

Short communication

Electro-oxidation of methanol, 1-propanol and 2-propanol on Pt and Pd in alkaline medium

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Abstract

Pd is investigated as electrocatalyst for 1-propanol and 2-propanol oxidation and compared with the conventional catalyst of Pt in alkaline medium. The results show that Pd is a good electrocatalyst for 1-propanol and 2-propanol oxidation. The oxidation reaction of 1-propanol and 2-propanol shows a very low activity on Pt electrode, however the oxidation reaction of 1-propanol and 2-propanol shows a high activity on Pd electrode in alkaline medium. The current densities of 1-propanol and 2-propanol oxidation on Pd electrode are much higher at corresponding potentials than that of methanol oxidation and the onset potentials of 1-propanol and 2-propanol oxidation on Pd electrode are more negative compared with that of methanol oxidation. The 1-propanol and 2-propanol oxidation on Pd electrode shows a stable performance. The results show that Pd can take the place of Pt for 1-propanol and 2-propanol oxidation in alkaline medium. The present study shows a promising choice of Pd as effective electrocatalyst for 1-propanol and 2-propanol electro-oxidation in alkaline medium.

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1. Introduction

Direct alcohol fuel cells (DAFCs) based on methanol as fuel have attracted enormous attention as power sources for portable electronic devices and transportation due to the much higher energy density than gaseous fuels such as hydrogen and natural gas [1,2]. However, the development of DAFCs based on methanol fuel is facing serious difficulties [3,4]: (i) slow electrokinetic of methanol oxidation, (ii) high-methanol crossover and (iii) high toxicity of methanol. Therefore, other alcohols were considered as alternative fuels. Here, the saturated C₃-alcohols (1-propanol and 2-propanol) were investigated as the fuels for DAFCs. Especially, direct 2-propanol fuel cells have attracted more and more attention as 2-propanol is the smallest secondary alcohol, less toxic than methanol and its electrochemical oxida-

tion is of great interest due to its particular molecular structure [5]. The direct alcohol fuel cells using 2-propanol as fuel show much higher performance than direct methanol fuel cells and a much lower crossover current [6–8].

Pt has been extensively investigated as the electrocatalyst for methanol, 1-propanol and 2-propanol electro-oxidation in acid medium [9–13]. However, Pt has a low activity for alcohol electro-oxidation in acid medium. If alcohol electro-oxidation proceeds in an alkaline instead of an acidic medium, the kinetics will be significantly improved [14–17]. However, alkaline medium is not stable for DAFCs owing to the carbonation of alkaline electrolyte. Thus, to avoid the carbonation alkaline membranes should be used [18–20]. The DAFCs with alkaline membrane show reasonable performance stability.

A lot of work has been done to study the electro-oxidation of methanol, 1-propanol and 2-propanol on Pt-based catalysts in alkaline medium [21–24]. However, the high price and limited supply of Pt constitute a major barrier to the development of DAFCs. Pt-free electrocatalysts such as Pd may be used as electrocatalysts for the methanol, 1-propanol and 2-propanol oxidation in alkaline medium. Pd-based electrocatalysts have been used for formic acid and hydrazine electro-oxidation in acid

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medium [25–27] and formaldehyde electro-oxidation in alkaline medium [28]. Our previous work on the development of Pt-free electrocatalysts for alcohol oxidation has focused on Pd-based catalysts and the results revealed that Pd is a good electrocatalyst for methanol and ethanol oxidation in alkaline medium [29,30]. However, there is little information on the electrocatalytic properties of 1-propanol and 2-propanol oxidation on Pd catalyst in alkaline medium. Here, Pd will be investigated as electrocatalyst for 1-propanol and 2-propanol oxidation and compared with the conventional catalyst of Pt in alkaline medium. The study of alcohol oxidation on different catalysts may provide valuable data for development of new, high-active catalysts for alcohol electro-oxidation in alkaline medium.

2. Experimental

Methanol, 1-propanol, 2-propanol and KOH in this work were of analytical grade purity. The experiments were carried out at 25 °C in a temperature-controlled water-bath. All electrochemical measurements were carried out in a three-electrode cell using CHI 700C electrochemical workstation (CHI Instrument, Inc., USA). Solutions were freshly prepared and purged with nitrogen (99.999%) before each experiment.

The working electrodes were platinum and palladium disk (99.999%) with a geometrical area of 0.03 cm². A platinum foil (3.0 cm²) and a saturated calomel electrode (SCE, 0.241 V versus RHE) were used as counter and reference electrodes, respectively. A salt bridge was used between the cell and the reference electrode.

3. Results and discussion

Fig. 1 shows the cyclic voltammograms of methanol, 1-propanol and 2-propanol oxidation in 1.0 M KOH solution containing 1.0 M alcohol on Pt electrode. The sweep rate is 5 mV s⁻¹ in the potential range from -0.9 V to 0.3 V. By comparing with the cyclic voltammogram in the absence of alcohol, an alcohol oxidation peak can be clearly observed. The electro-

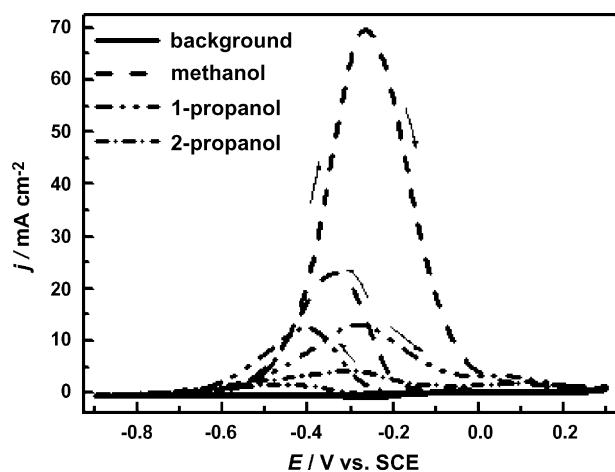


Fig. 1. Cyclic voltammograms of methanol, 1-propanol and 2-propanol oxidation on Pt electrode in 1.0 M KOH solution containing 1.0 M alcohol at a sweep rate of 5 mV s⁻¹.

oxidation of alcohol on Pt electrode was characterized by two well-defined current peaks on the forward and reverse scans. In the forward scan, the oxidation peak is corresponding to the oxidation of freshly chemisorbed species which come from alcohol adsorption. The reverse scan peak is primarily associated with removal of carbonaceous species which are not completely oxidized in the forward scan [31,32]. The magnitude of the peak current on the forward scan indicates the electrocatalytic activity of the electrocatalysts for the oxidation reaction of alcohol in alkaline medium.

The electrochemical performances of the oxidation reaction of methanol, 1-propanol and 2-propanol on Pt electrode were given in Table 1. It is clear that the current densities of methanol oxidation at corresponding potentials are higher than that of 1-propanol and 2-propanol oxidation on Pt electrode. The current density at -0.4 V of methanol oxidation is 2.7 times and 6.4 times than that of 1-propanol and 2-propanol oxidation on Pt electrode. The activity order of alcohol oxidation on Pt electrode is methanol > 1-propanol > 2-propanol. The oxidation reaction of 1-propanol and 2-propanol shows a very low activity on Pt electrode in alkaline medium.

The stability of methanol, 1-propanol and 2-propanol oxidation on Pt electrode in 1.0 M KOH + 1.0 M alcohol was investigated by chronoamperometry at a potential of -0.4 V. The results are shown in Fig. 2. The rapid current decay shows the poisoning of Pt electrode. Nevertheless, at the end of the test, the oxidation current of methanol is larger than that of 1-propanol and 2-propanol on Pt electrode. In the same time, the oxidation current of 2-propanol is smaller than that of 1-propanol on Pt electrode. This indicates that Pt is not a stable and poisoning-tolerance electrocatalyst for 1-propanol and 2-propanol oxidation in alkaline medium.

Fig. 3 shows the cyclic voltammograms of methanol, 1-propanol and 2-propanol oxidation in 1.0 M KOH solution containing 1.0 M alcohol on Pd electrode. The electrochemical performances of the oxidation reaction of alcohol on Pd electrode were given in Table 1. It is clear that the current densities of

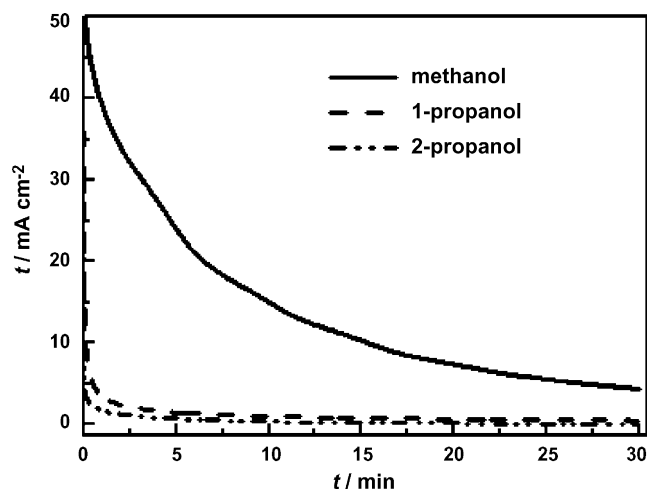


Fig. 2. Chronoamperometric curves for methanol, 1-propanol and 2-propanol oxidation at -0.4 V on Pt electrode in 1.0 M KOH solution containing 1.0 M alcohol.

Table 1

Electrochemical performances of methanol, 1-propanol and 2-propanol oxidation on Pt and Pd electrodes in 1.0M KOH solution containing 1.0M alcohol

Alcohol	E_s (V)		E_p (V)		j_p (mA cm ⁻²)		j at -0.4 V (mA cm ⁻²)	
	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
CH ₃ OH	-0.62	-0.52	-0.26	-0.27	70	80	21.4	2.9
1-propanol	-0.65	-0.62	-0.28	-0.31	13	78	7.8	23.9
2-propanol	-0.72	-0.78	-0.30	-0.39	4	52	3.4	51

1-propanol and 2-propanol oxidation at corresponding potentials are higher than that of methanol oxidation on Pd electrode. The current densities at -0.4 V of 1-propanol and 2-propanol oxidation are 8.2 times and 17.6 times than that of methanol oxidation on Pd electrode. The onset potentials (E_s) of 1-propanol and 2-propanol oxidation are more negative about 100 mV and 260 mV compared with that of methanol oxidation on Pd electrode. The peak currents of 1-propanol and 2-propanol oxidation on Pd electrode begin to rise much more sharply at more negative potential, which will directly improve the fuel cell efficiency. The results show that 1-propanol and 2-propanol oxidation has much higher catalytic activity than methanol electro-oxidation on Pd electrode in alkaline medium. The activity order of alcohol oxidation on Pd electrode is 2-propanol > 1-propanol > methanol. The 2-propanol oxidation shows the highest activity on Pd electrode in alkaline medium.

On the other hand, the current densities at -0.4 V for 1-propanol and 2-propanol oxidation on Pd electrode are about 3.1 times and 15.1 times than that on Pt electrode, respectively. The onset potential for 2-propanol oxidation on Pd electrode is more negative about 60 mV compared with that on Pt electrode. Pd shows better performances than Pt for 1-propanol and 2-propanol oxidation in alkaline medium.

The kinetics for methanol, 1-propanol and 2-propanol oxidation in alkaline medium on both electrodes are determined by the Tafel plots which are shown in Fig. 4. The Tafel slopes for alcohol oxidation on Pt electrode were obtained as 121 mV dec⁻¹ for methanol, 230 mV dec⁻¹ for 1-propanol and

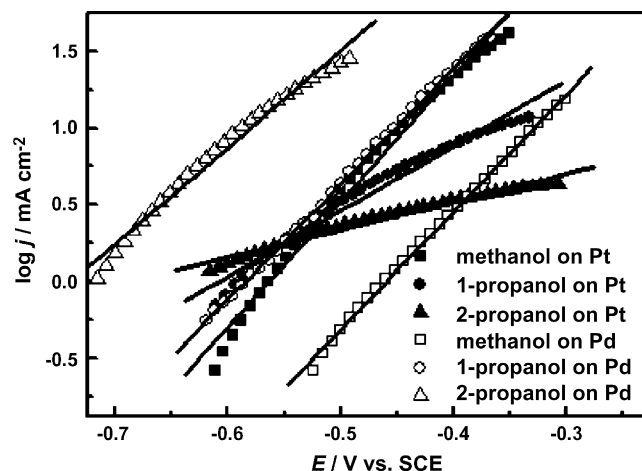


Fig. 4. Tafel plots for methanol, 1-propanol and 2-propanol oxidation on Pt and Pd electrodes in 1.0M KOH solution containing 1.0M alcohol.

542 mV dec⁻¹ for 2-propanol in alkaline medium. The oxidation of 2-propanol on Pt electrode shows a low-reaction activity. The Tafel slopes for alcohol oxidation on Pd electrode were obtained as 131 mV dec⁻¹ for methanol, 134 mV dec⁻¹ for 1-propanol and 156 mV dec⁻¹ for 2-propanol in alkaline medium. The almost identical Tafel slopes for three alcohols oxidation indicate the same reaction mechanism on Pd electrode. The Tafel slope for 2-propanol oxidation on Pd electrode was much lower than that on Pt electrode. The results show that the 2-propanol oxidation on Pd electrode has a higher reaction activity than that on Pt electrode in alkaline medium.

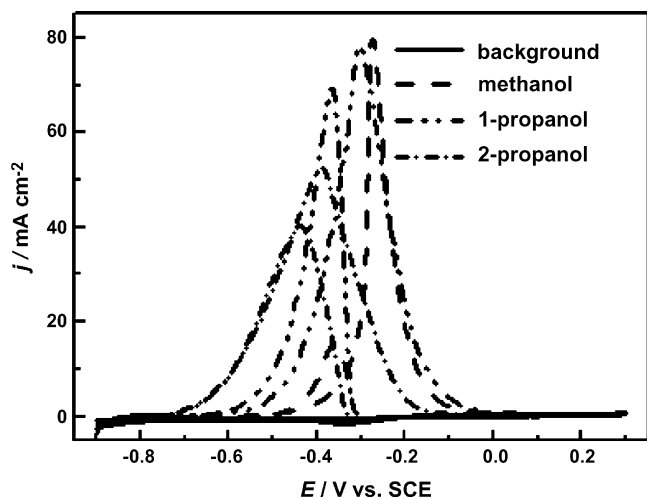


Fig. 3. Cyclic voltammograms of methanol, 1-propanol and 2-propanol oxidation on Pd electrode in 1.0M KOH solution containing 1.0M alcohol at a sweep rate of 5 mV s⁻¹.

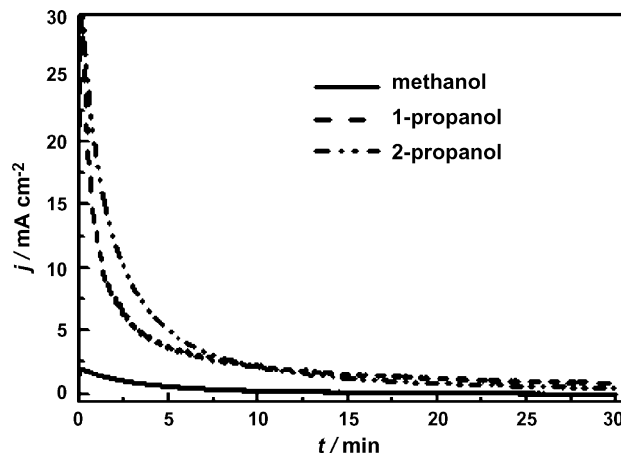


Fig. 5. Chronoamperometric curves for methanol, 1-propanol and 2-propanol oxidation at -0.4 V on Pd electrode in 1.0M KOH solution containing 1.0M alcohol.

The stability of methanol, 1-propanol and 2-propanol oxidation on Pd electrode in 1.0 M KOH + 1.0 M alcohol was investigated by chronoamperometry at a potential of -0.4 V. The results are shown in Fig. 5. The currents of 1-propanol and 2-propanol oxidation are larger than that of methanol oxidation on Pd electrode. This indicates that Pd is a stable and poisoning-tolerance electrocatalyst for 1-propanol and 2-propanol oxidation in alkaline medium.

4. Conclusions

The preliminary results in the present study show that Pd is a good electrocatalyst for 1-propanol and 2-propanol oxidation. The activity order of alcohol oxidation on Pt electrode is methanol > 1-propanol > 2-propanol. The 1-propanol and 2-propanol oxidation shows a very low activity on Pt electrode in alkaline medium. The activity order of alcohol oxidation on Pd electrode is 2-propanol > 1-propanol > methanol. The 2-propanol oxidation shows the highest activity on Pd electrode in alkaline medium. The current densities at corresponding potentials of 1-propanol and 2-propanol oxidation on Pd electrode are much higher than that on Pt electrode and the onset potential of 2-propanol oxidation on Pd electrode is more negative compared with that on Pt electrode. The results show that Pd can take the place of Pt for 1-propanol and 2-propanol oxidation in alkaline medium.

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