Supporting Information

Improved OER performance of an Anderson-supported Cobalt Coordination Polymer by Assembling with Acetylene Black

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1. Experimental Section

All the reagents and solvents used were purchased of the highest grade available from commercial sources and were used without any extra purification.

1.1. Synthesis of $[Co(2\text{-}pzc)(H_2O)_2\}_2\{H_7AlMo_6O_{24}\}].10(H_2O).2.5(CH_3OH)$ (PS-13):

Initially, two different aqueous solutions were prepared. The experimental conditions were optimized to enable homogeneity of the solution before and after mixing. Solution A was prepared by adding $Na_2MoO_4 \cdot 2H_2O$ (2.35 mmol, Merck, 99%) to the solution of $AlCl_3$ (anhydrous) (1.57 mmol, CDH, 99%) in 15 mL of water; this was further acidified by 5 mL of glacial acetic acid. Solution B was prepared by mixing 2-pyrazine carboxylic acid (2.52 mmol, Merck, 99%) to the solution of $CoCl_2 \cdot 6H_2O$ (1.68 mmol, Merck, 99%) in 10 mL of water and 10 mL of methanol. The solution A was then added to the solution B with stirring. The resulting solution was filtered and clear orange colored solution was left for crystallization at room temperature. The orange block crystals were obtained after 1 week approximately in about 75% yield (based on Mo). The product was filtered, washed with distilled water and dried in air.
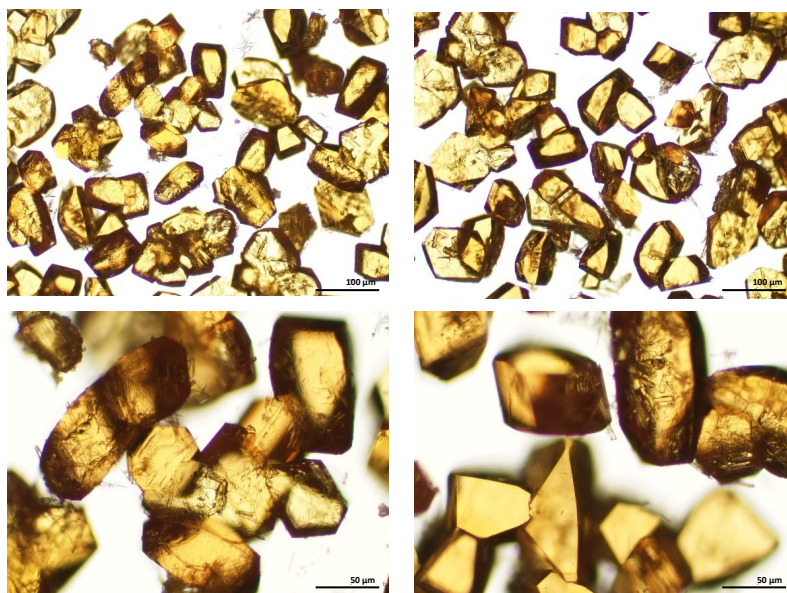

Figure S1. Optical microscopic images of **PS-13**.

1.2. Synthesis of composite materials: The composite materials were synthesized by 30 minutes mechanical griding, using a mortar pestle. The as-synthesized crystals of PS-13 (40 mg) were ground to powder and then mixed with acetylene black (AB, 10, 20, 30, 40 and 50 mg) uniformly, followed by the 30 minutes homogeneous grinding in mortar pestle.

1.3. Single Crystal X-ray Diffraction: Single crystal X-ray data were collected on an Agilent Super Nova diffractometer, equipped with a multilayer optics monochromated dual source (Cu and Mo) and an Eos CCD detector, using Cu-Ka radiation (1.54184 Å) at 150 k. Data acquisition, reduction and absorption correction were performed by using CrysAlisPRO.[1] The structure was solved with ShelXS[2] program using direct methods and refined on F 2 by full matrix least-squares techniques with ShelXL[2] through the Olex 2 (v.1.2) program package.[3] Anisotropic displacement parameters were applied for all the atoms, except for hydrogen atoms. The hydrogen atoms were placed in calculated positions and refined as riding atoms using isotropic displacement parameters. The crystal and structure refinement data are summarized in Table S1.

1.4. Physical Methods: Powder X-Ray Diffraction (PXRD) studies were carried out on a Bruker D8 – Advance Eco X-ray Diffractometer with Cu-Kα radiation (1.5418 Å). The morphological analysis of the catalyst was done by using a scanning electron microscope (SEM) from JEOL (JSM IT-300) provided with energy-dispersive X-ray diffractometer (Bruker) and transmission electron microscopy (TEM); a JEM-2100 instrument equipped with an energy-dispersive X-ray spectrometer, operated at an accelerated voltage of 200 kV. Valence states of the elements were found by NEXSA X-Ray Photoelectron Spectrometer (XPS) system of the Thermo scientific.

1.5. Electrochemical Study: All electrochemical measurements were executed on a Multi Autolab/M204 potentiostat/galvanostat (Metrohm) electrochemical workstation. In the conventional three electrode setup graphite electrode is used as a counter electrode, a saturated Ag/AgCl electrode as a reference electrode. The ink for the coating of graphitic strip electrode was prepared by using 5 mg of the catalyst in 500 μL of ethanol containing 20 μL of 5 wt% Nafion. The mixture was sonicated for 120 min and the homogeneous suspension was prepared. Out of this solution only 80 μL was coated on graphitic strip electrode and dried in vacuum. All the polarization data were collected at the scan rate of 5 mV s^{-1} in 1 M KOH. The equation used for the conversion to reversible hydrogen electrode is $E_{RHE} = E_{Ag/AgCl} + 0.197 + 0.059*pH$. The determination of Tafel slope was done by fitting the

linear region of the Tafel plot to the Tafel equation ($\eta = b \log(j) + a$) by again plotting the polarization curve. The double layer capacitance was calculated for the determination of electrochemically active surface area (ECSA) analysis by the CV scans in a non-Faradaic potential range of as-prepared catalysts electrodes in 1 M KOH at a scan rate of 10 to 100 mV/s. Half of the differences in current density variation ($\Delta J = (J_{anodic} - J_{cathodic})/2$) at a potential of 1.16 V vs RHE plotted against scan rate fitted to a linear regression that allows the determination of double layer capacitance (C_{dl}). The faradic efficiency was determined by calculating the ratio of the experimental and theoretical oxygen evolution.
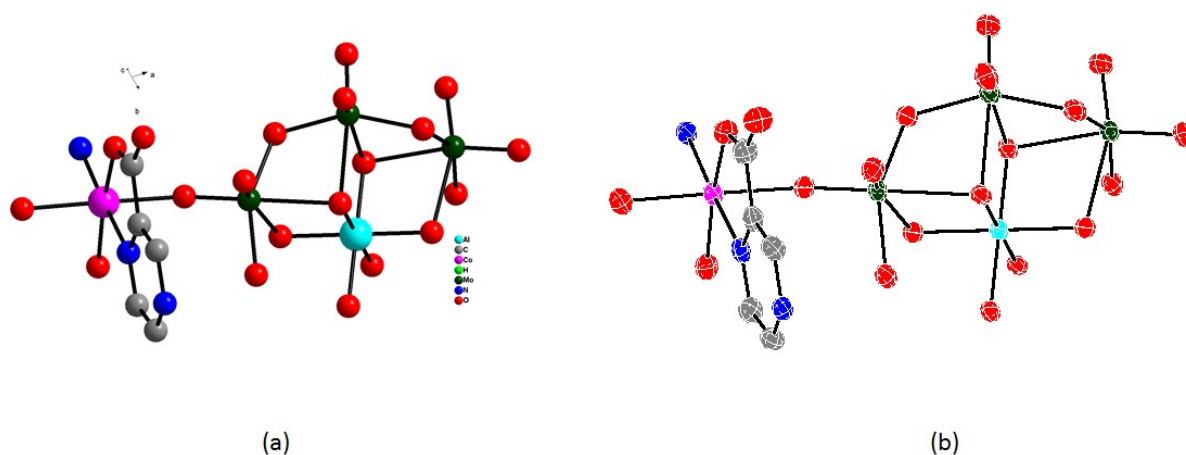

(a)   (b)

Figure S2. (a) Asymmetric unit of **PS-13.** Hydrogens are removed for clarity. (b) Thermal ellipsoid diagram.
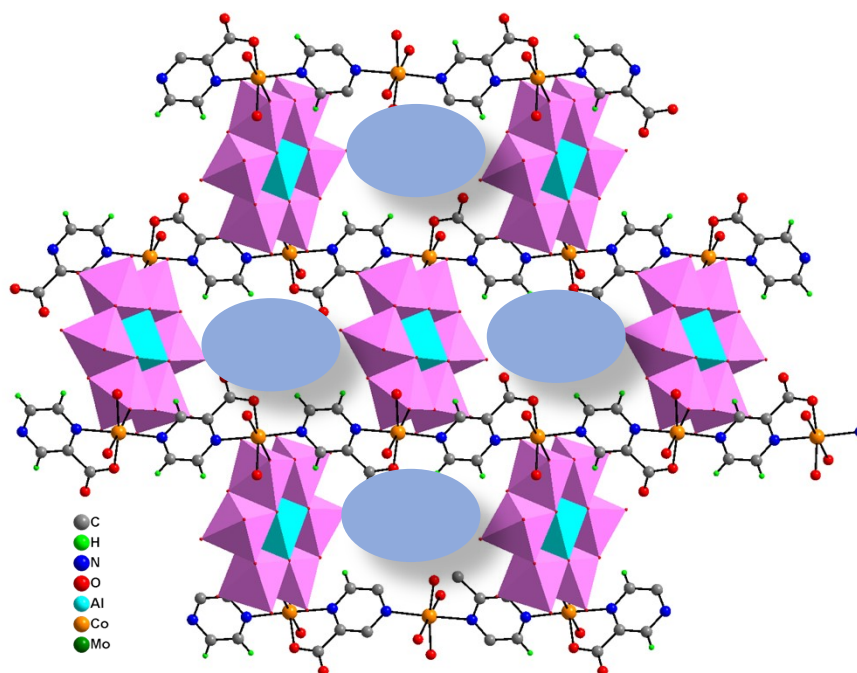
Figure S3. 1-D Cobalt pyrazine carboxylate coordination polymer covalently linked to Anderson-Evans cluster forming a 2-D sheet like structure. The sheet containing the cavities projecting along *a* axis, purple polyhedra represents MoO_6 whereas cyan colored polyhedra is the representation of AlO_6 octahedra. Hydrogen atoms have been omitted for clarity.
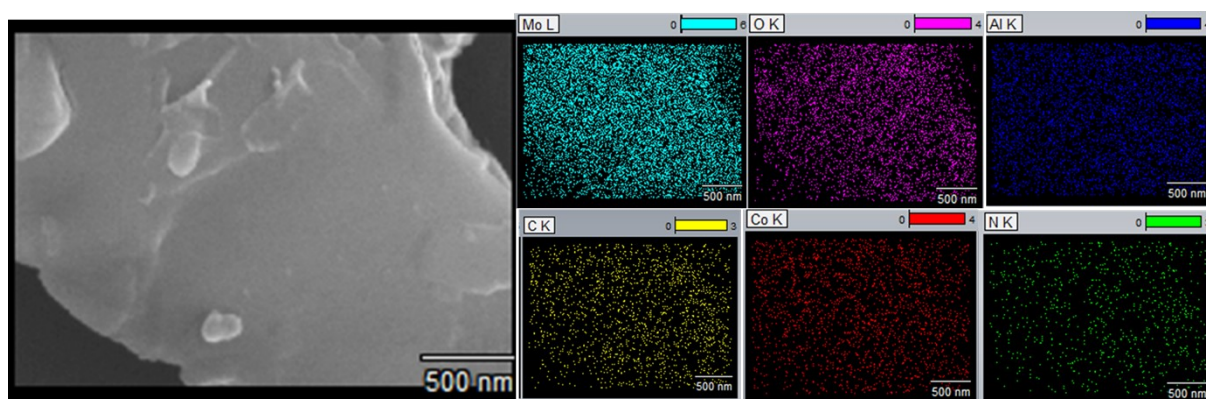
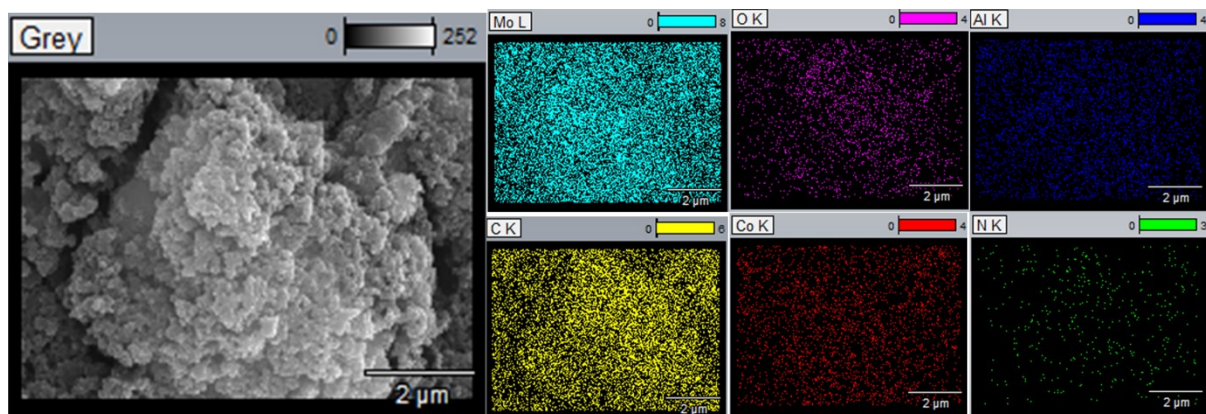**Figure S4.** FESEM image and elemental mapping of **PS-13**.

Figure S5. FESEM image and elemental mapping of **AB&PS-13 (1:2).**
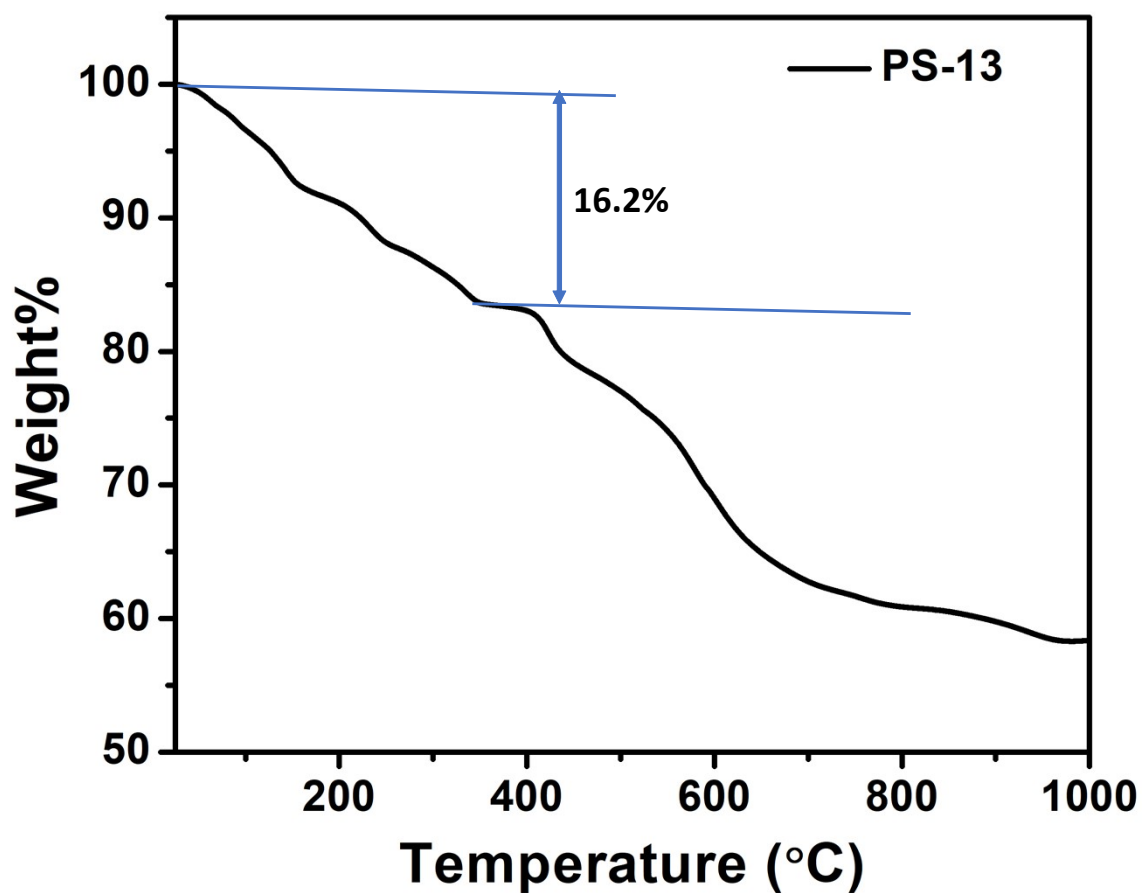
Figure S6. Thermogravimetric analysis (TGA) curve of PS-13. First weight loss was observed between 50 – 320 °C, which corresponds to the removal of solvent molecules i.e., 20 water molecules and 5 methanol molecules (cal. 15.5% and exp. 16.2%). For structure refinement a solvent mask was calculated and 299 electrons were found in 1 void per unit cell. This is consistent with the presence of 5[CH_4O], 20[H_2O] per Formula Unit which account for 290 electrons per unit cell and this is also supported by thermogravimetric analysis.
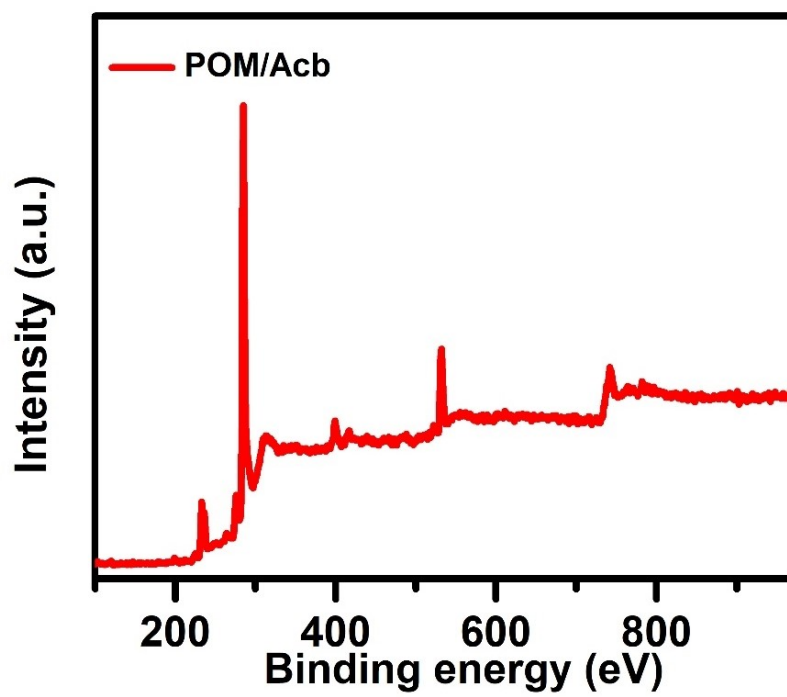
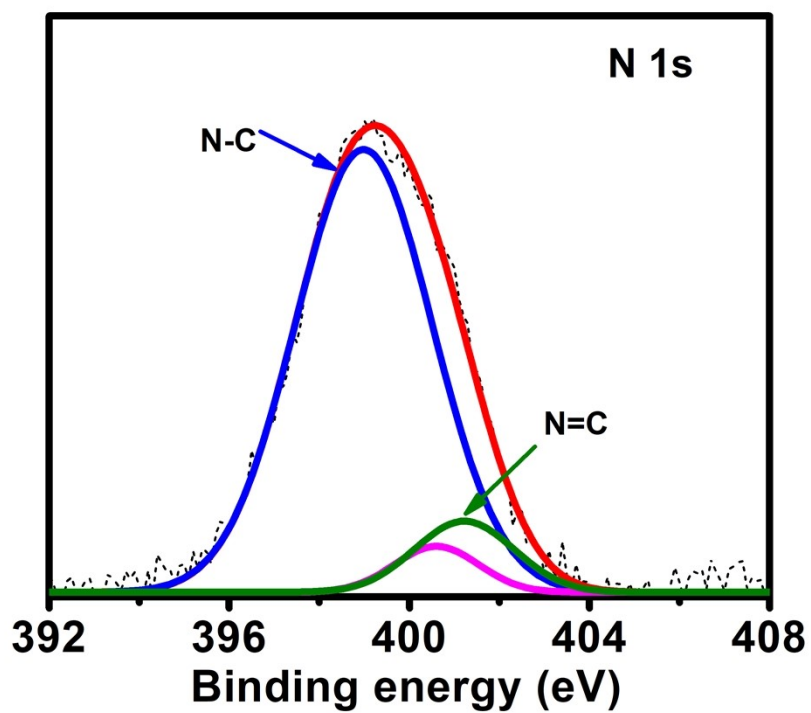**Figure S7.** XPS survey spectrum of **AB&PS13 (1:2).**

Figure S8. The high-resolution spectra of N 1s. The dotted curve was used to demonstrate the experimental data, while the solid line was used to demonstrate the fitting results.

Table S1. Comparison of OER performance by different **PS-13** and acetylene black composites.

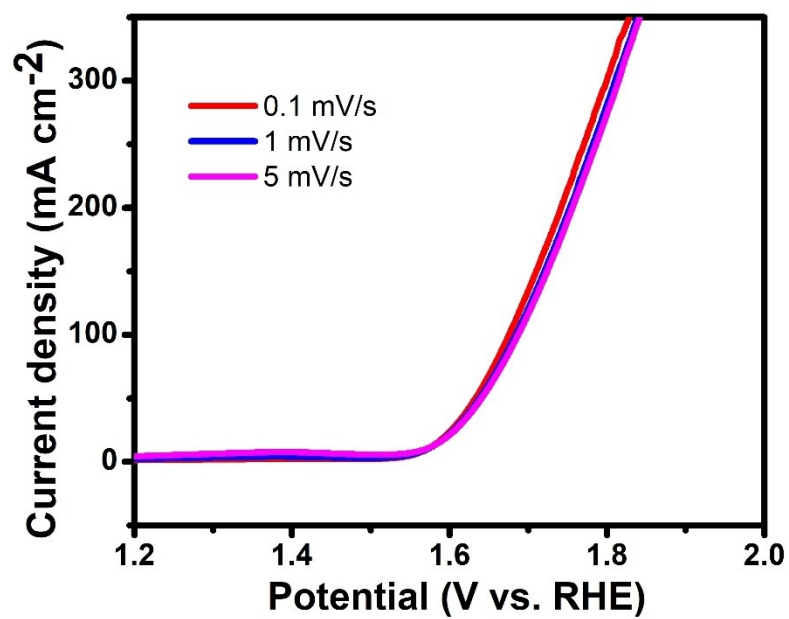| Catalysts[a]	η [mV] at 10 mA cm^{-2}
AB&PS-13 (1:4)	353
AB&PS-13 (1:2)	330
AB&PS-13 (3:4)	345
AB&PS-13 (1:1)	351
AB&PS-13 (5:4)	340

Figure S9. Polarization curves of AB&PS-13 (1:2) modified electrode in aqueous 1 M KOH at different scan rates, showing no change in the onset of the OER at ca. 1.5-1.6 V.
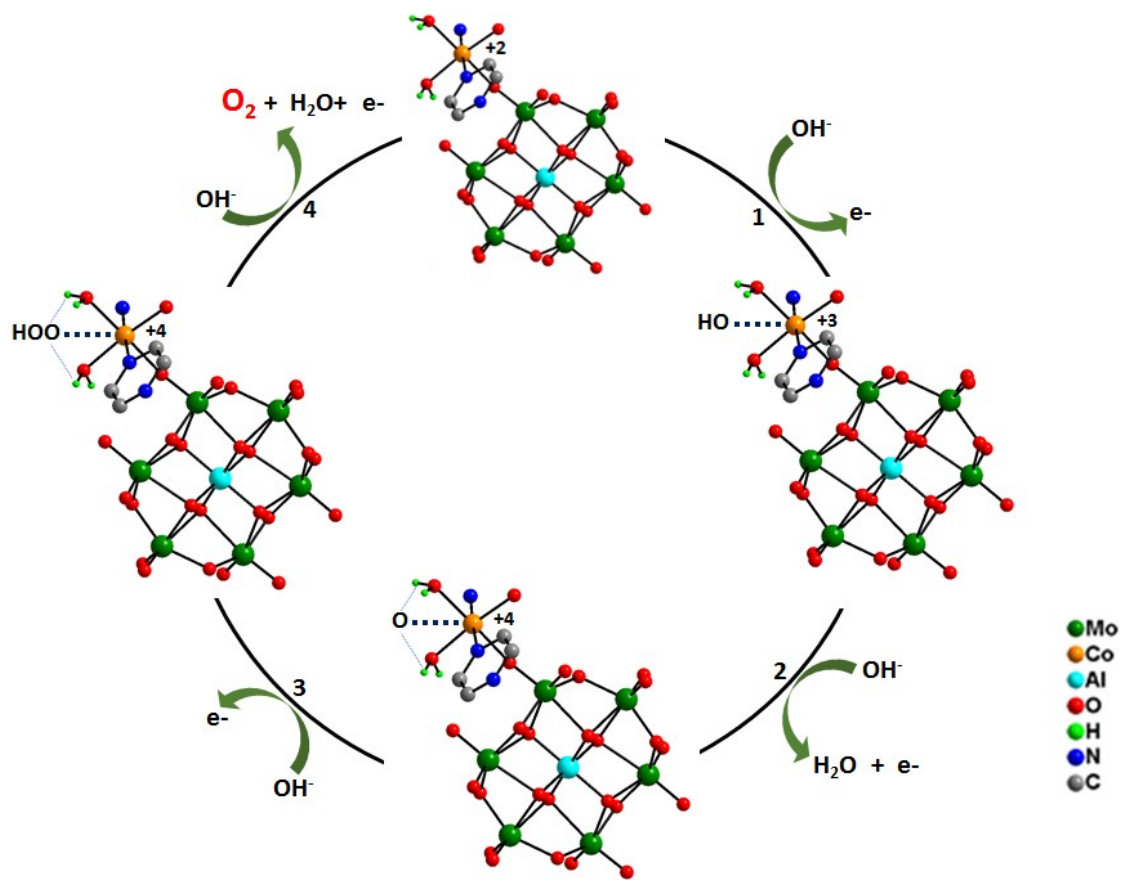
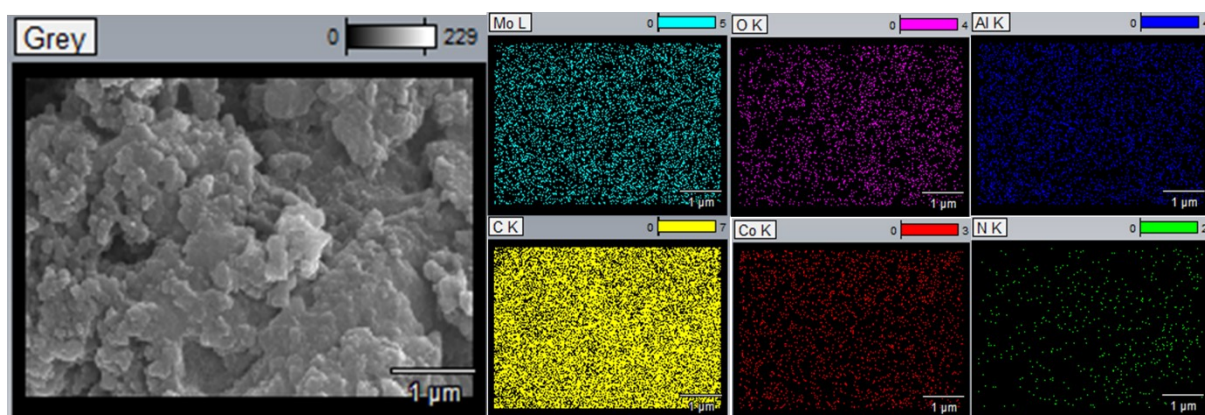**Figure S10.** Possible mechanistic pathway of oxygen evolution by PS-13.

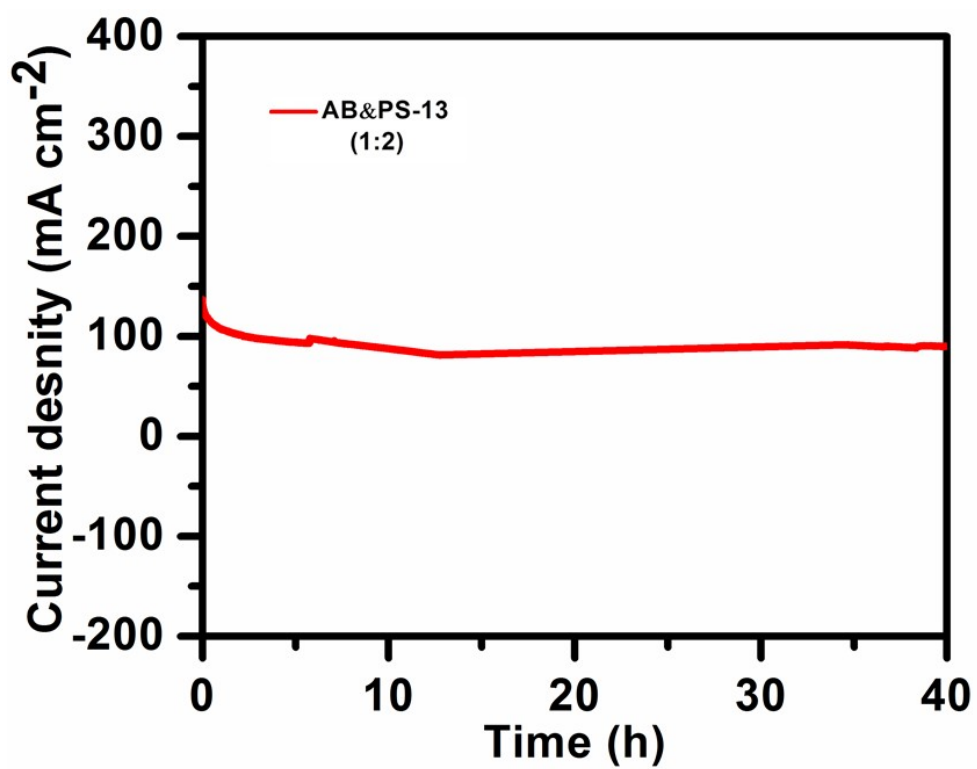**Figure S11.** FESEM image and elemental mapping of AB&PS-13 (1:2) after OER.

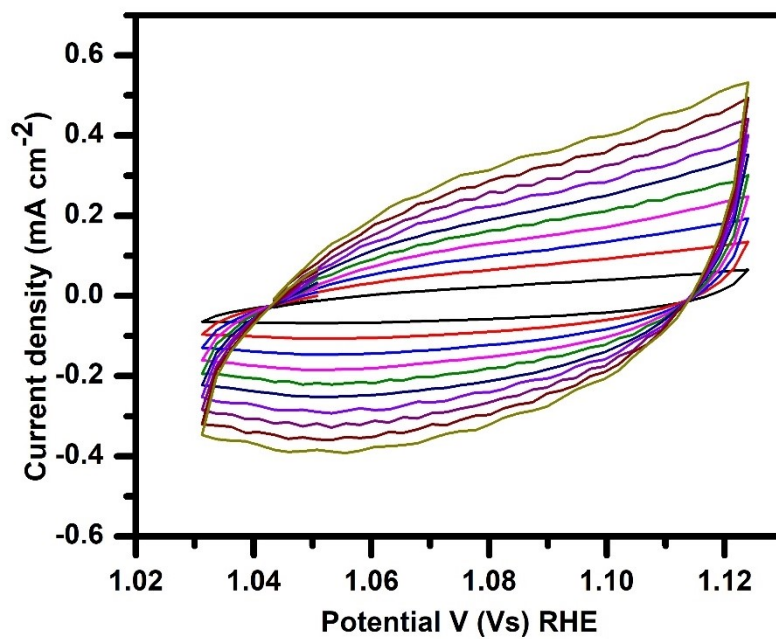**Figure S12.** Chronoamperometry cure of AB&PS-13 (1:2) at 100 mA cm^{-2}.

Figure S13. CV cycles for **PS-13** at different scan rates increasing from 10 to 100 mV s^{-1}.
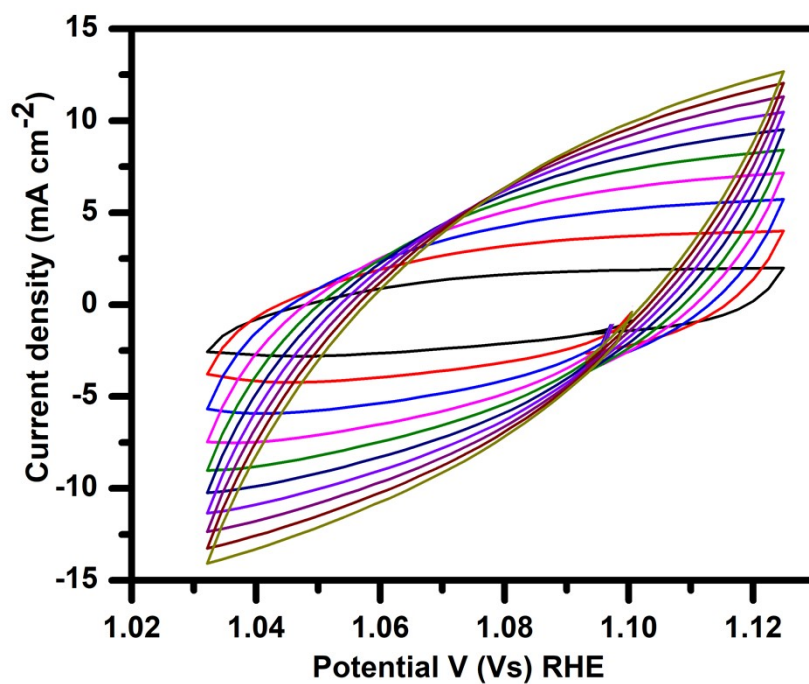
Figure S14. CV cycles for AB&PS-13 (1:2) at different scan rates increasing from 10 to 100 mV s^{-1}.

References:

[1] CrysAlisPro Program, version 171.37.33c, Agilent Technologies, Oxford, UK, **2012**.

[2] G. M. Sheldrick, Acta Crystallogr. **2008**, A64, 112-122.

[3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. J. Puschmann, J. Appl. Crystallogr. **2009**, 42, 339-341.