

***Electronic Supporting Information***

***High yield electrooxidation of 5-hydroxymethyl furfural catalysed by unsaturated metal sites  
in Co-Fe Prussian Blue Analogue films***

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## Materials

All commercially available reagents and materials were used without further purification unless otherwise stated. Nickel foam (99.9% purity) used as an electrode substrate was purchased from MTI corporation.  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NaNO}_3$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , Hydroxymethylenetetramine (HMT),  $\text{KOH}$ , 5% w/w Nafion, 5-hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA), formic acid and trichloroacetic acid were purchased from Merck | Sigma-Aldrich®. HPLC grade solvents methanol and acetonitrile were sourced from Honeywell Research Chemicals (Chem-Supply, Sydney, NSW, Australia). Milli-Q water (18.2 M $\Omega$ .cm resistivity) was used for solution preparation, washing, and electrochemical measurements.

### Preparation of CoFe PBA derived $\text{Co}(\text{OH})_x$ anodes

Nickel foam (NF) sheets were first compressed using a hydraulic press at 10MPa for 30s to achieve an average thickness of 0.6mm. These were then cut into  $3 \times 3$  cm pieces and sequentially sonicated in 0.1M  $\text{HCl}$ , acetone, iso-propyl and deionised (DI) water to remove impurities. The cut pieces were then oven dried at 80 °C for 4 hours. Cobalt-hexacyanoferrate (CoFe) films were electrodeposited onto the pre-treated NF surface in a 3-electrode cell consisting of the NF electrode as the working electrode ( $3\text{cm} \times 3\text{cm}$ ), a platinum foil ( $1\text{cm} \times 1\text{cm}$ ) as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode.

A deposition electrolyte was prepared containing 1 M  $\text{NaNO}_3$ , 0.5mM  $\text{K}_3\text{Fe}(\text{CN})_6$ , and 0.5mM  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  dissolved with milli-Q water (60mL). In this study, the PBA films were electrodeposited by applying an alternating on & off pulse (-0.4 & 0 V vs. SCE) at 10 Hz and 50% pulse duty for 300 seconds with magnetic stirring at 500 rpm. The electrode was submersed in the solution at a fixed depth of 2.5 cm during this process. The as obtained PBA anodes were dried in ambient air for at least 12 hours to minimize stress on the thin film structure. The average mass loading was found to be 23.8mg/ mg of Ni (**Table S 1**) Prior to reaction with HMF, the electrodes were exposed to potential cycling by cyclic voltammetry (-0.2 to 0.8V vs Hg/Hg O) for 20 cycles at 100 mV<sup>-1</sup> scan rate in 1.0 M  $\text{KOH}$  (pH 14.0) solution to transform them into the hydroxide form

### **Preparation of Bulk CoFe PBA catalyst ink**

In a typical synthesis procedure, a 10mL (0.075M)  $\text{Co}(\text{NO})_3 \cdot 6\text{H}_2\text{O}$  solution was introduced dropwise into a 100mL (0.5mM)  $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$  solution under magnetic stirring (600 rpm). The CoFe PBA particles were separated by centrifugation, washed with DI water, and then dried. A catalyst ink was prepared by mixing ground PBA powder (40mg) with ethanol (960  $\mu\text{l}$ ) and Nafion solution (40  $\mu\text{l}$  5% w/w). The ink was then sonicated for 10 mins to ensure homogeneity. To obtain a roughly similar mass loading to the pulse electrodeposited samples, 175  $\mu\text{l}$  of the ink was micro-pipetted on both sides of a bare nickel foam active surface (2.5 $\times$ 3.0 cm). The drop-casted ink was left to dry under a heat lamp for 15 mins before electrochemical testing.

### **Preparation of $\beta$ - Co (OH)<sub>2</sub> bulk particles**

Synthesis protocols reported by Liu, Z., et al <sup>1</sup> were used to prepare  $\beta$ -  $\text{Co}(\text{OH})_2$  using  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (5mM) as a cobalt precursor and HMT (60mM) as a hydrolysis agent . Both compounds were magnetically stirred together in a DI water/ethanol (9:1) 200ml solution and heated at 90°C for an hour. The resulting suspension were centrifuged, and oven dried to obtain the  $\beta$ -  $\text{Co}(\text{OH})_2$  solids.

## Physicochemical characterization

Scanning electron micrographs (SEM) of the deposited catalyst films were obtained using a FEI Nova SEM230 microscope with an accelerating voltage of 5kV. Transmission electron microscopy (TEM) images, scanning transmission electron microscopy (STEM) images and energy dispersive X-ray spectroscopy (EDS) maps were obtained using a JEOL JEM-F200 microscope with an accelerating voltage of 200kV. Samples for TEM imaging were prepared by drop casting an ethanol dispersion containing scrapped thin-films or powders onto a carbon coated copper grid using a micropipette and dried under atmospheric conditions. X-ray Diffraction (XRD) patterns of the thin-films were measured using an Empyrean-2 diffractometer (Co K $\alpha$  radiation,  $\lambda=1.790$  Å) in the  $2\theta=10-80^\circ$  range, to determine the phases and crystallinity of the catalyst. Surface chemistry of the electrodes was analysed using a Thermo Scientific ESCALAB250Xi X-Ray Photoelectron spectrometer (XPS). Additional surface composition analysis of the electrodes was performed using a Perkin Elmer series 400 ATR- FTIR spectrometer scanning between 600 to 4000cm<sup>-1</sup> IR wavelength. Raman analysis was performed using a Renshaw InVia II microscope with a 532nm laser source scanning between 100 to 4000 cm<sup>-1</sup>.

## XAS measurements

X-ray absorption spectroscopy measurements were performed at the 10-ID-B beamline of the Advanced Photon Source, Argonne National Laboratory. 10 Hz PBA film synthesized by PED method and conventionally precipitated PBA were measured using fluorescence geometry at the Fe K edge (7112.0 eV) from 200 eV below to 550 eV above the edge, as well as the Co K edge (7708.9 eV) from 100 eV below to 800 eV above the edge. Data was processed and modeled using the Demeter XAS software package.<sup>2</sup> For EXAFS modeling, the reported structure for FeCo PBAs was used to generate Co-N, Co-C and Fe-C, Fe-N contributions, and three N atoms were substituted by O atoms in the structure to generate the Co-O and Fe-O contributions.<sup>3</sup> S<sub>0</sub><sup>2</sup> values for Co (0.877) and Fe (0.93) were obtained by modeling the EXAFS of reference Co and Fe foils, respectively.

## Electrochemical characterization

Electrochemical measurements were done using a divided glass H-cell connected to a CHI760E workstation (CH instruments Inc.) in 1M KOH at 25 °C (pH 14.0) separated by an anion exchange membrane (Fumatech). A Hg/HgO (0.1M KOH) reference electrode and a platinum foil (1×1cm) counter electrode were used. The fabricated electrode was used as the working electrode with a depth of 2.5 cm submersed in the electrolyte solution. Electrocatalytic activity of the electrodes for HMF oxidation was studied using Linear sweep voltammetry (LSV) in the 1M KOH solution with and without HMF (10mM & 100mM). An open circuit potential at the rate of 50mV/s was applied in the positive direction for the LSV studies. The potential recorded was converted to V (vs. RHE) using equation (1).

$$E(\text{vs. RHE})\text{mV} = E(\text{vs. Hg/HgO}) + 0.059(\text{pH}) + 0.098\text{V} \quad (1)$$

Aliquots of the anode electrolyte were taken from the cell directly after the addition of HMF at 10-minute intervals for HPLC analysis. The current density for each electrode in the polarization curves for OER and HMF oxidation was normalized against the geometric surface area exposed to the reaction media.

## HPLC analysis of HMF oxidation products

Chromatographic analysis of HMF and FDCA were conducted using a Shimadzu<sup>®</sup> LC-20-AD HPLC system interfaced with a photodiode array detector. Separation of the analytes was performed on Kinetex EVO column (5 $\mu$ m 150mm x 4.6mm, Phenomenex, Sydney, NSW, Australia). The HPLC was a 10-minutes isocratic run and the mobile phase composed of 0.1% (v/v) TFA in 5% (v/v) methanol in Milli Q water. The column oven was set at 60 °C. The flow rate and injection volume were 1 mL/min and 10  $\mu$ L, respectively. Identification of the different compounds was monitored at 265nm and the absorption spectra at 283nm and 263nm were used for quantification of corresponding 5-HMF and FDCA.

Stock standard solutions of 5-HMF and FDCA (10 mM) were prepared in 0.1% (v/v) TFA in 5% (v/v) methanol in a UV-free laboratory. Stock solutions and standard calibrants were prepared fresh on the day of analysis. The 11-points external calibration curve had a range from 0.01 to 1.0 mM. Samples (1 mL) obtained from two experiments were collected every ten minutes from the H-cells. The sample aliquots were consequently diluted 10-fold with the mobile phase solution and analysed on the same day using HPLC. The conversion of HMF, product yield and faradaic efficiency of the electrolyser were determined using equations (2-4)

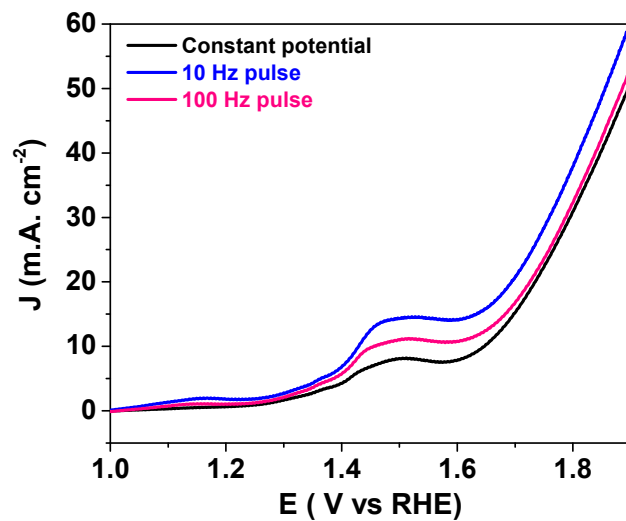
$$\text{HMF conversion (\%)} = \frac{\text{Moles of HMF consumed}}{\text{Initial moles of HMF}} \times 100\% \quad (2)$$

$$\text{Product yield (x) (\%)} = \frac{\text{Moles of x formed}}{\text{Initial moles of HMF}} \times 100\% \quad (3)$$

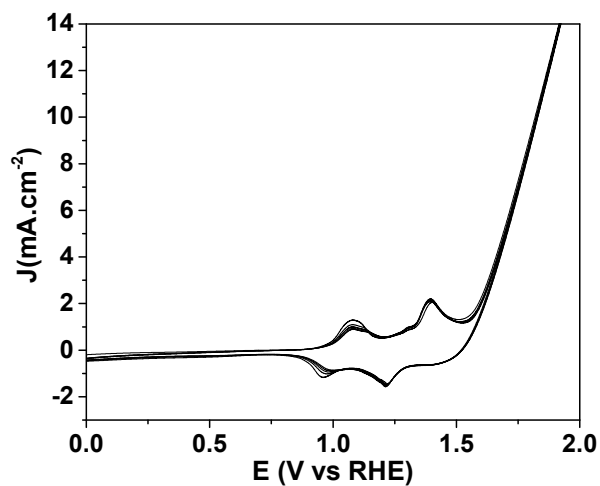
$$\text{Faradaic efficiency (\%)} = \frac{\text{Moles of x formed}}{\frac{\text{Charge}}{6F}} \times 100\% \quad (4)$$

Where, x corresponds to HMFCA, FFCA or FDCA

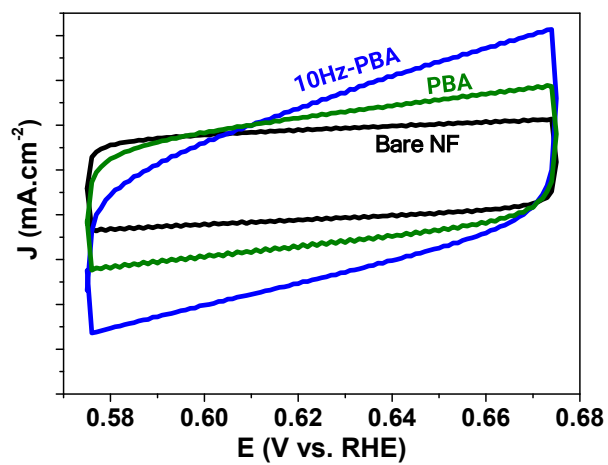
### Additional characterization Data



**Fig. S 1:** LSV of electrodeposited PBA at constant potential, 10Hz, and 100 Hz measured in 50mL 1.0M KOH+10mM HMF solution at 50mV.s<sup>-1</sup> with no stirring



**Fig. S 2:** CV scan of Pulse electrodeposited (10Hz) Co-Fe PBA on Ni foam measured in 50mL 1.0 M KOH solution at 100mV.s<sup>-1</sup> scan rate for 20 cycles



**Fig. S 3:** Specific areal capacitance of precipitated PBA and 10-Hz PBA on Ni-foam, and bare Ni-foam measured in 50mL 1.0 M KOH at 100mV.s<sup>-1</sup>



**Table S 1:** Sample mass-loading data for Co-Fe PBA thin films grown on a Ni-foam anode support immersed in a 60ml deposition electrolyte stirred at 500rpm at ambient conditions

<b>Sample name</b>	<b>Before(g)</b>	<b>After (g)</b>	<b>Mass loading (g CoFe/ g Ni)</b>
<b>Pulse 10Hz 1</b>	0.3152	0.3228	0.0241
	0.3154	0.3225	0.0225
	0.3154	0.3227	0.0231
	<b>Average</b>		0.0233
<b>Pulse 10Hz 2</b>	0.3197	0.3267	0.0219
	0.3199	0.3266	0.0209
	0.3201	0.3268	0.0209
	<b>Average</b>		0.0213
<b>Pulse 10Hz 3</b>	0.3070	0.3152	0.0267
	0.3072	0.3155	0.0270
	0.3071	0.3153	0.0267
	<b>Average</b>		0.0268

**Table S 2:** Summary of structural parameters obtained from EXAFS data

Sample		10 Hz- PBA		Bulk-PBA
Co K-edge	Coordination number	Co-N	4.12 ± 0.35	4.78 ± 1.24
		Co-O	1.14 ± 1.65	0.73 ± 0.64
		Co-C	3.78 ±1.38	5.33 ± 1.49
	Bond length (Å)	Co-N	2.07 ± 0.019	2.02 ± 0.022
		Co-O	3.06 ± 0.106	2.74 ± 0.067
		Co-C	3.30 ±0.036	3.30 ± 0.031
	Debye waller factor (Å²)	-	0.007	0.011
	R-factor	-	0.011	0.006
	Fe K-edge	Coordination number	Fe-C	3.87 ± 0.39
Fe-O			1.70 ± 0.46	2.79 ± 1.14
Fe-N			3.61 ± 0.40	5.56 ± 0.59
Bond length (Å)		Fe-C	1.89 ± 0.006	1.91 ± 0.011
		Fe-O	2.73 ± 0.017	2.76 ± 0.025
		Fe-N	3.17 ± 0.009	3.17 ± 0.016
Debye waller factor (Å²)		-	0.002	0.002
R-factor		-	0.0003	0.004

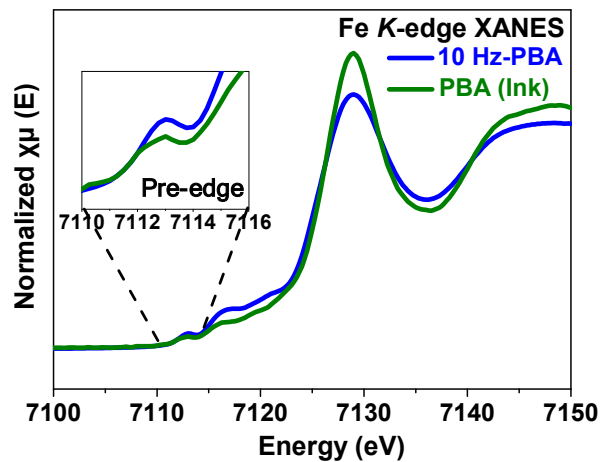


Fig. S 4: Fe K-edge XANES of PBA & 10Hz-PBA

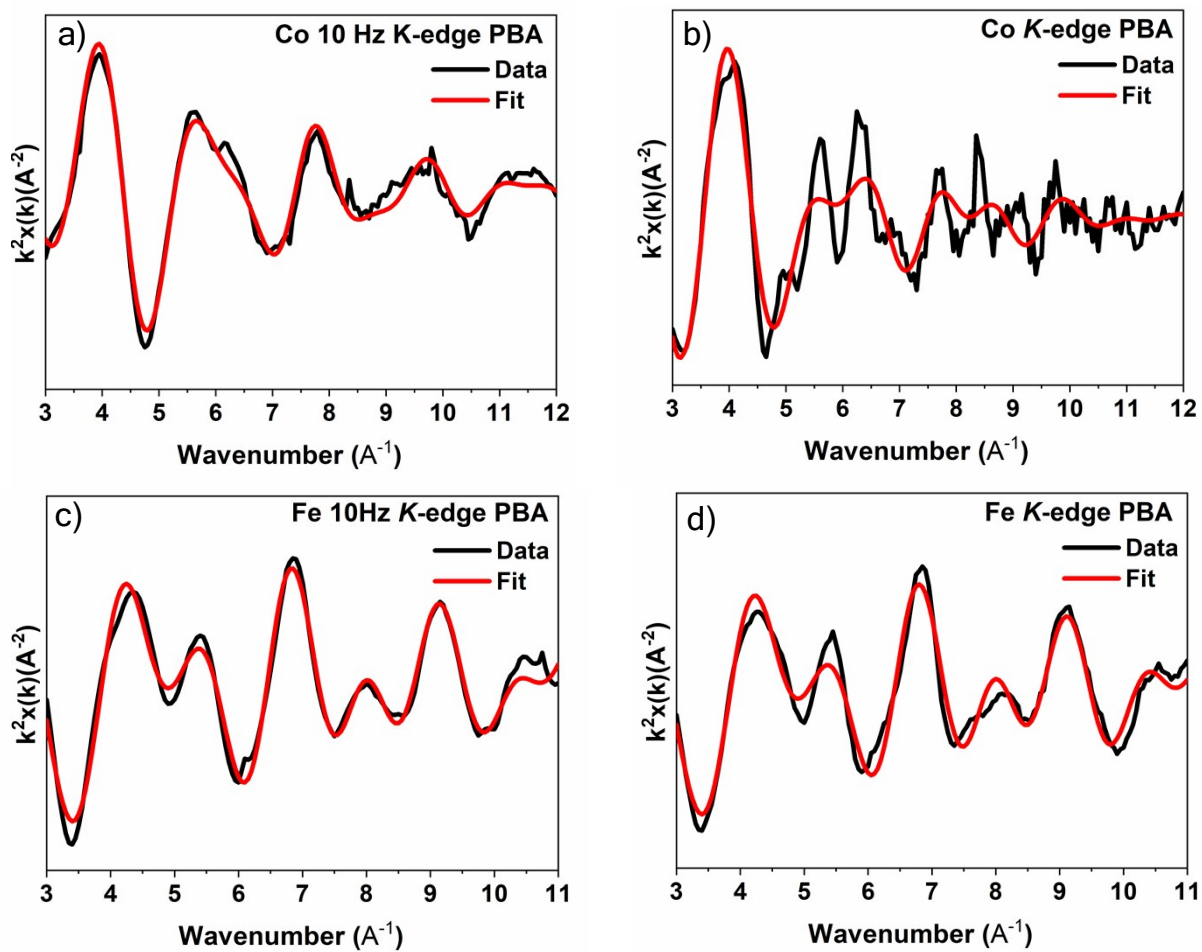
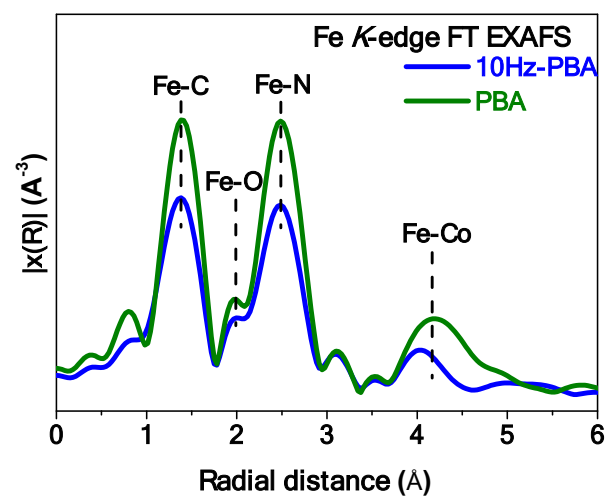
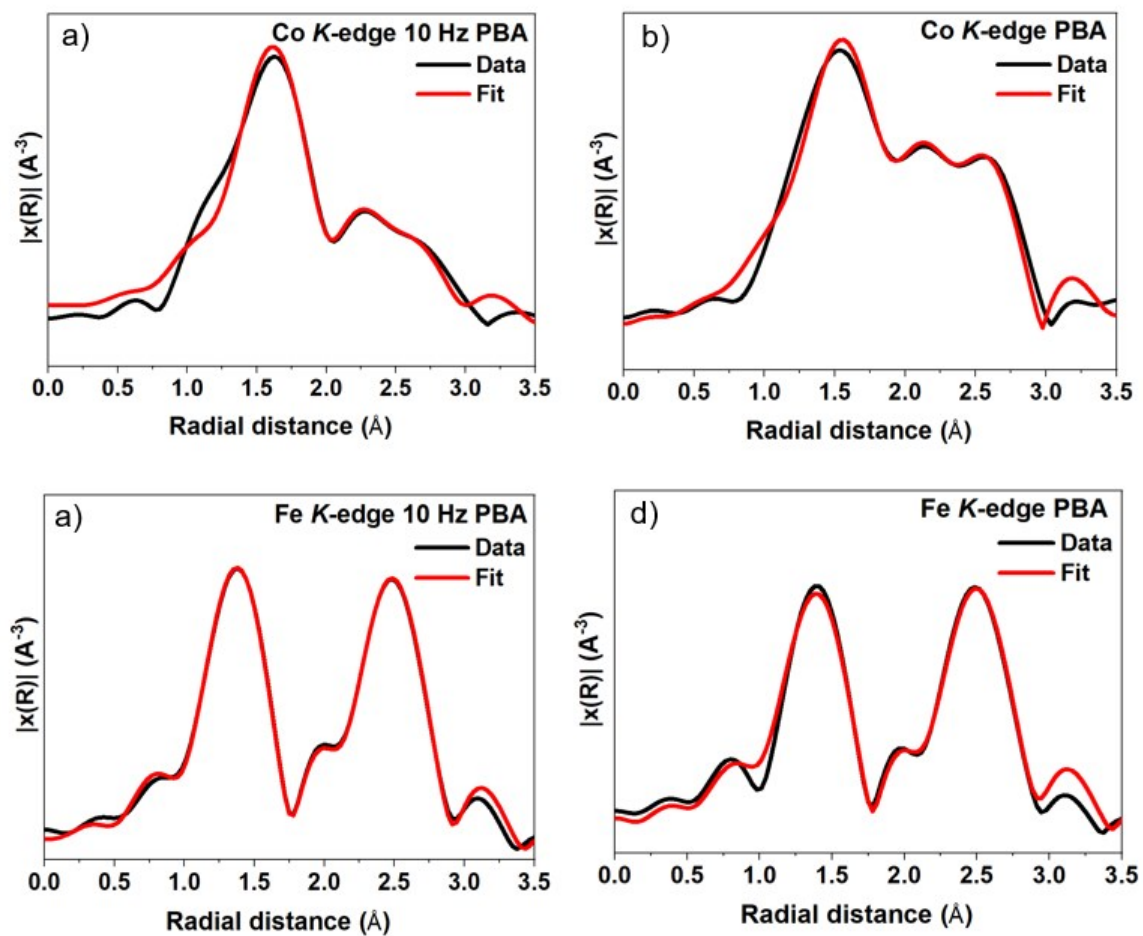


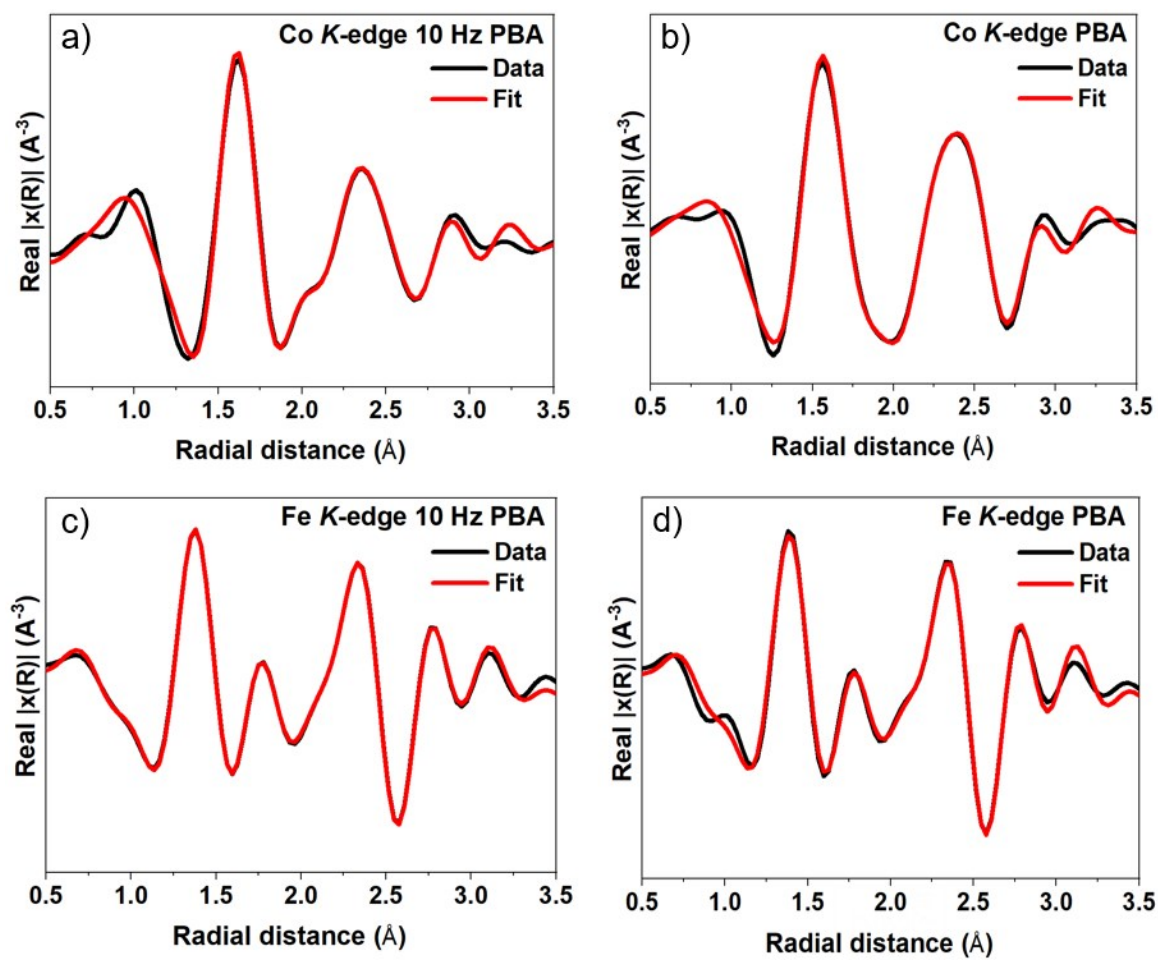
Fig. S 5:  $k^2$  space fits for (a) 10-Hz PBA Co (b) PBA Co (c) 10-Hz PBA Fe (d) PBA Fe



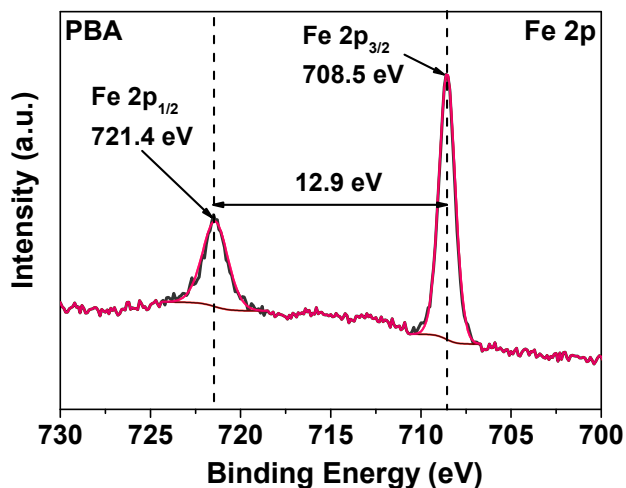
**Fig. S 6:** Fe K-edge EXAFS spectra of precipitated PBA & 10Hz-PBA



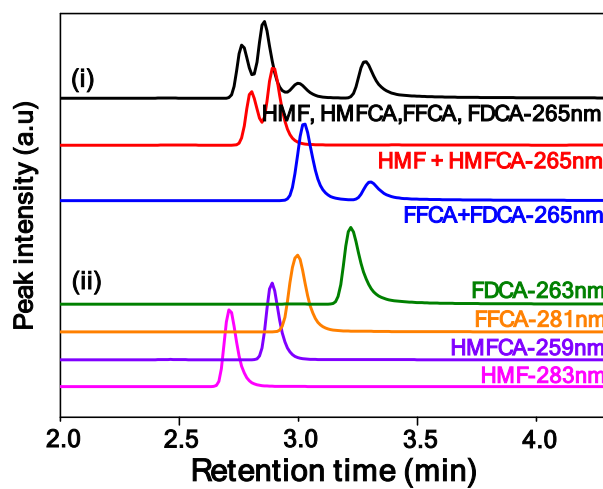
**Fig. S 7 :** Rmag fits for (a) 10-Hz PBA Co (b) PBA Co (c) 10-Hz PBA Fe (d) PBA Fe



**Fig. S 8 :**  $R_{\text{real}}$  fits for (a) 10-Hz PBA Co (b) PBA Co (c) 10-Hz PBA Fe (d) PBA Fe



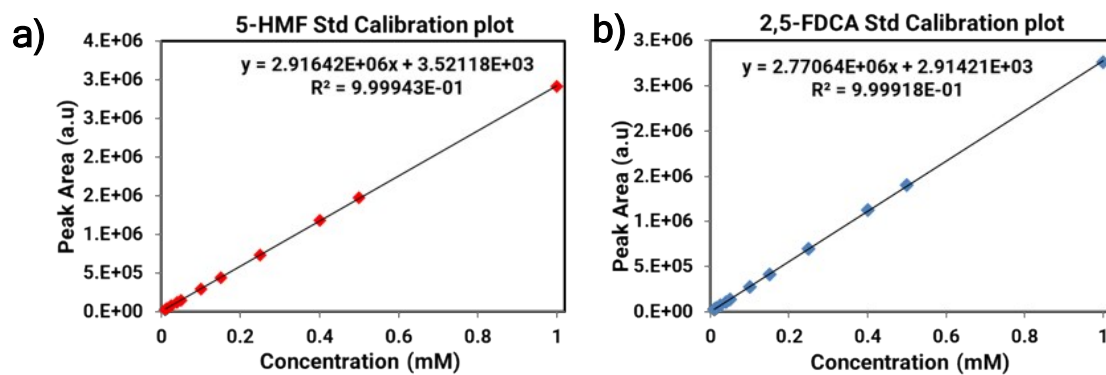
**Fig. S 9:** High resolution XPS spectra of Fe2p region for electrodeposited PBA film before exposure to 1.0 M KOH



**Fig. S 10 :**Chromatograms (i) show peaks of HMF, HMFA, FFCA and FDCA mixed standards when monitored at 265 nm. The chromatograms (ii) show the peak of each compound monitored at its maximum spectrum, e.g FDCA peak at 263 nm.



**Fig. S 11:** Digital photographs of Anion Exchange Membrane after the end of each batch conversion of HMF at 1.42 V vs RHE in 1.0M KOH.



**Fig. S 12 :** a) 5-HMF standard calibration curve b) 2,5-FDCA standard calibration curve



**Table S 3:** Signal intensities obtained from the HPLC were used for calculating the 5-HMF concentration between 0 to 160 mins during constant potential electrolysis at 1.42 V vs RHE (1st batch cycle)

Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
<b>0</b>	0	2406354	8.24	8.24	4.97E-03
		2406882	8.24		
		2404147	8.23		
<b>5</b>	16	2247791	7.70	7.68	1.76E-02
		2244909	7.69		
		2237804	7.66		
<b>10</b>	31	2115238	7.24	7.26	3.89E-02
		2134073	7.31		
		2113658	7.24		
<b>30</b>	77	1479201	5.06	5.04	1.97E-02
		1472463	5.04		
		1467771	5.02		
<b>40</b>	99	1236425	4.23	4.22	9.54E-03
		1231946	4.21		
		1237042	4.23		
<b>50</b>	118	1055423	3.61	3.59	1.52E-02
		1046649	3.58		
		1052032	3.60		
<b>60</b>	139	854124	2.92	2.92	4.88E-03
		854167	2.92		
		856608	2.93		
<b>70</b>	158	687485	2.35	2.34	7.30E-03
		683521	2.33		
		686848	2.34		
<b>80</b>	171	579023	1.97	1.98	2.50E-03
		579239	1.97		
		580378	1.98		
<b>90</b>	184	475002	1.62	1.62	2.98E-03
		476386	1.62		
		476607	1.62		
<b>100</b>	196	390932	1.33	1.33	8.31E-03
		392320	1.33		
		387605	1.32		

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Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
<b>110</b>	207	309442	1.05	1.04	7.52E-03
		307106	1.04		
		305058	1.03		
<b>120</b>	217	233645	0.79	0.795	5.49E-03
		236850	0.80		
		235267	0.79		
<b>130</b>	226	171072	0.57	0.569	4.51E-03
		168528	0.57		
		169225	0.57		
<b>140</b>	234	131494	0.44	0.432	5.78E-03
		129115	0.43		
		128238	0.43		
<b>160</b>	242	77992	0.26	0.257	1.50E-03
		78503	0.26		
		78865	0.26		

**Table S 4:** Signal intensities obtained from the HPLC were used for calculating the 2,5-FDCA concentration between 0 to 160 mins during constant potential electrolysis at 1.42 V vs RHE (1st batch cycle)

Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
0	0	N/A	N/A	N/A	N/A
5	16	65004	0.2241	0.224	7.04E-04
		65323	0.2253		
		64969	0.2240		
10	31	146350	0.5177	0.513	1.19E-02
		147495	0.5218		
		141295	0.4995		
30	77	423137	1.5167	1.51	6.25E-03
		422205	1.5133		
		419783	1.5046		
40	99	585847	2.1040	2.10	3.41E-03
		584194	2.0980		
		584232	2.0981		
50	118	747661	2.6880	2.68	3.35E-03
		745979	2.6819		
		746140	2.6825		
60	139	942089	3.3897	3.39	4.38E-03
		939981	3.3821		
		939994	3.3822		
70	158	1147703	4.1319	4.13	4.65E-03
		1148046	4.1331		
		1145663	4.1245		
80	171	1275588	4.5934	4.58	1.31E-02
		1269103	4.5700		
		1269569	4.5717		
90	184	1419968	5.1145	5.12	6.75E-03
		1421363	5.1196		
		1423672	5.1279		
100	196	1563606	5.6330	5.63	3.92E-03
		1564234	5.6352		
		1562120	5.6276		

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Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
<b>110</b>	207	1703949	6.1395	6.13	1.21E-02
		1699558	6.1237		
		1697359	6.1157		
<b>120</b>	217	1819019	6.5548	6.56	5.51E-03
		1821265	6.5629		
		1821933	6.5653		
<b>130</b>	226	1914672	6.9001	6.90	1.48E-02
		1918598	6.9142		
		1910400	6.8846		
<b>140</b>	234	2024954	7.2981	7.31	8.78E-03
		2029711	7.3153		
		2028220	7.3099		
<b>160</b>	242	2157947	7.7781	7.77	8.09E-03
		2153970	7.7637		
		2157753	7.7774		

**Table S 5:** Signal intensities obtained from the HPLC were used for calculating the 5-HMF concentration between 0 to 160 mins during constant potential electrolysis at 1.42 V vs RHE (2<sup>nd</sup> batch cycle)

Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
<b>0</b>	0	2469719	8.46	8.44	2.02E-02
		2464887	8.44		
		2458007	8.42		
<b>10</b>	31	2182819	7.47	7.46	1.73E-02
		2180561	7.46		
		2173171	7.44		
<b>30</b>	89	1338968	4.58	4.54	3.65E-02
		1329862	4.55		
		1317754	4.51		
<b>60</b>	173	557128	1.90	1.89	5.65E-03
		556054	1.89		
		553895	1.89		
<b>90</b>	226	169395	0.569	0.568	1.72E-03
		168493	0.566		
		169330	0.569		
<b>160</b>	243	5721	0.00754	0.00704	4.38E-04
		5485	0.00673		
		5518	0.00685		

**Table S 6:** Signal intensities obtained from the HPLC were used for calculating the 2,5-FDCA concentration between 0 to 160 mins during constant potential electrolysis at 1.42 V vs RHE (2<sup>nd</sup> batch cycle)

Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
0	0	N/A	N/A	N/A	N/A
10	31	130964 131774 131987	0.462 0.465 0.466	0.464	1.95E-03
30	89	516982 516500 510275	1.86 1.85 1.83	1.85	1.35E-02
60	173	1330050 1329464 1329826	4.79 4.79 4.79	4.79	1.07E-03
90	226	2012313 2011179 2012876	7.25 7.25 7.25	7.25	3.12E-03
160	243	2200186 2197693 2200768	7.93 7.92 7.93	7.93	5.90E-03

**Table S 7:** Signal intensities obtained from the HPLC were used for calculating the 5-HMF concentration between 0 to 160 mins during constant potential electrolysis at 1.42 V vs RHE (3<sup>rd</sup> batch cycle)

Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
0	0	1990819	6.81	6.29	6.49E-01
		1894593	6.48		
		1625379	5.56		
20	76	1085163	3.71	3.97	2.33E-01
		1188110	4.06		
		1213831	4.15		
30	88	813584	2.78	2.99	1.93E-01
		885344	3.02		
		924687	3.16		
100	181	158507	0.531	0.532	6.88E-02
		138716	0.464		
		178822	0.601		

**Table S 8:** Signal intensities obtained from the HPLC were used for calculating the 2,5-FDCA concentration between 0 to 160 mins during constant potential electrolysis at 1.42 V vs RHE (3<sup>rd</sup> batch cycle)

Time (mins)	Charge (C)	Peak Area (a.u)	Concentration (mM)	Mean (mM)	Std Dev
0	0	1287	0	0	0.00E+00
		1601	0		
		1247	0		
20	76	300672	1.07	1.15	6.87E-02
		329892	1.18		
		336404	1.20		
30	88	454845	1.63	1.76	1.14E-01
		496419	1.78		
		516883	1.86		
100	181	1466128	5.28	5.24	5.81E-02
		1435565	5.17		
		1459589	5.26		

## Supporting References

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