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Supplementary Information for:

Mechanochemical synthesis of cobalt/copper fluorophosphate generates a multifunctional electrocatalyst

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Experimental details

Synthesis

$Cu_{1.8}Co_{0.2}PO_4F$ was synthesized by mechanical ball-milling. Stoichiometric amounts of copper phosphate ($Cu_3(PO_4)_2$ prepared from CuO and $(NH_4)_2HPO_4$), copper fluoride (CuF_2, Alfa Aesar, 99.5%), and cobalt fluoride (CoF_2, Alfa Aesar, 99.99%), were carefully weighed inside an Ar glove box. The total weight (400 mg) was transferred into a zirconia (ZrO_2) mill (Fritsch) filled with zirconia balls (diameter: 2 mm, balls weight: ~2 g). The mixture was then ball-milled into a Fritsch Pulverisette 7 planetary Micro Mill at 500 rpm for 18h (36 cycles consisting in 25 min milling and 5 min break). The same synthesis procedure was used for the preparation of cobalt-free Cu_2PO_4F.

Characterization methods

X-Ray powder diffraction (XRPD): X-ray diffraction patterns were collected in the range $10° \leq 2\theta \leq 135°$ on a PANalytical X'Pert3 Powder diffractometer (monochromatized Cu $K\alpha$=1.5406 Å). Le Bail refinements were performed by using the Fullprof profile refinement program.[1, 2]

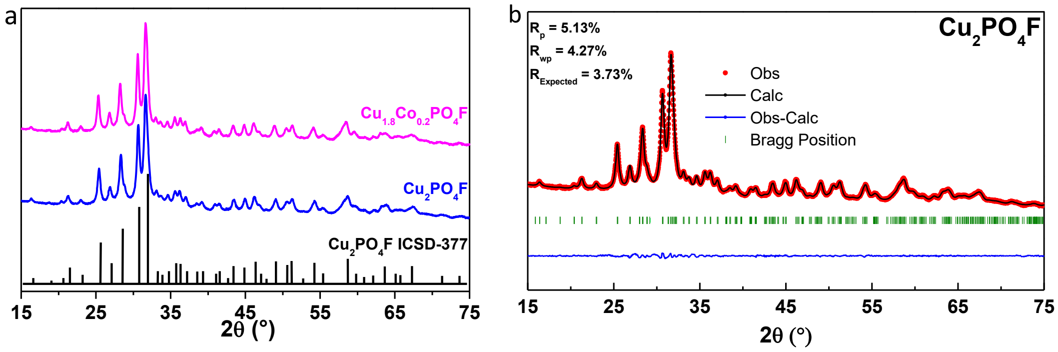

Figure S1: (a) X-ray diffraction patterns of $Cu_{1.8}Co_{0.2}PO_4F$ Cu_2PO_4F and (b) Le Bail refinement of Cu_2PO_4F.

Table S1: Cell parameters obtained from the Le Bail refinements.

$Cu_{1.8}M_{0.2}PO_4F$	a (Å)	b (Å)	c (Å)	β (°)	V ($Å^3$)
M = Cu	12.7847(1)	6.1878(1)	9.9809(1)	119.211(1)	689.17(1)
M = Co	12.8363(1)	6.2040(1)	9.9643(1)	119.241(1)	692.41(1)

Scanning Electronic Microscopy (SEM): SEM images of the powders were obtained using a JEOL microscope (JSM 6510LV) at an acceleration voltage of 20 kV. Elementary quantitative microanalyses were performed using an Energy Dispersive Spectrometry (EDS) OXFORD detector (AZtec software). The microscope belongs to the "Electron Microscopy" technical platform of IMMM (Le Mans University).

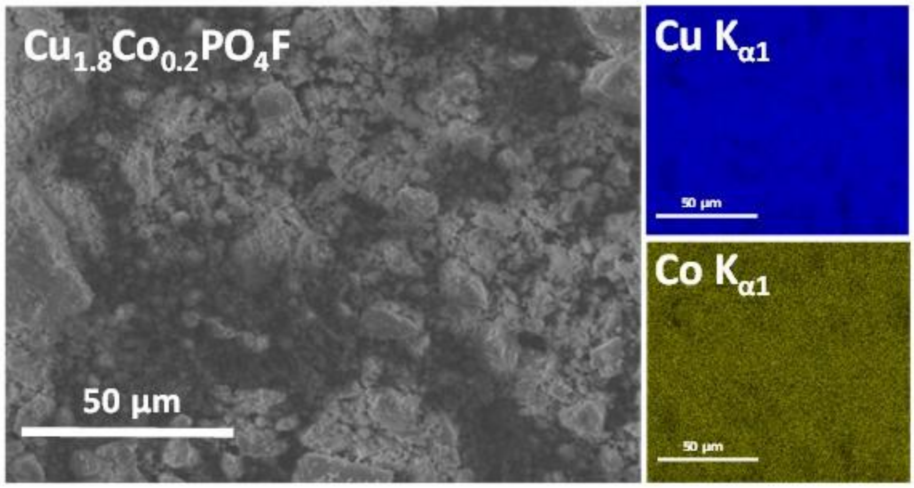

Figure S2: EDS-SEM elemental mapping images of $Cu_{1.8}Co_{0.2}PO_4F$.

Electrochemical measurements:

To make functional electrode from $Cu_{1.8}Co_{0.2}PO_4F$, $Cu_{1.8}Co_{0.2}PO_4F$ powders (1 mg/mL) were mixed with 1% wt. relative to the catalyst carbon nanotubes (40 nm diameter, Sigma Aldrich) in a 1:1 (v:v) ethanol:water mixture. The mixture was sonicated for 20 minutes, then drop cast onto Toray carbon paper, then dried under ambient conditions. The final loading of the $Cu_{1.8}Co_{0.2}PO_4F$ was approximately 3 mg/cm^2. Cu_2PO_4F electrodes were prepared in an identical fashion. To generate an Ir electrode for comparison, a 0.5% Ir on activated carbon powder was commercially purchased (Alfa Aesar) and dispersed in ethanol. This was loaded on the carbon paper electrode in the same manner as the $Cu_{1.8}Co_{0.2}PO_4F$.

In all electrochemical measurements, 1.0M KOH was used as the electrolyte. A graphite rod was used as a counter electrode and a Ag/AgCl reference was employed, due institutional restrictions on the use of Hg/HgO electrodes. However, the Ag/AgCl reference was periodically checked vs. a master reference electrode to exclude the possibility of potential drifts. A biologic VMP 150 was the potentiostat used with EC-Lab software employed to record data. All electrochemical measurements were corrected for ohmic drop losses at 85% through the EC-lab software, through measuring the impedance at open circuit at 1KHz.

HMF oxidation was also carried out in 1.0M KOH. The same electrochemical setup was employed. Products were quantified with NMR, using D_2O with acetate as an internal standard.

XPS Characterization:

XPS measurements were performed using a VG Escalab 220i-XL system in the Institute National de la Recherche Scientifique Centre Énergie Matériaux et communications. For this, Mg was used as a X-ray source. The data were calibrated to the C 1s peak at 284.6 eV to set the x-axis (binding energy).

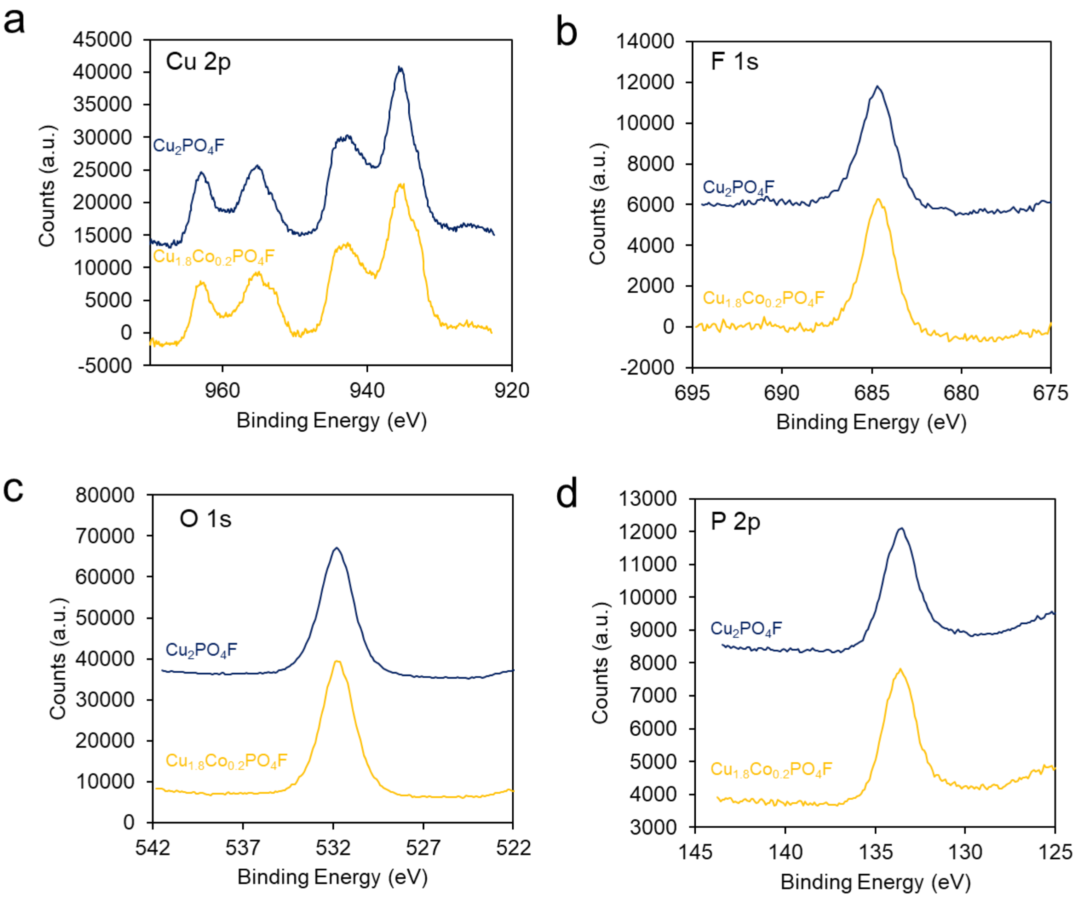

Figure S3: XPS spectra of the Cu 2p (a), F 1s (b), O 1s (c) and P 2p (d) peaks of the $Cu_{1.8}Co_{0.2}PO_4F$ and Cu_2PO_4F samples show largely similar peak positions indicating a similarity in the electronic structure of the constituent elements. The only exception is Cu, which features an additional shoulder on the high energy side of the peaks for $Cu_{1.8}Co_{0.2}PO_4F$ which may indicate that a portion of the Cu atoms have a slightly more electron-poor configuration in this material relative to Cu_2PO_4F.

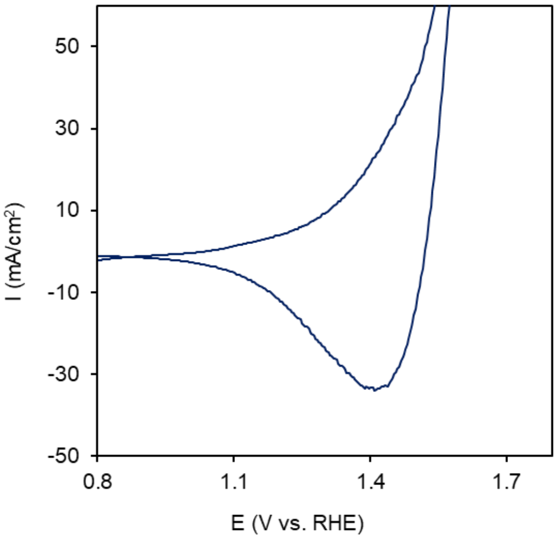

Figure S4: CV of $Cu_{1.8}Co_{0.2}PO_4F$ in 1.0M KOH, zoomed in to illustrate the Co redox peak. The asymmetry of the peak is typical for many Co-oxide based OER catalysts as the kinetics of the oxidation and reduction of the Co material are not equal. Typically this peak is attributed to the Co(II)/Co(III) redox couple and involves not only electron transfer but also counter ion adsorption/desorption.

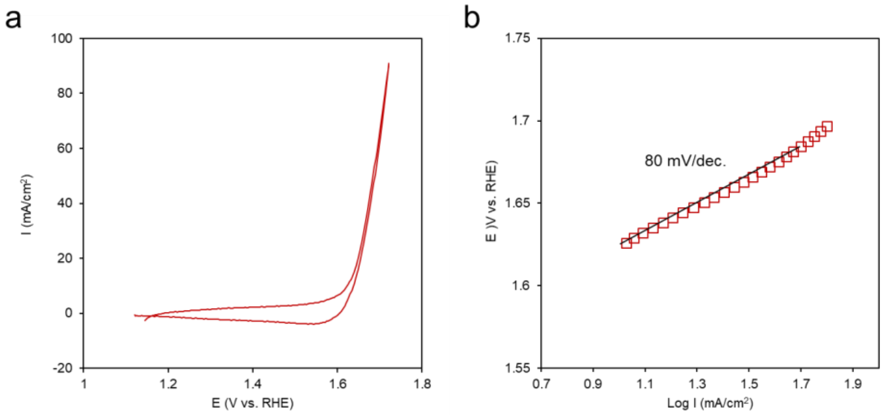

Figure S5: CV of Cu_2PO_4F in 1M KOH electrolyte (a) in the same conditions as Fig. 3 in the main text and the corresponding tafel slope (b).

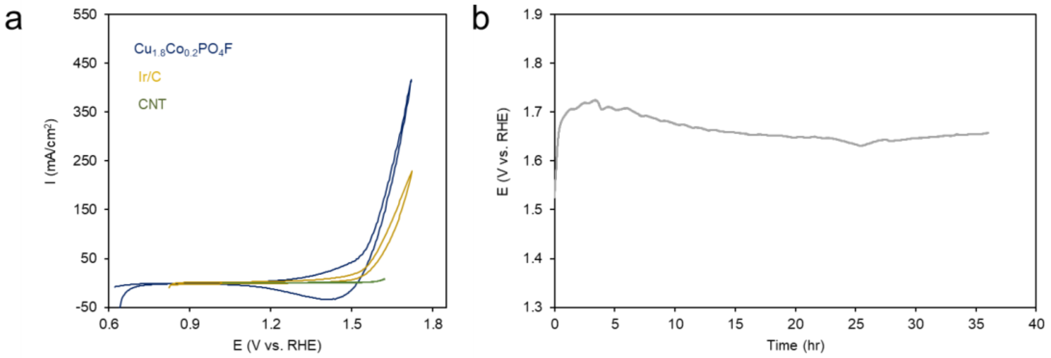

Figure S6: CVs of Cu_2PO_4F in 1M KOH electrolyte alongside of a commercially purchased Ir/C catalyst and a catalyst-free CNT film deposited onto the carbon paper electrode (a), and a chronopotentiometric scan of the Ir/C catalyst at 10mA/cm^2 (b).

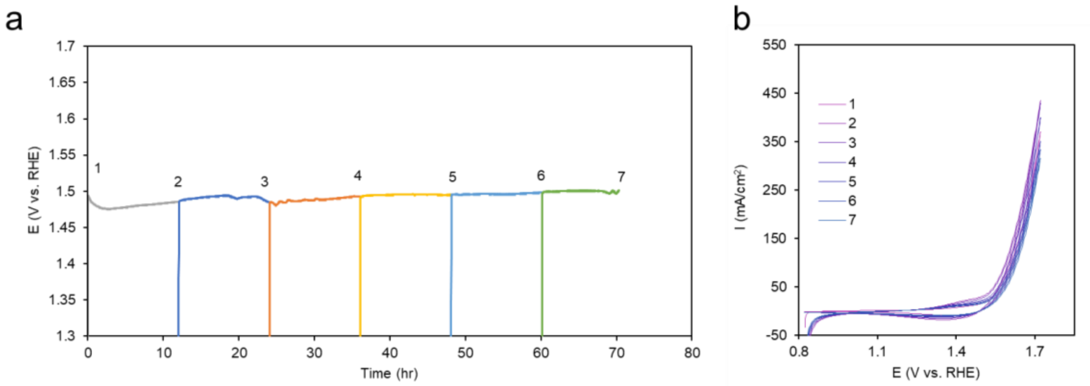

Figure S7: Chronopoteniometric scan of Cu_2PO_4F in 1M KOH electrolyte at 10 mA/cm^2 (a), with CVs taken intermittently (b).

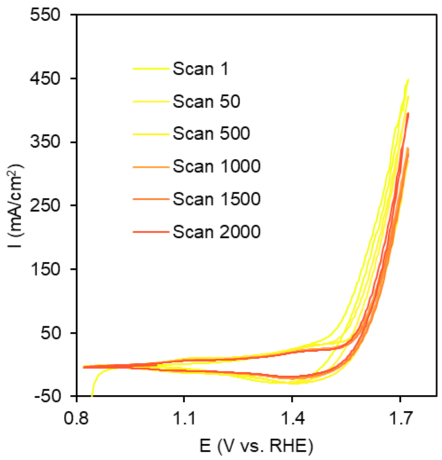

Figure S8: Stability test conducted by running successive CVs

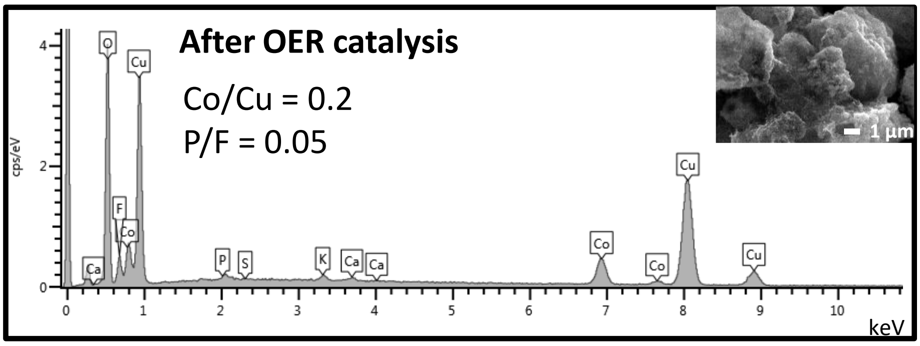

Figure S9: EDX-SEM of $Cu_{1.8}Co_{0.2}PO_4F$ after OER electrocatalysis

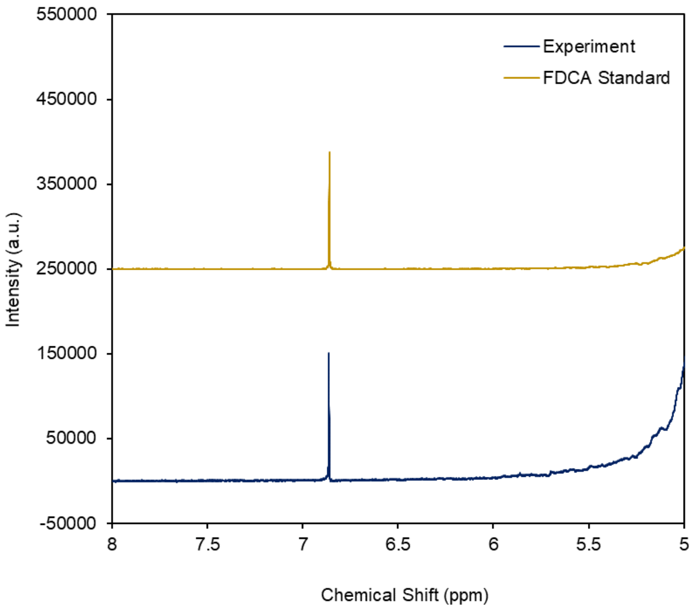

Figure S10: NMR spectra of a FDCA standard (top, yellow) and of the reaction solution following electrolysis from Fig. 4 in the main text (bottom, blue).

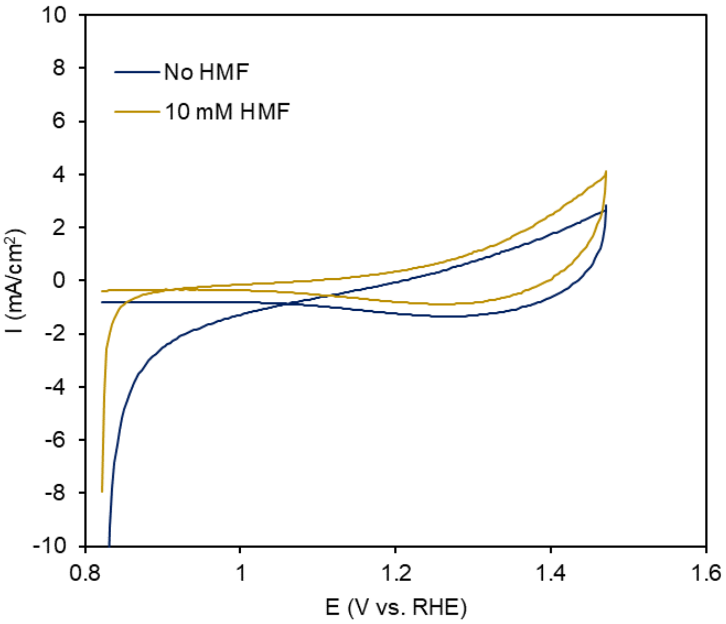

Figure S11: CV of Cu_2PO_4F in 1.0M KOH with and without HMF added to the electrolyte solution.

References:

1. A. Le Bail, H. Duroy and J. L. Fourquet, *Mater. Res. Bull.*, 1988, **23**, 447-452.
2. A. Le Bail, *Powder Diffr.*, 2005, **20**, 316-326.