Effects of alkali metal cations on the hydrogen oxidation reaction in alkaline electrolytes

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Introduction

Spectator ionic species in electrolyte solutions can affect the rate and selectivity of cathodic reactions. For example, it is well known that many cations, including alkali metal cations, can promote the adsorption of hydroxide onto the Pt(110) surface. We have shown that alkali metal cations can favorably specifically adsorb to the Pt(110) surface, as implemented in the Vienna Ab initio Simulations Package (VASP), and show it is dependent on the cation present in the electrolyte solution, even at low potentials. We develop and support a mechanism that alkaline metal cations can favorably specifically adsorb to the Pt(110) surface, through their impact on the stability of surface intermediates, providing a rationale for a combined design of electrolyte/electrodes to allow promotion of electrocatalytic reactions.

Materials and Methods

The rate of the hydrogen oxidation reaction is measured over a Pt(pc) rotating disk electrode at 22°C in 0.1 M LiOH, 0.1 M NaOH, 0.1 M KOH, and 0.1 M CsOH. Exchange current densities are calculated from triplicate runs at 2500 rpm, using data corrected for hydrogen mass transport. Density functional theory (DFT), as implemented in the Vienna Ab initio Simulations Package (VASP), is used to evaluate our proposed mechanism. Equilibrium adsorption potentials are calculated for the adsorption of Li, Na, K, and Cs onto Pt(110) surface as well as for the adsorption of hydroxide next to these adsorbed cations.

Results and Discussion

We find that the rate of the hydrogen oxidation reaction over Pt(pc), as quantified by the exchange current density, is affected by the presence of alkali metal cations. Using DFT, we have found that alkali metal cations can favorably specifically adsorb to the Pt(110) surface at low potentials and can compete with hydrogen adsorption in high pH electrolytes. Furthermore, we find that the presence of specifically adsorbed cations can promote the adsorption of hydroxide onto the Pt(110) surface. We derive a hydrogen oxidation reaction rate equation based on a Langmuir-Hinshelwood type mechanism and find that the trend in which cations promote hydroxide adsorption matches our experimentally measured trend in the rate of hydrogen oxidation. This is illustrated in Figure 1.

Figure 1. Experimentally measured exchange current density for the hydrogen oxidation reaction over Pt(pc) in 0.1 M LiOH, 0.1 M NaOH, 0.1 M KOH, 0.1 M CsOH and the DFT calculated equilibrium adsorption potential for hydroxide at 1/9 ML coverage onto Pt(110) next to 1/9 ML specifically adsorbed alkali metal cation.

Figure 1 shows specifically adsorbed Li (at 1/9ML coverage) best promotes hydroxide adsorption, and gives the highest experimentally measured hydrogen oxidation rate. Cs promotes hydroxide adsorption the least, and gives the lowest hydrogen oxidation rate.

Significance

We demonstrate that spectator cations may affect electrocatalysis through their impact on the stability of surface intermediates, providing a rationale for a combined design of electrolyte/electrodes to allow promotion of electrocatalytic reactions. The specific observations reported are of relevance to alkaline fuel cell development, where the rate of the hydrogen oxidation reaction is typically thought to be sluggish relative to acid fuel cells; we find the rate is comparable to that measured in acid in Li+/Na+ containing alkaline electrolytes.

References