Supplemental Information for:
Origin of anomalous activities for electrocatalysts in alkaline electrolytes
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I. ICPMS results for various alkaline electrolytes

We analyzed the concentration of various transition metals such as Fe, Co, Cu, Ni, Cr using Inductively Coupled Plasma Mass Spectroscopy (ICPMS). We have summarized the results here, listing the ranges for various transition metals in different electrolytes. In light of the variations with different batches of chemicals as well as the grades of chemicals, we have only listed the ranges in which these chemicals were detected in an aqueous solution of these chemicals.

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
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<tbody>
<tr>
<td>Commercial KOH samples</td>
<td>160±60</td>
<td>10±5</td>
<td>15±7</td>
<td>7±3</td>
<td>10±4</td>
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Table 1: All ion contents are shown in (µg/l) units. The variations were obtained over 4 different suppliers and at least 2 batches of the electrolyte. Only the ranges of the values are given to avoid ambiguities due to differing batches of the same chemicals from various suppliers.

II. Cleanliness of ultra-high purity electrolytes

High purity electrolytes, such as Fluka TraceSelect and Merck Suprapur sodium hydroxide were also used for this study. The main purpose was to determine if it is possible to obtain a control or baseline for the alkaline experiments. We once again used Pt(111), given its high sensitivity, to see if the lower level of impurities (specifications for metal cations <0.01 ppm), can avoid contamination of the electrode with time/cycling. We once again used our non-glass based alkaline cells to avoid any possible interaction of alkaline electrolytes with glass components. The results with cycling, both with and without rotation, as well as higher
concentration are shown in figure S1. Under quiescent conditions, i.e., absence of gas bubbling and rotation, the electrodes are minimally contaminated after 50 cycles. With added convection, or higher concentration of the electrolytes, the degree of contamination is comparable to those observed with the commercial quality KOH. Therefore, it is clear that it is very difficult to truly establish a “control” system to create baseline activities. In order to avoid this difficulty, we have used the first sweeps as our standards and as shown in the next section, this appears to be valid.

Figure S1: Impact of cycling Pt(111) electrode in high purity NaOH electrolytes at room temperature. In the absence of any convection (quiescent) conditions, 50 sweeps shows very “low” levels of contamination of the surface. In the presence of rotation (and/or strong gas bubbling), and higher concentration of the electrolyte, the degree of contamination is comparable with the commercial quality KOH electrolytes. All CVs were conducted at 50 mV/s.

III. The use of first scans for “control” for the alkaline measurements

In the manuscript, we emphasize the validity of the first scan for the measurements (either for voltammetry, or for the polarization curves to measure activities for the ORR and HOR). In order to demonstrate that this indeed is a valid approach, we compared the first scan obtained for
freshly prepared Pt(111) electrodes (annealed, see experimental section), and performed the CV, ORR and HOR experiments. As can be clearly seen, the values for the activities obtained for the HOR, HER and the ORR are well within experimental variations across all these electrolytes. This validates our approach of using the first scan as the baseline for our measurements. This also provides an added benefit of better understanding the role of long term contamination effects on observed activities etc… Figure S2 shows the comparison between the first scans for various electrolytes for both the HOR/HER and the ORR for Pt(111) surface.

IV. CO oxidation induced cleaning of Pt(111) surfaces

Cycling under CO saturated conditions was found to clean the surface of the Pt(111) electrode. The STM for before and after CO cycling was shown in figure 1 in the manuscript. In order to confirm that the effect of CO is the removal of the Co hydr(oxy)oxides and not due to any other processes such as growth/migration of these Co clusters, we compare the CVs both before and after CO cycling in figure S3. As shown clearly in Fig S3, the features corresponding to the hydr(oxy)oxides, the OH peaks at 0.7V and the suppression of the H\textsubscript{upd} disappear on cycling in CO saturated solutions. It is important to note that, the electrode is never completely “clean” in alkaline electrolytes due to the presence of residual impurities. The use of CO oxidation reaction was simply to demonstrate the nature of the impurity

**Figure S2:** Comparing the first scans for the HOR/HER and ORR for Pt(111) electrode in different electrolytes of different purities. The values obtained are nearly identical validating our approach of using the first scan as the control for our experiments. All experiments were conducted at 50 mV/s.
species and how this provides insights into the behavior of Pt-3d metal alloy nanoparticles in alkaline electrolyte, especially related to the CO annealing of the Pt-alloy nanoparticles with relative segregation of the Pt atoms to the surface.

**Figure S3:** CVs for the as-prepared electrode, Co modified electrode and the CO cycled electrode. As can be clearly seen, on cycling in CO the hydr(oxy)oxide clusters are removed from the surface, indicative of cleaning of the surface by CO oxidation reaction. All experiments were conducted at 50 mV/s.