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Electrooxidation of Methanol, Ethanol and 1-Propanol on Pd Electrode in Alkaline Medium

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Here, the oxidation activity of ethanol and 1-propanol compared methanol on Pd electrode has been studied in alkaline medium. We have used the amount of coulombs (coulometry) and apparent activation energy (E_a) to measure the activity of alcohol electrooxidation. The amount of coulombs during alcohol electrooxidation for ethanol and 1-propanol is much higher than that of methanol showing that ethanol and 1-propanol is more easily electrochemically oxidized than methanol. The E_a values of ethanol and 1-propanol are lower than that of methanol at the potential from -0.45 V to -0.325 V indicating that ethanol and 1-propanol shows better electrooxidation.

Keywords: Fuel cells; Alcohol electrooxidation; Palladium; Ethanol; 1-propanol

1. INTRODUCTION

Much effort has been devoted to the development of direct methanol fuel cells (DMFCs) [1-3]. At the same time, direct ethanol fuel cells (DEFCs) have attracted more and more attention because ethanol is less toxic compared to methanol and can be easily produced in great quantity by the fermentation of sugar-containing raw materials [4-8]. The saturated C_3-alcohols (1-propanol and 2-propanol) have also been investigated as the fuels for DAFCs due to they are less toxic than methanol [9,10]. The DAFCs using C_3-alcohols as fuel show better performance than DMFCs and a much lower crossover current [11,12].

A lot of work has been done to study the electrooxidation of methanol, ethanol and 1-propanol on Pt-based catalysts in alkaline medium [13-17]. However, the activity of ethanol and 1-propanol electrooxidation on Pt-based catalysts is very low and the high price and limited supply of Pt constitute 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 and 1-propanol oxidation in alkaline medium [18-20].

The methods of comparison activity of alcohol electrooxidation are usually used cyclic voltammogram (CV), onset potential (E_s), peak potential (E_p), peak current density (j_p) and so on. However, the alcohol electrooxidation is an electron loss process, so it's more appropriate to use the amount of coulombs to measure the activity and the capacity of electrochemical oxidized for alcohol electrooxidation. Here, we use the amount of coulombs released during alcohol electrooxidation to compare the activity of methanol, ethanol and 1-propanol. Investigation of alcohol electrooxdation reaction mechanisms on electrode is important. However, there is little information on the mechanistic study of methanol, ethanol and 1-propanol oxidation on Pd catalyst in alkaline medium. Here, E_a values for methanol, ethanol and 1-propanol oxidation on Pd electrode will be investigated in alkaline medium. The study of apparent activation energies of alcohol oxidation may provide valuable data for development of new, high active catalysts for alcohol electrooxidation in alkaline medium.

2. EXPERIMENTAL PART

Methanol, ethanol, 1-propanol 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 electrode was 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 CVs of methanol, ethanol and 1-propanol oxidation in 1.0 M KOH solution containing 1.0 M alcohol on Pd electrode. The sweep rate is 0.05 V s^{-1} in the potential range from -0.95 to 0.17 V. The background is the CV of the Pd electrode in 1.0 M KOH solution without alcohol. By comparing to the CV in the absence of alcohol, an alcohol oxidation peak can be clearly observed for both alcohols. The electrooxidation of alcohol 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 [21,22]. The magnitude of the peak current on the forward scan indicates the electrocatalytion activity of the electrocatalyst for the oxidation reaction of alcohol. The electrochemical performances of the oxidation reaction of alcohol on Pd electrode were given in Table 1. It is clear that the current density at -0.4 V ($j_{-0.4V}$) of ethanol and 1-propanol oxidation are 34.6 and 39.2 mA cm^{-2} which are 7.2 and 8.2 times than that of methanol oxidation. The E_s of ethanol and 1-propanol oxidation is more negative about 210 mV and 240 mV compared to that of methanol oxidation. More than 200 mV reduction on the onset potential for anodic reaction is significant for liquid fuel cell. The current of ethanol and 1-propanol oxidation on Pd electrode begins to rise at more negative potential. Here, we firstly used the amount of coulombs released during alcohol electrooxidation to measure the activity of alcohol electrooxidation. The amount of coulombs (Q) is obtained from following integrated equation

$$Q = \frac{1}{v}\int_{E_0}^{E} j dE \qquad (1)$$

Here, Q is the amount of coulombs released during alcohol electrooxidation integrated from the begin potential to the given potential in CV (mC cm^{-2}), the E_0 is begin integrated potential (V), E is given potential (V), j is current density (mA cm^{-2}) and v is scan rate (V s^{-1}).

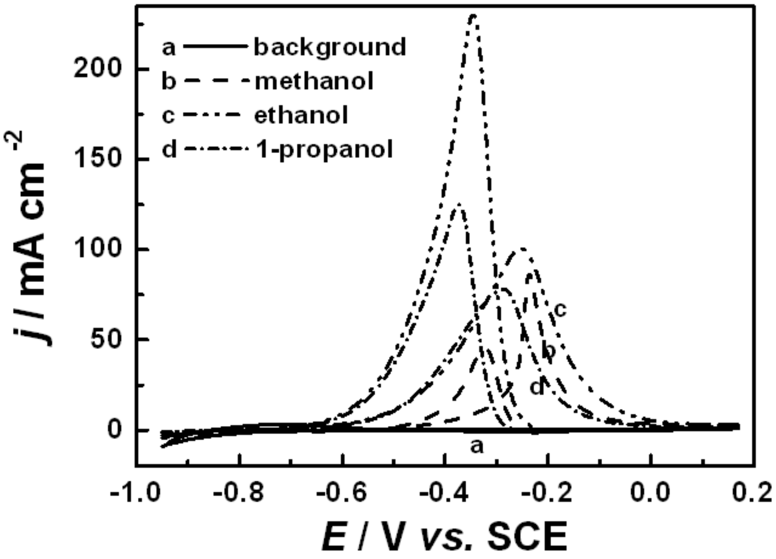

Figure 1. CV curves of Pd electrode in 1.0 M KOH + 1.0 M alcohol, 298 K, 0.05 V s^{-1}.

The amount of coulombs during alcohol electrooxidation which is integrated from -0.8 V to -0.4 V in the CV is 6.9 mC cm^{-2} for methanol, 55.9 mC cm^{-2} for ethanol and 62.3 mC cm^{-2} for 1-

propanol. The onset potential of ethanol and 1-propanol oxidation is more negative and the ethanol and 1-propanol electrooxidation occurs at significantly higher current at low potential than methanol. Ethanol and 2-propanol are more easily electrochemically oxidized than methanol. The amount of coulombs for ethanol and 1-propanol is much higher than that of methanol at low potential. The results show that ethanol and 1-propanol is more easily electrochemically oxidized than methanol. The results also show that 1-propanol oxidation has much higher catalytic activity than methanol and ethanol electrooxidation on Pd electrode in alkaline medium. The activity order of alcohol oxidation on Pd electrode is 1-propanol > ethanol > methanol. The 1-propanol oxidation shows the highest activity on Pd electrode in alkaline medium.

Table 1. Comparison of the electrochemical performances of methanol, ethanol and 1-propanol oxidation on Pd electrode with a sweep rate of 0.05 V s^{-1}, 298 K

Alcohol	E_s / V	E_p / V	j_p / mA cm^{-2}	$j_{-0.4\,V}$ / mA cm^{-2}	$Q_{-0.4V}$/ mC cm^{-2}
methanol	-0.46	-0.24	86.5	4.8	6.9
ethanol	-0.67	-0.25	100.6	34.6	55.9
1-propanol	-0.70	-0.29	78.0	39.2	62.3

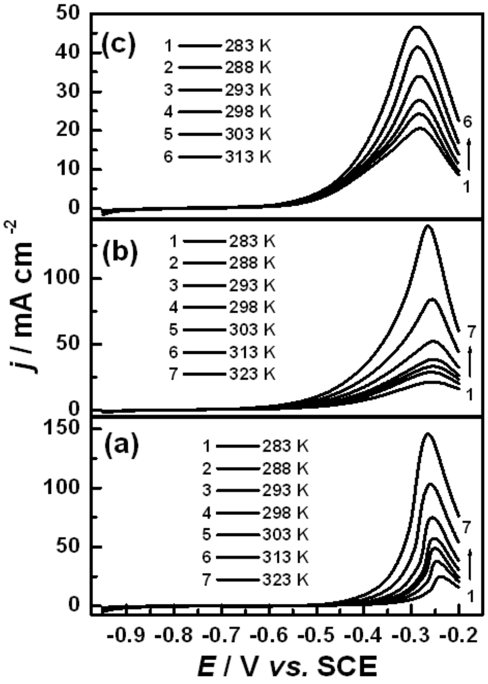

Figure 2. Linear sweep curves of Pd electrode in 1.0 M KOH + 1.0 M alcohol (a. methanol, b. ethanol, c. 1-propanol) from 283 K to 323 K with a scan rate of 0.005 V s^{-1}.

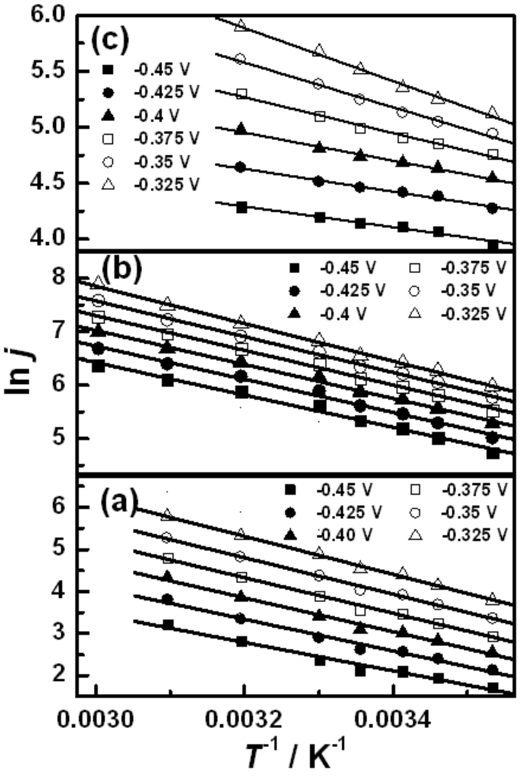

Figure 3. Arrhenius plots of alcohol (a. methanol, b. ethanol, c. 1-propanol) eletrooxidation on Pd at various potentials.

The E_a has been used to compare to the Pt and Pt alloy activity for methanol and ethanol oxidation [23,24]. The results showed that E_a values of Pt alloys are lower than that of Pt. Linear sweep voltammetry (LSV) at a number of different temperatures will be employed in this work to obtain the data needed to calculate E_a values. The determination of E_a values is carried out by increasing the temperature of the solution and obtaining the current density as a function of temperature at a given potential. Fig.2 shows the comparison the electrooxidation activity of methanol, ethanol and 1-propanol on Pd electrode in the temperature range of 283 ~ 323 K. In order to minimize anion adsorption and CO poisoning, as well as to minimize any contributions from double layer charging, the potential was swept at a relatively slow sweep rate of 5 mV s^{-1} [25]. With elevating temperature, the activity of all alcohols oxidation on Pd is markedly increased with the negative shift of the onset potential and the increase in oxidation current.

With respect to the inverse of temperature (1/T) at a fixed potential, E_a value is obtained as follows [26]

$$E_a = -R\left(\frac{\partial \ln j}{\partial (1/T)}\right)_E \qquad (2)$$

Fig.3 represents Arrhenius plots for methanol, ethanol and 1-propanol oxidation current at various potentials for Pd electrode. Linear relationships exist between ln$j$ and $1/T$ thereby indicating that the reaction mechanism at each potential is not changed with temperature. The E_a values were calculated in the potential range of -0.45 V to -0.325 V and shown in Table 2. The E_a values were found to be 33.6 kJ mol^{-1} for methanol, 26.3 kJ mol^{-1} for ethanol and 10.5 kJ mol^{-1} for 2-propanol at -0.4 V. The E_a values of 1-propanol are lower than that of methanol and ethanol at the potential from -0.45 V to -0.325 V indicating that 1-propanol shows better electrooxidation activity than methanol and ethanol. The E_a values are in the following order: 1-propanol < ethanol < methanol. 1-propanol has the lowest E_a value and shows the best electrooxidation activity.

Table 2. The E_a values (kJ mol^{-1}) of alcohol in 1.0 M KOH + 1.0 M alcohol on Pd electrode under various potential

Alcohol	E / V					
	-0.45	-0.425	-0.4	-0.375	-0.35	-0.325
methanol	28.1	31.6	33.6	35.4	35.9	37.9
ethanol	25.7	26	26.3	27.2	28.2	29.2
1-propanol	7.68	8.23	10.46	13.04	16.5	19.9

4. CONCLUSIONS

In this paper, we have used the amount of coulombs (coulometry) and E_a to measure the activity of alcohol electrooxidation. The current density at -0.4 V ($j_{-0.4V}$) of ethanol and 1-propanol oxidation are 34.6 and 39.2 mA cm^{-2} which are 7.2 and 8.2 times than that of methanol oxidation. The E_s of ethanol and 1-propanol oxidation is more negative about 210 mV and 240 mV compared to that of methanol oxidation. The amount of coulombs which is integrated from -0.8 V to -0.4 V is 6.9 mC cm^{-2} for methanol, 55.9 mC cm^{-2} for ethanol and 62.3 mC cm^{-2} for 1-propanol. The E_a values of ethanol and 1-propanol are lower than that of methanol at the potential from -0.45 V to -0.325 V indicating that ethanol and 1-propanol shows better electrooxidation activity than methanol. The activity order of alcohol oxidation on Pd electrode is 1-propanol > ethanol > methanol. The 1-propanol oxidation shows the highest activity on Pd electrode in alkaline medium.

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