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Nano-structured Pd_xPt_{1-x}/Ti anodes prepared by electrodeposition for alcohol electrooxidation

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ABSTRACT

Nano-structured Pd_xPt_{1-x} ($x = 0–1$) composite catalysts supported on Ti substrate are successfully prepared by electrodeposition method, and the morphology and phase of the catalysts are analyzed by field emission scanning electron microscope (FE-SEM) and X-ray energy dispersion spectroscopy (EDS). The activity and stability of the Pd_xPt_{1-x}/Ti composite catalysts are assessed for the electrooxidation of alcohols (methanol, ethanol and 2-propanol) in alkaline medium using cyclic voltammetry and chronoamperometry techniques. The results show that the Pd and Pt form Pd_xPt_{1-x} nano-structured composite catalysts, uniformly distributed on the Ti substrate. The electrocatalytic activity and stability of the Pd_xPt_{1-x} nanocatalysts depend strongly on the atomic ratios of Pd and Pt. Among the synthesized catalysts, the $Pd_{0.8}Pt_{0.2}$/Ti displays the best catalytic activity and stability for the electrooxidation reaction of alcohols investigated in alkaline medium under conditions in this study, and shows the potential as electrocatalysts for direct alcohol fuel cells.

1. Introduction

Direct alcohol fuel cells (DAFCs) based on liquid fuels have attracted much attention as power sources for portable electronic devices and fuel-cell vehicles due to the much higher energy density of liquid fuels than gaseous fuels such as hydrogen [1–4]. Among the different possible alcohols, methanol is the most promising liquid fuel because it has several advantages, such as an abundant availability at low cost, easy handling, transportation and storage, high theoretical density of energy comparable to that of gaseous hydrogen. Other alcohols, such as ethanol, propanol, etc. have also been considered as fuels in fuel cells [5–12].

Almost all low-temperature polymer electrolyte membrane fuel cells (PEMFCs) use platinum or platinum alloys as electrocatalyst materials. Carbon supported and unsupported PtRu alloys are commonly used as electrocatalysts for methanol oxidation in direct methanol fuel cells (DMFCs) [13–16]. PtSn bimetallic catalysts for the electrooxidation of ethanol have been investigated by several research groups [17–19]. However, they have a limited ability to break the C–C bond. Besides adsorbed CO, several intermediates with C–C bonds have been reported for the ethanol oxidation. The partial blocking of the catalyst surface by these intermediates causes the rapid decrease in the oxidation currents with time [20–22]. It has been shown that the electrooxidation of ethanol is more sluggish than that of methanol oxidation reaction on Pt-based catalysts in acidic medium [5,23]. In addition, the high price and limited source of Pt constitute a major barrier to the development of DAFCs. Therefore, there are several approaches employed to reduce the amount of platinum used in fuel cells, including new MEA fabrication methods, introducing a new supporting material to produce the maximum platinum activity, discovering a new catalyst or an alloyed catalyst based on platinum, etc. [24].

On the other hand, if DAFCs are operated in an alkaline instead of an acidic medium, the kinetics of the electrode reactions will be significantly enhanced and Pt-free catalysts with low cost can be used [25,26]. It is reported that the greater availability of OH^- ions and a higher OH^- coverage on the electrode surface will contribute to the considerable increase in the kinetics of the alcohol oxidation reaction in alkaline medium [27]. There is an increasing interest in the research of alkaline membrane fuel cells due to the fact that the electrode reaction is significantly facile and fast at the cathode as well as at the anode and cheaper non-noble metal catalysts can be used, thus significantly reducing the cost of fuel cells. It has long been known that the anodic oxidation of methanol in alkaline medium is much faster than that in acidic medium. We have reported that Pd has higher electrocatalytic activity and better stability for the electrooxidation of ethanol and 2-propanol than Pt in alkaline medium [20,28–33].

It is well known that the electrodeposition is one of the most efficient methods for the growth of metal nanoparticles. This is a

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powerful technique for the deposition of many metals since it is rapid and facile, allowing easy control of the nucleation and growth of metal nanoparticles with various sizes, shapes and distributions [20,34]. In this paper, Pd_xPt_{1-x} nanoparticles with different atomic ratios were electrodeposited on the Ti substrate surface and applied as electrocatalysts for methanol, ethanol and 2-propanol oxidation in alkaline medium. There are several reports on the novel electrode structures for DMFCs based on Ti mesh [35,36] due to its excellent conductivity and chemical stability.

2. Experimental

The chemical reagents (methanol, ethanol, 2-propanol, potassium hydroxide, ammonia, hydrochloric acid, hydroperoxide, $PdCl_2$ and $H_2PtCl_6{\cdot}xH_2O$, etc.) used in this experiment were analytical grade purity and Ti foils were 99.99% purity. All the above materials were purchased from Sigma–Aldrich. The solutions used were freshly prepared with deionized water of ≥18.2 MΩ cm.

The PdPt electrocatalysts on Ti substrates surface were synthesized by the electrodeposition method using a solution containing designed ratio of Pd and Pt. The surfaces of the Ti foils were polished with 50 nm alumina grinding powers, and then the Ti foils were rinsed by a mixture solution of HCl (7.4 wt%) and H_2O_2 (5.0 wt%) for 10 min to remove oxidized layer and contaminations. After that, the Ti foils were dipped into the precursor solution. The pH value of precursor solution was controlled at 9.5 and the metal ions concentration (Pd^{2+} and Pt^{4+}) was controlled at 5 mM with the designated Pd^{2+} and Pt^{4+} stoichiometric composition. The electrodeposition was performed by cyclic voltammetry (CV) from 0 to −0.8 V at a scan rate of 5 mV s^{-1} and the process was repeated five times.

The electrochemical experiments were carried out using Autolab PGSTAT30 electrochemical workstation. A standard three-electrode cell was used and controlled at 25 °C using a water bath during the experiments. The cell consisted of a titanium foil of 0.5 cm^2 coated by Pd, Pt and Pd_xPt_{1-x} catalyst as the working electrode, a Pt foil of 3 cm^2 as the counter electrode, and a saturated calomel electrode (SCE, 0.241 V versus SHE) as reference electrode. A salt bridge with a Luggin capillary closing to the working electrode was used between the cell and the reference electrode.

FE-SEM (JEOL JSM-6340F, Japan) was performed to characterize the morphology and the particle size distribution of the catalyst. EDS (Oxford, UK) was used to determine the atomic ratio of Pd and Pt in Pd_xPt_{1-x}.

3. Results and discussions

3.1. Physical characterizations of Pd_xPt_{1-x}/Ti electrocatalysts

The morphologies and size distributions of $Pd_{0.8}Pt_{0.2}$/Ti catalysts were observed by FE-SEM and the result is given in Fig. 1. It can be observed that the particles of the catalysts are spherical in shape and there is no obvious conglomeration, which means that PdPt catalysts possess a good three-dimensional structure and good specific surface area. The average particle size is ~10 nm, quite uniform and narrow-dispersed (see the inset of Fig. 1). We also found that the morphology and particle size of the PdPt electrocatalysts did not change significantly with the Pd/Pt atomic ratio of the catalysts.

The element composition analysis of the catalysts was conducted by EDS and the results are given in Fig. 2. As shown in Fig. 2, Pt and Pd elements can be distinctly detected in the respective Pt and Pd catalyst and can also be observed in the bimetallic catalysts ($Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti and $Pd_{0.2}Pt_{0.8}$/Ti). Ti element still showed the relatively high diffraction peaks, which means the surface of the Ti substrate have not been completely covered by the PdPt catalyst layer. This is consistent with the SEM results as shown in Fig. 1. The atomic ratio calculated from the relative intensity of the EDS spectra is in excellent agreement with that of the targeted ratio during the electrodeposition process, proving that the electrodeposition is an easy and feasible method to control the catalyst's composition and to produce nano-structured and composite of PdPt electrocatalysts on the Ti substrate.

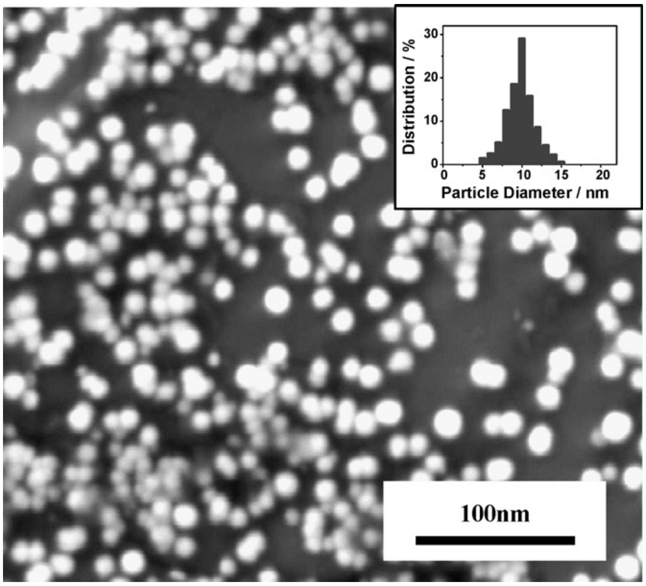

Fig. 1. FE-SEM image of the $Pd_{0.8}Pt_{0.2}$/Ti catalyst and the inset is the histogram of the particle size distribution.

3.2. Methanol electrooxidation on Pd_xPt_{1-x}/Ti electrodes

Fig. 3 shows the CV curves of the methanol oxidation in a N_2-saturated 1.0 M KOH solution containing 1.0 M methanol on the as prepared Pd_xPt_{1-x}/Ti electrodes. The CV curves were measured at a sweep rate of 50 mV s^{-1} in the potential range from −0.9 to 0.3 V. The reaction kinetics parameters of the Pd_xPt_{1-x}/Ti catalysts, including the onset potential (E_s), the peak potential (E_p), the peak current density (j_p) and the current density at −0.4 V ($j_{-0.4\,V}$) are given in Table 1. The alcohol electrooxidation on the electrodes is characterized by two well-defined current peaks in the forward and reverse scans. The forward scan peak currents present the electrochemical oxidation reaction of the freshly chemisorbed species coming from alcohol solution (i.e., the methanol in this case). The reverse scan peak is primarily related with removal of carbonaceous species which are not completely oxidized in the forward scan. The magnitude of current density at −0.4 V in the forward scan indicates the catalytic activity of the electrocatalysts for the methanol oxidation reaction. The comparison of the electrochemical performances of Pd/Ti, $Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti, $Pd_{0.2}Pt_{0.8}$/Ti and Pt/Ti as electrocatalysts for methanol oxidation is shown in Table 1. The highest peak current density at −0.4 V obtained for the methanol oxidation is 2.1 mA cm^{-2} on $Pd_{0.8}Pt_{0.2}$/Ti, which is four times higher

Table 1
The electrochemical performances of as-synthesized catalysts for the methanol electrooxidation in a 1.0 M methanol + 1.0 M KOH solution at a sweep rate of 50 mV s^{-1}, 298 K.

Catalysts	E_s/V	E_p/V	j_p/mA cm^{-2}	j at −0.4 V/mA cm^{-2}
Pd/Ti	−0.51	−0.22	7.7	0.5
$Pd_{0.8}Pt_{0.2}$/Ti	−0.53	−0.23	22.3	2.1
$Pd_{0.5}Pt_{0.5}$/Ti	−0.53	−0.25	13.2	0.7
$Pd_{0.2}Pt_{0.8}$/Ti	−0.53	−0.24	7.4	0.8
Pt/Ti	−0.52	−0.27	5.4	1.0

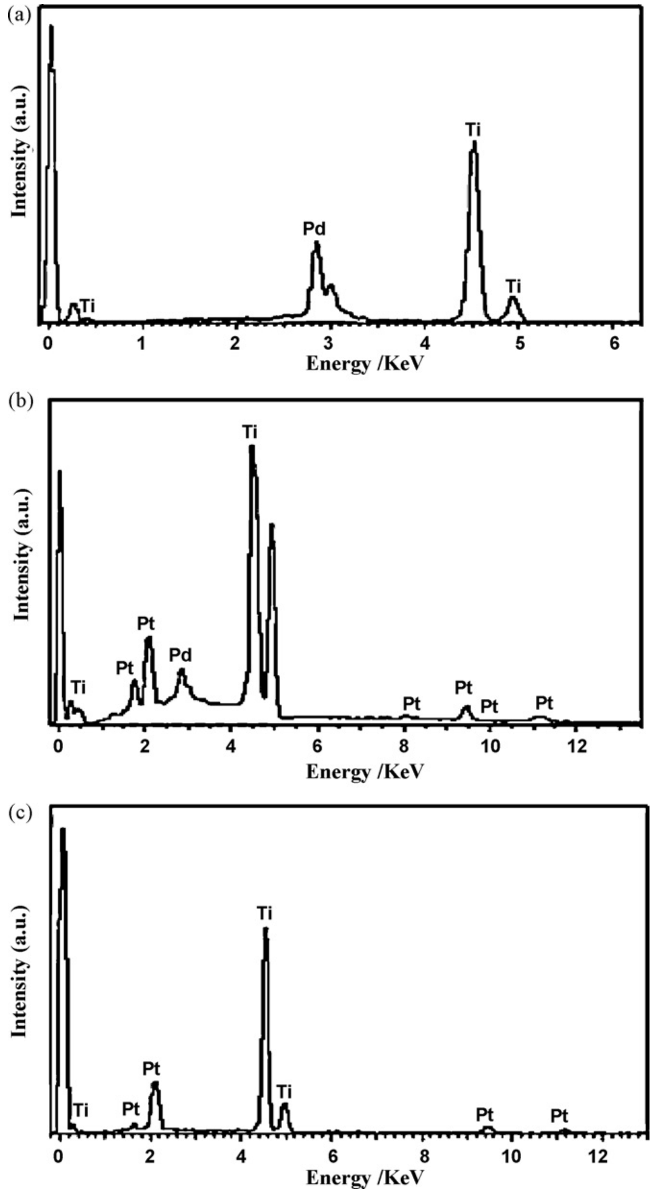

Fig. 2. EDS curves of (a) Pd/Ti catalyst, (b) $Pd_{0.8}Pt_{0.2}$/Ti catalyst and (c) Pt/Ti catalyst.

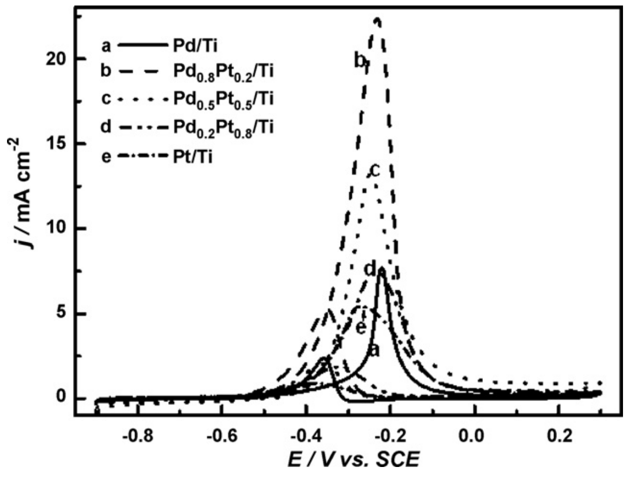

Fig. 3. Cyclic voltammograms of Pd/Ti, $Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti, $Pd_{0.2}Pt_{0.8}$/Ti and Pt/Ti electrodes in a 1.0 M methanol + 1.0 M KOH solution at a scan rate of 50 mV s^{-1} and 298 K.

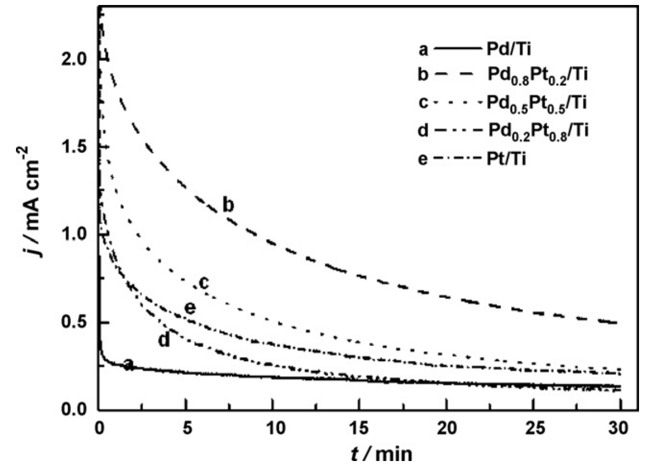

Fig. 4. Chronoamperometric curves for the methanol oxidation measured at −0.4 V on Pd/Ti, $Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti, $Pd_{0.2}Pt_{0.8}$/Ti and Pt/Ti electrodes in a 1.0 M methanol + 1.0 M KOH solution at 298 K.

than that on Pd/Ti electrode and two times higher than that on Pt/Ti electrode. The onset potential (E_s) of methanol oxidation is −0.55 V on Pd/Ti and −0.56 V on Pt/Ti electrode and it negatively shifts to −0.68 V on $Pd_{0.8}Pt_{0.2}$/Ti electrodes. More than 100 mV reduction on the onset potential for anodic reaction is significant for liquid fuel cell. The change in the onset potential shows an improvement in the kinetics due to synergistic effect by the interaction between Pd and Pt for the methanol electrooxidation reaction.

Fig. 4 is the chronoamperometry (CA) curves showing the different stabilities of the Pd_xPt_{1-x}/Ti electrodes for methanol electrooxidation. The potential was constantly held at −0.4 V and the change in current with time was recorded and plotted. As can be seen, there is a continuous current drop with test time elapsing, very rapid at the initial stage and then followed by a much slower decay. The rapid current decay means the quick poisoning effect on the catalyst surface, indicating the low tolerance to poisoning by carbonaceous or CO intermediates formed during the methanol oxidation reactions. As shown from Fig. 4, the $Pd_{0.8}Pt_{0.2}$/Ti electrode shows the best stability and this is consistent with the high catalytic activity of the catalyst (see Fig. 3).

3.3. Ethanol electrooxidation on Pd_xPt_{1-x}/Ti electrodes

The ethanol electrooxidation reactions on the Pd_xPt_{1-x}/Ti electrodes were performed in 1.0 M ethanol + 1.0 M KOH solution at a scan rate of 50 mV s^{-1}. The curves were shown in Fig. 5 and the corresponding performance data of E_s, E_p, j_p and $j_{-0.4\,V}$ are listed in Table 2. The catalytic activity and stability of $Pd_{0.8}Pt_{0.2}$/Ti is higher than that of Pd/Ti. The j_p of $Pd_{0.8}Pt_{0.2}$/Ti is 20.0 mA cm^{-2}, which is much higher than 11.1 mA cm^{-2} of Pd/Ti and Pt/Ti. The highest peak current density at −0.4 V obtained for ethanol oxidation is 8.8 mA cm^{-2} on $Pd_{0.5}Pt_{0.5}$/Ti, which is about two times higher than that on Pd/Ti electrode and six times higher than that on Pt/Ti electrode. The onset potential (E_s) of ethanol oxidation is −0.66 V

Table 2
The electrochemical performances of as-synthesized catalysts for the ethanol electrooxidation in a 1.0 M ethanol + 1.0 M KOH solution at a sweep rate of 50 mV s^{-1}, 298 K.

Catalyst	E_s/V	E_p/V	j_p/mA cm^{-2}	j at −0.4 V/mA cm^{-2}
Pd/Ti	−0.68	−0.26	11.1	4.8
$Pd_{0.8}Pt_{0.2}$/Ti	−0.69	−0.24	20.0	6.4
$Pd_{0.5}Pt_{0.5}$/Ti	−0.74	−0.42	9.2	8.8
$Pd_{0.2}Pt_{0.8}$/Ti	−0.64	−0.29	4.7	2.5
Pt/Ti	−0.63	−0.30	1.9	1.3

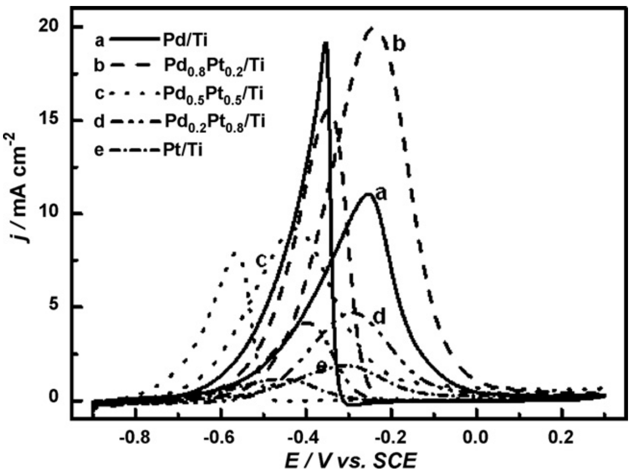

Fig. 5. Cyclic voltammograms of Pd/Ti, $Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti, $Pd_{0.2}Pt_{0.8}$/Ti and Pt/Ti electrodes in a 1.0 M ethanol + 1.0 M KOH solution at a scan rate of 50 mV s^{-1} and 298 K.

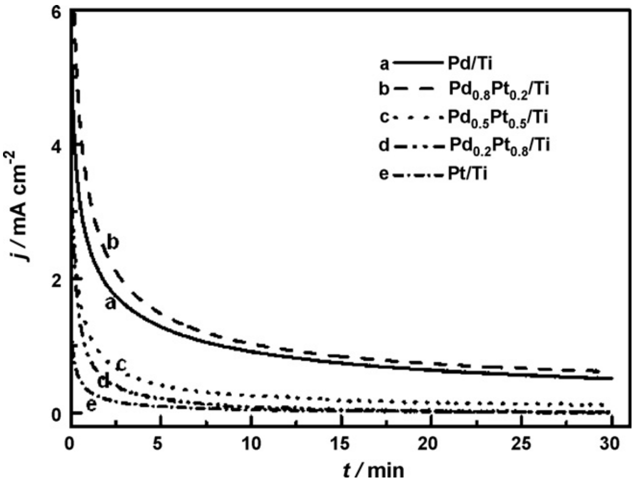

Fig. 6. Chronoamperometric curves for the ethanol oxidation, measured at −0.4 V on Pd/Ti, $Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti, $Pd_{0.2}Pt_{0.8}$/Ti and Pt/Ti electrodes in a 1.0 M ethanol + 1.0 M KOH solution at 298 K.

on Pd/Ti and −0.64 V on Pt/Ti electrode and it negatively shifts to −0.79 V on $Pd_{0.5}Pt_{0.5}$/Ti electrodes, more than 100 mV reduction on the onset potential for the ethanol electrooxidation reaction as compared to that on pure Pd and Pt. The change in the onset potential shows an improvement in the kinetics due to synergistic effect by the interaction between Pd and Pt for ethanol electrooxidation. The results also show that Pd/Ti has higher catalytic activity than Pt/Ti for ethanol oxidation in alkaline media, similar to the previous work [29,30]. The ratio of Pd to Pt in the Pd_xPt_{1-x}/Ti catalysts affects the catalytic activity for ethanol oxidation. The best performance was found when the ratio of Pd to Pt is from 0.5:0.5 to 0.8:0.2 in the Pd_xPt_{1-x}/Ti. The $Pd_{0.8}Pt_{0.2}$/Ti has the highest electrooxidation current and $Pd_{0.5}Pt_{0.5}$/Ti has the most negative onset potential for ethanol electrooxidation in alkaline medium. This has an important implication for the development of DEFC because ethanol is a more attractive and friendly fuel.

Pure Pt/Ti displays the lowest catalytic activity for ethanol oxidation in alkaline medium. The overall oxidation reaction equation for the direct ethanol fuel cell (DEFC) in alkaline medium is:

$$CH_3CH_2OH + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^- \qquad (1)$$

However, in reality the oxidation reaction of ethanol proceed in multiple steps. According to the literature, the electrooxidation reaction of ethanol is considered to be very complex because several reaction products and intermediates will be formed for reaction on Pt-based catalysts. High yields of partial oxidation products such as CH_3CHO and CH_3COOH are formed at the catalysts and these parallel reactions will cause a considerable reduction of the fuel efficiency and produce undesirable by-products [37]. The most possible anodic reactions of the ethanol oxidation in alkaline medium could be written as follows:(2)$CH_3CH_2OH + 3OH^- \rightarrow CH_3CO_{ads} + 3H_2O + 3e^-$

$$OH^- \leftrightarrow OH_{ads} + e^- \qquad (3)$$

$$CH_3CO_{ads} + OH_{ads} \rightarrow CHCOOH \qquad (4)$$

The reactive intermediates formed during the ethanol dehydrogenation react with OH_{ads} formed by the OH^- anion adsorption to produce acid in acidic solution or anion in alkaline solution. The acetic acid formed which is the main intermediate for ethanol oxidation in alkaline medium may not be further oxidized. The breaking of the C–C bond in ethanol for total oxidation to CO_2 is a major problem in the electrochemical oxidation reaction of ethanol [38].

The stability for the ethanol electrooxidation on Pd_xPt_{1-x}/Ti electrodes was investigated with CA method. The results are shown in Fig. 6. The current decays rapidly on Pt/Ti, however, the current decays relatively slowly on Pd/Ti. That results show that Pd/Ti has better steady-state electrocatalytic activity than Pt/Ti for ethanol oxidation in alkaline media. The results are same to the previous work [29,30]. The ratio of Pd to Pt in the Pd_xPt_{1-x}/Ti catalysts affects the stability for ethanol oxidation. The catalytic activity and stability increases with the increase in the amount of Pd. The best performance was found when the ratio of Pd to Pt is 0.8:0.2 in the Pd_xPt_{1-x}/Ti. The catalytic activity and stability of $Pd_{0.8}Pt_{0.2}$/Ti is higher than that of Pd/Ti.

3.4. Propanol electrooxidation on Pd_xPt_{1-x}/Ti electrodes

Fig. 7 illustrates the CV curves of 2-propanol electrooxidation on the Pd_xPt_{1-x}/Ti electrodes. The corresponding performance data of E_s, E_p, j_p and $j_{-0.4\,V}$ are listed in Table 3. Similarly to methanol and ethanol oxidation, the electrooxidation of 2-propanol is also characterized by two well-defined current peaks in the forward and reverse scans. The highest peak current density at −0.4 V obtained

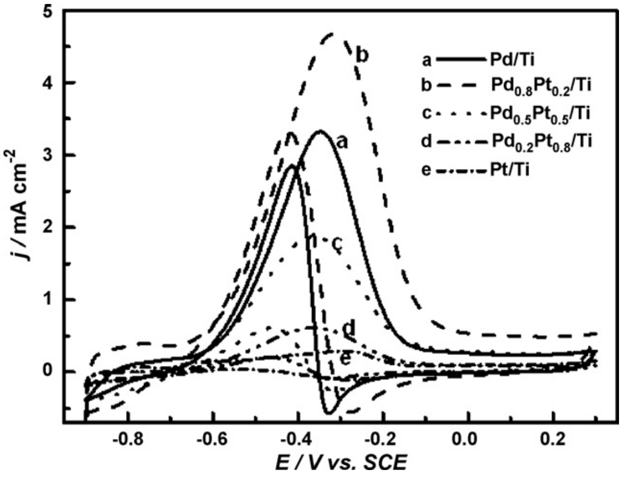

Fig. 7. Cyclic voltammograms of Pd/Ti, $Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti, $Pd_{0.2}Pt_{0.8}$/Ti and Pt/Ti electrodes in a 1.0 M 2-propanol + 1.0 M KOH solution at a scan rate of 50 mV s^{-1} and 298 K.

Table 3
The electrochemical performances of as-synthesized catalysts for the 2-propanol electrooxidation in a 1.0 M 2-propanol + 1.0 M KOH solution at a sweep rate of 50 mV s^{-1}, 298 K.

Catalyst	E_s/V	E_p/V	j_p/mA cm^{-2}	j at −0.4 V/mA cm^{-2}
Pd/Ti	−0.65	−0.34	3.3	2.8
$Pd_{0.8}Pt_{0.2}$/Ti	−0.68	−0.32	4.7	3.7
$Pd_{0.5}Pt_{0.5}$/Ti	−0.70	−0.36	1.9	1.8
$Pd_{0.2}Pt_{0.8}$/Ti	−0.69	−0.35	0.6	0.6
Pt/Ti	−0.69	−0.31	0.3	0.2

for 2-propanol oxidation is 3.7 mA cm^{-2} on $Pd_{0.8}Pt_{0.8}$/Ti electrode. The stability of the Pd_xPt_{1-x}/Ti electrodes for 2-propanol electrooxidation was also studied by CA method and the results were shown in Fig. 8. Similarly, the currents decay fast initially and reach a steady state after tested for some period. From the results, the Pt/Ti electrode shows the worst stability for 2-propanol electrooxidation in alkaline medium. Pd/Ti has a better steady-state activity than Pt/Ti for the 2-propanol oxidation reaction in alkaline media. The ratio of Pd to Pt in the Pd_xPt_{1-x}/Ti catalysts also affects the catalytic activity and stability for 2-propanol oxidation. The best performance was obtained when the ratio of Pd to Pt is 0.8: 0.2 in the Pd_xPt_{1-x}/Ti. The catalytic activity and stability of $Pd_{0.8}Pt_{0.2}$/Ti is higher than that of Pd/Ti. The $Pd_{0.8}Pt_{0.2}$/Ti manifests the highest current value in the catalysts. The current become relative stable after about 10 min, exhibiting that adsorption and desorption of intermediates on the catalysts surfaces reach a temporary equilibrium.

By comparing to methanol, ethanol and 2-propanol electrooxidation, Pd/Ti shows higher activity and better stability than Pt/Ti for the electrooxidation reactions of ethanol and 2-propanol, while Pt/Ti shows a better stability towards the methanol electrooxidation as compared to Pd/Ti in alkaline medium. The bimetallic catalyst, $Pd_{0.8}Pt_{0.2}$/Ti displays the highest catalytic activity and the best stability for the electrooxidation of alcohols investigated. Meantime, through the comparison of the electrochemical parameters, the peak current densities of the bimetallic catalysts reduce monotonously with the decreasing of the Pd content. It shows that the composition of the bimetallic catalysts possesses an obvious influence on the catalytic activity, and the presence of the second component exhibits evident enhancing effect, which can be interpreted by the bifunctional mechanism or ligand effect involved in the alcohol electrooxidation [39].

Considering both aspects of performance and price, palladium would be a good alternative electrocatalyst for low-temperature fuel cells. The results in the present study clearly show that the $Pd_{0.8}Pt_{0.2}$/Ti has best activity and stability for the electrooxidation of methanol, ethanol and 2-propanol and is a promising catalyst for DAFCs in alkaline medium. Nevertheless, more detailed studies of the mechanism and intermediate and product formation will be in the future works, which can be expected to give an important insight into the factors that determine the relative rates of the multiple pathways for alcohol electrooxidation in alkaline medium.

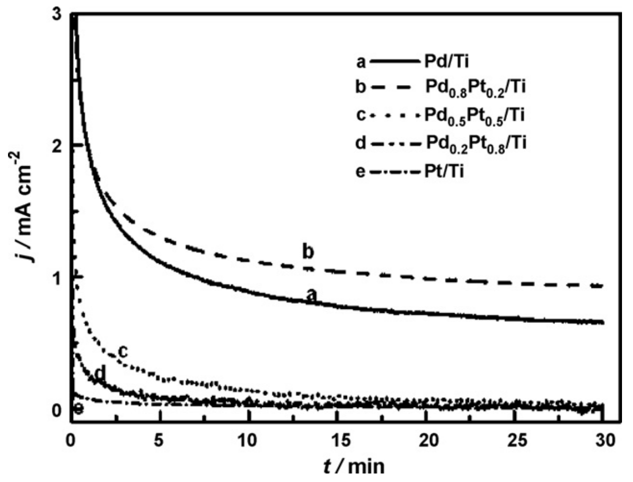

Fig. 8. Chronoamperometric curves for 2-propanol oxidation, measured at −0.4 V on Pd/Ti, $Pd_{0.8}Pt_{0.2}$/Ti, $Pd_{0.5}Pt_{0.5}$/Ti, $Pd_{0.2}Pt_{0.8}$/Ti and Pt/Ti electrodes in a 1.0 M 2-propanol + 1.0 M KOH solution at 298 K.

4. Conclusions

Nano-structured bimetallic Pd_xPt_{1-x} catalysts supported on Ti substrate with varying Pd:Pt atomic ratios have been prepared by electrodeposition. The electrodeposition method is found to be convenient for synthesizing nanocomposite catalysts on metal substrate surface. The particle size of the as synthesized bimetallic catalysts is ∼10 nm and uniform distributed without coagulation. The electrochemical results indicate that the molar ratio of Pd and Pt possesses the evident influence to the catalytic activities. $Pd_{0.8}Pt_{0.2}$/Ti displays the highest electrocatalytic activity and it presents the best tolerance to carbonaceous intermediates for the investigated alcohols in alkaline medium.

Acknowledgements

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