Evaluation of ethanol oxidation catalysts by rotating disc voltammetry

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ABSTRACT

Rotating disk voltammetry of ethanol at PtRu black and carbon supported Pt (Pt/C) catalyst layers has been investigated in 1 M sulfuric acid. When thick catalyst layers were used, increasing the rotation rate resulted in significant increases in current and produced linear Koutecky-Levich plots. However, a mass transport limited current was not reached due to inhibition of ethanol oxidation by oxide formation at high potentials. For PtRu black, the slopes of Koutecky-Levich plots gave an average number electrons transferred (n_{av}) of 3.6 that was independent of potential and indicated that the predominant product was acetic acid. Similar n_{av} values were obtained for Pt/C at high potentials, but decreased at potentials below 0.78 V vs. SHE, where the Koutecky-Levich plots began to show significant curvature. Non-linear Koutecky-Levich plots were observed at all potentials for thinner Pt/C layers, and accurate n_{av} values could not be obtained. This appears to be due to an increase in the kinetic current with rotation rate. Since acetaldehyde is known to inhibit ethanol oxidation at Pt, its convective removal appears to be responsible for the increased kinetic current.

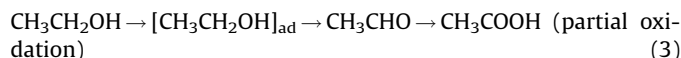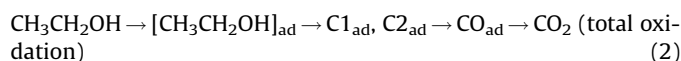© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Ethanol is an attractive liquid fuel for sustainable energy systems since it is renewable, readily available, and non-toxic. It is currently produced on a large scale from biomass, and since it is a liquid, storage and transportation are not issues for concern [1]. Ethanol has a high energy density ($8.0 \, \text{kWh kg}^{-1}$), high solubility in aqueous electrolytes, and is a promising green energy source for direct ethanol fuel cells (DEFC) [1–4]. A comprehensive understanding of the ethanol oxidation reaction (EOR) is of fundamental importance in determining and enhancing the commercial potential of these fuel cells.

The complete EOR to carbon dioxide produces twelve electrons according to equation 1.

$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12 \, e^- \qquad (1)$$
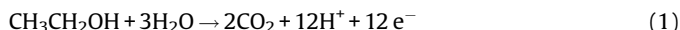
However, this reaction has not been achieved exclusively on the surface of any anode material at temperatures that are compatible with proton exchange membrane fuel cell (PEMFC) technology. To understand this, numerous experimental techniques have been applied [5,6] and there have been a number of computational studies [7–13]. For example, in situ Fourier transform infrared spectroscopy (FTIRS) [14–26] and differential electrochemical mass spectrometry (DEMS) [27–33], have been used to identify adsorbed intermediates on the electrode, and DEMS and chromatography [16,17,34–39] have been used to determine product distributions. As a result of these and many other studies, the oxidation mechanism of ethanol in acid solution may be summarized in the parallel reactions shown in Eqs. (2) and (3), where $C1_{ad}$ and $C2_{ad}$ represent adsorbed fragments with one and two carbon atoms, respectively.

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow C1_{ad}, C2_{ad} \rightarrow CO_{ad} \rightarrow CO_2 \text{ (total oxidation)} \qquad (2)$$

$$CH_3CH_2OH \rightarrow [CH_3CH_2OH]_{ad} \rightarrow CH_3CHO \rightarrow CH_3COOH \text{ (partial oxidation)} \qquad (3)$$

Due to the strong bond between the two carbon atoms in the ethanol molecule, the complete electro-oxidation of ethanol to CO_2 occurs to only a small extent under ambient conditions [5,30,40]. Instead, acetaldehyde (two-electron oxidation) and acetic acid (four-electron oxidation) are the main products, which decreases the faradaic efficiency due to the lower number of electrons transferred per molecule [40]. Although the yield of CO_2 can be increased to >80% at elevated temperatures [41–43], and catalyst activity can be increased by alloying platinum with other metals, such as Ru and Sn [5,6], better catalysts are needed for the development of efficient DEFCs.

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Electrochemical investigations of ethanol oxidation have largely relied on cyclic voltammetry and chronoamperometry which provide details of both the potential and time dependence of the reaction rate. However, data analysis and interpretation of the results is hampered by the time dependent interplay of electrode kinetics and mass transport. In other areas, rotating disk voltammetry (RDV) is commonly used to separate kinetic and mass transport currents [44]. RDV is a hydrodynamic method in which a rotating disk electrode (RDE) provides well-defined, steady-state mass transport of the reactant to the electrode surface. Generally, the Koutecky-Levich equation (Eq. (4)) can be applied to separate the kinetic and mass transport parameters,

$$1/i = 1/i_k + 1/(0.62 n_{av} FAD^{2/3} \nu^{-1/6} C \omega^{1/2}) \tag{4}$$

where i is the measured current, i_k is the kinetic current, n_{av} is the average number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, ν is the kinematic viscosity (1.0×10^{-2} cm^2 s^{-1}) [44], ω is angular velocity and C is the concentration of the reactant. The mass transport limited current ($i_{lim} = 0.62 n_{av} FAD^{2/3} \nu^{-1/6} C \omega^{1/2}$) and kinetic current are obtained from the slope and intercept, respectively, of a plot of i^{-1} vs. $\omega^{-1/2}$. RDV has become a particularly important technique in the evaluation and study of catalysts for oxygen reduction [45–48]. It is surprising therefore that there have only been a few reports of ethanol oxidation at RDEs [49–53].

Shieh and Hwang [49] reported that the current for ethanol oxidation at ruthenium oxide in KOH(aq) decreased as the rotation rate was increased, and became constant above 500 rpm. This was attributed to convective removal of the acetaldehyde intermediate ($n = 2$) before it could be further oxidized to acetic acid ($n = 4$). In contrast, rotation had an insignificant effect on ethanol oxidation at a nickel electrode in NaOH(aq) [52], but increased the current at a Pt electrode [53]. In the latter work, a rotating ring-disc electrode was used to monitor pH changes during ethanol oxidation in NaOH (aq) [53]. For ethanol oxidation at a Pt disc electrode in H$_2$SO$_4$, Seland et al. [50] found that electrode rotation decreased the current on the forward voltammetric scan but increased it on the reverse scan. This difference was attributed to slow formation of adsorbed intermediates during the reverse scan, since it was concluded that the decrease in the forward scan was due to the accumulation of strongly adsorbed intermediates (e.g. CO) that block ethanol oxidation. Zheng et al. [51] have reported linear Koutecky-Levich plots ($i^{-1} \propto \omega^{-1/2}$) for ethanol oxidation at glassy carbon electrodes coated with Pt and PtSn nanoparticles, but did not analyze the mass transport characteristics.

Similarly contradictory effects have been reported for RDV of methanol oxidation [50,51,54–56], and this can be attributed largely to the thickness of the catalytic layer on the electrode. Flat Pt electrodes generally show decreased currents with increasing rotation rate [54], due to removal of intermediates by convection, while thick layers of higher surface area catalysts provide normal Koutecky-Levich behavior [56]. In the latter work, n_{av} was determined to be 6.0 for methanol oxidation at a PtRu black catalyst layer and 3.1 at a carbon supported Pt layer [56].

In this work we investigate ethanol electro-oxidation by RDV using thick layers of carbon supported Pt and PtRu black catalysts on a glassy carbon (GC) electrode, in order to explore the interplay between kinetic and mass transport effects and determine parameters that will be useful in the development of anode catalysts for DEFCs. The use of thick catalyst layers on the electrode not only increases current densities into the range required for DEFCs, but also provides total coverage of the electrode surface, which improves the accuracy of the kinetic and mass transport parameters [56]. Of particular importance is the average number of electrons (n_{av}) transferred, which plays a central role in

determining the energy efficiency of a DEFC [57]. It is clear from studies of the film thickness dependence of n_{av} for oxygen reduction [58], and borohydride oxidation [59], that thicker catalyst layers favor the conversion of intermediates to the final product. Consequently, n_{av} increases with increasing catalyst layer thickness, and values obtained with thick catalyst layers are more representative of the behavior of the catalyst in a fuel cell.

2. Experimental

2.1. Materials

Anhydrous ethanol and sulfuric acid were obtained from ACP Chemicals Inc. Catalyst inks were prepared from a Nafion^{TM} solution in a mixture of lower aliphatic alcohols (5.14%; DuPont), 1-propanol (J.T. Baker), and commercial carbon supported platinum (20% Pt; Etek) or commercial platinum-ruthenium black (Ru: Pt = 50:50, Alfa Aesar). Prior to application of each catalyst ink, the electrode was polished with an alumina slurry (0.3 μm; Sturbridge Metallurgical Services, Inc.).

2.2. Electrode preparation

Catalyst inks were prepared by dispersing weighed amounts of catalyst powder (ca. 62 mg mL^{-1}) homogenously in either a Nafion solution or a mixture of 1-propanol and Nafion solution by sonication in an ultrasonic bath for 1 h. The electrode was prepared by applying the required amount of catalyst ink, with an Eppendorf micropipette, onto the polished surface of a glassy carbon disk electrode (0.196 cm^2; Pine Instruments). Each catalyst layer was allowed to dry for at least 30 min at ambient temperature. Where loadings higher than 1.5 mg cm^{-2} were required, the catalyst ink was applied in several aliquots, with ultrasonic re-dispersion of the ink for 10 min. Specified catalyst loadings do not include the mass of Nafion used as a binder, which varied from 17% to 50% of the catalyst layer mass as specified.

2.3. Electrochemistry

Electrochemical experiments were conducted at ambient temperature in a three-compartment glass cell operated with a Pine Instruments RDE4 potentiostat and ASR Analytical Rotator The working electrode was a catalyst coated glassy carbon electrode, the counter electrode was a platinum wire and a mercury sulfate electrode in 3.8 M sulfuric acid (Koslow; 635 mV vs. SHE) was used as a reference electrode. All potentials are given relative to the standard hydrogen electrode (SHE). Rotating disk cyclic voltammetry and constant potential experiments were carried out in 0.1 M ethanol solutions with 1 M sulfuric acid as the electrolyte. Prior to all experiments, the solution was de-aerated by passing N$_2$ into the solution for 15 min, and then over the surface of the solution continuously during the experiments. Steady-state cyclic voltammograms, obtained after repeated potential sweeps, are shown.

3. Results and discussion

3.1. Comparison of thick layers of carbon supported Pt and PtRu black catalysts

Carbon supported Pt was employed here as a typical baseline catalyst for ethanol oxidation, while PtRu black was chosen for comparison due to its higher activity, particularly at low potentials. PtRu was previously shown to provide very efficient oxidation of methanol in RDE experiments [56]. Initially, high catalyst loadings