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Elucidation of the Oxygen Reduction Volcano in Alkaline Media using a Copper-Platinum(111) Alloy


Abstract: Herein, we experimentally explore the relationship between the binding of the reaction intermediates and oxygen reduction activity in alkaline media. By introducing Cu into the 2nd surface layer of a Pt(111) single crystal, we tune the surface reactivity. We demonstrate that in both 0.1 M NaOH and 0.1 M KOH, the optimal catalyst should exhibit OH binding ~0.1 eV weaker than Pt(111), via a Sabatier volcano; this observation suggests that the reaction is mediated via the surface bound intermediates as in acid, in contrast to previous reports. In 0.1 M KOH, the alloy catalyst at the peak of the volcano exhibits a maximum activity of 101±8 mA/cm² at 0.9 V vs. a reversible hydrogen electrode (RHE). This activity constitutes a ~60-fold increase over Pt(111) in 0.1 M HClO₄.

Oxygen reduction is ubiquitous. It limits the efficiency of low temperature fuel cells and metal-air batteries for renewable energy conversion.[11,12] A huge body of research has been devoted towards elucidating the factors controlling this all-important reaction[2,3,7–9], most studies focus on acidic media, where only Pt-based catalysts are able to provide the stability and activity required for technological applications.[8] A theoretical model was developed to show that a Sabatier volcano relationship exists between the binding of *OH (where * denotes an adsorbed species) and the catalytic activity[10,11]; the most optimal metal catalyst should bind *OH, 0.1 eV weaker than Pt(111). This volcano exists because the reaction proceeds via a series of proton-coupled electron transfers to the surface-bound reaction intermediates, *OH, *O and *OH; the binding energies of all these intermediates scale linearly together.[8] In an earlier work, we experimentally verified that the oxygen reduction volcano holds in 0.1 M HClO₄, by modifying a Pt(111) single crystal with subsurface Cu to form a Cu/Pt(111) near-surface alloy[12] (see Fig. 1a). By lieu of the ligand effect,[11,12] we systematically tuned OH-adsorption, which we monitored through the position of the voltammetric peak for this process. The experimental relationship between the voltammetric shift for *OH adsorption and oxygen reduction activity extends to Pt-based single-crystalline surfaces reported by others,[13] including stepped single crystals[14,15] and PtNi(111)[16]. Knowledge of the volcano has provided catalyst developers with the key design principle for the reaction. It has led to the huge decrease in the amount of Pt required in commercial fuel cells today.[18–20]

The scope of oxygen reduction reaction (ORR) research is increasingly extending beyond acidic media[21–25] augmented by advances in hydroxide conducting polymer membranes.[26] At high pH, a much wider range of materials are stable, including Ag,[21] and Fe-based[27] electrodes. Shao-Horn and coworkers have elucidated the factors controlling oxygen reduction on oxide surfaces in basic electrolytes.[29,30] Nonetheless, there is little consensus regarding the factors that control oxygen reduction on metal surfaces in alkaline media. For example, one recent study[31] suggested that oxygen reduction proceeds via an *OOH surface intermediate, similar to acid. However, other reports suggest that the trends in activity in alkaline media are different from those in acid. Bulk polycrystalline and nanoparticulate Pt, for example, was a factor of ~2 less active in 0.1 M KOH than in 0.1 M HClO₄[32]. In 0.1 M HClO₄, stepped surfaces exhibited improved activity over Pt(111)[33]; in 0.1 NaOH they are less active than Pt(111).[23] Conversely, PtNi(111), exhibits a ~130-fold enhancement in 0.1 M KOH over Pt(111) in 0.1 M HClO₄.[17,24] Au(100), which is relatively inactive in 0.1 M HClO₄,[34] exhibits an activity equal to Pt(111) in 0.1 M KOH.[24] Several authors have proposed that in base, oxygen reduction proceeds via a proton-decoupled electron transfer step involving the superoxide anion species, O₂*; rather than *OOH.[21,23,32] meaning a Sabatier volcano would not be applicable.

Aside from pH, non-covalent interactions induced by the electrolyte cation[26,27] also govern *O and *OH formation on single crystal surfaces. Such phenomena seem to play a strong role on catalytic activity, both for oxygen reduction and other electrochemical reactions.[25,39,40] However, on Pt(111), when changing the cation, there is no clear trend between the positions of the peaks for OH-adsorption and the oxygen reduction activity[30]; this observation suggests that the cation changes the oxygen reduction activity by means that go beyond simply adjusting the binding of the reaction intermediates.

The seemingly discordant observations described above provide the motivation for our current work. In particular, we aim to determine whether the catalytic activity follows a Sabatier volcano in alkaline media. Moreover, we compare the role of changing the electrolyte[41] with changing the binding of surface intermediates.

In brief, we prepared the Cu/Pt(111) near-surface alloys using our previously developed methodology, as follows:[32] a Pt(111) single crystal was annealed and positioned in the headspace above the electrolyte in a custom electrochemical cell (see Fig. S1 and S2). Up to a monolayer (ML) of Cu was electrodeposited on the crystal and inductively annealed in the headspace in N₂/Ar (95/5 %), driving the Cu subsurface. Using angle resolved X-ray photoelectron spectroscopy (AR-XPS), we verified that the desired near-surface alloy structure[33] had formed and that it was stable in alkaline solution — within the range of experimental error.
— as shown in Fig. 1 (see SI for details). The AR-XPS derived Cu:Pt ratios of Fig. 1b are in line with earlier reports.[10,43] They indicate that when more than 0.5 ML Cu is initially deposited, some Cu may be lost into the Pt(111) bulk.

Following the formation of the near-surface alloy, the sample was mounted into the arbor of a rotating ring-disk electrode assembly and transferred to a three-electrode cell containing 0.1 M HClO4 to perform base voltammetry. Subsequently the electrodes were transferred to another cell, containing 0.1 M KOH (pH=12.8±0.3).

Electrodes were transferred to another cell, containing 0.1 M KOH saturated 0.1 M KOH following exposure to 35° with standard deviation error compared to the surface structure. Utilized, O1s and C1s contributions are not shown). Inset: schematic illustration of a model ~0.77 ML Cu in the 2nd atom layer. Open point represents a sample following exposure to electrochemical tests in KOH.

We used CVs in N2-saturated KOH to probe the interaction of the surface with the electrolyte, as shown in Fig. 2. We focus on the peak(s) positive of 0.6 V, which is associated with *OH or *O adsorption.[44] For the purpose of brevity, we will assume it is due to *OH; this assumption will not significantly affect our analysis. Clearly, increased amounts of Cu in the subsurface destabilize *OH or *O; this phenomenon is manifested as the positive shift in the peak associated with *OH or *O adsorption, at potentials positive of 0.6 V. In Fig. 3a and 4 we quantify this destabilization by comparing the shift in potential required to form 1/6 ML OH (equivalent to 40 µC/cm2) relative to Pt(111) given by $\Delta U_{\text{OH}} = \Delta E_{\text{OH/ML}} = \Delta E_{\text{H2O/ML}} - \Delta E_{\text{H2O/ML}}$ (see Fig. 2 and S7).

On Fig. 3a, we have co-plotted (i) the average experimental shift, $\Delta U_{\text{0.1M KOH}}$ in 0.1 M KOH and 0.1 M HClO4 as a function of the amount of Cu initially deposited (ii) the theoretical shift, $\Delta E_{\text{OH}}$ as a function of Cu in the 2nd surface layer, from our earlier publication.[10] All three curves are in qualitative agreement; however, as we noted in our previous work,[10] the theoretical destabilization is more pronounced than the experimental value, particularly at $\theta_{\text{Cu}}>0.5$ ML; this divergence is consistent with the XPS analysis in Fig. 1b, which indicated that high coverages of Cu cannot be sustained in the 2nd surface layer of Pt(111).

The shift in 0.1 M HClO4 is up to 0.02 V more pronounced than in 0.1 M KOH, possibly due to the different local environments of *OH and *O induced by each electrolyte.

Following the base CV measurements in N2, we saturated the electrolyte with O2 and rotated the electrode at 1600 rpm, 23 °C and 50 mV/s) in order to probe the kinetics of oxygen reduction. We compare the activities at 0.9 V vs. RHE. As shown in Fig. 3b and S14, the oxygen reduction activity is improved in the presence of subsurface Cu. We found up to a ~10-fold improvement over Pt(111) in KOH, with a maximum at the initial coverage of ~0.77 ML Cu.
Fig. 4 shows the activity enhancement as a function of the voltammetric shift in the OH-adsorption peak in various alkaline electrolytes. Despite a small shift in the peak position, the trend in alkaline is remarkably similar to 0.1 M HClO as seen in Fig. S12c and S13.

Keywords: oxygen reduction · Sabatier principle · surface chemistry · electrocatalysis · platinum · single crystal
Alloying Cu into the subsurface of Pt(111) tunes the oxygen reduction activity in basic electrolytes. Just the same as in acid, the key descriptor controlling the reaction is the binding to the intermediates.