

Influence of Interfacial Water Activity in the Electro catalysis of CO and Methanol Oxidation: Combination of Electrochemistry and Synchrotron based *In-situ* XAS Data

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The adsorption properties of carbon monoxide on metal surfaces have been investigated in great detail using modern spectroscopic and Ultra High vacuum (UHV) techniques.¹ It has been well established from these studies that the surface structure of adsorbed CO (CO_{ads}) and the oxidation of adsorbed CO species on Pt single crystal surfaces is potential dependant above 0.5 V. The kinetics of CO_{ads} on Pt depend on many factors including CO_{ads} surface coverage and its surface structure, its mobility on the electrode surface and the presence of anions on the electrode surface. Of all these factors that affect the kinetics of CO oxidation, the current state of the art CO tolerant electrocatalysts rely on the 'bifunctional approach' where a second alloying element such as Ru, Sn and Mo can initiate the oxidation of CO due to the presence of surface oxygenated species even at lower potentials.²⁻⁴ A model based on the bifunctionality of an alloying metal such as Ru are however poor for methanol oxidation.^{5,6}

Previously, a 3-fold enhancement in activity for CO oxidation was shown on a PtMo/C relative to a PtRu/C in a PEMFC operating at 85°C under an anodic H₂ stream mixed with 100ppm CO. Two distinct CO stripping peaks were observed both in a PEM half cell and a flooded electrolyte cell.^{7,8} This suggests that the CO stripping occurs on both the Mo and the Pt atoms on the surface, however at different potentials. From kinetic studies of H₂ and CO oxidation on smooth and well defined PtMo surfaces, it was concluded that the oxidation states of the Mo surface atoms determine the electrocatalytic activity on these alloys.^{9,10} *In-situ* X-ray absorption data (XANES and EXAFS) at the Pt L and Ru and Mo K edges confirm an increase in Pt d-band vacancy concentration and a lower Pt-Pt bond distance on these type of alloys.⁸ It was concluded that, while there is a competition between oxide species and CO adsorption for Ru surface sites on a PtRu/C, the Mo surface on a PtMo/C was shown to have no affinity for CO and as a result is available for efficient CO oxidation. However, a more complicated interaction was envisaged for methanol oxidation which results in a build up of C₁ oxide species on a PtMo/C in contrast to a PtRu/C. Mechanistic studies on decomposition of methanol on Pt surfaces by Wieckowski *et. al.*¹¹ in UHV and electrochemical environments suggests that the cleavage of the C-H bond on Pt surface is a more favorable rate determining step (rds) in an electrochemical environment than the O-H bond breakage due to the hydrophilic interactions between the methanol OH and surrounding water.

Previously, the inherent activity for ORR on supported Pt and Pt alloy nanoparticles without the effect of oxide formation via activation of water was investigated using higher concentrations of trifluoromethane sulfonic acid (TFMSA).^{12,13} The enhancement of ORR activity under low water content was shown to agree well with the lowering of oxide formation.¹⁴ The present investigation focuses on the study of CO and methanol electro-oxidation pathways on

supported Pt and Pt based electrocatalysts in different concentrations of TFMSA and to compare and correlate the influence of water activation on the electrocatalysis of CO and CH₃OH. The kinetics of CO oxidation would also be discussed in detail using rotating disk electrode (RDE) polarization data and stripping voltammetry. The short range atomic order and the electronic properties of the Pt and the alloying metals based on *in-situ* XAS would be discussed under surface adsorbed/poisoned conditions.

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