



Short communication

Electrooxidation of 2-propanol compared ethanol on Pd electrode in alkaline medium

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ABSTRACT

Here, the oxidation activity of 2-propanol compared ethanol 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 2-propanol is much higher than that of ethanol showing that 2-propanol is more easily electrochemically oxidized than ethanol. The E_a values of 2-propanol are lower than that of ethanol at the potential from -0.45 to -0.375 V which is usually used in direct alcohol fuel cells (DAFCs) indicating that 2-propanol shows better electrooxidation activity than ethanol.

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1. Introduction

Much effort has been devoted to the development of direct methanol fuel cells (DMFCs) [1,2]. 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 [3–7]. The saturated C₃-alcohols (1-propanol and 2-propanol) have also been investigated as the fuels for DAFCs [8,9]. Especially, direct 2-propanol fuel cells have attracted more attention as 2-propanol is the smallest secondary alcohol, less toxic than methanol and its particular molecular structure [10]. The DAFCs using 2-propanol 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 2-propanol on Pt-based catalysts in alkaline medium [13–17]. However, the activity of ethanol and 2-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 2-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 is 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 ethanol and 2-propanol.

2. Experimental

Ethanol, 2-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 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 CVs of ethanol and 2-propanol oxidation in 1.0 M KOH solution containing 1.0 M alcohol on Pd electrode. By comparing to the CV in the absence of alcohol, an alcohol oxidation peak can be clearly observed for both alcohols. The magnitude of

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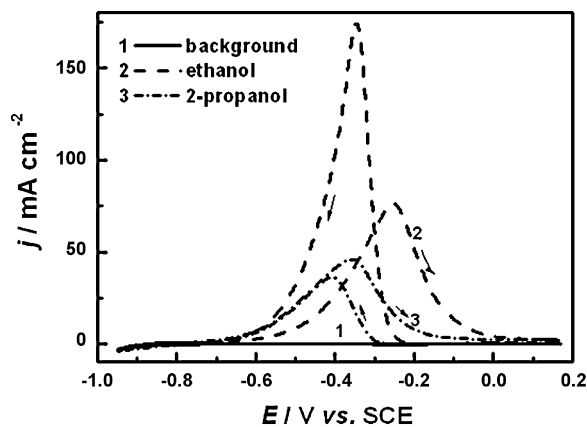


Fig. 1. CVs of Pd electrode in 1.0 M KOH + 1.0 M alcohol, 298 K, 0.005 V s⁻¹.

the oxidation current on the forward scan indicates the activity of the electrocatalyst for the oxidation reaction of alcohol [21,22]. The electrochemical performances of the oxidation reaction of alcohol on Pd electrode were given in Table 1.

The j_p of ethanol oxidation is 76 mA cm⁻² and more higher than that of 2-propanol oxidation which is 46 mA cm⁻². However, the current density at -0.4 V ($j_{-0.4V}$) of 2-propanol oxidation is 1.5 times than that of ethanol oxidation. The E_s of 2-propanol oxidation is more negative about 40 mV compared to that of ethanol oxidation. The current of 2-propanol oxidation on Pd electrode begins to rise at more negative potential. Here, we 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

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

Here, ν is scan rate (V s⁻¹).

The amount of coulombs released during alcohol electrooxidation which is integrated from -0.8 to -0.25 V in the CV is 2018 mC cm⁻² for ethanol and 2054 mC cm⁻² for 2-propanol. The amount of coulombs during alcohol electrooxidation which is integrated from -0.8 to -0.4 V in the CV is 466 mC cm⁻² for ethanol and 996 mC cm⁻² for 2-propanol. The onset potential of 2-propanol oxidation is more negative and the 2-propanol electrooxidation occurs at significantly higher current at low potential than ethanol. 2-Propanol is more easily electrochemically oxidized than ethanol. The concentration of alcohol around electrode decreases with the electrooxidation time. It is well known that the diffusion coefficient of ethanol is higher than that of 2-propanol due to the molecular structure, so the electrooxidation current of 2-propanol decreases faster than that of ethanol with the electrooxidation time. The amount of coulombs for 2-propanol is much higher than that of ethanol at low potential and close to that of ethanol at high potential. The results show that 2-propanol is more easily electrochemically oxidized than ethanol.

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

Table 1

Comparison of the electrochemical performances of ethanol and 2-propanol oxidation on Pd electrode with a sweep rate of 0.005 V s⁻¹, 298 K.

Alcohol	E_s/V	$j_{-0.4V}/\text{mA cm}^{-2}$	$Q_{-0.25V}/\text{mC cm}^{-2}$	$Q_{-0.4V}/\text{mC cm}^{-2}$
Ethanol	-0.65	26.6	2018	466
2-Propanol	-0.69	41.1	2054	996

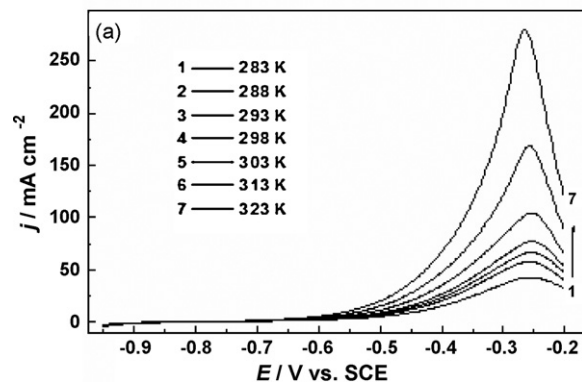
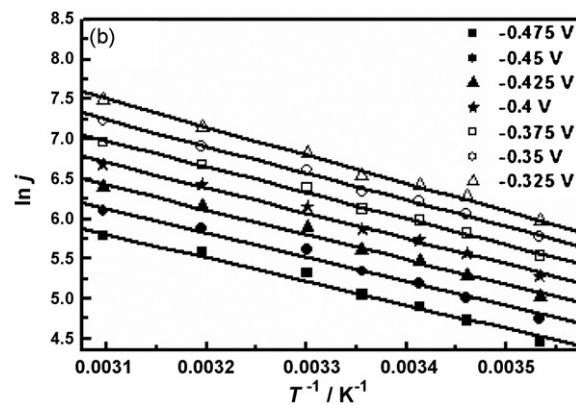


Fig. 2. (a) LSVs of Pd electrode in 1.0 M KOH + 1.0 M ethanol from 283 to 323 K with a scan rate of 0.005 V s⁻¹; (b) Arrhenius plot of ethanol electrooxidation on Pd at various potentials.

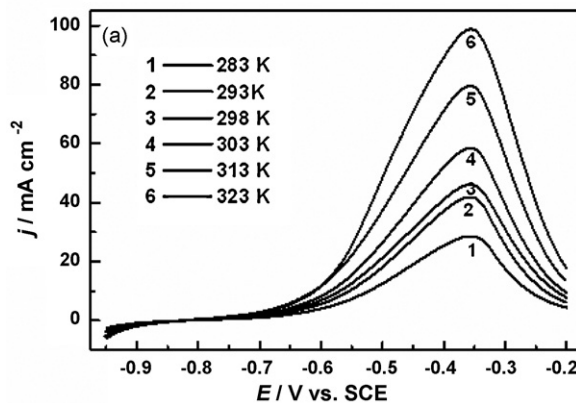
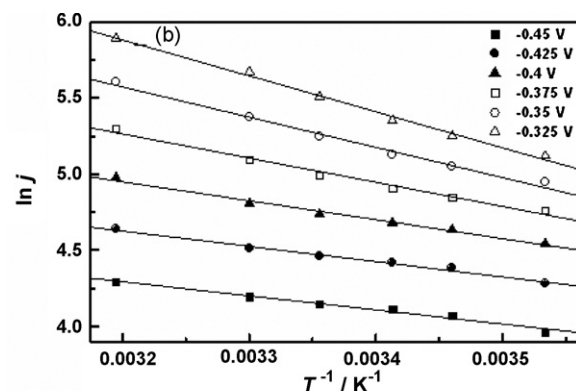


Fig. 3. (a) LSVs of Pd electrode in 1.0 M KOH + 1.0 M 2-propanol from 283 to 323 K with a scan rate of 0.005 V s⁻¹; (b) Arrhenius plot of 2-propanol electrooxidation on Pd at various potentials.

Table 2

The E_a values of ethanol oxidation in 1.0 M KOH + 1.0 M ethanol on Pd electrode under various potential.

E/V	$E_a/kJ\ mol^{-1}$
-0.475	23.9
-0.45	25.7
-0.425	26
-0.4	26.3
-0.375	27.2
-0.35	28.2
-0.325	29.2

Table 3

The E_a values of 2-propanol oxidation in 1.0 M KOH + 1.0 M 2-propanol on Pd electrode under various potential.

E/V	$E_a/kJ\ mol^{-1}$
-0.55	24.4
-0.525	25.9
-0.5	26.2
-0.475	25.4
-0.45	25.2
-0.425	24.6
-0.4	24.1
-0.375	23

voltammetry (LSV) at a number of different temperatures will be employed in this work to obtain the data needed to calculate E_a values. Figs. 2a and 3a show the influence of ethanol and 2-propanol electrooxidation on Pd electrode with the change of temperature range of 283–323 K. With elevating temperature, the oxidation activity of ethanol and 2-propanol 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 [25]

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

Figs. 2b and 3b represent Arrhenius plots for ethanol and 2-propanol oxidation current density (j) at various potentials on Pd electrode. Linear relationship exists between $\ln j$ and $1/T$ thereby indicating that the reaction mechanism at each potential is not changed with temperature. The E_a values for ethanol electrooxidation were calculated at the potential range of -0.475 to -0.325 V and shown in Table 2. The E_a values increase with potential. The E_a values for 2-propanol electrooxidation were calculated at the potential range of -0.55 to -0.375 V and shown in Table 3. The E_a values increase with potential and then begin to decrease with potential. The E_a values were found to be 26.3 kJ mol⁻¹ for ethanol and 24.1 kJ mol⁻¹ for 2-propanol at -0.4 V. The E_a values of 2-propanol are lower than that of ethanol at the potential from -0.45 to -0.375 V which is usually used in DAFCs indicating that 2-propanol shows better electrooxidation activity than ethanol.

4. Conclusions

In this paper, we have used the amount of coulombs (coulometry) and E_a to measure the activity of alcohol electrooxidation. The amount of coulombs released during alcohol electrooxidation which is integrated from -0.8 to -0.25 V is 2018 mC cm⁻² for ethanol and 2054 mC cm⁻² for 2-propanol. The amount of coulombs which is integrated from -0.8 to -0.4 V is 466 mC cm⁻² for ethanol and 996 mC cm⁻² for 2-propanol. The onset potential of 2-propanol oxidation is more negative than that of ethanol oxidation and the 2-propanol electrooxidation occurs at significantly higher current at low potential than ethanol. 2-Propanol is more easily electrochemically oxidized than ethanol. The E_a values were found to be 26.3 kJ mol⁻¹ for ethanol and 24.1 kJ mol⁻¹ for 2-propanol at -0.4 V. The E_a values of 2-propanol are lower than that of ethanol at the potential from -0.45 to -0.375 V which is usually used in direct alcohol fuel cells (DAFCs) indicating that 2-propanol shows better electrooxidation activity than ethanol.

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