

## Supporting Information

**The Role of Phosphate Functionalization on the Oxygen Evolution Reaction Activity of Cobalt-Based Oxides at Different pH Values**

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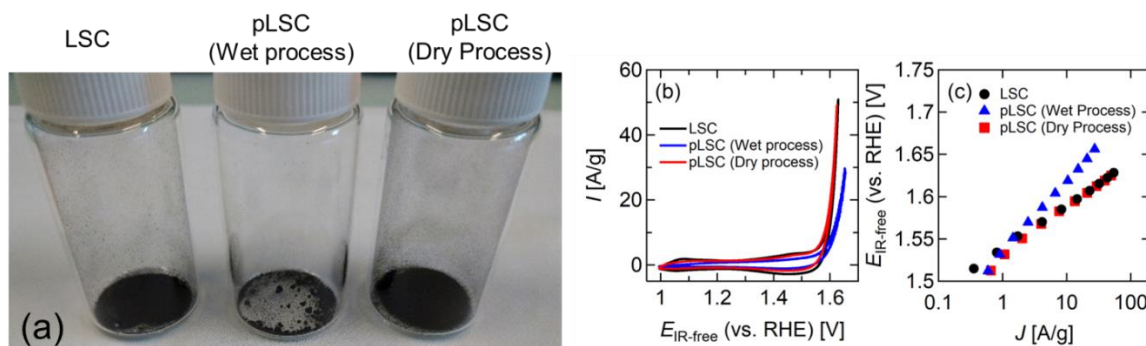
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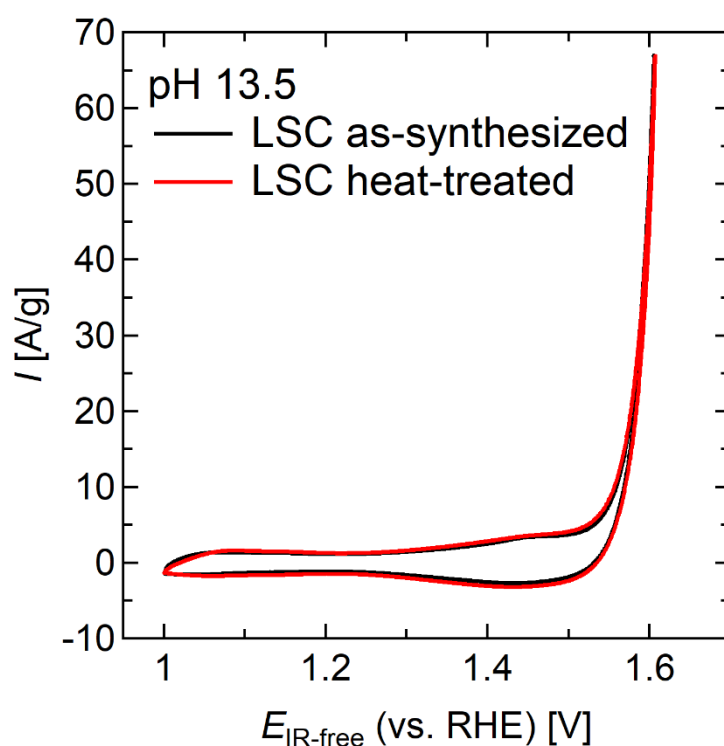
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**S1 and S2. Effect of different phosphate treatment routes and heat treatment without P sources on OER activities**



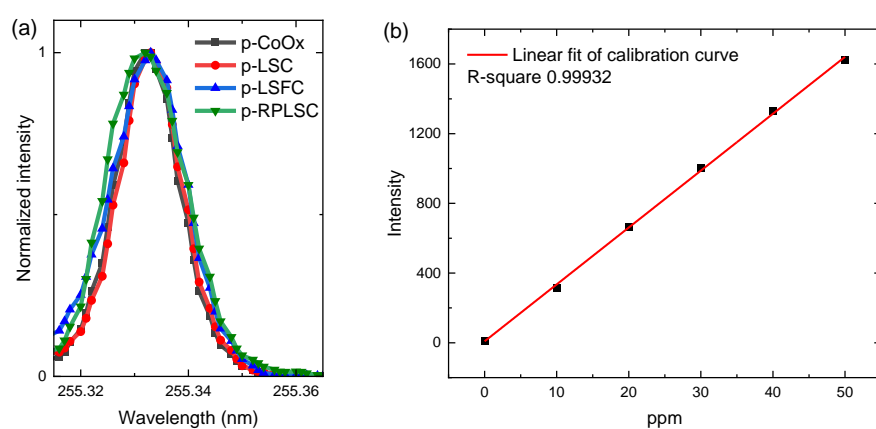
**Figure S1.** (a) Photograph of as-synthesized  $\text{La}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$  (LSC) and wet/dry phosphate-treated LSC (pLSC). (b) Cyclic voltammograms (25<sup>th</sup> cycles at  $10 \text{ mV s}^{-1}$ ) and (c) Tafel plots of LSC and pLSC in synthetic air-saturated 0.1 M KOH at 900 rpm.



**Figure S2.** The cyclic voltammograms (25<sup>th</sup> cycle at  $10 \text{ mV s}^{-1}$ ) at pH 13.5 of LSC as-synthesized and heat-treated ( $300^\circ\text{C}$  for 1 h in  $\text{N}_2$  flow) catalysts without P sources in a synthetic air-saturated electrolyte at the rotation speed of 900 rpm.

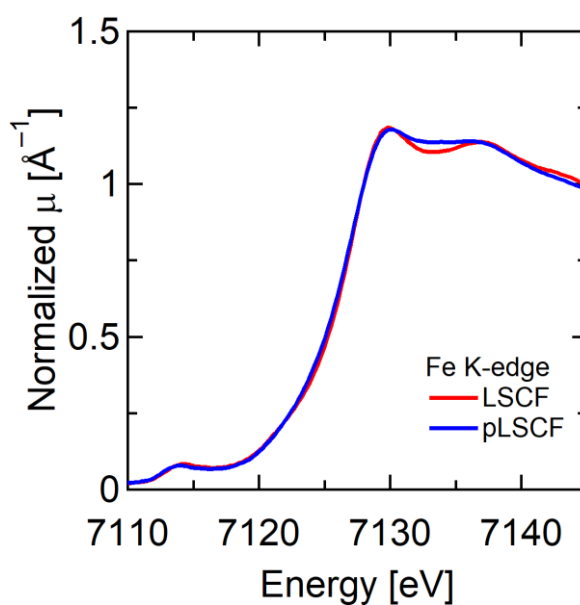
### S3. Inductively coupled plasma optical emission spectrometer (ICP-OES) measurements of the P incorporated in the catalyst surface

Elemental analysis for P was carried out using ICP-OES to quantify the amount of P in the treated samples. The measurements were performed to probe the wavelength of 255 nm for P (Figure S3a). The trace element was determined using a calibration curve with six points of P standard solutions, diluted with 2% sub-boiled  $\text{HNO}_3$ . Regression coefficient for the calibration curve were better than 0.999.



**Figure S3.** (a) Phosphorus bands collected for the phosphate-treated catalyst samples. (b) Calibration curve of P standard solutions.

#### S4. Fe K-edge X-ray absorption near-edge spectroscopy (XANES) Profiles

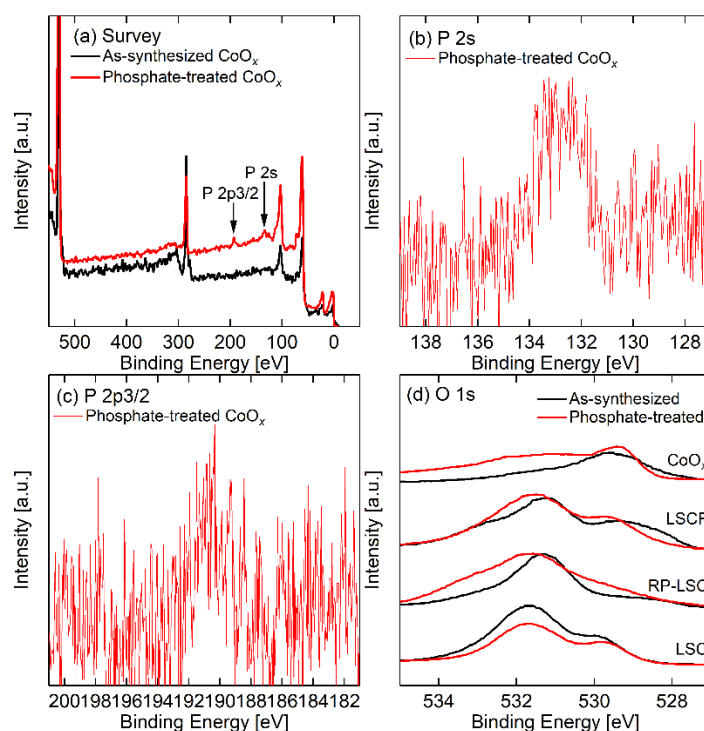


**Figure S4.** Fe K-edge XANES profiles:  $\text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$  (LSCF) and pLSCF.

#### S5. X-ray Photoelectron Spectroscopy (XPS) Profiles

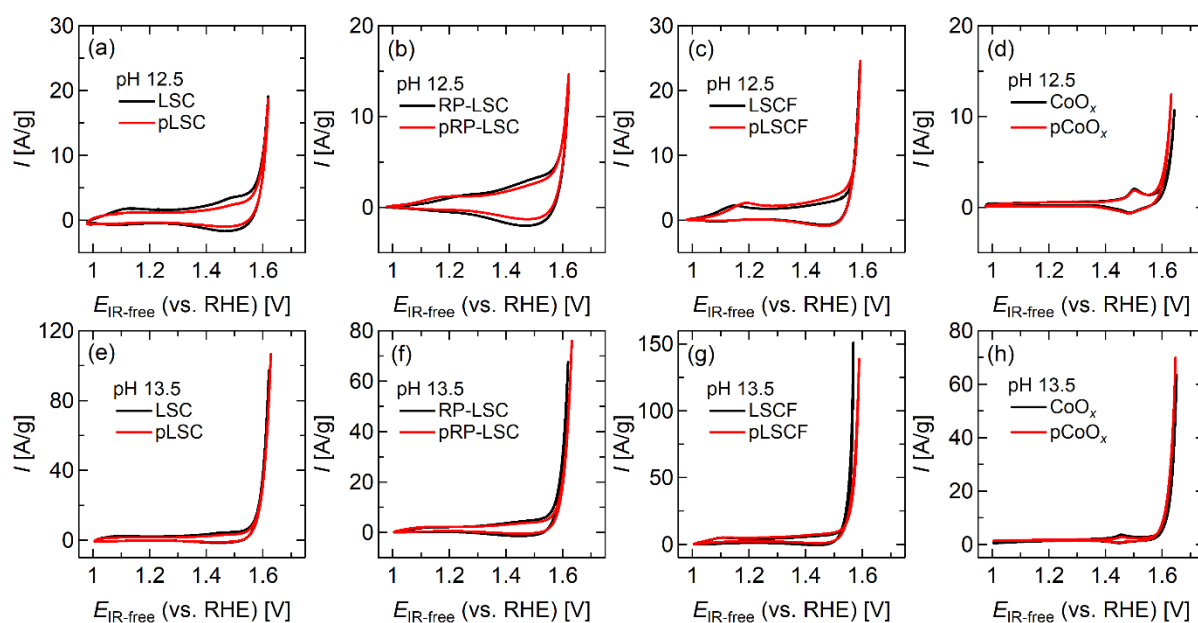
Figure S5a shows the survey XPS profiles for  $\text{CoO}_x$  and  $\text{pCoO}_x$ . In the profile of  $\text{pCoO}_x$ , small peaks attributed to P 2s and P 2p<sub>3/2</sub> peaks appeared in the profile (see also Fig S5b and c). It should be noted that Sr 3d and La 4p<sub>3/2</sub> peaks overlapped these P-peaks in the system of LSC, LSCF, and RP-LSC.

Figure S5d shows the O 1s XPS profiles. The peak at  $\sim 529$  eV can be assigned to lattice oxygen ( $O^{2-}$ ) in the oxide structure (Ref. 17a of the manuscript). The second peak at a binding energy of 531 eV corresponds to adsorbed oxygen species ( $O^{2-}$ ,  $O^-$ ,  $-OH$ ,  $O_2$ ) (Ref. 9b of the manuscript). However, compared to the identified lattice oxygen peak, attributing the broad O 1s peak at higher binding energy is difficult due to the numerous possible contamination species. For the perovskite samples, the O 1s peak at higher binding energy is at  $\sim 531.5$  eV, which could match with the O 1s binding energy of  $SrCO_3$  at  $\sim 531.5$  eV,  $Sr(OH)_2$  at  $\sim 530.5$  eV,  $SrO_2$  at  $\sim 531.1$  eV or other contaminants with C–O bonds at  $\sim 532.2$  eV and C=O bonds at  $\sim 533.7$  eV (Ref. 17a of the manuscript). For the oxygen species of  $H_2PO_4^-$  and  $PO_3^-$  ions, the peak O 1s peaks are centered at 531.6 and 532.6 eV, respectively (Ref. 18a of the manuscript).

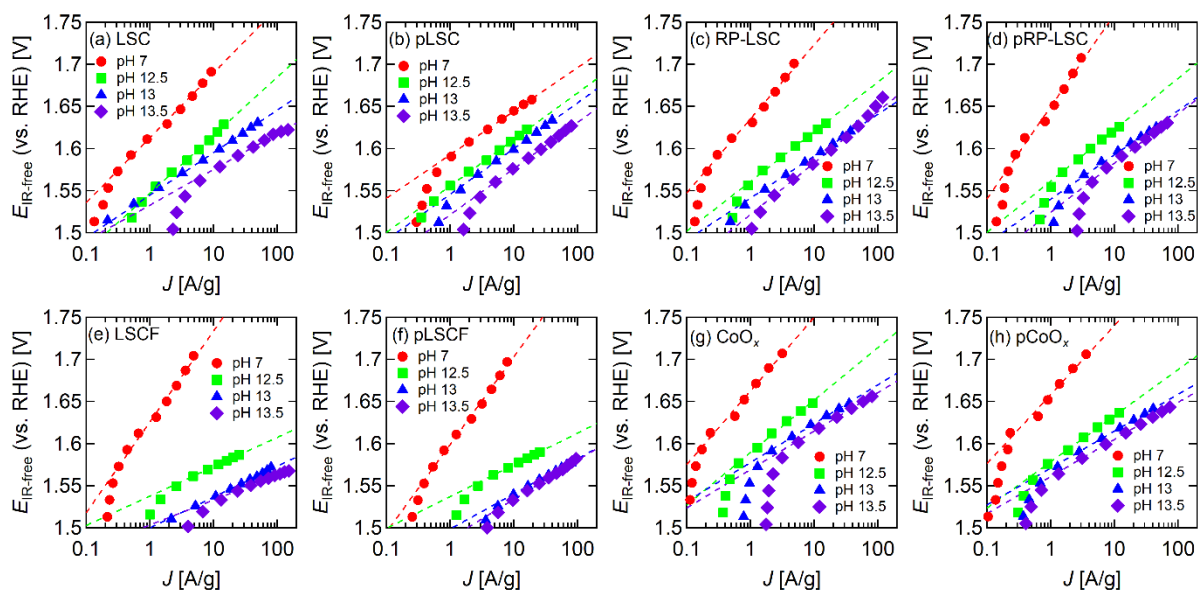


**Figure S5.** (a) Survey XPS profiles for  $CoO_x$  and  $pCoO_x$ , and (b) P 2s (c) P 2p3/2 (d) O 1s XPS core levels for all the investigated samples.

## S6 and S7. Summary of Electrochemical Study



**Figure S6.** Cyclic voltammograms (25<sup>th</sup> cycles at 10 mVs<sup>-1</sup>) for each catalyst at (a-d) pH 12.5 and (e-h) pH 13.5.



**Figure S7.** Tafel plots constructed from a series of chronoamperometry measurements at different pHs for each catalyst.