



Effects of acetone on electrooxidation of 2-propanol in alkaline medium on the Pd/Ni-foam electrode

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ABSTRACT

Acetone is the main product of 2-propanol electrooxidation in both acid and alkaline electrolytes; it always co-exists with 2-propanol in the reaction solution due to its liquid nature. Whether acetone will affect the electrooxidation of 2-propanol has not been well documented, which is a key issue that needs to be addressed for the direct 2-propanol fuel cell. In this study, the influence of acetone on the electrooxidation of 2-propanol in alkaline medium is investigated, using state-of-the-art Pd electrode, by cyclic voltammetry and chronoamperometry. The electrode is prepared using a chemical replacement method, by dipping nickel foam into acidified PdCl₂ solution, and characterized by scanning electron microscopy. We found that the presence of acetone adversely affects electrooxidation performance of 2-propanol and substantially reduces the oxidation current of 2-propanol on Pd in alkaline medium. The acetone poisoning effect is interpreted by a competitive adsorption mechanism, in which acetone adsorbs onto Pd surface and occupies the active sites for 2-propanol electrooxidation, leading to a significant decrease in the number of these sites for 2-propanol electrooxidation. The results of this study point out that efficient electrocatalysts for 2-propanol electrooxidation in alkaline electrolytes must be non-adsorptive to acetone besides being highly active to 2-propanol oxidation.

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1. Introduction

Direct alcohol fuel cells (DAFCs) are promising power sources for portable electronic devices because liquid alcohol fuels have higher energy density, and are easier to handle and store than hydrogen gas fuel. Direct methanol fuel cells (DMFCs) are the most studied type of DAFC because methanol contains no C–C bonds and can therefore be oxidized completely to CO₂ with relative ease. However, the problems of CO poisoning and methanol crossover have severely hindered the progress of DMFC developments [1–3]. Using 2-propanol, the smallest secondary alcohol, as DAFC fuel, has caught the researcher's attention recently. Cao and Bergens [4] and Qi and Kaufman [5] have reported that the performance of acidic DAFC operating on 2-propanol is substantially higher than operating on methanol, particularly at current densities lower than 200 mA cm⁻². The electrical efficiency of the acidic direct 2-propanol fuel cell is nearly 1.5 times that of DMFC using acidic electrolytes at power densities below 128 mW cm⁻².

If 2-propanol is electrooxidized only to acetone (CH₃CHOHCH₃ → CH₃COCH₃ + 2H⁺ + 2e⁻), there would be no CO₂ generation; thus the fuel cell can use alkaline, instead of acidic, electrolytes. Since electrooxidation of alcohol and elec-

troreduction of oxygen have faster kinetics in alkaline medium than in acid medium [6–10], the alkaline direct 2-propanol fuel cell is expected to have higher performance than its acid counterpart. This has inspired researchers to carry out studies on electrocatalysts for 2-propanol oxidation in alkaline electrolytes and studies on alkaline direct 2-propanol fuel cells. Several noble metals, including Pt, Pd, Ru, Au, Pt–Ru, Pt–Au, Pd–Au, have been found to be effective catalysts for 2-propanol electrooxidation in alkaline electrolytes [11–17]. Of these, Pd-based catalysts show better catalytic performance (higher current density, lower onset potential, better stability) than others and also favor the formation of acetone instead of CO₂ [14–16].

It is generally agreed that, at low polarization potentials, acetone is the dominant product of 2-propanol electrooxidation, independent of the nature of electrocatalysts, and the formation of acetone does not involve strongly adsorbed intermediates that could poison the catalyst [11,18–20]. However, chronoamperometric curves of 2-propanol electrooxidation in alkaline medium reported in the literature clearly demonstrated that currents for 2-propanol electrooxidation at a fixed low potential exhibit a quick and dramatic decay, the steady state current being sustained only at a very low level [11,12,16,17]. This general observation implies that the catalysts are rapidly poisoned by species from 2-propanol electrooxidation. What would be the poisoning species, if acetone formation does not involve stable adsorbed intermediates, has not been well discussed [12]. It has been reported that acetone can

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strongly adsorb onto surfaces of Pt, Ru, Rh and Ir via an $\eta^2(\text{O,C})$ configuration (bonded side-on to the metal through both carbon and oxygen atoms) [21–25]. So there is a possibility that acetone, the product of 2-propanol electrooxidation and always co-existing with 2-propanol in the electrolytes, could poison the electrocatalysts. A preliminary study found that 2-propanol electrooxidation on Pt in acid electrolyte was inhibited by strong adsorption of acetone [26]. Unfortunately, this result was ignored and not mentioned by researchers in this area. We believe that the influence of acetone on the electrooxidation of 2-propanol in alkaline medium is an important and worthwhile pursuit for the development of alkaline direct 2-propanol fuel cells.

In this work, the effect of acetone on electrooxidation of 2-propanol at Pd electrode in alkaline electrolytes was investigated. Clear evidence about the poisoning effect of acetone was provided. The acetone poisoning mechanism was discussed in terms of competitive adsorption. Our results suggest that efficient electrocatalysts for 2-propanol electrooxidation must be acetone tolerant and non-adsorptive to acetone in order to sustain their high activity and stability.

2. Experimental

Pd on nickel foam electrodes (Pd/Ni-foam) were prepared by a facile chemical replacement method. A piece of nickel foam (10 mm \times 10 mm \times 1.1 mm, 110 PPI, 320 g m⁻², Changsha Lyrun Material Co., Ltd., China) was degreased with acetone, etched with 6.0 mol dm⁻³ HCl for 15 min and rinsed thoroughly with ultrapure water (18 M Ω cm, Millipore). The pre-treated nickel foam was immersed in an aqueous solution containing 0.25 mmol dm⁻³ PdCl₂ and 4 mol dm⁻³ HCl for 4 min at room temperature to let the Pd deposition to occur. After deposition, the electrode was removed from the solution, washed thoroughly with ultrapure water, and then cycled between -0.9–0.2 V in 2.0 mol dm⁻³ KOH until a stabilized cyclic voltammogram was obtained. The loading of Pd was measured using inductively coupled plasma mass spectroscopy (ICP-MS, Thermo XSeries II) by dissolving the electrode in aqua regia. The surface morphology of the Pd/Ni-foam electrode was examined using scanning electron microscopy (SEM, JEOL JSM-6480) equipped with an energy dispersive X-ray spectrometer (EDX). Images were acquired using a 20 kV accelerating voltage.

Electrochemical measurements were performed in a standard three-electrode electrochemical cell using a computerized potentiostat (Autolab PGSTAT302, Eco Chemie) controlled by GPES software. Pd/Ni-foam (1 cm² nominal planar area) acted as the working electrode. A glassy carbon rod behind a D-porosity glass frit was employed as the counter electrode and a saturated Ag/AgCl, KCl electrode served as the reference. Prior to 2-propanol electrooxidation measurements, the Pd/Ni-foam electrode was kept at -0.9 V for 5 min to reduce surface oxides. All potentials were referred to the reference electrode. Current densities were normalized to the geometrical area of the working electrode. The electrolyte is 2.0 mol dm⁻³ KOH. All solutions were made with analytical grade chemical reagents and ultrapure water. The reaction temperature was controlled by a thermostatic bath with the precision of ± 0.1 °C. The solutions were purged by bubbling ultra high purity nitrogen (99.999%) for 20 min prior to measurements and maintained under nitrogen atmosphere during the measurements.

3. Results and discussion

3.1. Characterization of the Pd/Ni-foam electrode

Fig. 1 shows the SEM images of the skeleton of nickel foam and Pd/Ni-foam electrode. After Pd spontaneous deposition, the

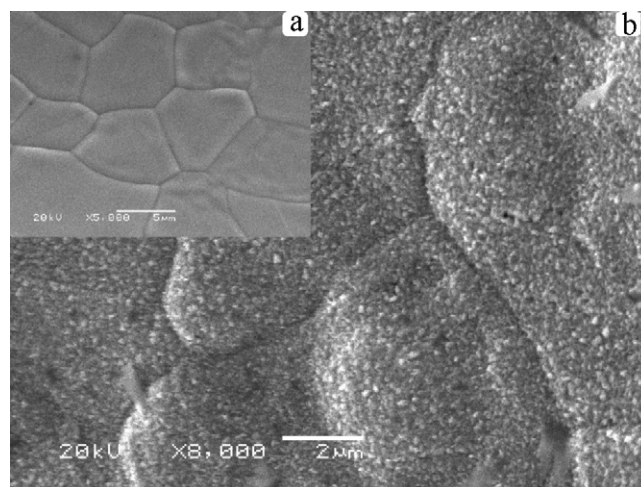


Fig. 1. SEM images of Ni foam substrate (a) and Pd/Ni-foam electrode (b).

smooth surface of nickel foam skeleton (Fig. 1a) disappeared and small particles formed and completely covered the surface, leaving no exposed nickel (Fig. 1b). EDX analysis indicated that the small particles are Pd, and with a loading of 0.5 mg cm⁻² determined by ICP-MS measurements. Compared with conventional fuel cell electrodes, which are generally fabricated by mixing and pressing powder of active material with conducting materials (e.g. carbon black) and polymer binders (e.g. polytetrafluorethylene), the Pd/Ni-foam electrode has better mass transport property owing to its reticulated structure and higher active material utilization efficiency because all Pd particles have direct contact with nickel foam, which serves as the current collector.

Fig. 2 shows cyclic voltammograms (CVs) of Ni foam substrate and Pd/Ni-foam electrode. The CV of the nickel foam substrate displayed no obvious oxidation and reduction peaks indicating that nickel substrate is stable in the potential range of -0.9 V to 0.2 V, which is the potential window for 2-propanol electrooxidation hereafter. The CV of Pd/Ni-foam displayed typical features of polycrystalline Pd. The peaks in the potential range of -0.9 to -0.4 V and -0.4 to 0.2 V correspond to the oxidation and reduction of hydrogen and Pd, respectively. Both the anodic and the cathodic currents of Pd/Ni-foam electrode are much higher than that of Ni foam substrate. So CV clearly demonstrated that Pd was deposited on Ni foam substrate. The surface area of the Pd/Ni-foam electrode is much larger than that of nickel foam substrate because the formation of small Pd particles (Fig. 1) on nickel foam significantly

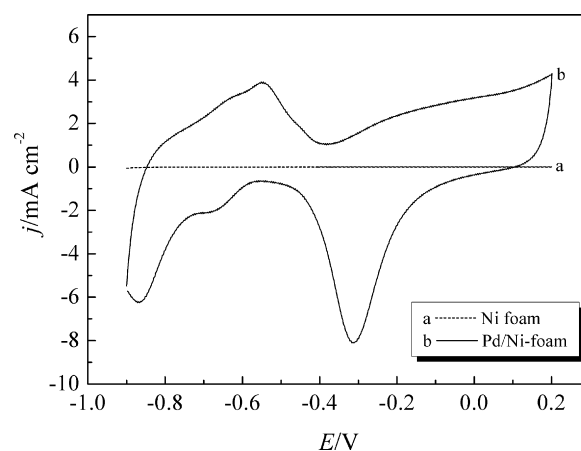


Fig. 2. Cyclic voltammograms of Ni foam substrate (a) and Pd/Ni-foam electrode (b) measured in 2.0 mol dm⁻³ KOH at 50 mV s⁻¹ scan rate and 25 °C.

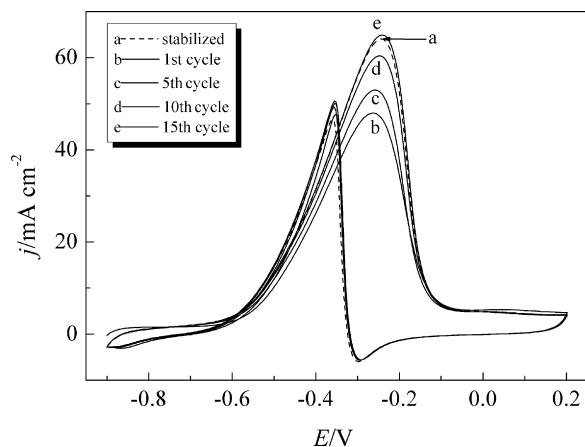


Fig. 3. Cyclic voltammograms of 2-propanol on Pd/Ni-foam electrode in $2.0 \text{ mol dm}^{-3} \text{ KOH} + 1.0 \text{ mol dm}^{-3} \text{ 2-propanol}$ at 50 mV s^{-1} before acetone adsorption (a: dash line) and after acetone adsorption (b–e: solid line).

increased the surface roughness of the nickel substrate. The influence of nickel foam substrate on the catalytic performance of Pd is thus neglectable.

3.2. Poisoning effects of acetone on the electrooxidation of 2-propanol at the Pd/Ni-foam electrode

In order to demonstrate effects of acetone on the electrooxidation of 2-propanol, a benchmark CV for the electrooxidation of 2-propanol on Pd/Ni-foam was first obtained in $2.0 \text{ mol dm}^{-3} \text{ KOH} + 1.0 \text{ mol dm}^{-3} \text{ 2-propanol}$ and shown in Fig. 3a. This stabilized CV is very similar to that reported in the literature for Pd electrode in alkaline solution [16,27]. It exhibits a peak current density of 64 mA cm^{-2} at -0.24 V in the positive going scan. After the benchmark CV measurements, the Pd/Ni-foam electrode was set at a potential of -0.8 V for 3 min to regenerate the active surface (removing surface adsorbed species from 2-propanol and Pd surface oxides), then removed from the electrolyte solution and immediately dipped into deoxygenated acetone for 3 min. The electrode was then put back into the electrochemical cell and the CV was immediately recorded starting from -0.9 V going positively (Fig. 3(b–e)). The first positive going scan after immersion in acetone generated a peak current density of 48 mA cm^{-2} at -0.24 V (Fig. 3b), which is obviously lower than that before acetone adsorption (64 mA cm^{-2} , Fig. 3a). In the subsequent scans, the peak current gradually increased and finally stabilized at 65 mA cm^{-2} after 15 cycles (Fig. 3(b–e)). The stabilized CV before and after acetone adsorption almost overlapped. This observation gives a preliminary indication that acetone can adsorb onto the Pd surface, occupy surface active sites and block the adsorption and electrooxidation of 2-propanol. The adsorbed acetone, however, can be desorbed by potential cycling between -0.9 and 0.2 V [18].

To gain further evidence about the poisoning effect of acetone, CVs of 2-propanol, acetone and a mixture of 2-propanol and acetone were measured on the Pd/Ni-foam electrode (Fig. 4). The CV of acetone (Fig. 4a) exhibits an anodic peak at 0.1 V with a peak current density of 12 mA cm^{-2} , which is much higher than the background current of Pd/Ni-foam electrode (3.5 mA cm^{-2} at 0.1 V , Fig. 2b), so this peak can be attributed to the electrooxidation of acetone. From a comparison of CV of acetone (Fig. 4a) and 2-propanol (Fig. 4b), the onset potential for acetone oxidation ($\sim -0.1 \text{ V}$) is much more positive than that for 2-propanol oxidation ($\sim -0.6 \text{ V}$), and the peak current density for acetone oxidation (12 mA cm^{-2} at 0.1 V) is much lower than that for 2-propanol oxidation (64 mA cm^{-2} at -0.24). This observation suggests that acetone is more difficult to be elec-

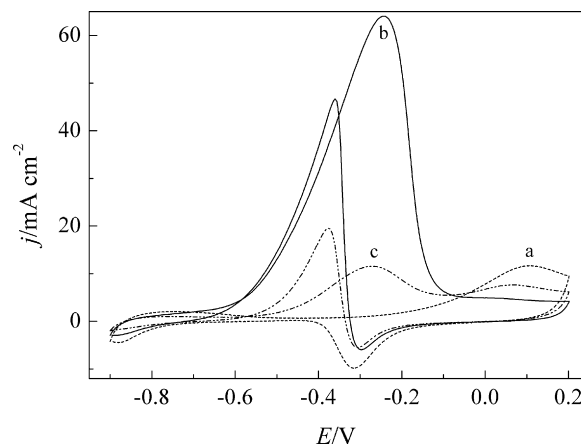


Fig. 4. Cyclic voltammograms of Pd/Ni-foam electrode measured in $2.0 \text{ mol dm}^{-3} \text{ KOH}$ solution containing $1.0 \text{ mol dm}^{-3} \text{ acetone}$ (a), $1.0 \text{ mol dm}^{-3} \text{ 2-propanol}$ (b) and $1.0 \text{ mol dm}^{-3} \text{ 2-propanol} + 1.0 \text{ mol dm}^{-3} \text{ acetone}$ (c). The scan rate is 50 mV s^{-1} .

trooxidized than 2-propanol on Pd/Ni-foam electrode. Therefore, acetone could be the stable product of 2-propanol electrooxidation, particularly at low potentials, such as lower than -0.1 V . The CV of the mixture of 2-propanol and acetone exhibits two peaks in the positive going scan (Fig. 4c). The one at $\sim -0.26 \text{ V}$ corresponds to 2-propanol oxidation and the one at $\sim -0.07 \text{ V}$ to acetone oxidation. Obviously, the peak current density for 2-propanol oxidation in the mixture of 2-propanol and acetone (11.5 mA cm^{-2} , Fig. 4c) is remarkably lower than that in pure 2-propanol (64 mA cm^{-2} , Fig. 4b). This clearly shows that acetone significantly hindered 2-propanol electrooxidation on the Pd/Ni-foam. This phenomenon can be explained by the competitive adsorption of acetone with 2-propanol on the Pd surface, whereas without the addition of acetone, the small amount of acetone formed on Pd surface from 2-propanol oxidation desorbed during potential cycling, diffused away from the electrode surface and had little opportunity to re-adsorb onto the electrode. So the clean Pd surface was regenerated after a complete potential cycle starting from and ending at -0.9 V . When acetone was introduced to the 2-propanol solution, it preferentially adsorbed onto the Pd surface and occupied the active sites for 2-propanol adsorption. Even though the adsorbed acetone can be desorbed via potential cycling, its re-adsorption can quickly take place to re-establish the adsorption equilibrium because there are large numbers of acetone molecules located near the Pd surface. Consequently, when considerable amount of acetone was present

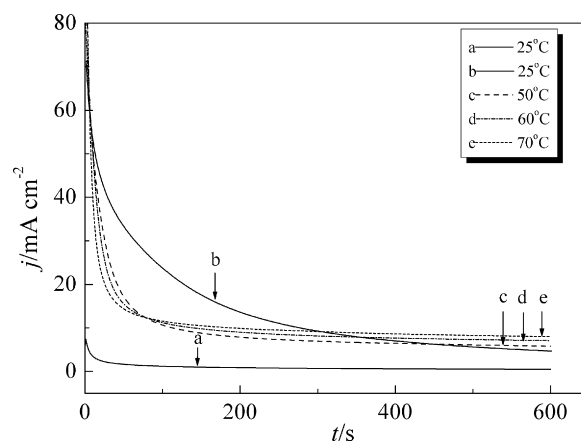


Fig. 5. Chronoamperometric curves for 2-propanol oxidation at -0.3 V on Pd/Ni-foam electrode in $1.0 \text{ mol dm}^{-3} \text{ 2-propanol} + 1.0 \text{ mol dm}^{-3} \text{ acetone}$ at 25°C (a) and in $1.0 \text{ mol dm}^{-3} \text{ 2-propanol}$ at different temperatures (b–e).

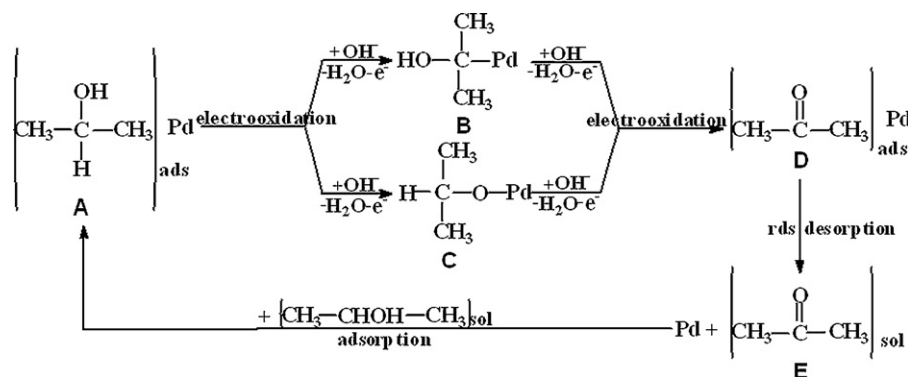


Fig. 6. The schematic reaction pathway for 2-propanol electrooxidation on Pd/Ni-foam electrode in alkaline medium with acetone as the sole product.

in 2-propanol solution, a large portion of Pd surface active sites was taken up by adsorbed acetone, leading to the remarkable catalyst poisoning. The confirmation of acetone poisoning effect is important for the research of direct 2-propanol fuel cells because acetone, the liquid product of 2-propanol electrooxidation, is continuously produced in the 2-propanol solution during fuel cell operation; the acetone's accumulated poisoning of the anode will largely deteriorate fuel cell performance. Accordingly, during the operation of an alkaline direct 2-propanol fuel cell, the timely removal of acetone product from the anolyte seems to be important for the maintenance of stable cell performance.

The acetone poisoning effect was further investigated by chronoamperometric measurements. Fig. 5 shows the current–time curves measured in 2-propanol solutions with and without acetone. The oxidation potential is -0.3 V, at which the electrooxidation of acetone will not occur. At 25°C , the initial and the quasi steady-state current densities measured in the absence of acetone (curve b) are much higher than those recorded in the presence of acetone (curve a), showing that the presence of acetone at high concentration significantly diminished the catalytic activity of Pd/Ni-foam for 2-propanol oxidation. This further confirmed the poisoning effect of acetone on the Pd catalyst, as demonstrated by CV (Fig. 4). Similar to results in the literature [11,12,16,17], a rapid and significant current decay was observed for 2-propanol electrooxidation in acetone-free solution (curve b–e). This is a clear indication of the poisoning of catalyst (the possibility of starvation of 2-propanol molecules near the electrode surface leading to the current decrease was ruled out because stirring the solution did not increase the current). Very recently, the poisoning species was attributed to CO-like intermediates without spectroscopic evidence [12]. As far as we know, acetone was not considered to be a poisoning species from the literature, except Ref. [26]. However, based on our experimental results and results in the literature [11,18–25,28], acetone is highly likely the poisoning substance because: (1) acetone is the predominate product of 2-propanol oxidation; (2) no strong adsorbed intermediates are involved from 2-propanol to acetone; (3) the cleavage of C–C bond can hardly occur at low over potentials; and (4) acetone can strongly adsorb onto noble metal surfaces.

Fig. 5 also shows the effect of reaction temperature on 2-propanol oxidation (curve b–e). Higher reaction temperature results in quicker current drop and larger steady state current. The quicker initial current decrease at higher temperature can be attributed to the faster formation and accumulation rate of acetone at higher temperature. When the acetone desorption rate and the 2-propanol oxidation rate are nearly equal, the current reaches a steady state. Since both rates increase with the increase of temperature, stabilized current is higher at higher temperature.

A reaction scheme for 2-propanol electrooxidation at low potential with acetone as the only product was postulated (Fig. 6)

based on the literature [18,29,30] to interpret our experimental results. The rate-determining step (rds) for electrooxidation of 2-propanol to dissolved acetone could be $A \rightarrow B$ (or C), B (or C) $\rightarrow D$ or $D \rightarrow E$. If $A \rightarrow B$ (or C) is the rds, then B or C and D will not accumulate on Pd surface, and the rapid current decay as shown in Fig. 5(b–e) should not be observed. If B (or C) $\rightarrow D$ is the rds, B or C will accumulate on Pd surface leading to catalyst poisoning, and thus a fast current decrease (Fig. 5(b–e)) will occur. However, in this case, the 2-propanol oxidation current should be independent of the presence of acetone in the reaction solution, which contrasts with the results shown in Figs. 4 and 5. If $D \rightarrow E$ is the rds, acetone will strongly adsorb onto Pd surfaces, occupy the active sites and prevent 2-propanol from adsorption. This assumption will explain the rapid decrease of current at constant potential as observed in Fig. 5(b–e) because adsorbed acetone from 2-propanol electrooxidation gradually accumulates onto the Pd surface, poisons the catalyst and results in a pronounced current reduction. On the other hand, the loss of catalytic activity of Pd caused by acetone adsorption (Fig. 3) and by the addition of acetone to the 2-propanol solution (Fig. 4c and Fig. 5a) can also be explained because the added acetone takes up Pd surface sites and inhibits 2-propanol adsorption and oxidation. Therefore, results obtained in this study suggest that 2-propanol electrooxidation rate is controlled by the desorption of adsorbed acetone. Efficient electrocatalysts for 2-propanol oxidation in alkaline medium should be able to promote the desorption of acetone.

4. Conclusions

One of the key advantages of using 2-propanol as an alternative to methanol as the fuel for alkaline DAFC is that acetone (the oxidation product of 2-propanol) does not react with alkaline electrolyte, while CO_2 (the oxidation product of methanol) does. On the other hand, gaseous CO_2 readily releases from methanol solution and has little negative effect on methanol oxidation performance. However, acetone is liquid and it accumulates in 2-propanol solution during 2-propanol oxidation below the boiling point of acetone. So the presence of acetone in 2-propanol must have no negative effect on the electrooxidation of 2-propanol except diluting 2-propanol; otherwise, the continuous power output of 2-propanol fuel cell cannot be sustained. In this study, clear evidence is provided showing that acetone significantly inhibits the electrooxidation of 2-propanol on Pd in alkaline electrolytes at ambient temperature. The poisoning effect of acetone is interpreted via a competitive adsorption mechanism with 2-propanol. Surface adsorbed acetone takes up active sites of Pd for 2-propanol oxidation and acetone desorption is likely the rare-determining step for the electrooxidation of 2-propanol to acetone on Pd in alkaline medium. Our results suggest that effective electrocatalysts for 2-propanol electrooxida-

tion must be acetone tolerant. The development of electrocatalysts for 2-propanol electrooxidation should take account of the acetone effect.

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