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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 reaction. 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.[11–13] A huge body of research has been devoted towards elucidating the factors controlling this all-important reaction,[14–27] most studies focus on acidic media, where only Pt-based catalysts are able to provide the stability and activity required for technological applications.[28] 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,[19] 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, *OOH, *O and *OH; the binding energies of all these intermediates scale linearly together. 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[20] (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[14,16] and PtNi(111)[17]. Knowledge of the volcano has provided catalyst developers with the key design principle for the reaction. It has led to the huge decreases 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 hydride conducting polymeric membranes.[26] At high pH, a much wider range of materials are stable, including Ag,[27] and Fe-based[28,29] 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 nanoscopic Pt 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[29,35–38] 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.[27,39,40] 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[25]; 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:[20] 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 Ar/H₂(5 %), driving the Cu subsurface. Using angle resolved X-ray photoelectron spectroscopy (AR-XPS), we verified that the desired near-surface alloy structure[10] 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 HClO\(_4\) to perform base voltammetry. Subsequently the electrodes were transferred to another cell, containing 0.1 M KOH (pH=12.8±0.3).

We used CVs in N\(_2\)-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 \(*\text{OH}^+\) or \(*\text{O}^+\) adsorption.\(^{[44]}\) For the purpose of brevity, here we will assume it is due to \(*\text{OH}^+\); this assumption will not significantly affect our analysis. Clearly, increased amounts of Cu in the subsurface destabilize \(*\text{OH}^+\) or \(*\text{O}^+\); this phenomenon is manifested as the positive shift in the peak associated with \(*\text{OH}^+\) or \(*\text{O}^+\) 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/cm\(^2\)) as a function of Cu in the 2\(^{nd}\) layer.

**Figure 1.** AR-XPS data. (a) Profile of a Cu/Pt(111) near-surface alloy with ~0.77 ML Cu in the 2\(^{nd}\) atom layer (Pt4f, Cu2p, O1s and C1s peaks were utilized. O1s and C1s contributions are not shown). Inset: schematic illustration of the surface structure. (b) Averaged Cu:Pt ratios derived at angles from 20 to 35° with standard deviation error compared to a model wherein all Cu is assumed to resides in the 2\(^{nd}\) atom layer. Open point represents a sample following exposure to electrochemical tests in KOH.

**Figure 2.** Base CVs of Pt(111) and Cu/Pt(111) near-surface alloys (N\(_2\)-saturated 0.1 M KOH at 400 rpm, 23 °C and 50 mV/s) with varying initial Cu coverages, \(\theta_{Cu}\). Filled areas represent the charge required to form 1/6 ML \(*\text{OH}^+\).

**Figure 3.** Cu/Pt(111) data as function of initial Cu coverage. (a) Potential shift in OH-adsorption (for 1/6 \(*\text{OH}^+\) ML) in 0.1 M HClO\(_4\) and KOH co-plotted with DFT model\(^{[10]}\) of the shift in OH binding energy compared to Pt(111) as function of Cu in the 2\(^{nd}\) atom layer (blue axis and plot); (b) Activity enhancement relative to Pt(111) in 0.1 M KOH. Lines have been inserted as guides for the eyes. Each experimental data point is based on two to four independent measurements; the error bar shows the standard deviation.

The shift in 0.1 M HClO\(_4\) is up to 0.02 V more pronounced than in 0.1 M KOH, possibly due to the different local environments of \(*\text{OH}^+\) and \(*\text{O}^+\) induced by each electrolyte.

Following the base CV measurements in N\(_2\), we saturated the electrolyte with O\(_2\) and rotated the electrode at 1600 rpm, 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.
Au(100) is equal to ~0.3 V, which approximates the DFT calculations. The shift between the peak for OH-adsorption on Pt(111) and Au(100) is equal to ~0.6 V (see SI for details), explaining the exceedingly low activity of Au(100) in acid.[23,24] Consequently, our analysis of the experimental data suggests that it may not be necessary to invoke the superoxide mechanism to describe the activity of Au(100) in base.[23,24] We offer a simpler explanation: in alkaline media, ORR proceeds via the same adsorbed intermediates as for Pt in acid, in particular *OH and *OH; the high activity of Au(100) in base is due to the favorable binding to these surface adsorbates, as described by the Sabatier volcano (see Fig. 4). Our observations suggest that the more pertinent question — beyond the scope of the current work — is why is *OH on Au(100) excessively destabilized in acid?

In conclusion, we have demonstrated that in alkaline media, it is possible to tune the activity of Pt(111) surfaces with subsurface Cu, consistent with a ligand effect. Pt(111) is ~4-fold more active in 0.1 M KOH than 0.1 M HClO4, the activity in 0.1 M NaOH is intermediate between the two. Capitalizing on the synergy between the electrode and electrolyte, we tailored the surface to achieve ORR activities of up to 1012 s m2 cm2 at 0.9 V vs. RHE.

Through voltammetric analysis of our data and those of others, we confirm experimentally, for the first time, that a Sabatier volcano exists for oxygen reduction on metal surfaces in alkaline media. We thus provide the key design principle for the reaction in base. The two significant outliers in our current understanding of oxygen reduction in acid[24] and stepped Pt surfaces in base.[23] We conclude that further studies are needed to understand the role of cations[41,44] and pH[27] at the electrochemical interface.

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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.