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Double layer effects in electrocatalysis: The oxygen reduction reaction and ethanol oxidation reaction on Au(1 1 1), Pt(1 1 1) and Ir(1 1 1) in alkaline media containing Na and Li cations

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ABSTRACT

Oxygen reduction and ethanol oxidation reactions were studied on Au(1 1 1), Pt(1 1 1) and Ir(1 1 1) in alkaline solutions containing sodium and/or lithium cations. By keeping the same (1 1 1) surface orientation and exploring oxophilicity trends and non-covalent interactions between OH_{ad} and alkali metal cations (AMCⁿ⁺), we were able to gain deep insights into the multiple roles that OH_{ad} plays in these important electrocatalytic reactions. Cyclic voltammetry experiments revealed that OH_{ad} formation initiates at distinct electrode potentials, governed by the oxophilicity of the specific metal surface, with further OH_{ad} adlayer stabilization by non-covalent alkali-cation interactions and affecting the formation of a “true oxide” layer at higher electrode potentials. Although OH_{ad} is a simple spectator for the ORR, it promotes the ethanol oxidation reaction (EOR) at lower potentials and act as spectator at high OH_{ad} coverages. By changing the alkali metal cation at the interface (Li⁺) on more oxophilic surfaces, it was possible to promote the EOR even more, relative to Na⁺, without changing the product distribution for the reaction. This cation effect suggests that OH_{ad}-Li⁺(H₂O)_x clusters can stabilize the ethoxide adlayer, thus improving the EOR activity. Our results indicate the importance of the entire electrochemical interface in determining the electrocatalytic activity during reaction.

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1. Introduction

Significant advances in the field of electrocatalysis over the past several decades have been driven by fundamental understanding, at atomic/molecular levels, of relationships between the structure of single crystal surfaces and their surface reactivity with respect to adsorption of spectator and intermediate species and catalytic processes [1]. These well-defined single crystal surfaces provide the ability to correlate interfacial reactivity with the structure of the double layer, bridging understanding of potential-dependent metal-adsorbate bonding (covalent forces) with the weaker, but equally important, electrostatic forces (van der Waals or non-covalent) between hydrated ions located in the outer Helmholtz plane (OHP) and covalently-bonded spectator/intermediate species located in the inner Helmholtz plane (IHP) [2–4]. Two classes of electrocatalytic reactions exhibiting strong relationships between interfacial properties and reactivity are the oxygen reduction

reaction (ORR) and the oxidation of small organic molecules such as the ethanol oxidation reaction (EOR). Although a great deal has already been learned with respect to the surface structure assumed by metal surfaces and the reactivity of the ORR and EOR [5–15], there are still many issues that must be resolved before these two reactions can operate at reasonably low overpotentials in alkaline and acid media. Here, overpotential is defined as the difference between the reversible potential for the reaction (ORR or EOR) and the operating potentials, e.g., a lower overpotential yields higher activity. Moreover, understanding selectivity trends for these reactions is crucial for highly efficient electrocatalysis – especially for the EOR – as effective breaking of the C–C bond has proven to be a challenge. Finally, the nature of the metal surface, effectively described by metal–oxygen interactions (degree of oxophilicity), has a key role in controlling the adsorption processes for relevant species such as OH_{ad}, O_{ad} and organic intermediates that are directly related to issues of activity and selectivity.

The EOR, in particular, is a complex reaction that requires an optimal balance between ensemble effects (i.e., surface site availability) and electronic effects (i.e., the d-band center), as

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well as the presence of oxygen source, usually provided by surface-adsorbed OH species (OH_{ad}). One of the main issues hampering the efficiency of the EOR is the breaking of C–C bonds required for complete oxidation to $\text{CO}_2/\text{CO}_3^{2-}$. Most catalysts only effectively produce $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$, diminishing the total number of electrons produced per ethanol molecule from 12 to 4 [12–15]. Moreover, the nature of the initial dehydrogenation step is still under debate, related to either bulk phase equilibria (alcohol pK_a) or surface adsorption processes that form adsorbed ethoxide (EtO_{ad}) species required for further oxidation [16]. Regardless of the specific mechanism, the kinetic rate depends on the metal– OH_{ad} and metal–intermediate interactions, as well as on the ensemble of free metal sites for adsorption of ethanol molecules. Of paramount importance is developing an understanding of the functional links between the coverage of OH_{ad} and the nature of EOR reaction intermediates.

Studies in alkaline solutions provide an ideal platform for investigating the dynamics of the OH_{ad} –ethanol interaction, as they exclude confounding effects arising from the specific adsorption of anions. Furthermore, interactions between hydrated alkali metal cations ($\text{AMC}^+(\text{H}_2\text{O})_x$) and OH_{ad} via non-covalent interactions may influence the reactivity of both ORR and EOR, providing another mechanism for probing the influence of OH_{ad} on the overall reaction kinetics. Indeed, these non-covalent interactions, which act at distances of tens of angstroms and involve dipole–dipole forces between adsorbed oxygenated species that are positioned in the IHP and $\text{AMC}^+(\text{H}_2\text{O})_x$ located in the OHP, have been shown to increase in magnitude in the same order as the hydration energy (surface charge density) of the corresponding cation ($\text{Li} \gg \text{Na} > \text{K}$) [2]. This increase also corresponds to an increase in the concentration of OH_{ad} – $\text{AMC}^+(\text{H}_2\text{O})_x$ clusters at the interface. Importantly, this trend is inversely proportional to activity of the ORR and methanol oxidation [2], as well as the oxidation of ethylene glycol [17], which suggests that these clusters block the active Pt sites for adsorption of reactants and production of intermediates. In contrast to the ORR and methanol oxidation, however, it has been shown that non-covalent interactions can also play a promoting role, affecting the rates of oxidative removal of CO [18] as well as of the discharge of water in the hydrogen evolution reaction (HER) on platinum covered by $\text{Ni}/\text{Co}(\text{OH})_2$ [19,20]. As a result, it is difficult to predict the role of non-covalent forces at electrochemical interfaces, as the nature of interfacial components, reactants, and intermediates can result in these effects either promoting or impeding reactivity of the interface.

Reported here are the salient findings from electrochemical and spectroscopic measurements of the role of non-covalent interactions in the ORR and EOR in alkaline solutions on Au(1 1 1), Pt(1 1 1) and Ir(1 1 1) single crystal surfaces. By performing both reactions in the presence of either Li^+ or Na^+ cations, it was possible to simultaneously investigate the effect of oxophilicity on the reversible and irreversible formation of oxides, where metal–oxygen interactions increases in the order $\text{Au} < \text{Pt} < \text{Ir}$, as well as the role of $\text{AMC}^+(\text{H}_2\text{O})_x$ on governing the adsorption of OH_{ad} and thus the formation of OH_{ad} – $\text{AMC}^+(\text{H}_2\text{O})_x$ clusters. The kinetics of the ORR on Pt and Ir are observed to be slower in the presence of Li^+ cations, confirming that OH_{ad} – $\text{AMC}^+(\text{H}_2\text{O})_x$ clusters play a critical role in ORR electrocatalysis. In contrast, we found that both OH_{ad} and hydrated Li^+ cations play a dual role in the EOR—promoting the reaction at low overpotentials while strongly suppressing the reaction at higher overpotentials. These overpotential-dependent differences are discussed in the context of surface coverage by OH_{ad} species and their interaction with hydrated cations. We also discuss how the nature of EOR intermediates and products depends on both the oxophilicity of the metal catalyst and the nature of the cation.

2. Experimental

Crystal preparation procedures and electrochemical measurements have been described in previous publications [2,3,19–23]. In short, all crystals were annealed up to 800 °C, 1100 °C and 1400 °C for Au(1 1 1), Pt(1 1 1) and Ir(1 1 1), respectively, in a 3% H_2/Ar atmosphere for 10 min. After slow cooling, a drop of ultra-pure deionized water (Milli-Q) was placed on the crystal surface before assembly into the RDE setup and transferring it to the electrochemical cell. Solutions of 0.1 M LiOH (Fluka, 99.998%) or 0.1 M NaOH (Fluka, 99.9995%) were used in all experiments. Ethanol (Pharmco–Aaper 200 proof) and Methanol (Fluka, 99.9%) were used to make solutions from 20 mM to 300 mM. All gases were 5N5 quality acquired from Airgas. Electrode potentials are given versus the reversible hydrogen electrode (RHE), calibrated using H_2 oxidation in a separate experiment. Note that the standard deviation in the onset potentials discussed in the text was around ± 3 mV while the relative standard deviation for the currents was about 5%, obtained after distinct measurements with freshly prepared solutions and crystals. The sweep rate for all electrochemical measurements was 50 mV s^{-1} . FTIR experiments were performed using the electrodes in a thin layer configuration pressed against a CaF_2 prismatic window, as described previously [22,24], with sweep rate of 1 mV s^{-1} . Electrodes used in FTIR experiments were prepared in the same way as described above. Each spectrum was the average of 16 individual scans acquired with 4 cm^{-1} resolution and an acquisition time of approximately 6.7 s. This allowed a good compromise between signal-to-noise and time resolution, which led to the use of sweep rates of 1 mV s^{-1} . The absorbance was calculated by using spectra taken at the starting potential (0.05 V) as the background. All experiments were performed at room temperature ($T = 25^\circ \text{C}$).

3. Results and discussion

We begin by exploring the effects of surface oxophilicity and alkali metal cations on formation of OH_{ad} and “true oxide” on Au(1 1 1), Pt(1 1 1), and Ir(1 1 1) in 0.1 M NaOH and 0.1 M LiOH electrolytes. We chose these three surfaces because there are clear trends in oxophilicity, and thus in the onset of adsorption of OH_{ad} and its transformation to metal– O_{ad} bonds at high positive potentials [25]. Cyclic voltammetric (CV) profiles for Au(1 1 1), Pt(1 1 1) and Ir(1 1 1) in 0.1 M NaOH and 0.1 M LiOH solution are shown in Fig. 1. In line with the literature [2,15,21,23], three important voltammetric features are noteworthy in Li^+ -free electrolytes: (i) for Pt(1 1 1), the adsorption of hydrogen (H_{upd} , ca. 0.05–0.35 V) is followed first by the double layer region, then by the reversible adsorption of OH_{ad} (ca. 0.60–0.85 V), and finally by irreversible oxide formation above 0.90 V; (ii) for Ir(1 1 1), H_{upd} stripping/adsorption (0.05–0.30 V) is followed by adsorption/desorption of OH_{ad} (sharp peak centered at 0.30 V), then with a wide featureless “double layer region,” and finally by the additional adsorption of $\text{OH}_{\text{ad}}/\text{O}_{\text{ad}}$ with a peak positioned at 0.90 V; (iii) for Au(1 1 1), a wide double layer region with a small pseudocapacitance corresponding to OH_{ad} formation (ca. 1.05 V) is followed by irreversible oxide formation (ca. 1.25 V). Interestingly, the effect of Li^+ on the formation of OH_{ad} and “true oxides” is substantial (Fig. 1): the onset of OH_{ad} formation is shifted toward more negative potentials and oxide formation is inhibited. As shown in Fig. 1C, there is a clear shift in potential by the sharp peak associated with OH_{ad} formation, indicating that OH_{ad} is formed even in the H_{upd} potential region. This behavior has been recently confirmed by CO displacement experiments [21]. Assuming that the maximum charge corresponding to H_{upd} on Pt(1 1 1) is approximately $160 \mu\text{C cm}^{-2}$, as is the case in Li^+ -free electrolytes, and subtracting

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