Role of Competitive Ion Adsorption in the Oxidation of Formic Acid on Au

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A key step in the electro-oxidation of formic acid to CO_2 on Au electrodes is the reversible formation of an adsorbed intermediate, proposed to be formate[1,2,3]. A central feature of this reaction is the marked dependence of anodic current onset and magnitude on supporting electrolyte identity[4] and concentration. Past studies show that increasing affinity of the supporting anion for Au drastically dampens reaction rates and formate vibrational intensities at a given potential[2,3,4].

A thus far untapped method for studying this adsorbed intermediate is collection of capacitance data. Using dynamic Electrochemical Impedance Spectroscopy (dEIS), capacitance data in solutions from 1 to 0.005 molal sulfuric or perchloric acid with 1 to 0.005 molal formic acid were acquired. Capacitance curves in sulfuric/formic acid and perchloric/formic acid solutions on Au reveal adsorption peaks for formate at higher potentials than supporting anions. This data suggests formate must adsorb onto previously anion-covered surfaces to undergo oxidation. The suppression of current onset and magnitude is discussed in terms of competition of formate with the supporting anions for sites on the Au electrode. This process is drastically different for each supporting electrolyte. Sulfate undergoes a disorder-order phase transition to a 2D solid-like adlayer at high coverages[5,6,7] along with co-adsorbed water. This phenomenon is not known for perchlorate. The sulfuric/formic acid system displays strongly inhibited formate adsorption, with formate adsorption peaks shifting to much higher potentials and decreasing in size as sulfuric acid activity increases. The perchloric/formic acid system shows near perfect co-adsorption, with nearly constant peak size as a function of perchloric acid activity.

Experimental results are compared with modelling results for competitive adsorption based on hard-hexagon and Frumkin isotherms.

Capacitance: Variable HCOOH in 0.1m H_2SO_4

Capacitance: Variable HCOOH in 0.09m $HClO_4$
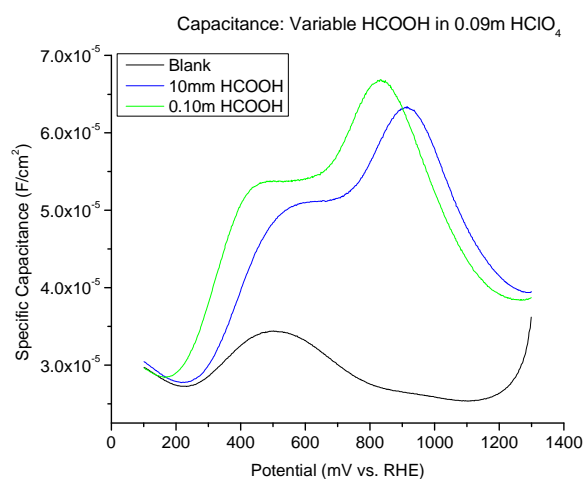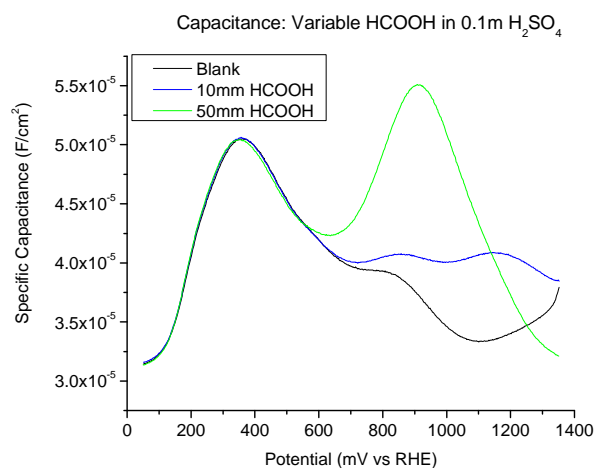
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