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# Influence of phosphate anion adsorption on the kinetics of oxygen reduction on low index Pt(hkl) single crystals

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**In-situ X-ray absorption spectroscopy.** *In situ* X-ray absorption spectroscopic data were collected on a Pt/C (30%, E-TEK) sample as a function of electrode potentials (+0.01 V, +0.24 V, +0.54 V, +0.84 V, and +1.04 V) in 0.1 M $HClO_4$ and 0.1 M $HClO_4$ + 100 mM phosphoric acid. All data were processed with standard procedures using the IFEFFIT suite (v.1.2.9) [1]. Briefly, the reference foils corresponding to each scan were calibrated to the standard Pt $L_3$ edge energy and then carefully aligned to a selected standard at +0.54 V. The energy shifts were then automatically applied to all the respective sample scans. Difference spectra were obtained to isolate the effect of adsorbate by using the following equation,

$$\Delta\mu(x,y) = \mu(y \text{ V, 0.1 M } HClO_4 + x \text{ M } H_3PO_4) - \mu(+0.54 \text{ V, 0.1 M } HClO_4) \quad (1)$$

where μ is the X-ray absorption coefficient at the electrode potential of *y* V and at $H_3PO_4$ concentration of *x* M. In a series of previous studies using the XANES-based $\Delta\mu$ technique [2-4], Pt catalyst surfaces were found to be the 'cleanest' and relatively free of any adsorbates at around

+0.5 V in acid media; therefore the data at +0.54 V in 0.1 M $HClO_4$ were used as the reference to generate the difference spectra in the present study.

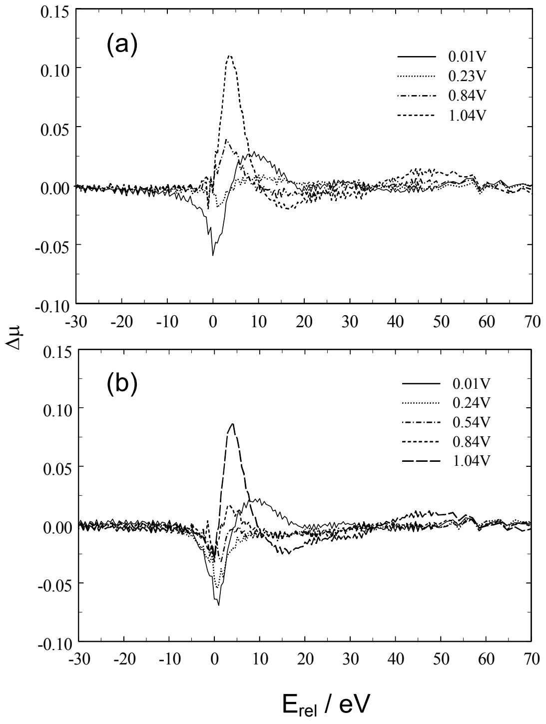

**Figure S1**. Pt $L_3$ edge $\Delta\mu$ spectra for Pt/C in (a) 0.1 M $HClO_4$ and (b) 0.1 M $HClO_4$ + 100 mM $H_3PO_4$ ($\Delta\mu = \mu(y \text{ V}, x \text{ M } H_3PO_4) - \mu(+0.54 \text{ V}, 0 \text{ M } H_3PO_4)$)

Figure S1 shows the $\Delta\mu$ curves for the Pt/C (E-TEK) catalyst samples in (a) 0.1 M $HClO_4$ and (b) 0.1 M $HClO_4$ + 100 mM $H_3PO_4$. The signatures correspond very well to H/Pt adsorbed in 3-fold sites [3], and the magnitude of the H/Pt signature decreased with increasing electrode potential. Note that the absorption spectrum at +0.54 V in 0.1 M $HClO_4$ was used as the reference spectrum in the calculation of $\Delta\mu$. In 0.1 M $HClO_4$ + 100 mM $H_3PO_4$, the $\Delta\mu$ curve at +0.54 V exhibits a small negative feature at ca. 0 eV followed by a small, broad positive feature of roughly the same magnitude at ca. 5 eV. Considering that oxygen did not bond to the Pt surface at such low potentials and that the magnitude of the positive feature was much smaller than for a strongly bonded 3-fold O/Pt, it is likely that this is due to the more weakly bonded $H_2PO_4^-$/Pt with the

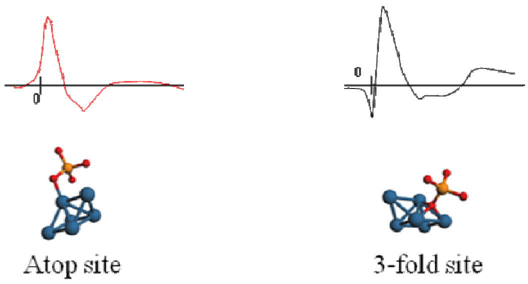

**Figure S2.** Theoretical simulations of $\Delta\mu$ signatures of $H_2PO_4^-$ adsorption on Pt by FEFF 8.0

oxygen occupying the 3-fold hollow sites on the Pt surface. This is very similar to the line shape found previously for 3-fold Cl/Pt [5]. As the potential was increased to +0.84 V and +1.04 V, the line shape approaches the theoretical 3-fold mode depicted in Figure S2, along with a negative peak close to 0 eV.

## Additional Electrochemical Data

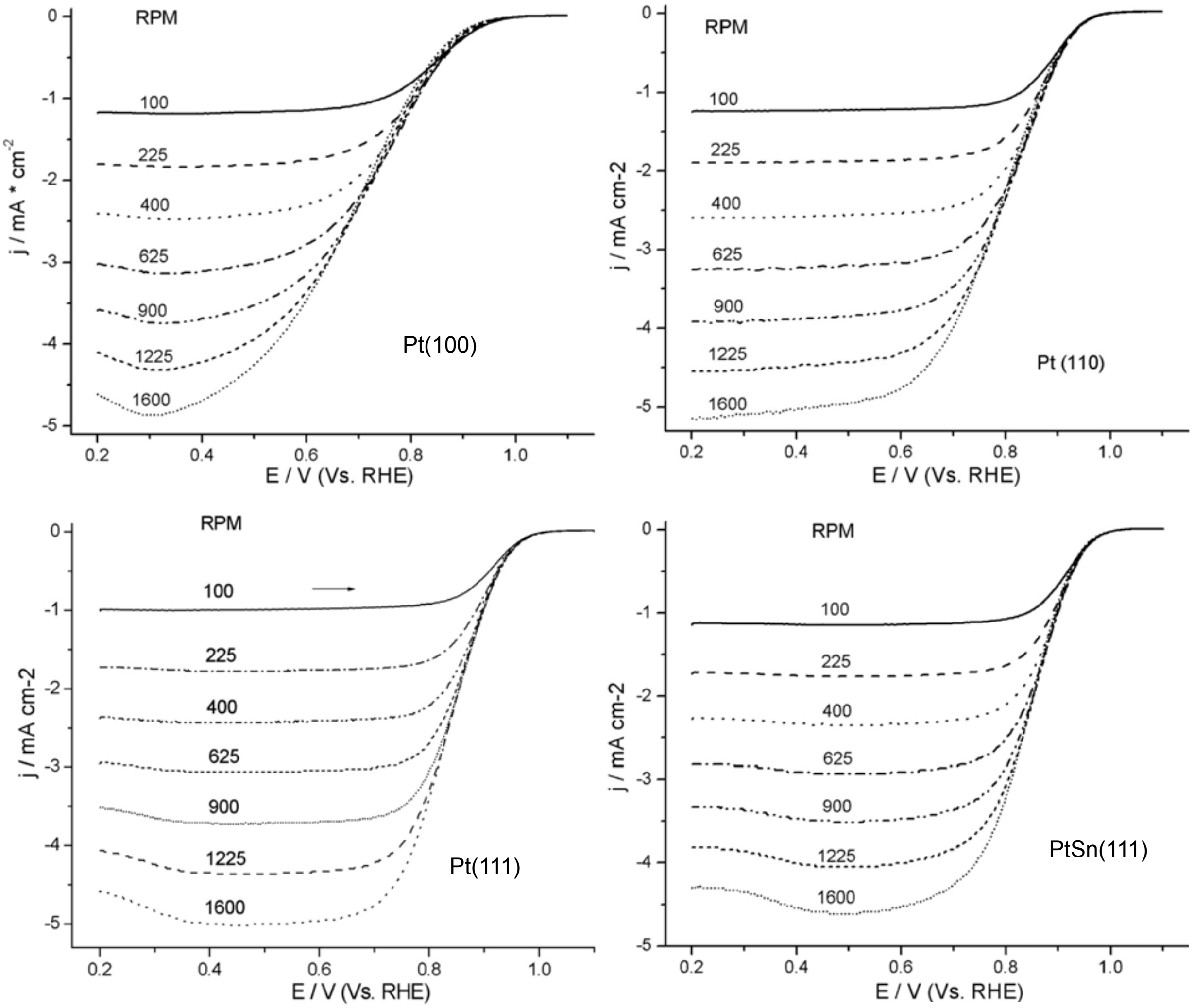

**Figure S3**. RDE voltammograms for the Pt(100), Pt(110, Pt(111), and PtSn(111) electrode in $O_2$ saturated 0.1 M $HClO_4$ at varied rotation rates. The current density was calculated by normalizing the voltammetric current to the geometrical area of the electrode. DC ramp 20 mV/s.

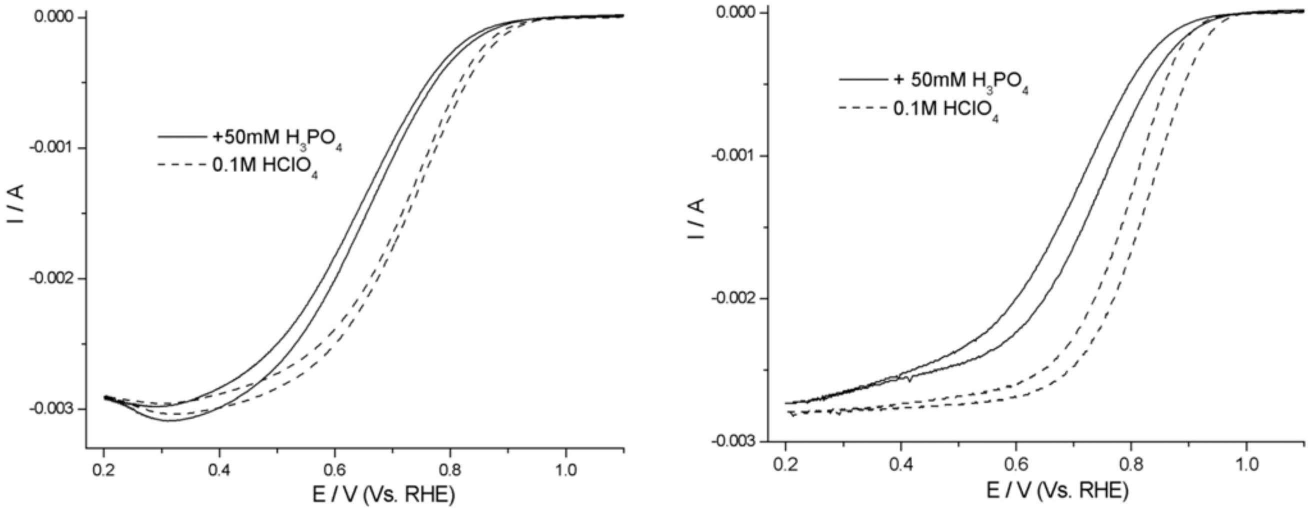

**Figure 4S.** RDE voltammograms of ORR at (left) Pt(100) and (right) Pt(110) electrodes in oxygen-saturated 0.1 M HClO4 and 0.1M $HClO_4$ + 50mM $H_3PO_4$. Rotation rate 900 RPM. DC potential ramp 20 mV/s.

## References

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