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Comparison of ethanol electro-oxidation on Pt/C and Pd/C catalysts in alkaline media

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ABSTRACT

The ethanol electro-oxidation behaviors of Pt/C and Pd/C in alkaline media were compared using potentiodynamic and potentiostatic methods. Various ethanol and alkaline concentrations were studied. In addition, the temperature effect of ethanol oxidation was investigated. The Pd/C showed a higher activity toward ethanol oxidation than the Pt/C, especially in the potentiostatic measurement. This is mainly due to the higher oxyphilic characteristics of the Pd/C and the relatively inert nature of the Pd/C on C–C bond cleavage. The apparent activation energies of the ethanol oxidation on the Pd/C in alkaline media varied from 26.6 to 30.4 kJ mol⁻¹, depending on the potentials. The Tafel slopes could be divided into two parts on both catalysts: at low overpotentials, the Tafel slope on both the Pt/C and the Pd/C was close to 120 mV dec⁻¹ at all temperatures; at high overpotentials, the Tafel slope was ca. 260 mV dec⁻¹ on the Pd/C at all temperatures, but was much higher on the Pt/C, especially at high temperatures. Based on these results, it is concluded that Pd/C has less poisoning effect and higher activity than Pt/C for selective oxidation of ethanol to acetate.

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1. Introduction

The electro-oxidation of ethanol has been studied extensively over the last few decades in the context of using ethanol as an anode fuel for low-temperature fuel cells [1–4]. Recently, due to the development of anion exchange membranes [5–11], there has been a growing interest in studying the electro-oxidation of ethanol in alkaline media [12–26]. Alkaline media presents several advantages compared to acidic media. The electrocatalytic activity for small organic molecule oxidation in alkaline media has been found to be much higher than that in acidic media. The oxidation of CO [27], methanol [28], ethanol [12,14–16,20], and ethylene glycol [20] in alkaline media has shown much higher current densities and smaller

overpotentials compared to those in acidic media. Furthermore, the selectivity for ethanol electro-oxidation to CO₂ could be improved significantly in alkaline media. For example, Rao et al. [19] reported that the complete electro-oxidation of ethanol to CO₂ at 0.8 V vs. RHE at 60 °C contributed 55% of the total currents in an alkaline membrane electrode assembly (MEA), compared to 2% in an acidic MEA under similar test conditions. More importantly, in addition to Pt, a wide range of electrode materials are stable in alkaline environments [27,29–31] and can be considered as electrocatalysts for ethanol oxidation reactions (EORs).

Among the non-platinum catalysts, Pd exhibits interesting catalytic activity for ethanol oxidation in alkaline media [17,21–26,32–40]. To improve the activity and stability toward

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ethanol oxidation, Pd-based catalysts including Pd-oxide composite catalysts [34] and Pd-based binary [35–38] and ternary [39,40] catalysts have been investigated by several research groups. To further improve EOR activity and durability, it is important to have a good fundamental understanding of the ethanol electro-oxidation behavior on Pd catalysts in alkaline media. Cyclic voltammetry [21], in-situ Fourier transform infrared (FTIR) reflection spectroscopy [22,23], high-performance liquid chromatography (HPLC) [17], and density functional theory calculation [24,25] have all been used to study the electro-oxidation of ethanol on Pd electrodes. It has been confirmed that acetate is the main product of ethanol electro-oxidation on Pd. However, compared to the comprehensive fundamental understanding of ethanol oxidation on Pt [12–15,18–20], knowledge related to the ethanol electro-oxidation on Pd is still quite limited, especially for nanoparticle Pd catalysts.

In the present work, we investigated the ethanol electro-oxidation behaviors of carbon-supported Pt (Pt/C) versus carbon-supported Pd (Pd/C) catalysts. The effects of ethanol concentration, NaOH concentration, and temperature on the EOR activities on Pt/C and Pd/C catalysts were studied using potentiodynamic and potentiostatic methods. The ethanol oxidation mechanism on Pt/C and Pd/C catalysts in alkaline media were discussed.

2. Experimental

2.1. Materials and electrode preparation

The carbon-supported electrocatalysts Pt/Vulcan XC 72 and Pd/Vulcan XC 72 (all 20 wt% metals on carbon) were purchased from E-TEK. Ethanol (99.5%, A.C.S reagent) was purchased from Acros Inc. NaOH (97 + %) and H₂SO₄ was purchased from Sigma–Aldrich. Ar gas (99.999%) was purchased from Praxair. All aqueous solutions and suspensions used in this study were prepared using Millipore ultrapure water (18.2 MΩ cm⁻¹).

To prepare the catalyst suspension, 4.0 mg of the catalyst was dispersed ultrasonically in 2 ml of diluted Nafion solution (2 mg/ml catalyst), which contains 950 μl ethanol, 950 μl ultrapure water, and 100 μl Nafion solution (Aldrich, 5% Nafion). The thin film electrodes were then prepared by pipetting and drying the 20 μl catalyst suspension on the surface of a mirror-polished glass carbon electrode with a 5 mm diameter (Pine Instruments). The resulting thin film electrodes had a metal loading of 40.76 μg cm⁻².

2.2. Electrochemical characterization

All the electrochemical measurements were conducted using a Solartron 1287 potentiostat. The electrochemical experiments were carried out in an Ar-purged NaOH solution (or NaOH + ethanol solution) using a standard three-electrode electrochemical cell with a jacket. A gold foil electrode and an Hg/HgO electrode (the concentration of NaOH varied according to the solution tested) served as the counter electrode and the reference electrode, respectively. However, all the potentials in this study were reported with respect to the reversible hydrogen electrode (RHE). The cell temperature was

controlled by recycling water in the jacket through a water pump (NESLAB).

Prior to the potentiodynamic and potentiostatic measurements for ethanol electro-oxidation, the prepared thin film electrodes were firstly cycled between 0.06 and 1.2 V in the Ar-saturated blank NaOH solution. For potentiostatic measurements, after the electrode was held at a potential of 0.09 V for 50 s to obtain the baseline, the Pt/C thin film electrodes were stepped to the potentials between 0.45 and 0.65 V in 0.1 V increments; for Pd/C, the thin film electrodes were stepped to the potentials between 0.45 and 0.55 V in 0.05 V increments. The quasi-steady state currents, which were normalized to mass-specific current density (mA per mg of noble metal), were recorded after 15 min of polarization in NaOH + ethanol solutions at each potential. Each data set was recorded with a single electrode, i.e. after stepping from 0.09 to 0.45 V, a further step to the following potential was performed [41]. All the potentials were IR corrected by Solartron operation software.

3. Results and discussion

3.1. Cyclic voltammetry

Fig. 1 shows cyclic voltammograms (CVs) obtained on the Pt/C and Pd/C electrodes in Ar-saturated 0.1 M NaOH and 0.5 M H₂SO₄ solutions. Both the Pt/C and Pd/C show well defined CV shapes in acidic solutions, in which the potential regions of hydrogen adsorption/desorption, double layer, and reversible/irreversible oxide formation are well separated. It is noticed that the CV of the Pt/C show a relatively ill-defined HUPD region as well as extra pseudo-capacitive features comparing to that of planar Pt electrode. This feature is mainly caused by the competitive adsorption of (bi)sulfate anions on the Pt/C catalysts with large surface areas [12,28]. The unusual high peak current of the Pd/C at the low potential (around 0.06 V) is due to the absorption/desorption of the large quantities of hydrogen in bulk Pd [42,43]. In alkaline solutions, however, hydrogen desorption is immediately followed by the adsorption of OH on both the Pt/C and the Pd/C. As shown in the enlarged plot of Fig. 1b, for Pt/C, after hydrogen desorption (0.06–0.45 V), the formation of surface oxides on the positive scan starts immediately (0.45 V), which is consistent with previous reports [12,18,28]; for Pd/C, the adsorption of OH may even start in the hydrogen desorption region, and gives rise to a small peak located around 0.49 V [44]. The typical CV shapes of the Pt/C and Pd/C in alkaline media indicate the test system is clean [18,28,44]. In the negative scan, the corresponding reduction peaks of the oxides are located at 0.7 and 0.68 V for the Pt/C and Pd/C, respectively, which are more negative than their counterparts in acidic solutions. Also, the peaks of hydrogen adsorption/desorption on the Pt/C and Pd/C are more positive in alkaline solutions than those observed in acidic solutions. All the CV shapes in alkaline solutions are compressed compared to their counterparts in acidic solutions. Moreover, in both acidic and alkaline solutions, the oxygen region (reversible/irreversible oxide formation and reduction) of the Pd/C is much larger than that of the Pt/C, and the reduction peak of Pd oxides is located at lower potentials

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