ L of the electrocatalyst ink on a glassy carbon electrode (GCE). The ink was prepared by ultrasonically mixing 4 mg of the electrocatalyst in 2 mL of ethanol. Then, 1 μ L of 0.5 wt.% Nafion solution in 2-propanol was added on top to fix the electrocatalyst. A Pt foil and Hg|HgO (1.0 M KOH) electrode were used as the counter and reference electrodes, respectively. All potentials in the present study are reported versus the Hg|HgO (1.0 M KOH) electrode. The CV and LSV tests were conducted at 20 mV s^{−1}, with the potential ranging from −0.8 to 0.3 V. The LSV was measured at different temperatures. The CA was conducted at −0.25 V for 3600 s. CO stripping was performed as follows: after purging the solution with N₂ for 20 min, CO was bubbled for 15 min to form a CO adlayer on the catalysts while maintaining the potential at −0.8 V. Excess CO in solution was purged with N₂ for 20 min and CO stripping voltammetry was recorded in 1.0 M KOH at 50 mV s^{−1}.

3. Results and discussion

Fig. 1(a) presents XRD patterns of the Pd–Pb(8:1)/C, Pd–Pb(4:1)/C and Pd–Pb(2:1)/C catalysts, as well as the Pd/C catalyst for comparison. The diffraction peak at ca. 25° is due to the C (002) plane. While the main Pd peaks are obvious for each catalyst, no Pb peaks can be seen. By contrast, EDX spectra of the Pd–Pb(8:1)/C catalyst clearly show the presence of Pb (Fig. 1(b)). This indicates that the Pb is either in an amorphous state, or alloyed with the Pd. The addition of Pb causes clear shifts of the Pd peaks for these catalysts, with the effect being greater for higher Pb

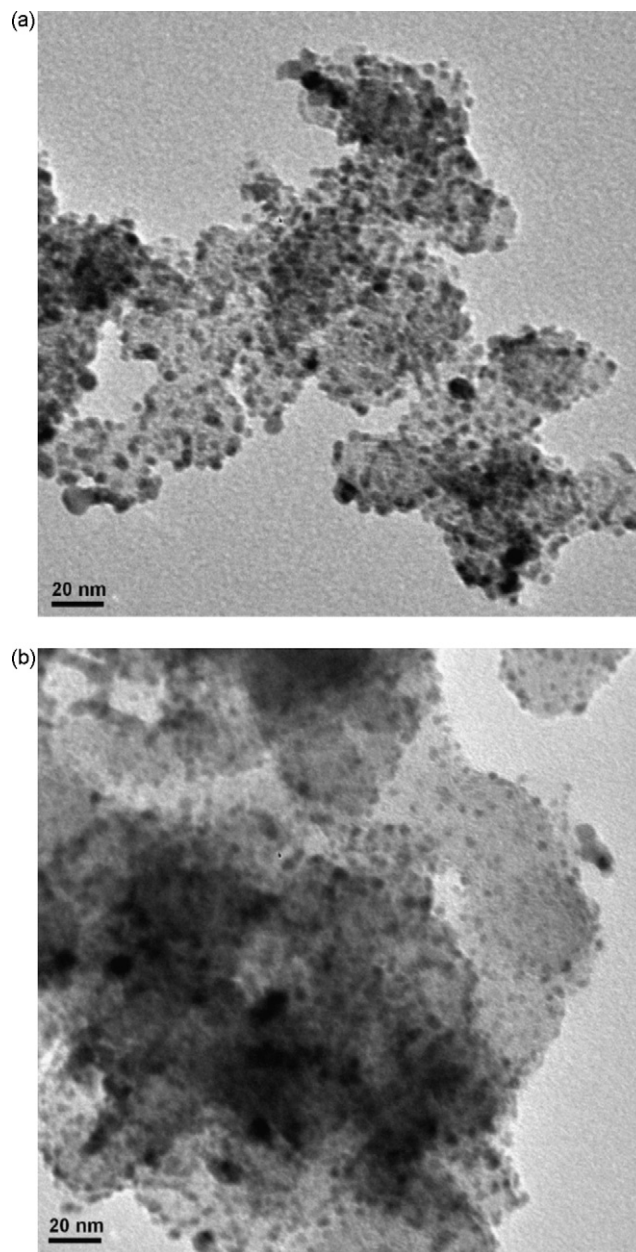


Fig. 2. TEM of images of: (a) Pd–Pb(8:1)/C and; (b) Pd–Pb(2:1)/C, catalysts.

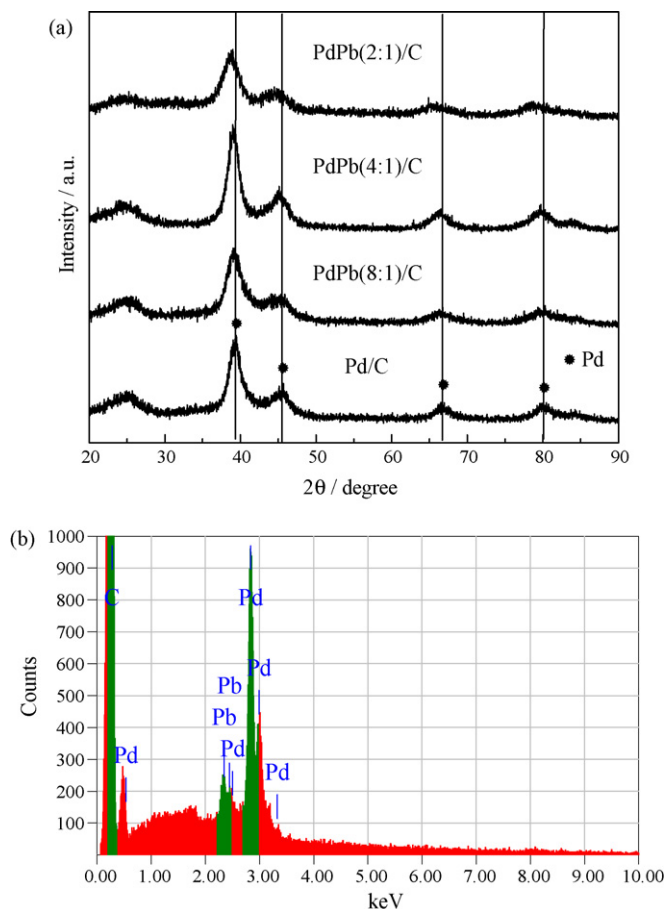


Fig. 1. (a) XRD patterns of Pd/C, Pd–Pb(8:1)/C, Pd–Pb(4:1)/C and Pd–Pb(2:1)/C catalysts; (b) EDX spectra of Pd–Pb(8:1)/C catalyst.

content, which indicates that alloying had occurred. According to the Scherrer equation $d = 0.9\lambda_{K\alpha 1} / B_{2\theta} \cos \theta_{\max}$, the crystallite sizes are estimated at 4.1, 2.8, 3.9 and 2.6 nm for the Pd/C, Pd–Pb(8:1)/C, Pd–Pb(4:1)/C and Pd–Pb(2:1)/C catalysts, respectively.

The morphologies and particle-size distributions for the Pd–Pb(8:1)/C and Pd–Pb(2:1)/C catalysts were also investigated by TEM. As shown in Fig. 2, the nanoparticles are evenly distributed on the carbon support. The average particle sizes seen in TEM images are in reasonable agreement with those estimated by XRD, although a quantitative comparison was not made.

The CVs of ethanol electrooxidation on the Pd/C and Pd–Pb/C electrodes are presented in Fig. 3(a). For clear observation, only the forward scan curves are shown. The results are normalized by the Pd oxide reduction peak area obtained from the CVs in blank solution. As seen from Fig. 3(a), the onset potential of ethanol oxidation on the Pd–Pb(4:1)/C is obviously more negative than those on the other samples. Furthermore, the current density on the Pd–Pb(4:1)/C catalyst is the highest. It is indicated that the

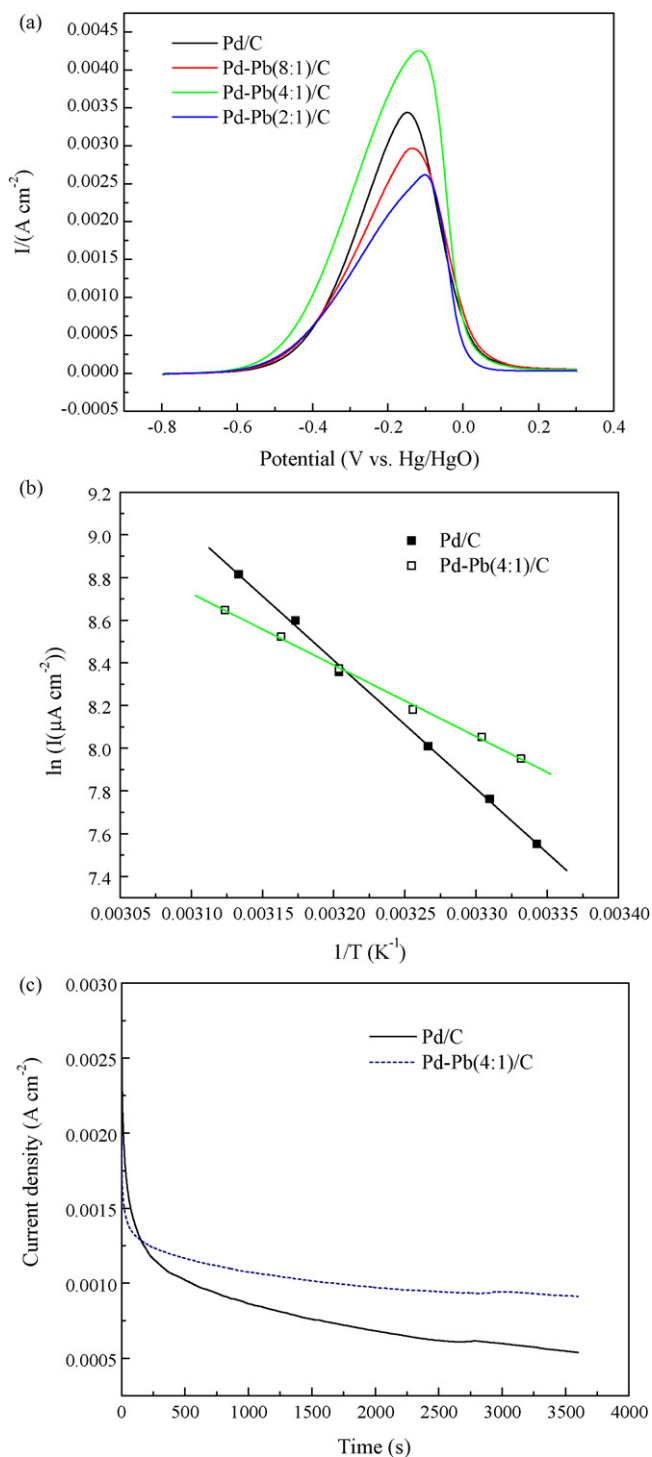


Fig. 3. (a) CVs of ethanol electrooxidation on Pd/C, Pd-Pb(8:1)/C, Pd-Pb(4:1)/C and Pd-Pb(2:1)/C catalysts in 1 M KOH + 1 M C₂H₅OH solutions; (b) plot of $\ln I$ vs. $1/T$ (I : current at -0.06 V; T : temperature in K); (c) CA for oxidation of 1 M ethanol in 1 M KOH at -0.25 V on Pd/C and Pd-Pb(4:1)/C catalysts.

Pd-Pb(4:1)/C catalyst exhibits the best catalytic activity for ethanol oxidation. For the other two Pd-Pb/C catalysts, no improvement is observed. Therefore, in the remaining session, attention is focused on the best-performing catalyst namely, Pd:Pb = 4:1.

To demonstrate further the excellent behavior of the Pd-Pb(4:1)/C catalyst, LSV tests were performed at several different temperatures on the Pd-Pb/C and Pd/C electrodes. The relationship of the reciprocal of temperature and the logarithm of current (at -0.06 V) is given in Fig. 3(b). An apparent activation

energy value can be calculated according to Arrhenius equation [11]:

$$I = Ae^{-E_a/RT} \quad (1)$$

where I is the current at a specific potential; R is the gas constant; T is the temperature in K; and E_a is the apparent activation energy. By linearly fitting the relationship of $\ln I$ and $1/T$, it can be obtained that the E_a for Pd/C and Pd-Pb(4:1)/C is 50.03 and 27.87 kJ mol⁻¹, respectively. It is clear that the E_a of the Pd-Pb/C catalyst is smaller than that of the Pd/C catalyst. A smaller activation energy indicates that, using the Pd-Pb/C electrocatalysts, the charge-transfer process is faster. In short, an appropriate amount of lead obviously promotes the kinetics of the electrooxidation of ethanol catalyzed by Pd/C.

Besides LSV, more representative information on the relative activities and stabilities of electrodes is obtained by chronoamperometry (CA). The results for ethanol oxidation on the Pd/C and Pd-Pb(4:1)/C catalysts at a potential of -0.25 V are given in Fig. 3(c). The currents for ethanol oxidation on both catalysts drop rapidly at first, and then become relatively stable. The initial surge of current is due to charging current [3]. The current for ethanol oxidation on the Pd-Pb(4:1)/C catalyst is significantly larger than that on the Pd/C catalyst over most of the time range. Moreover, the decay rate becomes low at longer time for the Pd-Pb(4:1)/C electrode, while for the Pd/C electrode, the current decays continuously and there is no apparent steady-state during the whole measurement. This indicates that the activity of the Pd-Pb(4:1)/C catalyst is truly remarkable.

The promoting effect of the second metal has been explained by a bi-functional mechanism and electronic (ligand) effects [1,12,13]. In the bi-functional mechanism, the second metal activates water at lower potentials than Pt or Pd and the activated water can oxidize the adsorbed intermediate and therefore liberate Pt or Pd active sites. This could be the first reason for the improved activity with the introduction of Pb. The reaction mechanism of the ethanol electrooxidation catalyzed by Pd-based metal in alkaline media has been proposed by Liang et al. [14], where oxidation of adsorbed intermediate, viz., ethoxi species, is regarded as the rate-determining step. The direct stripping experiment with the ethoxi species is difficult to realize. Since both CO and ethoxi species are strongly bound to the catalyst surface, CO stripping may be used to indicate the capability of the catalyst to remove adsorbed poisoning species. Therefore, CO stripping curves were collected and the results are shown in Fig. 4. The onset potential of CO oxidation on the Pd-Pb(4:1)/C catalyst is obviously more negative than that on the Pd/C catalyst. This means that the addition of Pb facilitates the removal of CO, or a similar poisoning intermediate, from the surface of the Pd-Pb(4:1)/C. This result helps to explain the higher activity of Pd-Pb(4:1)/C for the oxidation of ethanol. Fig. 4(b) shows the appearance of two peaks for CO stripping on the Pd-Pb(4:1)/C catalyst. The possible reason for this fact is that perhaps some Pd is not alloyed with Pb and still remains beside the Pd-Pb domain. The second metal can also promote ethanol oxidation by changing the electronic properties of Pt or Pd [3]. According to d-band theory of Nørskov and co-workers [15–17], there is a direct correlation between the reactivity and the d-band centre value of the overlayer and impurity atoms. When metals with small lattice constants are overlayed on, or alloyed with metals with larger lattice constants, the d-band centre shifts up and vice versa. If the d-band centre is shifted up, the adsorption ability of the adsorbate (ethanol) on the metals will be stronger and this may help to improve the electrooxidation of ethanol on the surfaces of the metals. The lattice values of Pd and Pb are 3.89 and 4.93 Å, respectively. Therefore, after Pb is combined with Pd, the d-band centre of Pd may be shifted up. This may contribute to the better catalytic performance of the Pd-Pb/C catalyst.

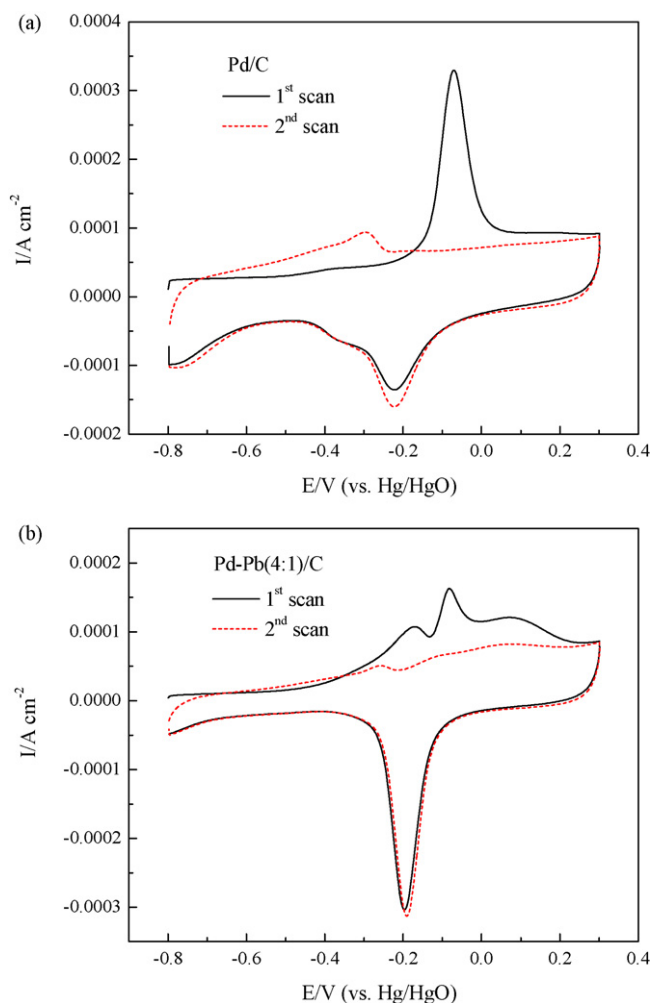


Fig. 4. CO stripping curves on Pd/C (a) and Pd-Pb(4:1)/C (b) catalysts recorded in 1 M KOH solution.

4. Conclusions

Pd-Pb/C catalysts with different amounts of Pb have been prepared, and the catalytic performances for ethanol electrooxidation in alkaline solution are investigated. The onset potentials of ethanol oxidation on the Pd-Pb/C catalysts are more negative than that on the Pd/C catalyst. According to the CV, LSV and CA results, it is found that the Pd-Pb(4:1)/C catalyst has a better activity than the Pd/C catalyst. From CO stripping results, the addition of Pb also facilitates the oxidative removal of CO. The promoting effect of Pb is explained by a bi-functional mechanism and d-band theory.

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