Mechanism study of the ethanol oxidation reaction on palladium in alkaline media

Z.X. Liang, T.S. Zhao *, J.B. Xu, L.D. Zhu

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

ABSTRACT

In this work, the mechanism of the ethanol oxidation reaction (EOR) on a palladium electrode was studied using the cyclic voltammetry method. The dissociative adsorption of ethanol was found to proceed rather quickly and the rate-determining step was the removal of the adsorbed ethoxi by the adsorbed hydroxyl on the Pd electrode. The Tafel slope was found to be 130 mV dec⁻¹ at lower potentials, which suggests that the adsorption of OH⁻ ions follows the Temkin-type isotherm on the Pd electrode. In comparison, the Tafel slope increased gradually to 250 mV dec⁻¹ at higher potentials. The change in the Tafel slope indicated that, at higher potentials, the kinetics is not only affected by the adsorption of the OH⁻ ions, but also by the formation of the inactive oxide layer on the Pd electrode.

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1. Introduction

Direct ethanol fuel cells (DEFCs) are electrochemical devices that directly convert the chemical energy stored in liquid ethanol into electricity. Based on the electrolyte used, DEFCs can be divided into two types: acid-type DEFCs and alkaline-type DEFCs. Over the past several years, attention has been focused on acid-type DEFCs, and significant progress has been made in their development [1–3]. For example, Xin et al. [1,2] developed a highly active PtSn catalyst for the ethanol oxidation reaction (EOR) in an acid medium, and they further demonstrated that a maximum power density of over 60 mW cm⁻² could be achieved with this catalyst, which is the highest performance reported in the open literature [1]. Although the performance seems appealing, the commercialization of acid-type DEFCs still remains a problem. One of the most critical issues with this type of fuel cell is that a considerable amount of Pt is needed to achieve decent performance. As Pt is scarce and expensive, the high loading of Pt in electrodes is a critical obstacle limiting the wide commercialization of acid-type DEFCs [1–3]. On the other hand, it has recently been demonstrated that some non-Pt catalysts for the ethanol oxidation reactions and the oxygen reduction reactions (ORR) can be exploited in alkaline media. Alkaline-type DEFCs have consequently attracted increasing attention [4–9]. In alkaline-type DEFCs, Pd based catalysts can be an alternative to the Pt-based catalysts for the alcohol oxidation reactions in alkaline media [10–21]. Takamura et al. [10–12] found that Pd catalysts exhibited high electrocatalytic activity to the methanol oxidation reaction (MOR) in the alkaline electrolyte. They further studied the kinetics of the MOR and suggested that the dehydrogenation of the methanol occurred quickly and the rate-determining step (r.d.s.) was the oxidative removal of the methoxi radicals by the hydroxide ions. Shen et al. [13–15] prepared a series of Pd-based catalysts and found that Pd catalysts exhibited higher activity and stability than did Pt catalysts in the EOR in alkaline solutions. They also demonstrated that the incorporation of an oxide, such as NiO and Ce₂O₃, as the support of the Pd catalyst was favorable to the EOR. The improvement in the activity was attributed to the enhanced anti-poisoning ability of the catalyst resulting from the introduction of the oxide.

Our literature review reveals that although Pd catalysts can be alternatives to Pt catalysts for the EOR in alkaline media, the catalytic activity, selectivity, and stability of a pure Pd catalyst are critical issues that need to be addressed so that the performance of such catalysts can be improved. To this end, it is essential to gain a better understanding of the reaction mechanism of the EOR on the Pd catalyst. The objective of this work was to study the mechanism of the EOR on Pd using the cyclic voltammetry (CV) method. Based on the CV results and the final product analysis, we propose a reaction sequence and the rate-determining step.

2. Experimental

The electrochemical experiments were conducted in a conventional three-electrode cell. A palladium disk electrode with an area...
of 0.125 cm² was used as the working electrode, while platinum foil was employed as the counter electrode. The reference electrode was Hg/HgO/KOH (1.0 mol L⁻¹) (MMO, 0.098 V vs. SHE), which was connected to the cell through a Luggin capillary. All the potentials refer to the MMO. The ethanol solution in the compartment was first deaerated by bubbling ultrahigh-purity nitrogen for 30 min before the CV experiments. A typical cyclic voltammogram was measured between the potential range of −0.926 and 0.274 V at the sweep rate of 20 mV s⁻¹ with a computer-aided potentiostat (Autolab PG30), and the quasi-steady-state polarization curve was recorded at a sweep rate of 3 mV s⁻¹.

Prior to experiments, the Pd disk electrode was polished with 0.3 and 0.05 μm alumina suspension, respectively, and was then sonicated in acetone and doubly distilled water thoroughly. In all of the experiments, stable voltammogram curves were recorded after scanning for 20 cycles in the potential region from −0.926 to 0.274 V in 1.0 M KOH solution.

3. Results and discussion

3.1. CV in the base solution

Fig. 1 shows the cyclic voltammogram of the Pd electrode in 1.0 mol L⁻¹ KOH solution. Three potential peaks can be observed during the positive-going sweep, which correspond to different electrochemical processes occurring on the surface of the Pd electrode. Peak I in the potential range between −0.9 and −0.7 V is due to the oxidation of the absorbed and adsorbed hydrogen ions [10,22–24]:

\[ \text{Pd} - \text{H}_{\text{ads/ads}} + \text{OH}^- \rightarrow \text{Pd} + \text{H}_2\text{O} + \text{e}^- . \quad (1) \]

Peak III, which emerges above −0.25 V, can be attributed to the formation of the palladium(II) oxide layer on the surface of the catalyst [22–24]. Although the mechanism of this oxidation process remains unclear, it has been widely accepted that OH⁻ ions are first chemisorbed in the initial stage of the oxide formation, and then they are transformed into higher valence oxides at higher potentials, as described by [24–26]:

\[ \text{Pd} + \text{OH}^- \rightarrow \text{Pd} - \text{OH}_{\text{ads}} + \text{e}^- \quad (2) \]

\[ \text{Pd} - \text{OH}_{\text{ads}} + \text{OH}^- \leftrightarrow \text{Pd} - \text{O} + \text{H}_2\text{O} + \text{e}^- \quad (3) \]

\[ \text{Pd} - \text{OH}_{\text{ads}} + \text{Pd} - \text{OH}_{\text{ads}} \leftrightarrow \text{Pd} - \text{O} + \text{H}_2\text{O}. \quad (4) \]

The adsorption of \( \text{OH}^- \) (Eq. (2)) starts at the far negative potential from the onset potential of the Pd oxidation (Eqs. (3) and (4)) and partially overlaps the hydrogen desorption peak, as seen in Peak II [27,28]. The adsorption of \( \text{OH}^- \) and the further oxidation process are rather important for the EOR, as discussed later.

Corresponding to the oxidation process, Peak IV, centered at −0.2 V, can be attributed to the reduction of the Pd(II) oxide during the forward scan. In the reverse scan, another current peak (designated as Peak A) centered at −0.12 V is observed during the forward scan. In the reverse scan, another current peak B is found centered at about −0.23 V. In the hydrogen region, the suppression of the peak can be attributed to the dissociative adsorption of ethanol in the low-potential region, i.e.:

\[ \text{Pd} + \text{CH}_3\text{CH}_2\text{OH} \leftrightarrow \text{Pd} - \text{(CH}_3\text{CH}_2\text{OH})_{\text{ads}} \quad (6) \]

\[ \text{Pd} - \text{(CH}_3\text{CH}_2\text{OH})_{\text{ads}} + 3\text{OH}^- \rightarrow \text{Pd} - \text{(CH}_3\text{)}_{\text{ads}} + 3\text{H}_2\text{O} + 3\text{e}^- \quad (7) \]

The resultant ethoxi, such as \( \text{(CH}_3\text{CO})_{\text{ads}} \), is strongly adsorbed onto the active sites of the Pd electrode, which blocks the adsorption of hydrogen, thereby reducing the hydrogen peaks. The steady-state oxidation current of Peak A can only be observed when the potential is above −0.7 V, well above the starting potential of the adsorption of the hydroxyl ions (Eq. (2)). This fact indicates that the adsorbed intermediates, which are formed during the dissociative adsorption of ethanol, can be stripped off the Pd electrode by the adsorbed oxygen-containing species (Pd-OHads). As a result, the EOR can proceed continuously such that the current continues to increase with the potential. At −0.12 V, the current reaches the maximum value and then starts to decline with a further increase in the potential. Previous studies suggested that the decrease in current was related to the formation of the Pd(II) oxide layer on the surface of the electrode at higher potentials (Eqs. (3) and (4)) [16,22–24]. The formation of the oxide layer can block
the adsorption of the reactive species onto the Pd surface and lead to a decrease in the electrocatalytic activity. As the positive-going sweep proceeds, more Pd(II) oxide covers the surface of the electrode. Consequently, the oxidation current of the EOR is further decreased with the increase in the potential. When the potential is above 0.2 V, the oxidation current nearly coincides with the base current in the supporting electrolyte solution, indicating that the EOR that occurs on the fully developed Pd oxide layer is negligible. Fortunately, the decrease in the electrocatalytic activity can be recovered during the negative-going sweep, as evidenced by the presence of Peak B at about −0.23 V. This reactivation can be attributed to the reduction of the Pd(II) oxide (Eq. (5)), which is similar to the behavior observed with the Pt-based catalyst.

### 3.3. Final product analysis

To analyze the final product of the EOR on Pd, the cyclic voltammograms of the Pd electrode in 1.0 mol L\(^{-1}\) KOH solution containing three fuels – ethanol, acetaldehyde and potassium acetate, are compared in Fig. 3. It can be seen that the electrocatalytic activity in the oxidation of acetaldehyde is the highest, while no oxidation current is drawn from the acetate solution. This fact suggests that acetate is the final product and acetaldehyde is an active intermediate for the EOR on the Pd electrode. We also analyzed the content of the carbonate ions in the solution and found that less than 5% of the ethano was converted to the carbonate ions. This result is consistent with the previous studies that the cleavage of the C–C bond be accelerated with an increase in ethanol concentration, thereby leading to an increase in the coverage of adsorbed ethoxi (\(k_{\text{r.d.s.}}\)). This increase in the coverage of adsorbed ethoxi yields an increase in the oxidation current of the EOR, as indicated by Eq. (10). Furthermore, the increase in the coverage of adsorbed ethoxi with an increase in the ethanol concentration can be further examined by the change in the hydrogen sorption peak in the CVs. Fig. 4b reveals that the hydrogen sorption peak centering at ca. −0.8 V is gradually suppressed as the ethanol concentration increases at potentials below −0.2 V. In contrast, at higher potentials (e.g. −0.1 V), the peak current first increases as the ethanol concentration increases, but when the ethanol concentration exceeds 3.0 mol L\(^{-1}\), the peak current starts to decrease. The increase in the current with the ethanol concentration below −0.2 V can be explained as follows. Eqs. (6) and (7) suggest that the adsorption of ethoxi on the Pd electrode can be accelerated with an increase in ethanol concentration, thereby leading to an increase in the coverage of adsorbed ethoxi (\(k_{\text{r.d.s.}}\)). This increase in the coverage of adsorbed ethoxi yields an increase in the oxidation current of the EOR, as indicated by Eq. (10). Furthermore, the increase in the coverage of adsorbed ethoxi with an increase in the ethanol concentration can be further examined by the change in the hydrogen sorption peak in the CVs. Fig. 4b reveals that the hydrogen sorption peak centering at ca. −0.8 V is gradually suppressed as the ethanol concentration increases. This indicates that more Pd sites can be occupied by the adsorbed ethoxi at higher ethanol concentrations and that the coverage of adsorbed ethoxi increases as the ethanol concentration increases.
To explain why the peak current decreases when the ethanol concentration is above 3.0 mol L\(^{-1}\), the change of the Pd-OH\(_{ads}\) coverage has to be considered with the increase in the ethanol concentration. At lower potentials, the coverage of hydroxyl can be considered to be independent of the ethanol concentration, as the adsorption of ethoxi on the Pd electrode is far from saturated and rarely blocks the adsorption of hydroxyl. In comparison, as the potential increases, the coverage of the adsorbates, including ethoxi and hydroxyl, gradually increases, and hence the competition between the two adsorption processes on the Pd electrode becomes more significant. The adsorption of ethoxi on the Pd electrode in high-concentration ethanol solutions will be dominant at high potentials, e.g., −0.1 V, and the adsorption of the hydroxyl ions will thus be largely blocked. As a result, the competition yields an excessive coverage of adsorbed ethoxi and an insufficient coverage of hydroxyl on the Pd electrode. As indicated by Eq. (10), the insufficient coverage of Pd-OH\(_{ads}\) will lead to a decrease in the peak current, as the peak current is only achieved at the intermediate coverage of the ethoxi and hydroxyl adsorbates.

### 3.5. Effect of KOH concentration

Fig. 5 shows the cyclic voltammograms of the EOR on the Pd electrode in a 1.0 mol L\(^{-1}\) ethanol solution containing KOH solutions of various concentrations ranging from 0.010 to 6.0 mol L\(^{-1}\). Fig. 5a shows the overall cyclic voltammograms for the whole potential range, while Fig. 5b shows the partial cyclic voltammograms for the potential range of −0.93 to −0.50 V. Fig. 5a shows that the peak potential has a continuous negative-shift with an increase in the KOH concentration. Furthermore, the peak current is observed to increase as the KOH concentration increases from 0.010 to 1.0 mol L\(^{-1}\). However, a further increase in the KOH concentration leads to a decrease in the peak current. The negative-shift in the peak potential suggests that the KOH concentration has a favorable effect on the oxidation of ethanol, which can be understood based on the mechanism. First, Eq. (7) indicates that the first step on the Pd electrode – the dehydrogenation process – can be accelerated at higher OH\(^{−}\) concentrations. Second, the increase in the KOH concentration can also lead to a higher coverage of the reactive Pd-OH\(_{ads}\), which, as indicated by Eq. (8), facilitates the EOR by the removal of the adsorbed ethoxi. As a result, the peak potential will shift negatively with the increase in the KOH concentration. For the same reason, the peak current increases as the KOH concentration increases from 0.010 to 1.0 mol L\(^{-1}\). At higher KOH concentrations, however, the adsorption of the hydroxyl ions will be dominant on the Pd electrode, thereby blocking the adsorption of ethanol on the Pd electrode. As a result, the coverage of hydroxyl is excessive on the Pd electrode, while the coverage of ethoxi is insufficient. Such an imbalance in the coverage of the two adsorbates will lead to a decrease in the peak current, as mentioned above. Additionally, Eqs. (3) and (4) suggest that the increase in the KOH concentration can also accelerate the formation of the Pd(II) oxide, which can further contribute to the decrease in the peak current at higher potentials.

Fig. 5b shows that the current increases monotonically when the potential is below −0.5 V. The increase in the current is associated with the increased coverage of the reactive Pd-OH\(_{ads}\) at higher KOH concentrations, as discussed earlier. Furthermore, it is noticeable that the current continues to increase without reaching a maximum value when the KOH concentration increases to 6.0 mol L\(^{-1}\), which is different from the change in the peak current. This is due to the fact that, at lower potentials (−0.5 V), the adsorption of ethanol can be considered as independent from the KOH concentration and is rarely blocked by the adsorption of the hydroxyl ions. In this potential region, the coverage of Pd-OH\(_{ads}\) is still rather small and far from being saturated even in the 6.0 mol L\(^{-1}\) KOH solution.

### 3.6. Tafel analysis

Fig. 6 shows a typical linear sweep voltammogram at the sweep rate of 3 mV s\(^{-1}\), which is close to a steady-state polarization curve of the EOR on the Pd electrode in the 1.0 mol L\(^{-1}\) KOH solution.
By combining Eqs. (12) and (14), the expression of the coverage of the reactive Pd-OH ($\theta_{OH}$) at higher potentials can be given by:

$$\theta_{OH} = \frac{1}{K_2c_{OH}^0} \exp \left( \frac{F}{RT\eta} \right).$$

Eq. (15) indicates that the Tafel slope of the EOR increases with the potential. Accordingly, the Tafel slope of 250 mV dec$^{-1}$ in Region II can thus be explained in terms of the formation of the oxide layer on the Pd electrode. Furthermore, at sufficiently high potentials, Eq. (15) suggests that the Tafel slope approximates the value of $-120$ mV dec$^{-1}$, which is close to $-160$ mV dec$^{-1}$ in Region III. In summary, the analysis of the Tafel slope indicates that the kinetics of the EOR is dominated by the adsorption on hydroxyl in the low-potential region of $-0.6$ to $-0.4$ V, and further affected by the formation of the inactive oxide layer on the Pd electrode at potentials above $-0.3$ V.

4. Conclusions

In this work, the mechanism of the ethanol oxidation reaction on a palladium electrode in alkaline media was studied using the cyclic voltammetry method. It was found that the dissociative adsorption of ethanol proceeds rather quickly and the rate-determining step is the removal of the adsorbed ethoxy by the adsorbed hydroxyl. At potentials below $-0.4$ V, the Tafel slope is found to be $130$ mV dec$^{-1}$. At higher potentials above $-0.4$ V, the Tafel slope increases to $250$ mV dec$^{-1}$, as the mechanism of the EOR is significantly complicated by the formation of the oxide layer on the Pd surface at higher potentials.

Acknowledgment

The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region, China (Project No. 622706).

References