E2-26: Electrocatalysis of polyaniline modified Pt surface towards methanol oxidation

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The adsorption of polar organic molecules such as methanol and ethanol on Pt surfaces and their subsequent heterogeneous reactions compete with electrochemical processes occurring on the Pt electrode surface in aqueous electrolytes. A study of this nature is useful in understanding electrocatalytic reactions, nature of electrochemical reactivity of fuel cells and electrosynthesis. The intermediates/products formed by the electron transfer between the Pt surface and the organic molecules, however, poison the Pt surface. This paper is based on the preventive measures taken for the poisoning problem due to methanol oxidation on Pt surface by modifying the Pt surface by electrodepositing a thin film of polyaniline.

Electrocatalytic methanol oxidation on bare Pt electrodes and those modified with polyaniline were studied in one compartment cell comprising the above electrode as working electrode (WE), a saturated calomel reference (SCE) and a Pt gauze auxiliary electrode. The electrolyte used was a deoxygenated solution containing 0.100 mol dm^{-3} $NaClO_4$ and required amount of methanol at pH 1 (adjusted with HCl). The cell also had an inert gas blanket to prevent the diffusion of O_2 into the solution. In a typical experiment, required quantities of methanol was injected into the background electrolyte and the solution was deoxygenated. Methanol oxidation on the WE was followed by cyclic voltametry and the peaks due to the process were identified by changing the methanol concentration and by continuous cycling experiments. The instrumentation adopted consists of an electrochemical analyzer (Oxford Electrodes) and an X-Y chart recorder (YEW Model 3022). $NaClO_4$ (Analar, Aldrich), $HClO_4$ (60%, Aldrich) and methanol (99.8%, Aldrich) were used as received while aniline (GPR, BDH) was distilled under N_2 prior to use.

Cyclic voltamogram (CV) of bare Pt electrode was severely affected by the presence of 1 mol dm^{-3} methanol in the electrolyte. Pt oxidation wave and subsequent reduction of PtO are inhibited. The hydrogen adsorption/desorption regions are altered and a new peak centered at 0.58 V is apparent.

Experiments conducted by changing the bulk concentration of methanol confirm that the new peak is due to methanol oxidation. CV recorded in the range when there is no sufficient overvoltage for PtO formation did not show the peak due to methanol oxidation. This result together with Freundlich adsorption studies showed that methanol is preferentially adsorbed on the clean Pt surface available after the reduction of PtO. The peak current at 0.58 V is enhanced with continued cycles in the full range of potentials. This enhancement was predominant at the early scans and is eventually levelled off after about 100 cycles. Further continuation of cycling resulted in gradual loss of the electrode activity completely. This is due to the poisoning of the electrode surface by the products/intermediates formed by the oxidation of methanol. In the presence of polyaniline on the surface of Pt, the adsorption of methanol follows the Langmuir adsorption isotherm suggesting a monolayer coverage in contrast to multilayer coverage on the bare Pt surface. The potential of methanol oxidation had no effect due to polyaniline. Methanol oxidation did not occur on polyaniline modified glassy carbon electrode surface showing that methanol oxidation does not take place on the polyaniline surface. Continuous cycling experiments done on polyaniline modified Pt electrodes did not show any loss of electrode activity even after the 200 cycles.

Electro-oxidation of methanol takes place on a clean Pt surface at 0.58 V in aqueous $NaCl0_4$ solution at pH 1 and methanol oxidation on the Pt surface forms multilayer coverage. The products/intermediates formed by the oxidation of methanol poison the electrode.

Electro-oxidation of methanol on polyaniline modified Pt occurs at the same potential under similar conditions. The adsorption is a monolayer coverage. The oxidation occurs on the Pt surface and not on the polyaniline surface. The polyaniline layer resists the poisoning of the electrode due to methanol oxidation.