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Comparison of Alcohol Electrooxidation on Pt and Pd Electrodes in Alkaline Medium

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Here, we have compared the activity of alcohol electrooxidation on Pt and Pd electrodes. Ethanol and isopropanol can be more easily electrochemically oxidized than other alcohol on the both Pt and Pd electrodes. The methanol shows a good activity of electrooxidation on the Pt electrode, however shows a very bad activity of electrooxidation on the Pd electrode. Ethylene glycol and glycerol show the best activity of electrooxidation on the Pt electrode, however show a very low current at low potential on the Pd electrode. The activity order on the Pd electrode is n-propanol > isopropanol > ethanol > ethylene glycol > glycerol > methanol.

Keywords: Fuel cell, Alcohol electrooxidation, Palladium, Ethanol, Propanol

1. INTRODUCTION

Much effort has been devoted to the development of direct alcohol fuel cells (DAFCs) [1-3]. Among the different possible alcohols, methanol is the most promising fuel because its use as a fuel has several advantages in aqueous electrolytes, available at low cost, easily handled, transported and stored, high theoretical density of energy comparable with that of gasoline [4]. Other alcohol such as ethanol has also been considered for use in fuel cells [5,6]. Ethanol is less toxic compared to methanol, and can be easily produced in great quantity by fermentation of sugar-containing raw material. The saturated C_3-alcohols (n-propanol and isopropanol) have also been investigated as the fuels for DAFCs due to they are less toxic than methanol [7-9]. The DAFCs using C_3-alcohols as fuel show better performance and a much lower crossover current than direct methanol fuel cells (DMFCs) [10,11]. Polyhydric alcohols such as ethylene glycol (EG) and glycerol have high boiling points and are much less volatile. They have higher theoretical energy density than methanol and can be easily electrochemically oxidized [12,13]. The application of EG and glycerol on DAFCs has attracted increased interests [14-16]. The DAFCs based on EG fuel show certain advantages such as low fuel cross-over and high power density [17,18].

A lot of work has been done to study the electrooxidation of alcohol on Pt-based catalysts in alkaline medium. However, the limited supply of Pt constitutes major barriers to the development of DAFCs. 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 ethanol, n-propanol and isopropanol oxidation in alkaline medium [19-21]. The similar results have been reported by many other researchers [22-24]. The alcohol electrooxidtion on the Pd electrode in alkaline medium has obtained more and more interest and been studied in the last five years. So the different performance of alcohol electrooxidation on different electrode must be further compared to obtain more formation. Here, we compare the electrooxidation activity of all saturated alcohols which can be dissolved in aqueous solution, such as methanol, ethanol, n-propanol, isopropanol, EG and glycerol on the Pt and Pd electrodes, just to find out the appropriate fuel on the different electrocatalyst.

2. EXPERIMENTAL DETAILS

Alcohol (methanol, ethanol, n-propanol, isopropanol, EG, glycerol) and KOH in this work were of analytical grade purity. The experiments were carried out in a temperature-controlled water-bath (Polyscience 9106, U.S.A.). All electrochemical measurements were carried out in a three-electrode cell using CHI 700C electrochemical workstation (CHI Instrument, Inc., U.S.A.). 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 cm^2. A platinum foil (3.0 cm^2) 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 linear sweep curves (LSCs) of alcohol (methanol, ethanol, n-propanol, isopropanol, EG and glycerol) oxidation in 1.0 M KOH solution containing 1.0 M alcohol on the Pt electrode. The sweep rate is 0.05 V s^{-1} in the potential range from -0.95 to 0 V. The electrochemical performance of the oxidation reaction of alcohol on the Pt electrode was given in Table 1. Fig. 2 shows Tafel curves from the LSCs of Pt electrode in 1.0 M KOH + 1.0 M alcohol with a scan rate of 0.005 V s^{-1}. The lowest point is the equilibrium potential which is the onset potential (Es) for alcohol electrooxidation. The values of Es for alcohol oxidation on the Pt electrode were given in Table 1. The lower value of Es shows more easily electrochemically oxidized for alcohol. The Fig. 2 and Table 1 show that methanol has the highest value of Es. The other alcohols are more easily electrochemically oxidized than methanol. The oxidized order for alcohol electrooxidation on the Pt electrode is isopropanol > ethanol > glycerol > EG > n-propanol > methanol. The isopropanol and ethanol show lower value of Es on the

Pt than other alcohol, which shows that isopropanol and ethanol can be more easily electrochemically oxidized than other alcohol.

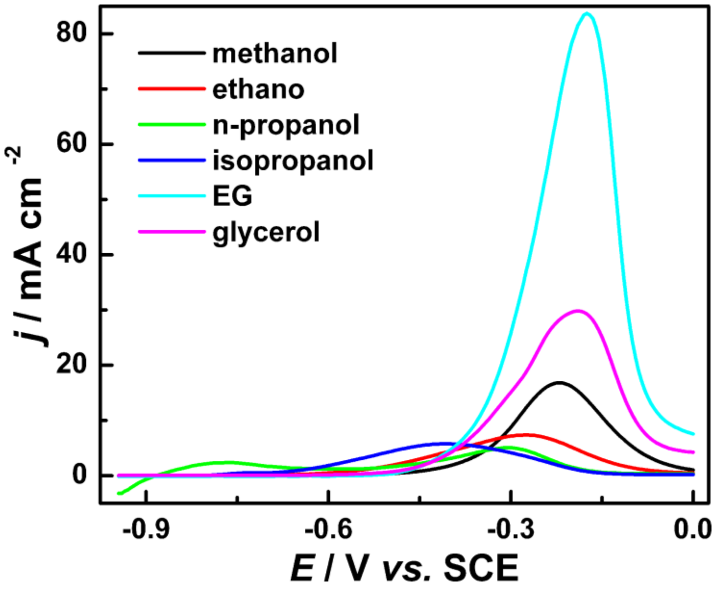

Fig.1 Linear sweep curves of Pt electrode in 1.0 M KOH + 1.0 M alcohol with a scan rate of 0.05 V s^{-1}, 298 K.

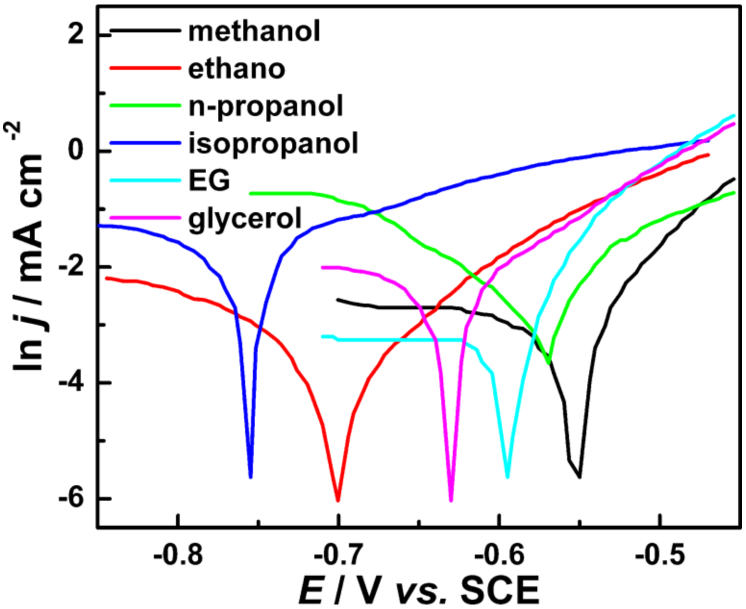

Fig.2 Tafel curves from the linear sweep curves of Pt electrode in 1.0 M KOH + 1.0 M alcohol with a scan rate of 0.005 V s^{-1}, 298 K.

The electrochemical performance of alcohol oxidation is different at different potential. The EG and glycerol show a better performance of electrooxidation than methanol for whole potential. The oxidation current of ethanol, n-propanol, isopropanol is higher than that of methanol at low potential such as -0.4 V. However, the intermediate species of ethanol, n-propanol and isopropanol electrooxidation will block the Pt surface and decrease the electrooxidation current of ethanol, n-propanol and isopropanol. So the oxidation current of ethanol, n-propanol and isopropanol electrooxidation will decrease rapidly at higher potential, and lower than that of methanol at higher potential such as -0.3 V.

Table 1 Comparison of the electrochemical performances of alcohol oxidation on the Pt and Pd electrodes, 298 K

Alcohol	E_s/V		E_p/V		j_p/mA cm^{-2}		$j_{-0.4\ V}$/mA cm^{-2}		$j_{-0.3\ V}$/mA cm^{-2}	
	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd	Pt	Pd
methanol	-0.549	-0.336	-0.220	-0.200	16.8	3.1	1.8	≈ 0	8.8	0.3
ethanol	-0.701	-0.663	-0.276	-0.235	7.4	5.1	4.4	2.2	7.2	4.3
n-propanol	-0.570	-0.636	-0.305	-0.285	5.1	14.2	3.1	6.6	5.1	13.8
isopropanol	-0.755	-0.709	-0.407	-0.343	5.7	4.1	5.8	3.5	4.2	3.3
EG	-0.595	-0.451	-0.175	-0.179	83.7	58.2	4.6	0.3	25.8	2.0
glycerol	-0.630	-0.478	-0.185	-0.178	29.8	29.6	4.1	≈ 0	15.0	0.7

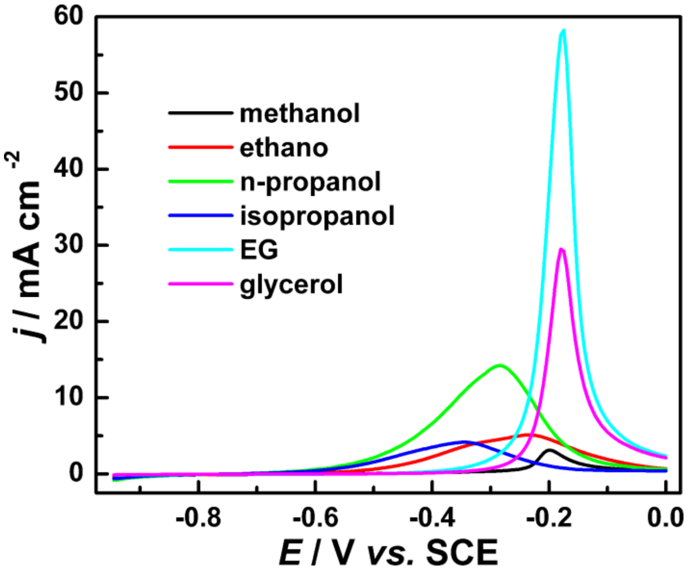

Fig.3 Linear sweep curves of Pd electrode in 1.0 M KOH + 1.0 M alcohol with a scan rate of 0.05 V s^{-1}, 298 K.

Fig. 3 shows the LSCs of alcohol (methanol, ethanol, n-propanol, isopropanol, EG and glycerol) oxidation in 1.0 M KOH solution containing 1.0 M alcohol on the Pd electrode. The electrochemical performance of the oxidation reaction of alcohol on the Pd electrode was given in Table 1. Fig. 4 shows the Tafel curves from the LSCs of the Pd electrode in 1.0 M KOH + 1.0 M alcohol with a scan rate of 0.005 V s^{-1}. The values of E_s for alcohol oxidation on the Pd electrode were given in Table 1. The Fig. 3 and Table 1 show that methanol has the highest value of *E*s on the Pd electrode, which is the same as that on the Pt electrode. The other alcohols are more easily electrochemically oxidized on the Pd electrode. The oxidized order for alcohol electrooxidation on the Pd electrode is isopropanol > ethanol > n-propanol > glycerol > EG > methanol. The isopropanol and ethanol show lower value of *E*s than other alcohol on the Pd electrode, showing that isopropanol and ethanol can be more easily electrochemically oxidized than other alcohol on the Pd electrode, which is the same as that on the Pt electrode.

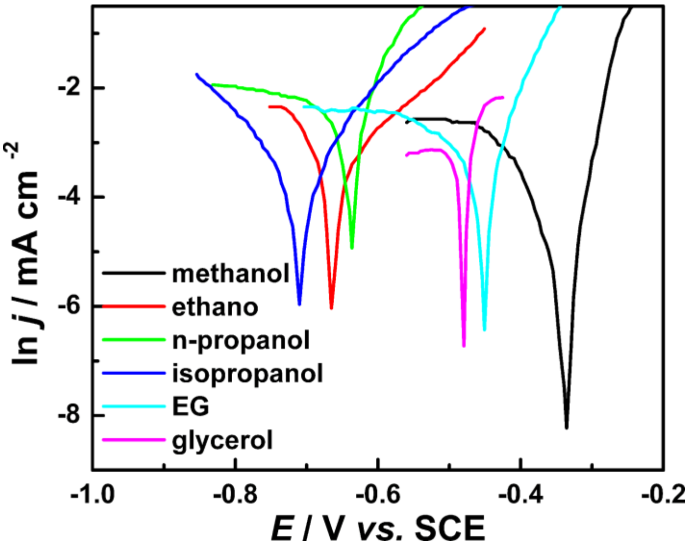

Fig.4 Tafel curves from the linear sweep curves of Pd electrode in 1.0 M KOH + 1.0 M alcohol with a scan rate of 0.005 V s^{-1}, 298 K.

The electrochemical performance of alcohol oxidation on the Pd electrode is different from that on the Pt electrode. The methanol shows a very bad activity of electrooxidation on the Pd electrode. The other alcohols show a better performance of electrooxidation than methanol for whole potential on the Pd electrode. EG and glycerol show a very low electrooxidation current at low potential. The potential of alcohol oxidation usually used in DAFCs is lower than -0.3 V. So EG and glycerol have poor electrocatalytic activity on the Pd electrode. The n-propanol shows the highest activity on the Pd electrode, which is different from that on the Pt electrode, showing a very low activity. The E_a values were found to be 31.6 kJ mol^{-1} for methanol, 26 kJ mol^{-1} for ethanol, 7.68 kJ mol^{-1} for n-propanol and 24.6 kJ mol^{-1} for isopropanol at -0.425 V, 33.6 kJ mol^{-1} for methanol, 26.3 kJ mol^{-1} for ethanol, 10.5 kJ mol^{-1} for n-propanol and 26.3 kJ mol^{-1} for isopropanol at -0.4 V, 35.4 kJ mol^{-1} for methanol, 27.2 kJ mol^{-1} for ethanol, 13.04 kJ mol^{-1} for n-propanol and 23 kJ mol^{-1} for isopropanol at -0.375 V in 1.0 M KOH solution containing 1.0 M alcohol on the Pd electrode [24,25]. The following order of E_a values at around -0.4 V is n-propanol < isopropanol < ethanol < methanol. n-Propanol has the lowest E_a value and shows the best activity of electrooxidation. The activity order on the Pd electrode is n-propanol > isopropanol > ethanol > EG > glycerol > methanol. By the way, the preliminary results show that Pt is a better electrocatalyst for methanol, EG and glycerol oxidation than Pd, and Pd is a better electrocatalyst for ethanol, n-propanol and isopropanol oxidation than Pt.

4. CONCLUSION

In this paper, we have compared the activity of alcohol electrooxidationon Pt and Pd electrodes. The ethanol, n-propanol, isopropanol, EG and glycerol are more easily electrochemically oxidized than methanol on both Pt and Pd electrodes. The oxidized order for alcohol electrooxidation on Pt electrode is isopropanol > ethanol > glycerol > EG > n-propanol > methanol. The oxidized order for alcohol electrooxidation on the Pd electrode is isopropanol > ethanol > n-propanol > glycerol > EG > methanol. Isopropanol and ethanol can be more easily electrochemically oxidized than other alcohol. The electrochemical performances of alcohol oxidation on the Pd electrode are different from that on the Pt electrode. The methanol shows a good activity of electrooxidation on the Pt electrode, however shows a very bad activity of electrooxidation on the Pd electrode. The other alcohols show a better performance of electrooxidation than methanol for whole potential on the Pd electrode. EG and glycerol show the best activity of electrooxidation on the Pt electrode, however show a very low current at low potential on the Pd electrode. The n-propanol shows the highest activity on the Pd electrode. The activity order on the Pd electrode is n-propanol > isopropanol > ethanol > EG > glycerol > methanol. By the way, the preliminary results show that Pt is a good electrocatalyst for methanol, EG and glycerol electrooxidation and Pd is a good electrocatalyst for ethanol, n-propanol and isopropanol oxidation.

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