

# Determination of Diffusion Coefficient of Isopropanol in Alkaline Medium using Electrochemical Methods on Pd Electrode

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**Abstract:** The diffusion coefficient of isopropanol in alkaline medium using electrochemical methods on Pd electrode has been studied by linear sweep voltammetry (LSV) with different sweep rate and chronoamperometry in 1.0 M KOH solution containing 1.0 M isopropanol. Isopropanol oxidation on the Pd electrode is an irreversible charge-transport process and controlled by a diffusion process. The diffusion coefficient of isopropanol on the Pd electrode is obtained as  $1.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  using the LSV method and  $1.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  using the chronoamperometry method. The average diffusion coefficient of isopropanol is  $1.04 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

**Keywords:** Fuel cells, Alcohol electrooxidation, Isopropanol, Palladium, Diffusion coefficient.

## 1. INTRODUCTION

Direct alcohol fuel cells (DAFCs) based on alcohol as fuel have attracted enormous attention as power sources for portable electronic devices and transportation due to a much higher energy density than gaseous fuels such as hydrogen and natural gas [1-4]. Direct isopropanol (2-propanol) fuel cells have attracted more and more attention as isopropanol is the smallest secondary alcohol, less toxic than methanol and its electrochemical oxidation is of great interest due to its particular molecular structure [5]. The DAFCs using isopropanol as fuel show much higher performance and a much lower crossover current than direct methanol fuel cells [6-8].

Some work has been done to investigate the electrooxidation of isopropanol on Pt-based catalysts in alkaline medium [9, 10]. However, Pt has a low activity for isopropanol electrooxidation. Our previous work on the development of Pt-free electrocatalysts for isopropanol oxidation has focused on the Pd catalyst and the results revealed that Pd is a good electrocatalyst for isopropanol oxidation in alkaline medium [11, 12].

The fundamental understanding of alcohol electrooxidation in alkaline medium is important for the development of new fuel for DAFCs. Here, we studied the electrooxidation of isopropanol on the Pd electrode and reported the determination of the diffusion coefficient of isopropanol using the LSV and chronoamperometry methods. The investigation of diffusion coefficient using electrochemical method has been reported [13-15]. Here, we firstly used the LSV method with different sweep rate and chronoamperometry method to invest the diffusion coefficient of isopropanol in 1.0 M KOH

solution containing 1.0 M isopropanol. The diffusion coefficient of isopropanol in different electrolyte and variational concentration isopropanol can be obtained by the same method. This electrochemical method to measure the diffusion coefficient of isopropanol is very facile and don't need intricate instruments.

## 2. MATERIALS AND METHODOLOGY

KOH, isopropanol and acetone 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 work electrode is palladium disk (99.999%) with a geometrical area of 0.03 cm<sup>2</sup>. A platinum foil (3.0 cm<sup>2</sup>) and a saturated calomel electrode (SCE, 0.241 V versus NHE) 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 LSVs of isopropanol oxidation in 1.0 M KOH solution containing 1.0 M isopropanol on the Pd electrode. The sweep rate is from 5 to 100 mV s<sup>-1</sup> at the potential range of -0.9 to 0.3 V. The electrochemical performances of isopropanol oxidation on the Pd electrode were given in Table 1.

The peak potential ( $E_p$ ) increases with the increase of sweep rate, indicating that isopropanol oxidation on the Pd electrode is an irreversible charge-transport process [16, 17]. For an irreversible charge-transfer electrode process, the following equation can be applied [16]

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$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha nF} \quad (1)$$

Where,  $E_p$  is peak potential,  $E_{p/2}$  the half peak potential at  $j = j_p / 2$ ,  $\alpha$  the transfer coefficient and  $n$  the charge electron number.

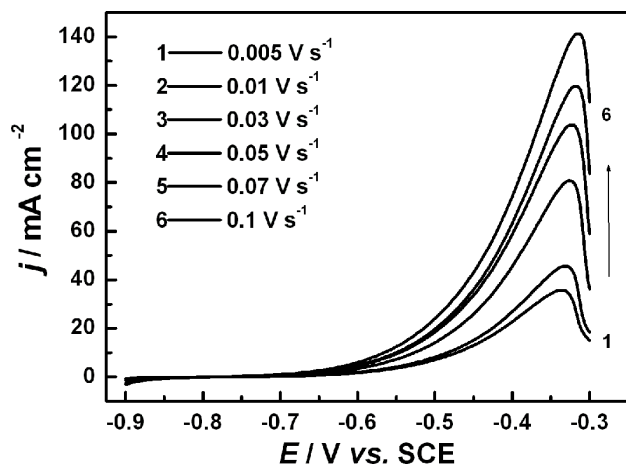


Fig. (1). LSVs of isopropanol oxidation on the Pd electrode in 1.0 M KOH solution containing 1.0 M isopropanol at a sweep rate from 5 to 100  $\text{mV s}^{-1}$ .

The average value of  $|E_p - E_{p/2}|$  for isopropanol oxidation on the Pd electrode in 1.0 M KOH is obtained as 0.089 over the sweep range of 5 to 100  $\text{mV s}^{-1}$ . The  $\alpha n$  of isopropanol oxidation on the Pd electrode is obtained as 0.536 from the Eq.(1). The isopropanol oxidation to acetone in alkaline medium is a fast reaction and corresponds to the following reaction [18, 19]



Fig. (2) shows the cyclic voltammogram (CV) of acetone oxidation in 1.0 M KOH + 1.0 M  $\text{CH}_3\text{COCH}_3$  on the Pd electrode. By comparing with the CV in the absence of acetone, no obvious acetone oxidation peak can be clearly observed. The anodic peak appearing between -0.8 and -0.6 V originates from the desorption of atomic hydrogen on the electrocatalyst. So the presence of acetone inhibits the hydrogen absorption. The acetone can be oxidized further into  $\text{CO}_2$  by the following reaction [10]

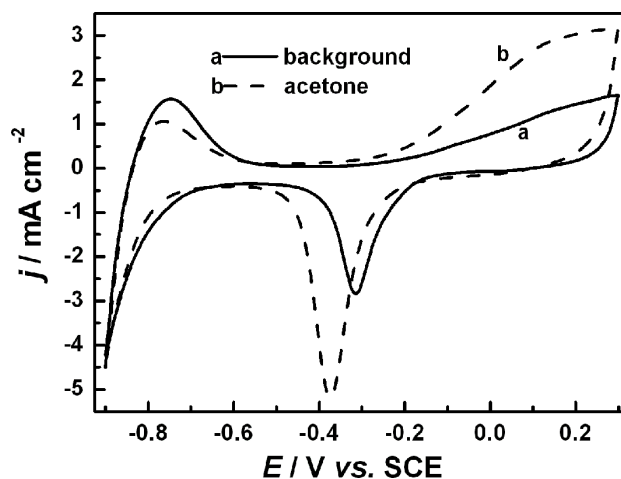
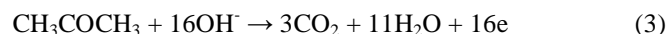


Fig. (2). Cyclic voltammogram of acetone oxidation on the Pd electrode in 1.0 M KOH solution containing 1.0 M acetone at a sweep rate of 50  $\text{mV s}^{-1}$ .



However, the acetone is difficult to further oxidize on the Pd electrode and the oxidation current for acetone is too small to compare with that for isopropanol. So the  $n$  is 2 and  $\alpha$  is 0.27 for isopropanol electrooxidation on the Pd at the potential range of -0.9 to 0.3 V.

The relationship between the peak current density ( $j_p$ ) of isopropanol oxidation on the Pd electrode and the square root of sweep rate ( $v^{1/2}$ ) is shown in Fig. (3). A linear relationship is observed. The result shows that isopropanol oxidation on the Pd electrode is controlled by a diffusion process [16, 20]. The relation between  $j_p$  and  $v^{1/2}$  can be expressed as following equation [16]

$$j_p = 0.496 nFC \left( \frac{\alpha nF}{RT} \right)^{1/2} D^{1/2} v^{1/2} \quad (4)$$

Where,  $C$  is the concentration of isopropanol and  $D$  is the diffusion coefficient of isopropanol.

The slope of  $dj_p / dv^{1/2}$  for isopropanol oxidation on the Pd electrode is obtained as  $4.39 \times 10^3 \text{ A m}^{-2} \text{ s}^{1/2} \text{ V}^{-1/2}$ . So we obtain

Table 1. Electrochemical Performances of Isopropanol Oxidation on the Pd Electrode in 1.0 M KOH Solution Containing 1.0 M Isopropanol

$v$ , $\text{mV s}^{-1}$	$E_p$ , V	$ E_p - E_{p/2} $ , V	$j_p$ , $\text{mA cm}^{-2}$
5	-0.336	0.086	34.8
10	-0.331	0.083	45.6
30	-0.325	0.086	80.8
50	-0.323	0.089	103.6
70	-0.318	0.087	119.7
100	-0.314	0.091	141.2

$$0.496 nFC \left( \frac{\alpha n F}{RT} \right)^{1/2} D^{1/2} = 4.39 \times 10^3 \quad (5)$$

The diffusion coefficient of isopropanol on the Pd electrode is obtained as  $1.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

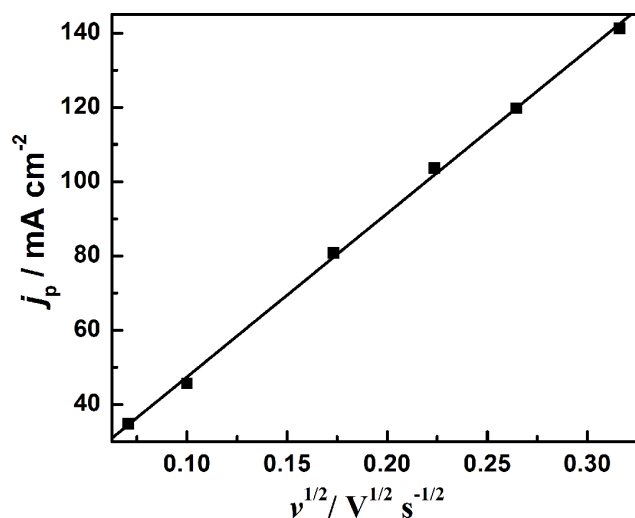


Fig. (3). The relationship of peak current density of isopropanol oxidation on the Pd electrode and square root of sweep rate.

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  $0.2 \text{ mV s}^{-1}$  of LSV for isopropanol oxidation on the Pd electrode. One current plateau at the potential region from  $-0.32$  to  $-0.28 \text{ V}$  is ascribed to mass transport-limited current in Fig. (4) [21]. Therefore, the potential step of chronoamperometry was selected to be from  $-0.6$  to  $-0.3 \text{ V}$ .

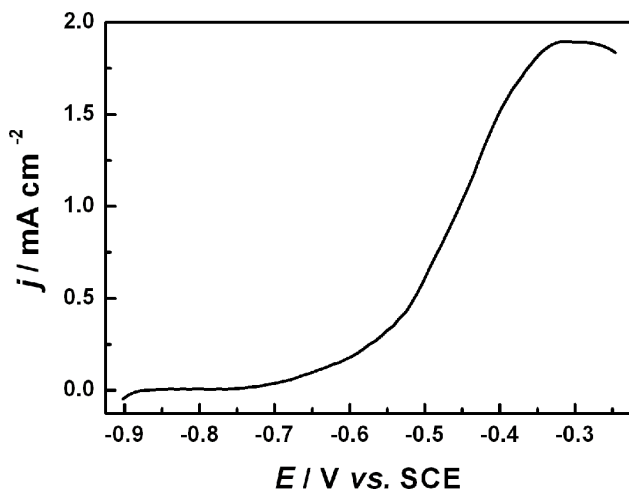


Fig. (4). LSV of isopropanol oxidation on the Pd electrode in  $1.0 \text{ M KOH}$  solution containing  $1.0 \text{ M}$  isopropanol at a sweep rate of  $0.2 \text{ mV s}^{-1}$ .

Fig. (5) shows the chronocoulometric experiment for isopropanol oxidation on the Pd electrode at  $-0.3 \text{ V}$ . The linear plot for charge ( $Q$ ) versus square root of time ( $t^{1/2}$ ) is

shown in Fig. (5). The slope of  $dQ/dt^{1/2}$  for the isopropanol oxidation is  $2.318 \times 10^3 \text{ C m}^{-2} \text{ s}^{-1/2}$ . The relation of  $Q$  versus  $t^{1/2}$  follows following relationship [13, 22].

$$dQ/dt^{1/2} = \frac{2nFD^{1/2}C}{\pi^{1/2}} \quad (6)$$

$$\text{So } \frac{2nFD^{1/2}C}{\pi^{1/2}} = 2.318 \times 10^3 \quad (7)$$

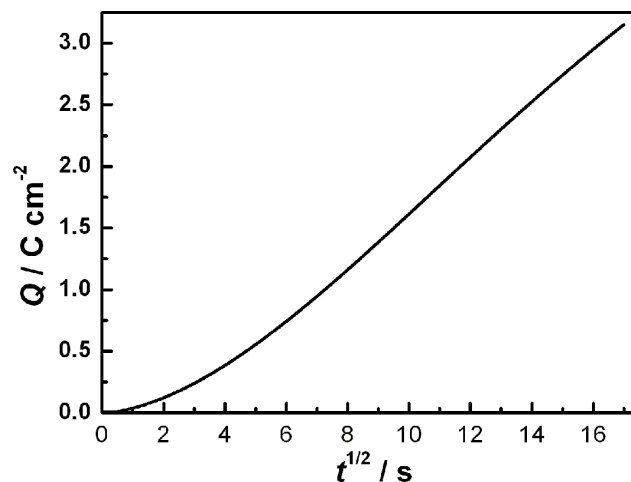


Fig. (5). Chronoamperometric curve of isopropanol oxidation on the Pd electrode in  $1.0 \text{ M KOH}$  solution containing  $1.0 \text{ M}$  isopropanol at  $-0.30 \text{ V}$ .

The diffusion coefficient of isopropanol is obtained as  $1.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . This value is close to the diffusion coefficient which is obtained using the LSV method. The average diffusion coefficient of isopropanol is  $1.04 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  in  $1.0 \text{ M KOH}$  solution containing  $1.0 \text{ M}$  isopropanol.

#### 4. CONCLUSION

The diffusion coefficient of isopropanol in alkaline medium using electrochemical methods on the Pd electrode was studied by LSV with different sweep rate and chronoamperometry in  $1.0 \text{ M KOH}$  solution containing  $1.0 \text{ M}$  isopropanol. The  $E_p$  increases with the increase of sweep rate, indicating that isopropanol oxidation on the Pd electrode is an irreversible charge-transport process. The relationship between the  $j_p$  and  $v^{1/2}$  of isopropanol oxidation on the Pd electrode is a linear relationship showing that isopropanol oxidation on the Pd electrode is controlled by a diffusion process. The charge electron number is 2 and the transfer coefficient is 0.27 for isopropanol electrooxidation on the Pd electrode at the potential range of  $-0.9$  to  $0.3 \text{ V}$ . The diffusion coefficient of isopropanol on the Pd electrode is obtained as  $1.01 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  using LSV method and  $1.06 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  using chronoamperometry method. The average diffusion coefficient of isopropanol is  $1.04 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

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