Potentiometric Measurements of
Adsorption Pseudocapacitance of Chlorine on Platinum

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The kinetics of chlorine adsorption on polycrystalline platinum was studied potentiometrically in aqueous potassium chloride solution. The potential of the platinum rose slowly to a plateau upon exposure of the platinum to chlorine at concentrations in the ppb to ppm regime (Figure 1). The plateau potential increased by 290 mV for every 10-fold increase in chlorine concentration, nearly two orders of magnitude greater than predicted by the Nernst equation (Figure 2).

The potential increase is believed to be due to the pseudocapacitance caused by the adsorption of chlorine atoms on to the platinum surface, as described by Conway.[1] Much weaker responses are observed gold and glassy carbon electrodes. At concentrations below 1 ppm, the kinetics of the adsorption, as determined from the potential response, was modeled by the adsorption of chlorine to two different types of sites. Higher concentrations of chlorine led to more complex kinetics involving at least two adsorption mechanisms. This is consistent with Müller's study of chlorine reduction kinetics.[2]

The pretreatment of the platinum with various organic adsorbates prior to use in the potentiometric experiments, led to potential responses that did not plateau, but instead, reached a maximum and slowly decayed in a manner that depended on the adsorbate (Figure 3). The decay suggests that the platinum sites are not simply blocked by the adsorbate, but that a surface reaction occurs between the adsorbate and the adsorbed chlorine atoms.

References:

1. B. E. Conway and P. Gu, J. Electroanal. Chem., 349 (1993) 233.

2. Von L. Müller and B. Kaiser, Z. phys. Chemie, Leipzig 261 (1980) 5, S1011

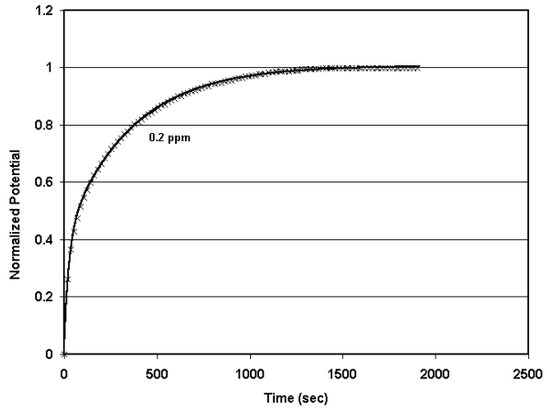

Fig. 1. Potentiometric response of polycrystalline platinum to 0.2 ppm chlorine in 1 M KCl (solid line). Simulation based on two site model (crosses).

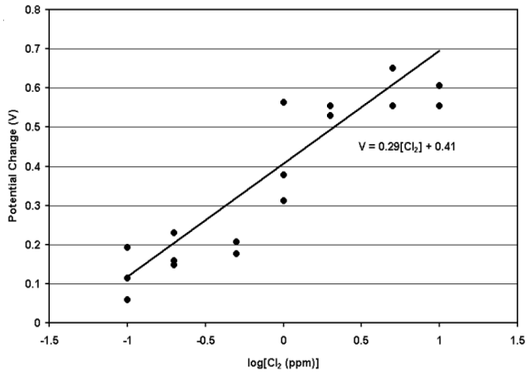

Fig. 2. Dependence of plateau potential on chlorine concentration.

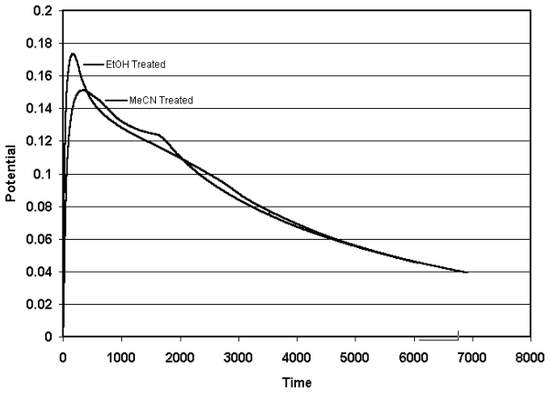

Fig. 3. Potentiometric response of ethanol and acetonitrile pretreated polycrystalline platinum electrodes to 1 ppm chlorine in 1 M KCl.