



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

Yuanhui Cheng, Yao Liu, Dianxue Cao*, Guiling Wang, Yinyi Gao

College of Material Science and Chemical Engineering, Harbin Engineering University, Natong St. #145, Harbin 150001, PR China

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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

* Corresponding author. Tel.: +86 451 82589036; fax: +86 451 82589036.
E-mail address: caodianxue@hrbeu.edu.cn (D. Cao).

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

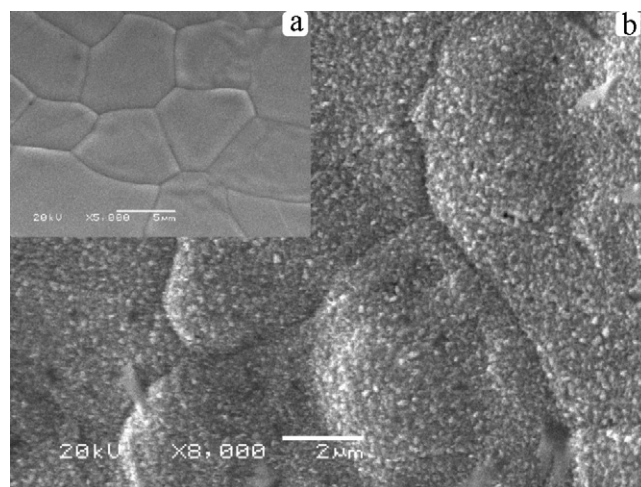


Fig. 1. SEM images of Ni foam substrate (a) and Pd/Ni-foam electrode (b).

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

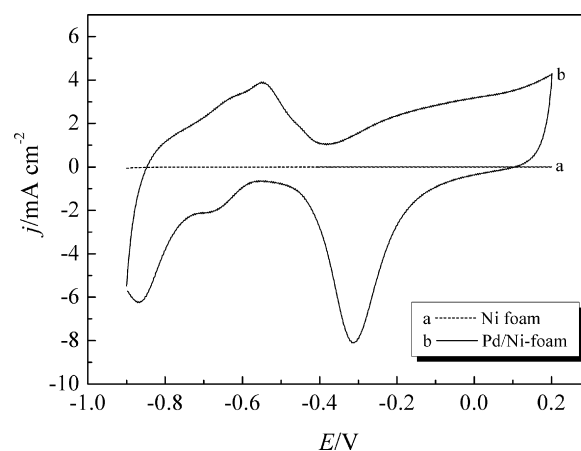


Fig. 2. Cyclic voltammograms of Ni foam substrate (a) and Pd/Ni-foam electrode (b) measured in 2.0 mol dm⁻³ KOH at 50 mV s⁻¹ scan rate and 25 °C.

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