Evaluation of methanol oxidation catalysts by rotating disc voltammetry

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ABSTRACT

Rotating disc voltammetry of 0.1 M methanol at thick catalyst layers shows significant increases in current with increasing rotation rate. Although a mass transport limited current was not reached, due to inhibition of methanol oxidation by Pt oxide at high potentials, linear Koutecky-Levich plots were obtain in the mixed kinetic-mass transport region. For a carbon supported Pt catalyst, the slopes of the Koutecky-Levich plots corresponded to a methanol oxidation efficiency of ca. 50% (average n-value of 3.1 electrons per molecule), while the efficiency was ca. 100% for a PtRu black catalyst. The methanol diffusion coefficient obtained with the PtRu black catalyst was in good agreement with literature values. Koutecky-Levich plots provide mass transport corrected kinetic currents, in the mixed kinetic-mass transport region, that complement values obtained at lower potentials by cyclic voltammetry or at constant potential.
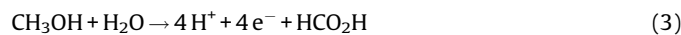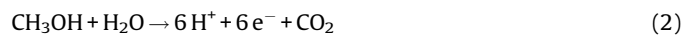
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1. Introduction

The electrochemical oxidation of methanol is of fundamental importance in the development of our understanding of the electrochemistry of small organic molecules [1–4], and central to the development of direct methanol fuel cells (DMFC) [5–9]. The development of more active catalysts for methanol oxidation [8,10] requires efficient methodologies for evaluating large numbers of new formulations in sufficient depth to identify candidates for further development [11]. Typically, new catalysts for methanol oxidation are assessed by cyclic voltammetry and chronoamperometry, with the latter method providing data most relevant to DMFCs [11]. However, neither of these techniques provides a clear separation of kinetic and mass transport effects. Rotating disc voltammetry (RDV) is much more suitable for this, and so has become the normal method for evaluating oxygen reduction catalysts [12–14]. Although it should be possible to apply RDV similarly to methanol oxidation, and extract both steady-state kinetic parameters and stoichiometry (the number of electrons per methanol molecule), there are a number of complications. Consequently, there are few reports on methanol oxidation at rotating electrodes.

Gojkovic reported that electrode rotation decreased the current for methanol oxidation at smooth Pt [15] and Pt_3Co alloy [16]

electrodes, and attributed this to convective removal of partially oxidized products (mainly formaldehyde). Oxidation of methanol to formaldehyde produces only two electrons (Eq. (1); n = 2) relative to the six electrons for complete oxidation to carbon dioxide (Eq. (2); n = 6), and formic acid (Eq. (3); n = 4) can also be produced. The number of electrons released during methanol oxidation (n_{av}), and hence the current produced, is therefore determined by the product distribution.

$$CH_3OH \rightarrow 2\,H^+ + 2\,e^- + HCHO \tag{1}$$

$$CH_3OH + H_2O \rightarrow 6\,H^+ + 6\,e^- + CO_2 \tag{2}$$

$$CH_3OH + H_2O \rightarrow 4\,H^+ + 4\,e^- + HCO_2H \tag{3}$$

Since both formaldehyde and formic acid can be further oxidized to CO_2, n_{av} depends strongly on the mass transport conditions, with thick catalyst layers and slow mass transport leading to more complete oxidation of the methanol (higher n_{av}) [17–19]. Consequently, rotation of the electrode had less (negligible) influence when the electrode is coated with a layer of carbon supported Pt catalyst [15,20]. Electrode rotation has also been reported to have an insignificant effect on methanol oxidation at a PtRu alloy on Vulcan XC-72 carbon black [21]. In contrast, a significant increase in current was seen with electrode rotation at a carbon supported Pt_9Sn catalyst [20]. In that work, a Koutecky-Levich plot was used to obtain the kinetic current, but the mass

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transport behaviour was not analysed. However, the methanol diffusion coefficient can be estimated to be ca. $1 \times 10^{-7} \, cm^2 \, s^{-1}$ from that plot, which is much too low (the literature value is ca. 1.5×10^{-5} [22]).

Experiments in a flow cell, with arrays of catalytically active cylindrical Pt nanostructures at two different densities, paralleled the RDV results at Pt disc electrodes [23]. Simultaneous measurement of the CO_2 produced by differential electrochemical mass spectrometry (DEMS) showed that the efficiency for complete oxidation of the methanol decreased with increasing flow rate, and increased when the density of Pt nanostructures was increased. This was explained by a "desorption-readsorption-reaction" model in which reactive intermediates that desorb from the electrodes can either be readsorbed or can diffuse into the bulk solution [23].

Seland et al. [24] found that an increase in rotation rate caused a transient increase in current for the oxidation of 1 M methanol in $0.5 \, M \, H_2SO_4$ at a Pt disc. This was attributed to the increased mass transport rate (i.e. the normal effect of electrode rotation), while the decrease in current with time was attributed to an increasing coverage of adsorbed intermediates.

Hou et al. [25] reported seemingly normal RDV behaviour for 1 M methanol (in $0.5 \, M \, H_2SO_4$) at a polycrystalline Pt rotating disc electrode (RDE). Substantial increases in current were obtained over the range of 400–1600 rpm, with the data providing parallel Koutecky-Levich plots over the range of 0.4–0.6 V vs. RHE, and a linear Tafel plot with a slope of 125 mV decade^{-1}. However, the slopes of Koutecky-Levich plots gave an unreasonably low number of electrons (ca. 10^{-5}) for the reaction, or an apparent diffusion coefficient of ca. $5 \times 10^{-12} \, cm^2 \, s^{-1}$ (for n = 6). This was attributed to "counter diffusion of gaseous CO_2 and other intermediates in a thin film adjacent to the electrode surface" [25]. Using a diffusion coefficient of $5.37 \times 10^{-12} \, cm^2 \, s^{-1}$, obtained from chronoamperometry, they found that n_{av} increased from ca. 1.8 at 0.41 V to ca 5.4 at 0.6 V. The reliability of these n_{av} values, however, must be questioned in light of the unreasonable diffusion coefficient that was employed.

The purpose of the work described here was to further develop RDV as a method for evaluating methanol oxidation catalysts, and in particular to address the very low apparent diffusion coefficient that has been reported [25] and the reliability of n_{av} values that are obtained. n_{av} is a central parameter in determining the energy efficiency of a DMFC, since the faradaic efficiency is proportional to n_{av} (efficiency for oxidation to $CO_2 = n_{av}/6$) [26,27]. It also provides an indication of by-product [28] and harmful emission levels [29]. However, it is very difficult to measure n_{av} experimentally [30]. Consequently, RDV would be a powerful technique for catalyst evaluation if it could provide reliable n_{av} values. Here we demonstrate that methanol oxidation at thick layers of a carbon supported Pt catalyst (20% Pt/C), and PtRu black, shows mixed mass transport and kinetic control of the current with a normal methanol diffusion coefficient. n_{av} values are consistent with reported product distributions.

2. Experimental

2.1. Materials and solutions

Solutions were prepared by using methanol (95–98% from ACP Chemical Inc.), sulfuric acid (98% from ACP Chemical Inc.) and deionized water. Nafion^{TM} solution in a mixture of lower aliphatic alcohols (5.14% from DuPont), commercial carbon supported platinum (20% Pt/C; Etek) and commercial platinum-ruthenium black (Ru:Pt = 50:50, Alfa Aesar) were used for catalyst ink preparation. Electrodes were 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. 50 mg mL^{-1} for carbon supported Pt; 63 mg mL^{-1} for PtRu) in a Nafion solution homogenously by sonicating in an ultrasonic bath for 1 h. For each experiment, the required amount of catalyst ink was applied with an Eppendorf micropipette (or fine paint brush for PtRu) onto the polished surface of a glassy carbon disk electrode (0.196 cm^2; Pine Instruments) in several small aliquots. Before depositing each aliquot, the catalyst ink was sonicated again for 10 min. Each aliquot was allowed to dry for 20 min at ambient temperature. To improve the catalyst attachment, 4 μL of Nafion solution was pipetted onto the catalyst layer and allowed to dry for 30 min at ambient temperature. The catalyst loading amounts were 7.6 and 10 mg cm^{-2} for the carbon-supported platinum catalyst and ca. 8 mg cm^{-2} for the PtRu black catalyst.

2.3. Electrochemistry

Electrochemical measurements were 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 loaded glassy carbon rotating disk electrode and the counter electrode was a platinum wire. The reference electrode was either a saturated calomel electrode or mercury sulfate electrode in 3.8 M sulfuric acid. However, all potentials are given relative to SHE. Rotating disk cyclic voltammetery and constant potential experiments were run in 0.1 M methanol solutions with 1 M sulfuric acid as the electrolyte. Before each experiment, the solution was de-aerated by passing N$_2$ gas into the solution for 15 min and over the surface of the solution continuously during the experiments.

3. Results and discussion

3.1. Carbon supported platinum (20% Pt/C)

From literature reports, it appears that electrode rotation begins to increase the current for oxidation of methanol when the Pt loading on the electrode reaches ca. 0.25 mg cm^{-2} [15,20]. Consequently, much higher loadings of a commercial carbon supported Pt catalyst were employed here, leading to significant
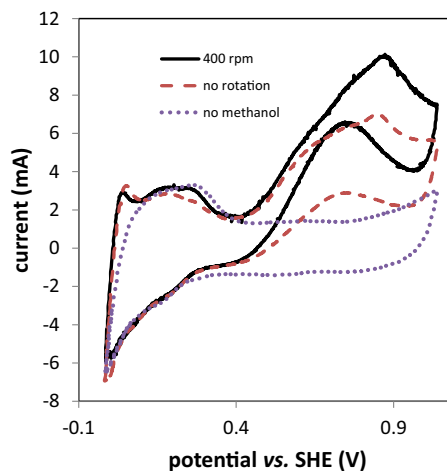
Fig. 1. Cyclic voltammograms (10 mV s^{-1}) of a GC/Pt/C (10 mg cm^{-2}) electrode in 1 M H$_2$SO$_4$(aq) (dotted), and with 0.1 M methanol without rotation (dashed) and at 400 rpm (solid).