

Studies of the role of water in the electrocatalysis of methanol oxidation

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Abstract

The oxidation of methanol has been carried out on electrodes prepared by evaporating Pt directly onto a Nafion membrane and then introducing the methanol either in the gas-fed mode or directly from the electrolyte in the electrolyte-fed mode. It was found that the oxidation carried out using a gas-fed electrode was shifted 100–150 mV more cathodic than the electrolyte-fed electrode. A similar set of experiments was carried out using hydrophobic gas-diffusion electrodes and similar results were obtained. These results suggest that the mechanism of the methanol oxidation reaction depends on the nature of the surroundings and the orientation of the methanol with respect to the electrode surface. In the electrolyte-fed configuration the methanol will be in a hydrogen-bonded water cluster allowing the carbon end of the molecule to more readily approach the catalyst surface. While in the gas-fed configuration the methanol will interact with the water or oxidic surface through the hydroxyl end of the molecule. Clearly, these two possible mechanisms will lead to different products and one may enhance the rate of the direct oxidation of methanol as observed in this work.

Keywords: Water; Methanol oxidation; Electrocatalysis

1. Introduction

The direct electrochemical oxidation of methanol in a proton-exchange membrane type fuel cell holds great potential because of the possibility of operating at low temperatures (<100 °C) without the necessity of a reformer. The major requirements necessary for this to be accomplished are the development of a more active catalyst for the oxidation of methanol, reducing the methanol crossover and improved water management in the cell. Not only is adequate hydration of the proton-exchange membrane required, but water is one of the reactants with methanol at the anode of this fuel cell. How the vaporized water and methanol molecules interact on the surface of the Pt in a highly dispersed Pt-carbon supported catalyst is still unclear. The performance of a direct methanol fuel cell successively decreases with time and this is believed to be due to the strong adsorption of certain species at the anode. These species result from the dissociative adsorption of methanol and have been well studied on polycrystalline Pt in acid electrolytes [1–6]. Prevention of the formation of such strongly adsorbed species could reduce the degradation of the catalyst activity and lead to a decrease in the overvoltage of methanol electro-oxidation. The identification of this adsorbed species has been investigated with a number of techniques including electrochemical thermal desorption

mass spectroscopy (ECTDMS) [7,8] and Fourier-transform infrared reflection-adsorption spectroscopy (FTIRAS) [9–11]. The results of these measurements indicate that the adsorbed intermediate is a –CO or –COH specie with the carbon end of the molecule bound to the Pt surface. The oxidation of this intermediate specie occurs in the same potential region where platinum oxide formation occurs. Prior to this oxidation two possible kinetic mechanisms can be postulated to occur. Methanol may be stepwise dissociatively adsorbed on Pt via the approach of the methanol molecule to the surface through the carbon leading to a –CO or –COH. Or alternatively, the methanol molecule approaches the Pt surface through the hydroxy end of the molecule leading to the formation of a formate-type species on the surface. The reaction mechanism would be different for these two hypotheses. For the system where methanol is present in the electrolyte, water molecules interact with the OH group of methanol via hydrogen bonds and prevent the OH end from approaching the Pt surface. For most transition metals studied in UHV, gas-phase methanol binds through oxygen with the scission of the O–H bond [12]. The methoxy species has been found to be stable on oxygen covered Pt surfaces [13]. The nature of water at the electrode surface and the approach of methanol to the Pt surface as well as the hydrogen bonding that can be formed between the methanol in the bulk water or the surface

water needs to be considered. Different experimental conditions as well as the electrolyte can influence the adsorbed species [1–5].

In this work different configurations were used to deliver the methanol to the Pt surface in order to determine the role of the process by which methanol interacts with the catalyst surface. To do this, methanol must be delivered to the Pt surface either directly from the electrolyte or from the gas phase [14]. In this work it was found that a metal deposited directly on a proton-exchange membrane, e.g. Nafion, and operated as an electrode in a gas-fed configuration gives rise to a lower poisoning effect than the same metal electrode operated in direct contact with a methanol electrolyte solution. Further, there appears to be different reaction mechanisms for the wet-protected carbon-supported electrodes operated in the backfeed exhaust configuration (BFE-type) [15] compared to the direct feed methanol electrolyte configuration. The electrochemical oxidation of methanol has also been studied on glassy carbon electrodes coated with Pt-carbon particles supported in Nafion in sulfuric and perchloric acid solutions.

2. Experimental

2.1. Pt electrodes deposited on Nafion and carbon-supported Pt gas-diffusion electrodes

The Pt film on proton-exchange membrane (PEM) electrodes were prepared by direct vacuum deposition of a 500 Å Pt metal film on a Nafion surface. Nafion 117 was used in all the experiments. A Pd/H electrode was used as the reference electrode. An Astris Quickcell (Electrosynthesis Co.) was used to study the electro-oxidation of methanol in two configurations: (i) methanol vapor gas-fed electrode, and (ii) 1 M H₂SO₄ solution containing 1 M CH₃OH. In the gas-fed configuration nitrogen was bubbled through methanol held at 50 °C at a fixed rate determined by a flow meter and the nitrogen/methanol mixture was introduced into the cell.

The gas-diffusion electrodes were prepared using carbon-supported Pt catalysts, 10 wt.% Pt on Vulcan XC72 carbon obtained from Prototech Corp. (now Etek Inc.). Using a procedure described in Ref. [16], a gas-diffusion electrode layer with a loading of 0.5 mg Pt/cm² loading was formed on a wet-proof carbon paper [16]. Two Astris Quickcells were combined to study the electro-oxidation of methanol in the backward feed and exhaust (BFE-type) configuration. A 2 M methanol/water solution was flowed past the back of the carbon paper side of the electrode. Since the electrode and backing carbon paper are waterproofed this BFE-type configuration supplies methanol to the catalyst surface similar to the way it is supplied in the methanol vapor gas-fed configuration. The solutions were deaerated with argon for a minimum of 30 min prior to the experiments. The cyclic voltammetry data were recorded at a sweep rate of 20 mV/s.

2.2. Electrode preparation for electrolyte studies

The electrodes used in this study were prepared by coating a glassy carbon (GC) disc electrode with a mixture of a Pt-C catalyst and solubilized Nafion. The Pt-C catalyst was obtained from Prototech Corp (now Etek Inc.). A Pt disc of known diameter was used for comparison to the mixture. The electrodes were mounted in a rotating disc electrode system. A microsyringe was used to deliver a known volume, usually 20 µl, of a diluted Nafion-catalyst mixture. The mixtures were prepared by combining a known mass of Nafion solution with a known mass of a mixture of solid catalyst powder dispersed in absolute ethanol. The mixture was placed in an ultrasonic bath to disperse the particles throughout the solution. The coated electrodes were air dried, dipped in Millipore water several times, air dried again, then dipped in 3 M H₂SO₄, and placed in water until needed for use. The ratio of Nafion to catalyst determined whether the mixture would adhere to the GC electrode surface. A 6:1 weight ratio of Nafion to catalyst was used. The electrodes were placed in an electrochemical cell for determination of the current-potential curves or cyclic voltammograms. The surface area of the coated Pt was calculated from the hydrogen absorption peaks in the cyclic voltammograms. The experiments were carried out with a Pd/H₂ reference electrode and a Pt gauze counter electrode and all the measurements were made at room temperature. Either a PAR model 173 or a Pine Instrument Co. RDE potentiostat/galvanostat was used. Oxygen was removed by deaerating with argon or ultrapure nitrogen and an inert gas atmosphere was maintained above the solutions during the electrochemical measurements. Cyclic voltammograms were recorded at a sweep speed of 50 mV/s. Current-potential curves were obtained at a sweep speed of 2 mV/s.

The HClO₄ and H₂SO₄ solutions were made up with ULTREX acids obtained from J.T. BAKER, Inc. and were used as-received. The CH₃OH was Spectrophotometric grade, Gold Label from the Aldrich Chemical Co.; it was used as-received. The Nafion was a 5% butanol solution, 1000 EW, from the DuPont Co. All the solutions were prepared using distilled water passed through a Millipore system. All glassware was soaked overnight in a cleaning solution of 1:1 molar ratio of concentrated H₂SO₄ and HNO₃ acids followed by a thorough rinsing and soaking in Millipore water.

3. Results and discussion

Comparison of the cyclic voltammograms of Pt deposited by evaporation on the PEM recorded in sulfuric acid in the absence of methanol for the two configurations (gas-fed and electrolyte-fed) showed no significant differences in the charge area of the oxide formation region or the hydrogen adsorption/desorption region.

The PEM-Pt-electrolyte configuration was then tested in 1 M CH₃OH–1 M H₂SO₄ electrolyte. In this electrolyte-fed

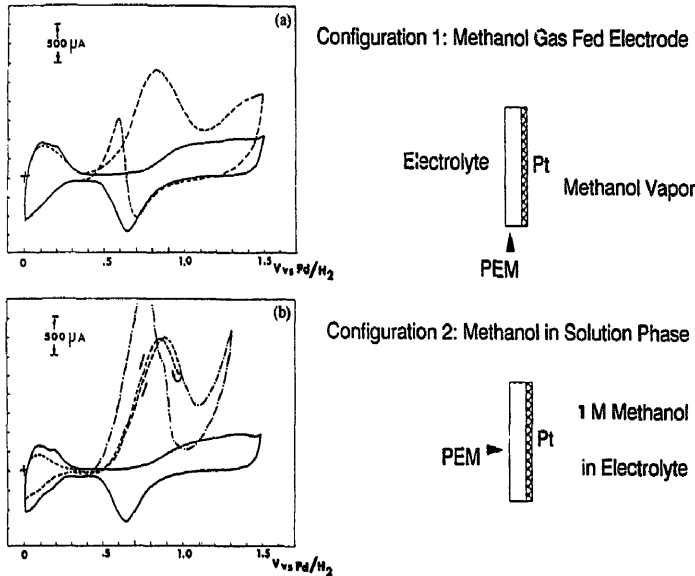


Fig. 1. Cyclic voltammograms of Pt evaporated on a proton exchange membrane (PEM): (a) vapor-fed configuration 1, and (b) solution-fed configuration 2.

configuration, the methanol oxidation begins at 0.4 V and the oxidation peak current occurs at 0.9 V. A commensurate decrease in the hydrogen adsorption/desorption charge current area was also observed. This voltammogram indicates that the Pt surface is partially blocked by the strongly adsorbed species see Fig. 1(b). The gas-fed Pt-PEM-electrolyte configuration was tested and the methanol oxidation begins at 0.4 V and the oxidation peak current occurs at 0.8 V, a lower potential than the initiation of Pt oxide growth, Fig. 1(a). The initial oxidation of methanol (or the half-wave potential) is shifted cathodically by 100 to 150 mV, cf. Fig. 1(a) and (b). The difference in oxidation current is due to the lower concentration of methanol in the gas-fed configuration. No poisoning effects are observed on the gas-fed Pt-PEM electrode even after several hours of cycling in the potential region shown in Fig. 1(a). These results suggest that gas-fed methanol does not poison the Pt surface and the oxidation reaction occurs at lower potentials than liquid-fed methanol.

A wet-proof gas-diffusion electrode was used in a backward feed and exhaust (BFE) configuration which had 1 M $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ solution on the carbon paper side of the electrode and 1 M H_2SO_4 electrolyte on the catalyst side of the electrode, Fig. 2. The methanol passes through the wet-proof carbon paper into the catalyst layer and behaves in a manner similar to a gas-fed electrode. The cyclic voltammetry of this configuration shows the methanol oxidation peak occurring at 0.85 V with a small decrease in the hydrogen adsorption/desorption area. For the electrolyte-fed configuration, where the 1 M H_2SO_4 is replaced with 1 M CH_3OH in 1 M H_2SO_4 on the catalyst side of the electrode and the carbon paper side of the electrode is exposed to nitrogen gas, the cyclic voltam-

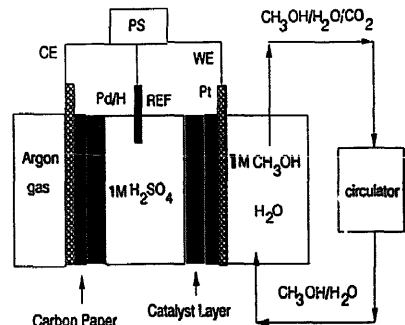


Fig. 2. Backward feed and exhaust configuration of carbon-supported Pt electrode in Astris electrochemical cell.

metry shows a decrease in the hydrogen adsorption/desorption area with the methanol oxidation peak occurring at 1.05 V with a shoulder at 0.85 V, Fig. 3(b). The difference in the oxidation currents is due to a lower concentration of methanol at the interface in the BFE configuration. Similar decreases in the hydrogen adsorption/desorption charge areas were observed for the two configurations. The decreases are very nearly the same and this is attributed to the fact that some methanol is transported through the BFE and passes into the electrolyte at the interface and then is oxidized in the same manner as that supplied directly from the electrolyte. The cyclic voltammograms of both configurations show a current peak at 0.85 V for methanol oxidation. It is clear that a cathodic shift of the methanol oxidation peaks at 1.05 V with a shoulder at 0.85 V in the electrolyte-fed configuration Fig. 3(b) shifts to 0.85 V with a shoulder at 0.7 V Fig. 3(a) in the BFE configuration. A similar cathodic shift is also

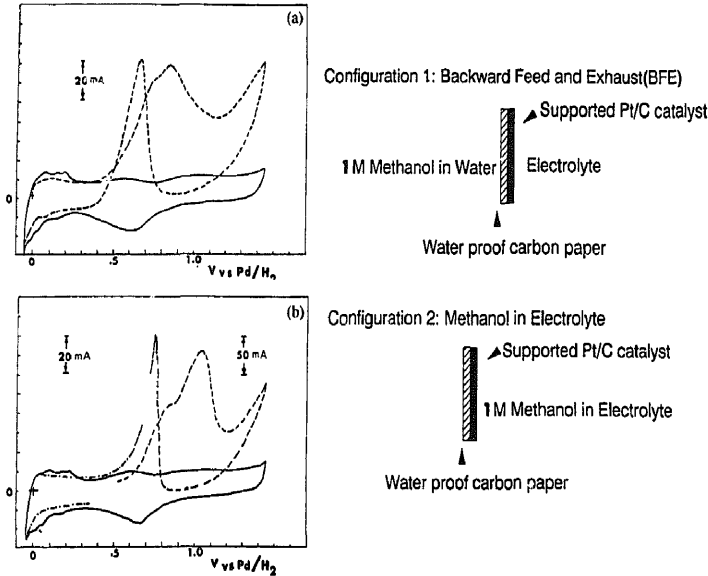


Fig. 3. (a) Cyclic voltammogram of Pt on carbon gas-diffusion electrode in the BFE configuration. (b) Cyclic voltammogram of Pt on carbon gas-diffusion electrode in electrolyte-fed configuration.

observed for the anodic oxidation peak at 0.75 V in the electrolyte-fed configuration Fig. 3(b) to 0.65 V in the BFE configuration Fig. 3(a). The differences observed for methanol oxidation in these two configurations imply that there may be different mechanisms involving the backward fed methanol as compared to the electrolyte-fed methanol. In the BFE configuration, the cathodic shifts of the methanol oxidation peaks indicate that the catalytic shift can be related to how the methanol is delivered to the catalyst layer of the supported carbon gas-diffusion electrode.

To further investigate the role of the interaction of the methanol with the electrolyte in the oxidation of methanol the relationships of the peak currents with the hydrogen ion activity, the water activity and the ratio of methanol to protonated methanol (CH_3OH^+) have been determined using the GC electrodes. There is an apparent difference in the dependence of the peak currents on the acid concentration. Also, there is a relationship between the cathodic shifts of the methanol oxidation peaks discussed earlier and the dependence of the peak currents on the activities of the water and hydrogen ions. In the vapor state, methanol is a stronger acid than water whereas in aqueous solution the order is reversed. Solvent effects due mostly to hydrogen bonding, make it more difficult for methanol in aqueous solution to give up a proton compared to water [17]. The mean activity coefficients in sulfuric acid and perchloric acid were available for use [18]. The activity of water in sulfuric acid has been reported [18] and the water activity in perchloric acid was determined from the freezing point data [19].

The trends in the dependence of the activity coefficients with acid concentration for sulfuric and perchloric acids are

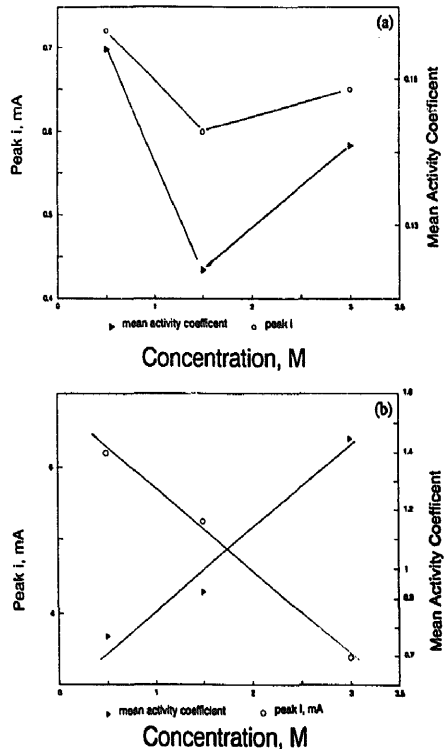


Fig. 4. Dependence of the activity coefficients and the anodic peak currents on acid concentration: (a) sulfuric acid with 1 M CH₃OH, and (b) perchloric acid with 1 M CH₃OH.

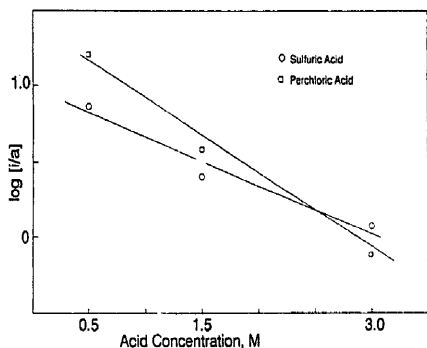


Fig. 5. Dependence of $\log [i_p/aH^+]$ vs. acid concentration for sulfuric and perchloric acids both containing 1 M CH_3OH .

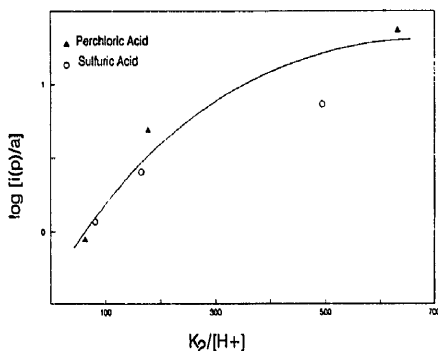
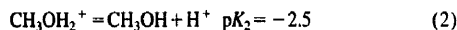
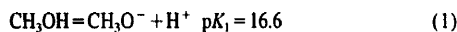


Fig. 6. Dependence of $\log [i_p/aH^+]$ on the $[CH_3OH]/[CH_3OH_2^+]$ ratio in sulfuric and perchloric acids both containing 1 M CH_3OH .

compared to the trends in the methanol oxidation peak currents with acid concentration in Fig. 4. If the hydrogen ion activities are used to correct the peak currents, i_p , a plot of $\log [i_p/aH^+]$ versus acid concentration is linear as shown in Fig. 5. Two separate lines are seen for perchloric acid and sulfuric acid where the slight difference in the two lines is a result of the weak second dissociation of sulfuric acid which was taken into account when the hydrogen ion activities were calculated.

The environment of the methanol as it approaches the electrode is important and determines how the methanol is delivered to the catalyst surface for oxidation. Protonation and hydrogen bonding can determine which end of the methanol can approach the Pt surface. Methanol is a weak base and can form the $CH_3OH_2^+$ ion. Consider the two equilibria [20]:



In acid electrolyte, the acidity of methanol is less than water by two orders of magnitude; however, the second equilibrium is important in determining the species of methanol present. The ratio of $[CH_3OH]/[CH_3OH_2^+]$ may be written as $K_2/[H^+]$. Fig. 6 shows the dependence of i_p/aH^+ on this ratio

of methanol species. The interaction of methanol with water and the catalytic surface are also dependent on this ratio. In the more acidic solutions, the ratio $[CH_3OH]/[CH_3OH_2^+]$ is low and there is a significant number of $CH_3OH_2^+$ ions with the $-OH_2^+$ end surrounded by water molecules, in this configuration the methanol is more likely to approach the catalyst surface via the CH_3 end. The oxidation rate would be dependent on the hydrogen ion activity and the ratio of species present. At low hydrogen ion concentrations, all of the methanol is present in the neutral form, CH_3OH , and the peak currents corrected for hydrogen ion activity reach a limiting value as seen in Fig. 6.

4. Conclusions

Based on these results, there are at least two possible mechanisms for the electrochemical oxidation of methanol that depend on how the methanol approaches the electrode surface, see Fig. 7. In the electrolyte, the OH end of methanol is expected to be surrounded by water molecules through hydrogen bonding, Fig. 7(a). This interaction with a water cluster would prevent the OH end of the methanol from approaching the surface and hence the CH_3 would interact with the surface leading to the formation of a $-CO$ or $-COH$ specie. When methanol is delivered from the vapor phase, the methanol molecule will tend to approach the surface via the OH end due to its interaction with the adsorbed water, Fig. 7(b), enhancing the direct oxidation to CO_2 . The hydrogen adsorption/desorption regions of the cyclic voltammetry indicate that there is a lower amount of the adsorbed intermediates produced when supplying the methanol from the vapor phase and the potential for methanol oxidation moves to a more negative value. In such a case, the orientation of surface-adsorbed water molecules at the applied potential play a significant role by interacting with the approaching methanol

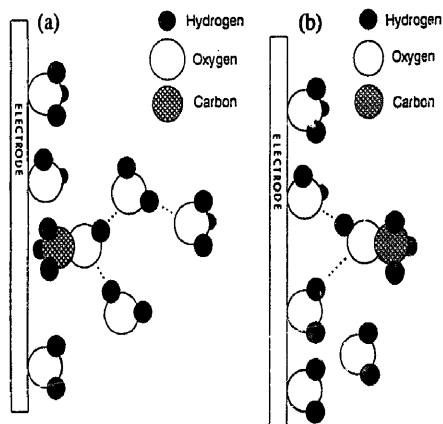


Fig. 7. Schematic representations of the orientations and interactions between methanol, water and surface-adsorbed water molecules in (a) electrolyte-fed configuration, and (b) in the BFE or gas-fed configuration.

molecule. When methanol is present in the electrolyte it interacts with the water through hydrogen bonding and approaches the Pt surface in a different manner, Fig. 7(a). We also see that there is a relationship between the current and the water activity as well as the proton activity. The nature of how methanol and water are hydrogen bonded as well as the nature of the water on the surface of the electrode determines the performance of the catalytic electro-oxidation of methanol.

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