Double layer effects in electrocatalysis: the oxygen reduction reaction and ethanol oxidation reaction on Au(111), Pt(111) and Ir(111) in alkaline media containing Na and Li cations

Pietro P. Lopes¹, Dusan Strmcnik¹, Jakub S. Jirkovsky¹, Justin G. Connell¹, Vojislav Stamenkovic¹, Nenad Markovic^{1§}

¹Materials Science Division, Argonne National Laboratory, Lemont, IL, USA

[§]corresponding author: +1-630-252-5181, nmarkovic@anl.gov

Abstract

Oxygen reduction and ethanol oxidation reactions were studied on Au(111), Pt(111) and Ir(111) in alkaline solutions containing sodium and/or lithium cations. By keeping the same (111) 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 role 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 acts as a 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 $\text{OH}_{\text{ad}}\cdots\text{Li}^+(\text{H}_2\text{O})_x$ 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.

Keywords: Electrocatalysis, surface spectators, non-covalent interactions, cation effect, oxygen reduction, ethanol

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 well as the presence of an 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 Ni/Co(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(111), Pt(111) and Ir(111) 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 $\text{OH}_{\text{ad}}\text{---AMC}^+(\text{H}_2\text{O})_x$ clusters. The kinetics of the ORR on Pt and Ir are observed to be slower in the presence of Li^+ cations, confirming that $\text{OH}_{\text{ad}}\text{---AMC}^+(\text{H}_2\text{O})_x$ 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.

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(111), Pt(111) and Ir(111), respectively, in an 3% H_2/Ar atmosphere for 10 minutes. 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 0.1M LiOH (Fluka, 99.998%) or 0.1M 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 20mM to 300mM. All gases were 5N5 quality acquired from Airgas.

Electrode potentials are given versus the reversible hydrogen electrode (RHE), calibrated using H₂ oxidation in a separate experiment. Note that the standard deviation in the onset potentials discussed in the text was around +/- 3mV 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 CaF₂ prismatic window, as described previously [22,24], with sweep rate of 1 mVs⁻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 seconds. 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°C).

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(111), Pt(111), and Ir(111) 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(111), Pt(111) and Ir(111) in 0.1M NaOH and 0.1 M LiOH solution are shown in Figure 1. In line with the literature [2,15,21,23], three important voltammetric features are noteworthy in Li⁺-free electrolytes: (i) for

Pt(111), the adsorption of hydrogen (H_{upd} , ca. 0.05-0.35V) is followed first by the double layer region, then by the reversible adsorption of OH_{ad} (ca. 0.60-0.85V), and finally by irreversible oxide formation above 0.90V; (ii) for Ir(111), H_{upd} stripping/adsorption (0.05-0.30V) is followed by adsorption/desorption of OH_{ad} (sharp peak centered at 0.30V), then with a wide featureless “double layer region,” and finally by the additional adsorption of $OH_{\text{ad}}/O_{\text{ad}}$ with a peak positioned at 0.90 V; (iii) for Au(111), 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 (Figure 1): the onset of OH_{ad} formation is shifted towards more negative potentials and oxide formation is inhibited. As shown in Figure 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(111) is approximately $160 \mu\text{C cm}^{-2}$, as is the case in Li^+ -free electrolytes, and subtracting this charge from the total charge passed in the entire H_{upd} potential region (up to 0.35 V), it is possible to extrapolate the charge corresponding to the adsorption of OH_{ad} , which is close to $\sim 135 \mu\text{C cm}^{-2}$. Certainly, further adsorption of OH_{ad} takes place at $E > 0.4 \text{ V}$, however, substantial OH_{ad} formation has already taken place in this lower potential region.

Further inspection of Figure 1 reveals that the potential difference between the formation of adsorbed hydroxyl species and the irreversible formation of oxide on all surfaces follows a clear trend. Ir(111) exhibits the formation of OH_{ad} at the lowest electrode potentials of all three metals in NaOH (Figure 1c), with formation of the irreversible O_{ad} taking place slightly above 0.75 V and completing around 0.9 V. For this surface, the $OH_{\text{ad}}-O_{\text{ad}}$ potential gap, defined as the

onset of OH_{ad} formation to the end of O_{ad} , is ca. 0.6 V. In contrast, this hydroxyl-oxide potential gap is only ca. 0.4 V on Pt(111) surfaces and is even narrower, ca. 0.25 V, on Au(111) (Figures 1b and 1a, respectively). In all cases, the presence of Li^+ increases this gap, initiating hydroxide formation at lower potentials and shifting the irreversible oxide formation to even higher electrode potentials as compared to Na^+ . These effects can be correlated to the strength of the OH_{ad} adlayer, which arises from both the oxophilicity of the surface (covalent surface interactions) and from stabilization by the $\text{OH}_{\text{ad}} \cdots \text{AMC}^+(\text{H}_2\text{O})_x$ network (non-covalent interactions). By increasing the oxophilicity of the surface ($\text{Au} < \text{Pt} < \text{Ir}$), the OH_{ad} adlayer is stabilized through a wider potential region, and by changing the nature of the cation, further stabilization of the OH_{ad} adlayer can be achieved. These trends serve to confirm the importance of non-covalent interactions in adsorption properties of metal surfaces and, as we shall see further, in activity of the ORR and EOR.

Although the details of the ORR on Au(111) and Pt(111) surfaces have been described extensively before [26], here we will briefly discuss how oxophilicity and cation effects influence the ORR in order to provide a framework for discussing how these trends impact the EOR in the results that follow. Figure 2 summarizes polarization curves for the ORR on Au(111), Pt(111) and Ir(111) (Figure 2a-c) along with a “volcano-like” trend for the ORR in both LiOH and NaOH electrolytes (Figure 2d). Briefly, the ORR on Au(111) proceeds as a 2e^- reduction pathway in the entire potential region, in contrast to what is observed on Pt(111), e.g. ORR initially occurs as a 4e^- process over a very wide potential region, showing characteristic diffusion-limited currents up to 0.4 V, but at more negative potentials the reaction pathway changes from a 4e^- process to 2e^- . This transition is directly correlated to the H_{upd} coverage, which is a known poison for breaking the O-O bond [26,27]. Interestingly, although Ir(111) is also covered with similar amount of

H_{upd} below 0.4 V, the ORR on Ir(111) always proceeds via a $4e^-$ process, indicating that there are fundamentally different reaction pathways for the ORR on Pt and Ir surfaces modified by H_{upd} . Figure 2 also shows that due to rather high coverages by OH_{ad} spectator species on Ir, the initial ORR activity is observed at higher overpotentials on Ir relative to Pt. The magnitude of the difference in activity between Au, Pt and Ir is depicted in Figure 2d, clearly showing a “volcano-like” behavior that is controlled by a combination of metal-intermediate interactions (oxophilicity), which are the weakest for gold, and surface coverage by spectator OH_{ad} (surface site availability), which increases from Au to Pt to Ir. The same type of “volcano-like” behavior is also observed in the presence of Li^+ ; however, the activities are significantly attenuated on both Pt and Ir surfaces, following the formation of $\text{OH}_{\text{ad}}\cdots\text{Li}^+(\text{H}_2\text{O})_x$ clusters that decrease the availability of free metal sites for the adsorption of O_2 and inhibit the formation of active intermediates [2]. Nevertheless, the results in Figure 2 confirm that the extent of the metal-oxygen interactions indeed play significant role in the ORR on metal surfaces, controlling both OH_{ad} and adsorption of other reaction intermediates. Unfortunately, these results also show that non-covalent effects, reflected by the extent and persistence of OH_{ad} surface coverage, strongly inhibit the ORR. The question arises if it would be possible, as in the case of the HER and CO oxidation [18–20], to catalyze the reaction if OH_{ad} can participate as a reaction intermediate, which we explore below for the case of the EOR.

In order to investigate the influence of OH_{ad} species on the kinetics of the EOR, voltammograms were collected as above using Au(111), Pt(111) and Ir(111) surfaces. Figures 3a–c show the polarization curves for the EOR on all three single crystal surfaces in both Na^+ and Li^+ electrolytes. Note that the concentration of EtOH used for Ir(111) is higher than that used for Pt(111) or Au(111), simply to observe higher oxidation currents and facilitate comparison (Figure

3d shows the small ethanol oxidation current for 20 mM EtOH on Ir. We discuss the effects leading to intrinsically smaller oxidation currents on Ir(111) below. From the results shown in Figure 3, two key points are noteworthy. First, Ir(111) shows the lowest overpotential of the three metals, with onset potential decreasing in the order $\text{Au} \gg \text{Pt} \gg \text{Ir}$ (Figure 3e). This trend can again be correlated to the oxophilicity of the surface; however, the initial current recorded for the EOR on Ir is fairly low, especially taking into account the higher EtOH concentration used in Figure 3c. Based on this observation alone, we conclude that the EOR follows desorption of H_{upd} and the formation of a relatively low surface coverage by OH_{ad} , implying that the EOR requires an ensemble of metal sites and reactive OH_{ad} . Notice that, in the case of Pt(111), the onset potential for the EOR also coincides with the “butterfly” region where the adsorption of OH_{ad} takes place and, as expected, on Au(111) the EOR starts at rather positive potentials, close to the small charge associated with the formation of OH_{ad} (Figure 1). This trend indicates the active role of OH_{ad} in the EOR, serving initially as an oxygen source, but also suggesting that metal-ethanol (adsorbed ethoxide formation, EtO_{ad}) or metal-intermediates interactions also scale with the degree of surface oxophilicity. Second, at higher overpotentials the reactivity decreases sharply, indicating that the reactive OH_{ad} transforms into a poisoning species, blocking metal sites for ethanol adsorption. While this is clearly observed at ca. 0.35 V on Ir(111), the same deactivation is seen only above 0.75 V on Pt(111) and above 1.1 V on Au(111) (Figures 1 and 3), following the same spectator effect as seen from the ORR results in Figure 2. This emphasizes the unique correlation between ensemble and electronic effects and how the same species (OH_{ad}) can have a dual role in electrocatalytic reactions.

Not surprisingly, a synergy between covalent and non-covalent effects leads to the “volcano-like” trend shown in Figure 3f, with more profound effects on the EOR than for the

ORR. Examining the impact of the nature of alkali metal cations (double layer structure) on the overall catalytic behavior reveals that Li^+ serves as a promotor for the EOR at lower potentials on Pt and Ir surfaces (Figure 3b-c). Notice also that this promoting effect strongly depends on the surface coverage by OH_{ad} – being almost undetectable for Au(111), exhibiting much stronger effect on Ir(111) and showing a particularly strong effect on Pt(111). Following the discussion of Figures 1 and 2, this cation effect again arises from the formation of $\text{OH}_{\text{ad}}\cdots\text{AMC}^+(\text{H}_2\text{O})_x$ clusters whose influence is strongly dependent on the nature of the cation. In particular, the non-covalent interaction between OH_{ad} and $\text{Li}^+(\text{H}_2\text{O})_x$ that stabilizes the hydroxyl adlayer relative to Na^+ (Figure 1) may also serve to promote the EOR, at least at low overpotentials. Providing that $\text{OH}_{\text{ad}}\cdots\text{AMC}^+(\text{H}_2\text{O})_x$ clusters are spectators at higher overpotentials, as observed for the ORR in Figure 2 as well for methanol and ethylene glycol oxidation [2,17], it is not surprising that very fast deactivation is observed on Ir and Pt in the presence of Li^+ cations. Regardless of the deactivation at higher OH_{ad} coverage, the promotion of the EOR by Li^+ at lower potentials raises an important question: does this effect originate from a higher concentration of $\text{OH}_{\text{ad}}\cdots\text{Li}^+(\text{H}_2\text{O})_x$ clusters, providing more OH_{ad} to the ethanol and its intermediates to continue the oxidation (ensemble effect), or do interactions of ethanol with these $\text{OH}_{\text{ad}}\cdots\text{Li}^+(\text{H}_2\text{O})_x$ clusters promote its adsorption and/or that of the reaction intermediates (steric effect)? The latter was proposed to be very important in the dissociation of H_2O on Pt surfaces modified by $\text{Ni}(\text{OH})_2$ [19,28].

To address this question we performed *in situ* FTIR spectroscopy in order to access information about the formation of adsorbed intermediate species during the EOR as well as the bulk end products. Here we will focus mainly on the nature of products formed during the EOR on Pt(111), and will compare these results with the two other metal surfaces when appropriate. FTIR investigations reveal that the main oxidation product on Pt(111) and Ir(111) is

acetate (Figure 4a and b, respectively), identified from the characteristic peaks shown at 1550 and 1415 cm^{-1} and the smaller “shoulder” at 1348 cm^{-1} . For clarity we do not include FTIR data for Au(111) in Figure 4, but the main product for the EOR on this surface is also acetate, in accordance to the literature [15]. Interestingly, Ir(111) clearly shows another small peak centered at ca. 1950 cm^{-1} , with a measured Stark slope (electric field induced shift in the vibration frequency) greater than 130 cm^{-1}/V . Such high Stark slope is consistent with adsorbed CO at low coverages that is formed with increasing electrode potential [29], a clear indication that Ir(111) promotes the oxidation of ethanol by C-C bond breaking. Although clear identification of carbonate or acetaldehyde was not possible on Pt and Au due either to band overlapping or homogenous chemical reactions that remove acetaldehyde from the solution [10,14,30], the results for Pt(111) and Au(111) are consistent with the literature; namely, on Pt there is evidence supporting a small amount of carbonate production while on Au this is far less pronounced. These results indicate that metal-ethanol (M-EtO_{ad}) and metal-intermediate interactions are stronger on more oxophilic surfaces, demonstrating that not only surface coverage by OH_{ad} (ensemble effect) is important for the EOR, but that electronic effects also play a decisive role in determining selectivity for the reaction. These results can also help to understand selectivity and activity differences observed in other surface orientations, especially for polycrystalline and nanoparticles samples, as the increased amount of defect sites will have higher oxophilicity degree and therefore, might affect how both OH_{ad} and ethanol adsorption or its intermediates interact at the surface. That could also be related to alloys or the presence of metal oxides in the same lines as discussed.

After establishing the importance of ensemble and electronic effects on the EOR, we turn our attention to the effect of the alkali metal cation on reaction promotion. We shall again focus

our discussion to the results obtained for Pt(111), as they follow the same trends as for Ir(111) (Figure 4b). As shown in Figure 4, the product distribution is independent of the nature of the cation and production of acetate begins at slightly lower overpotentials in Li^+ as compared to Na^+ . The same selectivity trend is observed in chronoamperometry results summarized in Figures 4e-g; showing acetate as the major product for both LiOH and NaOH solutions. We note that any meaningful quantitative effort to correlate the band intensities to the current density of chronoamperometric experiments is beyond the scope of the present discussion. Nonetheless, this observation is consistent with the voltammetry results discussed earlier in Figure 3b. Taken together, these data suggest that the presence of $\text{OH}_{\text{ad}}\cdots\text{Li}^+(\text{H}_2\text{O})_x$ facilitates a steric effect that either directs the ethanol molecule to the surface and/or promotes one of its initial dehydrogenation steps by stabilizing the EtO_{ad} intermediate. This effect would be similar to the stabilization of the OH_{ad} adlayer by the formation of the $\text{OH}_{\text{ad}}\cdots\text{Li}^+(\text{H}_2\text{O})_x$ clusters (Figure 1), but instead, interacting with the EtO_{ad} adlayer by creating a $\text{OH}_{\text{ad}}\cdots\text{Li}^+(\text{H}_2\text{O})_x\cdots\text{EtO}_{\text{ad}}$ network. Moreover, as suggested for the role of hydrated alkali cations in the water dissociation step for the HER on $\text{Ni}(\text{OH})_2$ modified Pt [19], these $\text{AMC}^+(\text{H}_2\text{O})_x$ clusters could promote EtO-H bond breaking as well, indicating that the surface formation of EtO_{ad} is more important than the bulk formation of ethoxide and its consequent adsorption on the surface. Therefore we emphasize that the role of non-covalent interactions and the structure of the double-layer is key in altering activity and these effects are dependent on the nature of the reactant and intermediate species involved in the reaction.

Conclusions

In this study we investigated the functional links between OH_{ad} present on a variety of metal surfaces with varying degree of oxophilicity, and the reactivity these surfaces for important electrochemical reactions such as the ORR and EOR in the presence of different alkali metal cations. By correlating the surface adsorption properties of Au(111), Pt(111) and Ir(111) with the activities for the ORR and EOR, we were able to identify that OH_{ad} plays several roles that are different for each reaction: it is purely a surface spectator for the ORR, and acts both as a promoter and spectator for the EOR. We also observe that oxophilicity trends are responsible for promoting the EOR at lower overpotentials via a combination of ensemble effects (e.g. formation of OH_{ad} at lower potentials) and electronic effects (e.g. alcohol adsorption, EtO_{ad} and other intermediates). In particular, we found that activity for the EOR is further enhanced at lower electrode potentials in LiOH vs. NaOH electrolytes, while still showing the same surface blockage effect due to $\text{OH}_{\text{ad}} \cdots \text{AMC}^+(\text{H}_2\text{O})_x$ clusters at higher overpotential. Spectroscopic data suggest that promotion of the EOR in the presence of Li^+ is related to the stabilization of EtO_{ad} induced by the formation of $\text{OH}_{\text{ad}} \cdots \text{Li}^+(\text{H}_2\text{O})_x$ clusters at lower potentials, without any change in reaction pathways or product distribution. These results highlight the importance of controlling the entire electrochemical interface when designing more active, selective and stable catalysts.

Acknowledgments

This work is supported by the Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences, under contract DE-AC0206CH11357.

References

- [1] N.M. Markovic, Electrocatalysis: Interfacing electrochemistry, *Nat Mater.* 12 (2013) 101–102.
- [2] D. Strmcnik, K. Kodama, D. van der Vliet, J. Greeley, V.R. Stamenkovic, N.M. Marković, et al., The role of non-covalent interactions in electrocatalytic fuel-cell reactions on platinum, *Nat. Chem.* 1 (2009) 466–472.
- [3] D. Strmcnik, D.F. van der Vliet, K.-C. Chang, V. Komanicky, K. Kodama, H. You, et al., Effects of Li⁺, K⁺, and Ba²⁺ Cations on the ORR at Model and High Surface Area Pt and Au Surfaces in Alkaline Solutions, *J. Phys. Chem. Lett.* 2 (2011) 2733–2736.
- [4] K. Müller-Dethlefs, P. Hobza, Noncovalent interactions: a challenge for experiment and theory., *Chem. Rev.* 100 (2000) 143–68.
- [5] C. Wang, G. Wang, D. van der Vliet, K.-C. Chang, N.M. Markovic, V.R. Stamenkovic, Monodisperse Pt₃Co nanoparticles as electrocatalyst: the effects of particle size and pretreatment on electrocatalytic reduction of oxygen, *Phys. Chem. Chem. Phys.* 12 (2010) 6933–6939.
- [6] V. Stamenkovic, B.S. Mun, K.J.J. Mayrhofer, P.N. Ross, N.M. Markovic, J. Rossmeisl, et al., Changing the Activity of Electrocatalysts for Oxygen Reduction by Tuning the Surface Electronic Structure, *Angew. Chemie Int. Ed.* 45 (2006) 2897–2901. .
- [7] V.R. Stamenkovic, B.S. Mun, M. Arenz, K.J.J. Mayrhofer, C. a Lucas, G. Wang, et al., Trends in electrocatalysis on extended and nanoscale Pt-bimetallic alloy surfaces., *Nat. Mater.* 6 (2007) 241–247.

- [8] V.R. Stamenkovic, B. Fowler, B.S. Mun, G. Wang, P.N. Ross, C. a Lucas, et al., Improved oxygen reduction activity on Pt₃Ni(111) via increased surface site availability., *Science*. 315 (2007) 493–497.
- [9] N.M. Marković, T.J. Schmidt, V. Stamenković, P.N. Ross, N.M. Markovic, T.J. Schmidt, et al., Oxygen Reduction Reaction on Pt and Pt Bimetallic Surfaces: A Selective Review, *Fuel Cells*. 1 (2001) 105–116.
- [10] S.C.S. Lai, M.T.M. Koper, Ethanol electro-oxidation on platinum in alkaline media., *Phys. Chem. Chem. Phys.* 11 (2009) 10446–10456.
- [11] S.C.S. Lai, M.T.M. Koper, The Influence of Surface Structure on Selectivity in the Ethanol Electro-oxidation Reaction on Platinum, *J. Phys. Chem. Lett.* 1 (2010) 1122–1125.
- [12] S.C.S. Lai, S.E.F. Kleyn, V. Rosca, M.T.M. Koper, Mechanism of the Dissociation and Electrooxidation of Ethanol and Acetaldehyde on Platinum As Studied by SERS, *J. Phys. Chem. C*. 112 (2008) 19080–19087.
- [13] C. Lamy, E.M. Belgsir, J.-M. Léger, Electrocatalytic oxidation of aliphatic alcohols: Application to the direct alcohol fuel cell (DAFC), *J. Appl. Electrochem.* 31 (2001) 799–809.
- [14] C. Busõ-Rogero, E. Herrero, J.M. Feliu, Ethanol oxidation on Pt single-crystal electrodes: Surface-structure effects in alkaline medium, *ChemPhysChem*. 15 (2014) 2019–2028.

- [15] S. Beyhan, K. Uosaki, J.M. Feliu, E. Herrero, Electrochemical and in situ FTIR studies of ethanol adsorption and oxidation on gold single crystal electrodes in alkaline media, *J. Electroanal. Chem.* 707 (2013) 89–94.
- [16] Y. Kwon, S.C.S. Lai, P. Rodriguez, M.T.M. Koper, Electrocatalytic Oxidation of Alcohols on Gold in Alkaline Media: Base or Gold Catalysis?, *J. Am. Chem. Soc.* 133 (2011) 6914–6917.
- [17] E. Sitta, B.C. Batista, H. Varela, The impact of the alkali cation on the mechanism of the electro-oxidation of ethylene glycol on Pt., *Chem. Commun.* 47 (2011) 3775–3777.
- [18] C. Stoffelsma, P. Rodriguez, G. Garcia, N. Garcia-Araez, D. Strmcnik, N.M. Marković, et al., Promotion of the oxidation of carbon monoxide at stepped platinum single-crystal electrodes in alkaline media by lithium and beryllium cations., *J. Am. Chem. Soc.* 132 (2010) 16127–16133.
- [19] R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C.C. Chang, M. Uchimura, A.P. Paulikas, et al., Enhancing hydrogen evolution activity in water splitting by tailoring Li^+ -Ni(OH)-Pt interfaces., *Science*. 334 (2011) 1256–60.
- [20] R. Subbaraman, D. Tripkovic, K.-C. Chang, D. Strmcnik, A.P. Paulikas, P. Hirunsit, et al., Trends in activity for the water electrolyser reactions on 3d M(Ni,Co,Fe,Mn) hydr(oxy)oxide catalysts., *Nat. Mater.* 11 (2012) 550–7.

- [21] D. Strmcnik, M. Uchimura, C. Wang, R. Subbaraman, N. Danilovic, D. van der Vliet, et al., Improving the hydrogen oxidation reaction rate by promotion of hydroxyl adsorption, *Nat Chem.* 5 (2013) 300–306.
- [22] D.S. Strmcnik, D. V Tripkovic, D. van der Vliet, K.-C. Chang, V. Komanicky, H. You, et al., Unique Activity of Platinum Adislands in the CO Electrooxidation Reaction, *J. Am. Chem. Soc.* 130 (2008) 15332–15339.
- [23] R. Subbaraman, N. Danilovic, P.P. Lopes, D. Tripkovic, D. Strmcnik, V.R. Stamenkovic, et al., Origin of Anomalous Activities for Electrocatalysts in Alkaline Electrolytes, *J. Phys. Chem. C.* 116 (2012) 22231–22237.
- [24] T. Iwasita, E. Pastor, A dems and FTir spectroscopic investigation of adsorbed ethanol on polycrystalline platinum, *Electrochim. Acta.* 39 (1994) 531–537.
- [25] G. Karlberg, Adsorption trends for water, hydroxyl, oxygen, and hydrogen on transition-metal and platinum-skin surfaces, *Phys. Rev. B.* 74 (2006) 153414.
- [26] T.J. Schmidt, V. Stamenkovic, M. Arenz, N.M. Markovic, P.N. Ross, P.N. Ross Jr., Oxygen electrocatalysis in alkaline electrolyte: Pt(hkl), Au(hkl) and the effect of Pd-modification, *Electrochim. Acta.* 47 (2002) 3765–3776.
- [27] N.M. Marković, P.N. Ross Jr., Surface science studies of model fuel cell electrocatalysts, *Surf. Sci. Rep.* 45 (2002) 117–229.
- [28] N. Danilovic, R. Subbaraman, D. Strmcnik, K.-C. Chang, A.P. Paulikas, V.R. Stamenkovic, et al., Enhancing the Alkaline Hydrogen Evolution Reaction Activity

- through the Bifunctionality of Ni(OH)₂/Metal Catalysts, *Angew. Chemie Int. Ed.* 51 (2012) 12495–12498.
- [29] X. Jiang, S. Changj, M.J. Weaver, In Situ Infrared Spectroscopy of Carbon Monoxide Adsorbed at Iridium(111)-Aqueous Interfaces: Double-Layer Effects on the Adlayer Structure, *J. Phys. Chem.* 95 (1991) 7453–7459.
- [30] A. Santasalo-Aarnio, Y. Kwon, E. Ahlberg, K. Kontturi, T. Kallio, M.T.M. Koper, Comparison of methanol, ethanol and iso-propanol oxidation on Pt and Pd electrodes in alkaline media studied by HPLC, *Electrochem. Commun.* 13 (2011) 466–469.

Figure Captions

Figure 1 –Cyclic voltammetry profile of (a) Au(111) , (b) Pt(111) and (c) Ir(111) in alkaline solutions containing 0.1 M LiOH or NaOH showing differences in OH_{ad} and O_{ad} formation related to surface oxophilicity and non-covalent interactions that further stabilizes OH_{ad} adlayer in the presence of Li⁺.

Figure 2 –Polarization curves for ORR on (a) Au(111), (b) Pt(111) and (c) Ir(111) in alkaline solutions containing 0.1 M LiOH or NaOH, and (d) “volcano-like” curve depicting oxophilicity trends in controlling ORR activity and selectivity. The standard deviation of the potentials shown in (d) was around +/- 3 mV. Note that non-covalent interactions between alkali metal cations at the interface further blocks the active sites required for the ORR on both Pt and Ir surfaces, increasing the reaction overpotential.

Figure 3 –Polarization curves for ethanol oxidation in alkaline solutions on (a) Au(111), b) Pt(111) and (c) Ir(111). The ethanol concentration was 20mM for Au and Pt, and 300 mM for Ir. (d) Polarization curve for ethanol oxidation on Ir(111) at a concentration of 20mM, showing the dramatically lower oxidation current at this concentration relative to the other surfaces. Oxophilicity trends for onset potential (e) and current density at high OH_{ad} coverages (f) during the EORshow the importance of metal-ethanol, metal-OH_{ad} and non-covalent interactions in

determining activity of ethanol oxidation. Here onset potential was defined as the potential at 0.4 mAcm^{-2} (standard deviation around $\pm 3 \text{ mV}$), and current density on (f) was defined as the value at the peak potential observed in NaOH solutions (with relative standard deviation of 5%), specifically to highlight the surface blockage effect caused by cation effect at high OH_{ad} coverages.

Figure 4 - *In situ* FTIR results of the EOR on (a)Pt(111) and (b)Ir(111) in both 0.1 M NaOH and 0.1M LiOH. (c, d) IR-voltammetry on Pt(111) in 0.1 M NaOH and 0.1M LiOH, respectively. (e) Electrochemical and (f, g) FTIR chronoamperometry results ($E = 0.60 \text{ V}$) in 0.1 M LiOH or 0.1 M NaOH electrolytes.

Figure 1

Figure 2

Figure 3

Figure 4