

Electrooxidation of Methanol on Platinum; Reaction Kinetics and Mechanism

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INTRODUCTION

The electrooxidation of methanol on platinum and a variety of other metals has been the subject of numerous studies, mainly due to its promise as a fuel cell feed. Several reaction mechanisms have been proposed, even a dual pathway mechanism, including both adsorbed catalytic poisons and reactive intermediates. In the case of methanol oxidation on platinum, adsorbed CO has been detected over wide potential ranges and is regarded as a catalytic poison. It is, however, a necessary intermediate in a serial pathway. The necessity of an adsorbed oxygen-containing species to complete the oxidation of methanol has pointed out the importance of studying the effect of surface states on the electrocatalytic properties. One part of this work has been to study the effect and nature of surface oxides on the electrooxidation of methanol by dc and ac voltammetry and determine an equivalent circuit from a simplified reaction sequence. A second part involves a chronoamperometric and a rotating disk experimental study.

EXPERIMENTAL

AC voltammograms were obtained by superimposing a 5-10 mV ac sine wave on a 10 mVs⁻¹ ramp voltage and applying this signal to the cell via a custom-made potentiostat. The ac component of the current was measured with a Stanford Research model SR530 lock-in amplifier. A polycrystalline platinum wire was sealed in glass and used as a working electrode in a glass cell of conventional design. A reversible hydrogen electrode was used as reference electrode.

Chronoamperometric measurements were made with a fast custom-built potentiostat, after a sequence of electrochemical pretreatments. Typically, one activating/cleaning potential step from the onset of hydrogen evolution to the oxide region was followed by a 10 ms prestep at a potential sufficiently low to reduce the oxide but short enough such that no noticeable methanol chemisorption occurred [1]. The potential step was then stepped to a selected value and the current measured.

Rotating disk and rotating ring disk experiments were obtained by using a rotator and bipotentiostat from Pine Instrument Company.

RESULTS AND DISCUSSION

Significant rates of electrooxidation of methanol on platinum are observed only above ca. 0.5 V_{RHE}. Adsorbed CO species produced in the methanol oxidation reaction are likely to form passive CO islands on platinum terrace sites, thus blocking the surface for further adsorption of

methanol and formation of underpotential deposited hydrogen. These adsorbed species are oxidatively removed in the positive sweep in the region above 0.5 V_{RHE}. The current peak in a cyclic voltammogram occurs at about 0.83 V_{RHE} in the positive scan, and coincides with the formation of a monolayer of Pt-OH at the platinum electrode, which commences at 0.75 V_{RHE}. This monolayer of oxide will deactivate the electrode surface by occupying free sites on the surface and inhibit methanol adsorption.

The impedance data were analysed using an equivalent circuit derived from a simplified reaction mechanism using the methodology of Harrington and Conway [2]. The ac voltammetry and the corresponding impedance spectra, with equivalent circuit analysis, showed only one faradaic capacitive or inductive element in addition to the double-layer capacity. This implies that only one kinetically significant adsorbed species is present at the surface at all potentials. This adsorbed species is assumed to be Pt-OH₂ at potentials lower than 0.75 V_{RHE}, and Pt-OH for potentials above 0.75 V_{RHE}.

Voltammetric reversal and sweep-hold experiments showed evidence for nucleation-collision-growth mechanisms in two potential regions, 0.67 to 0.75 V_{RHE} and 0.77 to 0.80 V_{RHE}. These results are consistent with the intuitive idea that the intermediate, surface-bonded carbon monoxide, reacts with surface-bonded water molecules at potentials lower than 0.75 V_{RHE} and with surface-bonded hydroxyl at higher potentials. The nucleation and growth behaviour observed can be explained by the reaction leading to CO₂ production occurring at the edge of an island consisting of Pt-OH₂ or Pt-OH.

The chronoamperometric data showed that the adsorption and deactivation of the platinum catalyst is a relatively slow process. The effect of different supporting electrolytes in the methanol decomposition reaction was apparent at short time, and attributed to anion adsorption. Surprisingly the initial (instantaneous) current was slightly higher in sulphuric acid than in perchloric acid. The transient from perchloric acid solution rapidly exceeded the current from sulphuric acid with time, most likely due to the increased anion adsorption strength obtained with sulphuric acid. Tafel slopes obtained from steady state measurements were varying around 120 mV decade⁻¹.

Rotating disk experiments clearly showed that mass transport has an impact on methanol electrooxidation. With methanol, the current peak in the anodic scan decreased with increased rotation rate, while in the case of formic acid and formaldehyde, this oxidation peak increased with increased rotation rate. A major kinetic difference between three possible fuel cell feeds is expected.

REFERENCES

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