Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Role of B site ion in bifunctional oxygen electrocatalysis: A structure property correlation study on doped $Ca_2Fe_2O_5$ brownmillerites

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1) Rietveld refinement of PXRD patterns

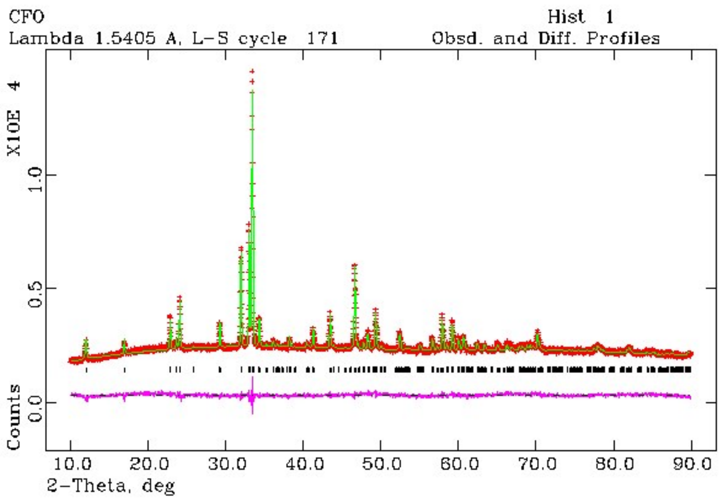

Figure S1: Resultant Rietveld refined pattern of CFO

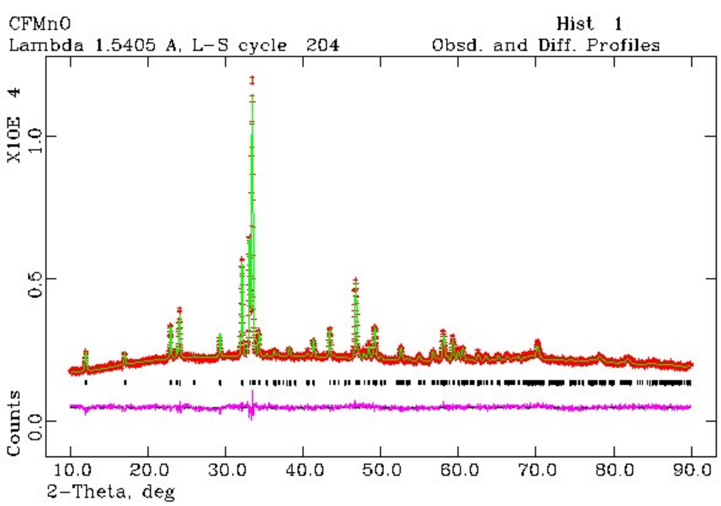

Figure S2: Resultant Rietveld refined pattern of CFMnO

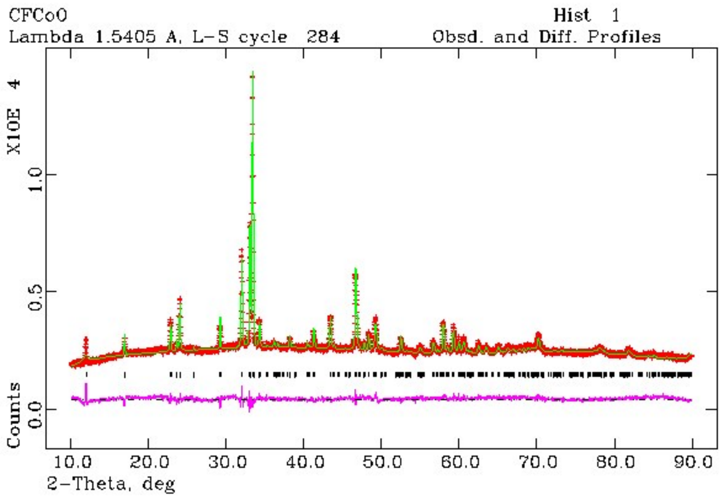

Figure S3: Resultant Rietveld refined pattern of CFCoO

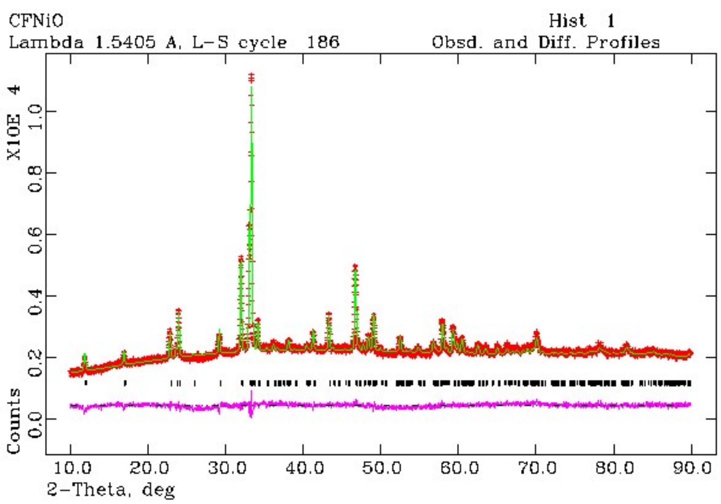

Figure S4: Resultant Rietveld refined pattern of CFNiO

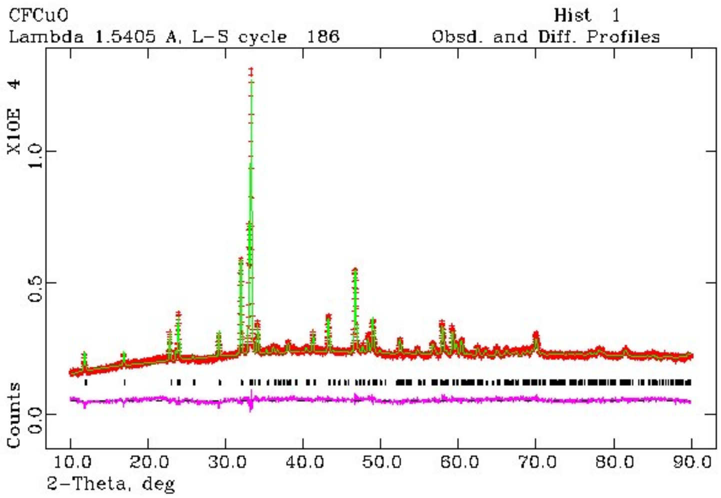

Figure S5: Resultant Rietveld refined pattern of CFCuO

2) Composition data :XPS, SEM-EDAX, MP-AES data

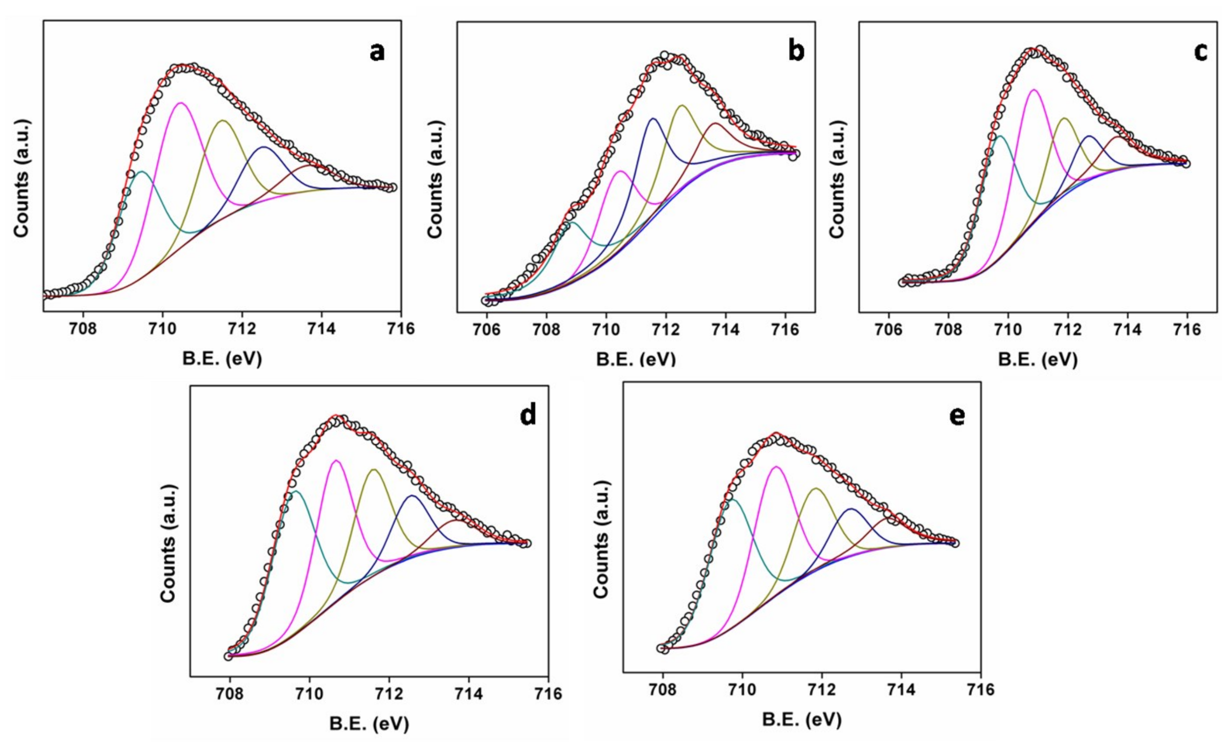

Figure S6 : Fe2p XPS spectra of a) CFO b) CFMnO c) CFCoO d) CFNiO e) CFCuO

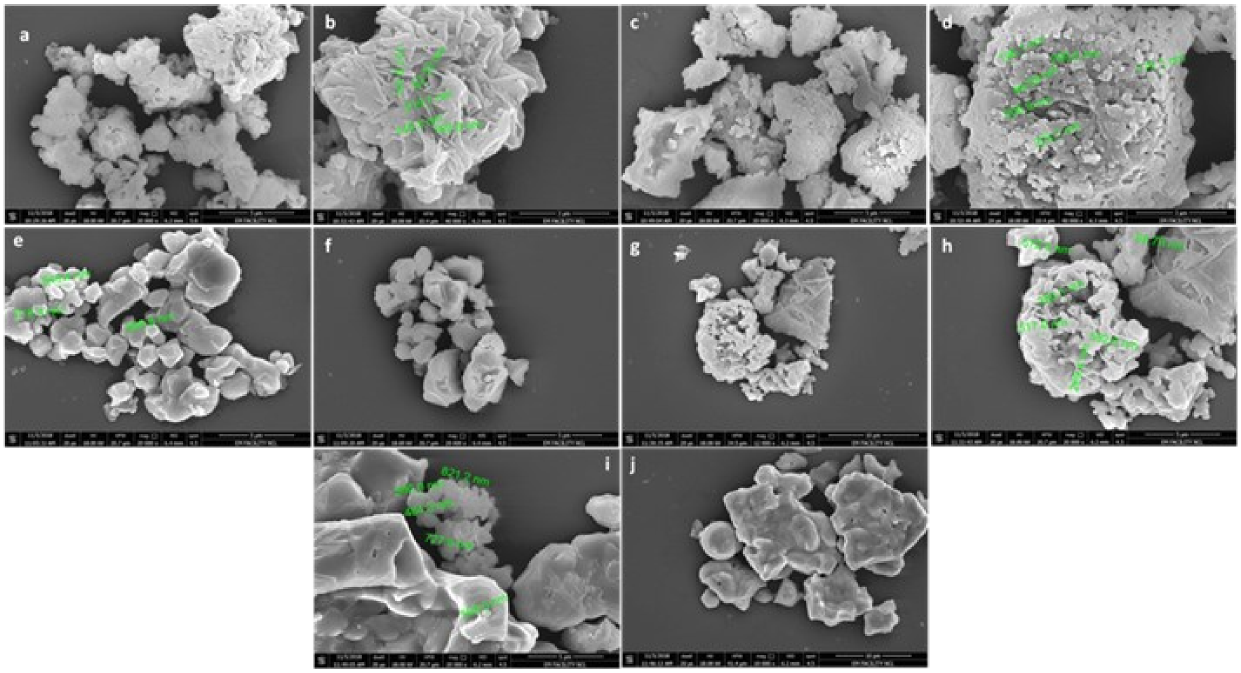

Figure S7 : SEM Images of a) and b) CFO c) and d) CFMnO e) and f) CFCoO g) and h) CFNiO i) and j) CFCuO. Few particle dimensions are given in green.

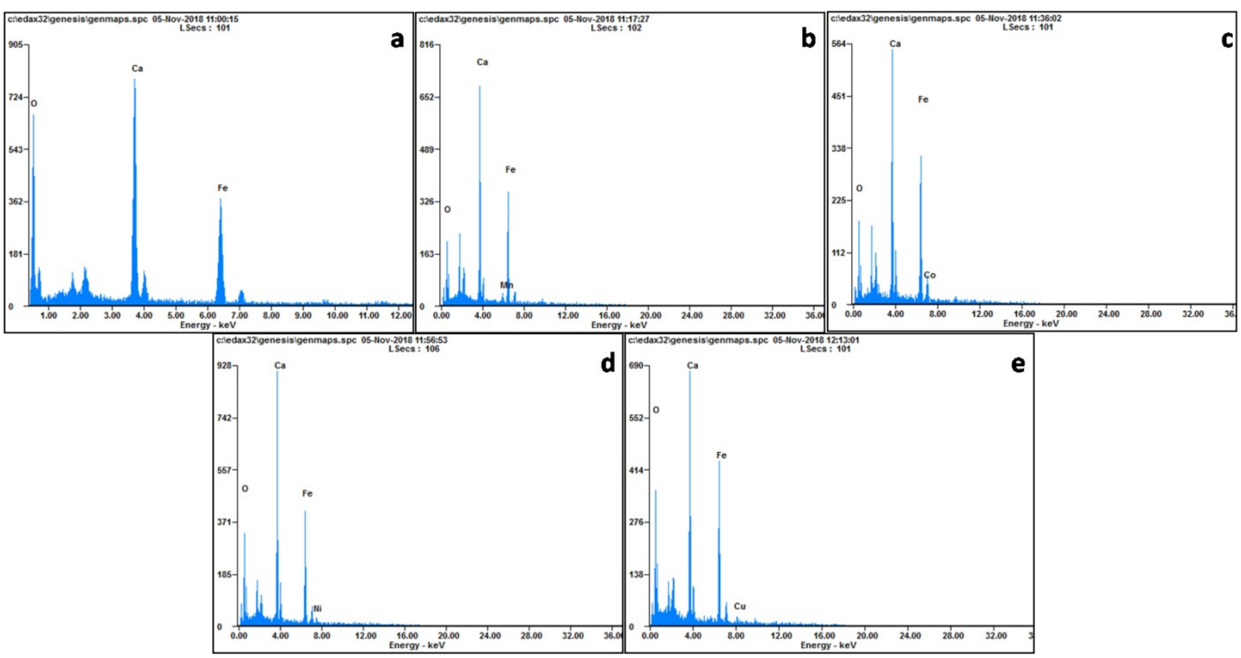

Figure S8: EDAX profiles of a) CFO b) CFMnO c) CFCoO d) CFNiO e) CFCuO

Table S1: EDAX Data

		Wt %	Calculated
CFO	Ca	21.51	29.48
	Fe	32.33	41.087
	O	46.16	29.47
CFMnO	Ca	26.56	29.49
	Fe	40.64	39.046
	Mn	2.01	2.02
	O	31.10	29.43
CFCoO	Ca	28.76	29.4524
	Fe	44.09	38.98
	Co	3.61	2.17
	O	23.53	29.39
CFNiO	Ca	25.04	29.45
	Fe	36.81	38.99
	Ni	2.74	2.16
	O	35.41	29.39
CFCuO	Ca	23.97	29.4
	Fe	36.43	38.92
	Cu	2.31	2.33
	O	37.30	29.34

Table S2: MP-AES Results

Catalyst	Experimental (PPM)			Calculated (PPM)		
	Ca	Fe	Mn/Co/Ni/Cu	Ca	Fe	Mn/Co/Ni/Cu
CFMnO	53.7	63.7	3.03	53.1	70.3	3.6
CFCoO	107.9	119.6	6.37	84.8	112.3	6.24
CFNiO	100.3	118.2	5.9	90.72	120.1	6.64
CFCuO	69.6	83.7	4.9	57.63	76.3	4.57

*4.5mg CFMnO, 7.2mg CFCoO, 7.7mg CFNiO, 4.9mg CFCuO separately dissolved in aquaregia and made upto 25ml MilliQ Ultrapure water.

3) Surface area data

Table S3: BET Surface area results

Catalyst	Surface area m^2/g
CFMnO	4.44
CFCoO	0.89

CFNiO	4.23
CFCuO	8.14

4) Electrochemical Data

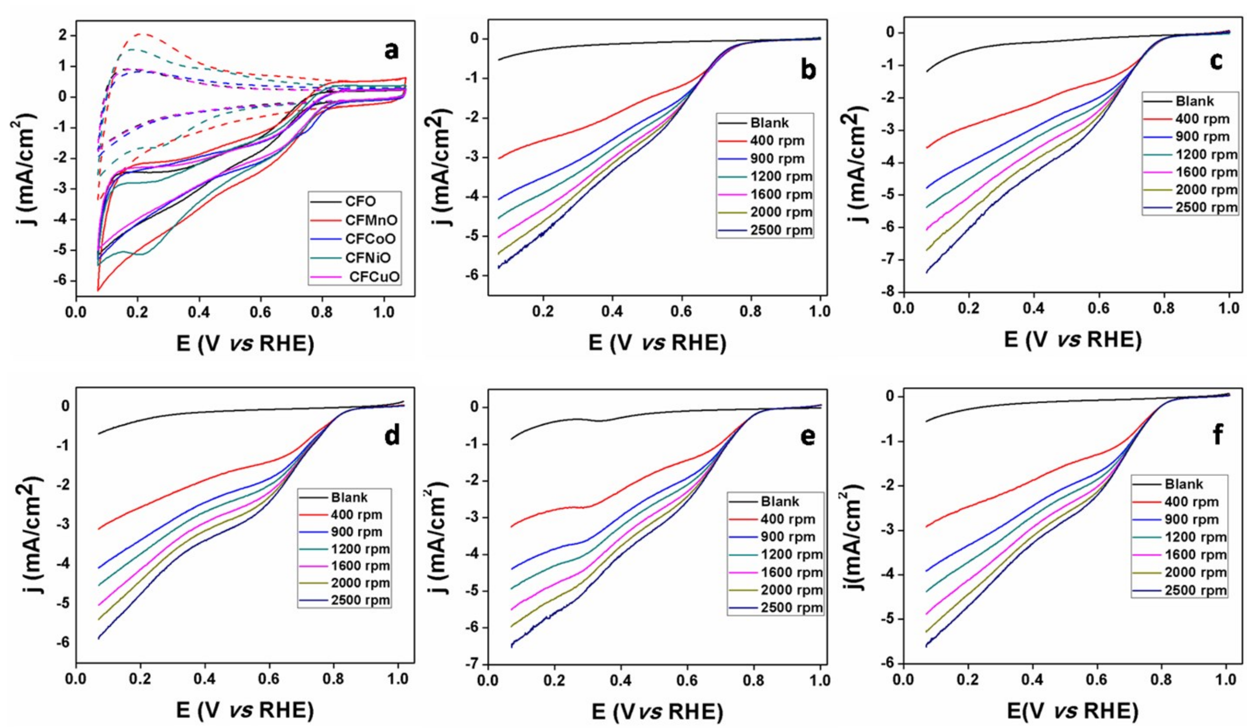

Figure S9: a) Cyclic voltammogram at 900 rpm with 50mV/s scan rate, the dashed profile with N_2 saturation and solid profile is in O_2 saturation. Linear sweep voltammogram at 1600 rpm in O_2 saturation and 10mV/s scan rate of b) CFO c) CFMnO d) CFCoO e) CFCNiO f) CFCuO, where blank data is recorded with N_2 saturation without rotation.

4.2) Koutechy-Levich equation

Koutechy Levich equation can be expressed as

$$\frac{1}{I_D} = \frac{1}{I_k} + \frac{1}{I_d} = \frac{1}{I_k} + \frac{1}{B\omega^{\frac{1}{2}}} \qquad (1)$$

$$B = 062nFAC_O D_O^{\frac{2}{3}} \upsilon^{\frac{-1}{6}} \qquad (2)$$

$$I_k = nAFKC_O \qquad (3)$$

Where I_D is the disk voltammetric current which has the contribution of the kinetic current (I_k) and diffusion controlled current (I_d), ω is the rotation speed, n is the electron transfer number F is Faradays constant, A is the geometric area of the electrode, CO is the oxygen concentration in the oxygen saturated solution, DO is the diffusion coefficient of oxygen υ is the kinematic viscosity of the solution and k is the electron transfer rate constant. K-L plot is the plot of inverse of disk current against inverse of square root of rotation. The slope value B, is 0.46 $mAcm^{-2}S^{1/2}$ for a perfect 4 electron transfer reaction.

4.3) Tafel equation

Tafel equation can be represented as

$$\eta_c = \frac{RT}{nF\alpha_c} lnj_0 - \frac{RT}{nF\alpha_a} lnj = a - blnj \qquad (4)$$

where j_0 is the exchange current density, R is the gas constant, n is the number of electrons involved in the overall reaction, α is the charge transfer coefficient and a and c in the subscripts indicate anodic and cathodic parts. The plot of η against lnj is called Tafel plot and the tafel slope -b from which the rate determining step can be predicted from the slope value.

$$O_2 \rightarrow O_{2(ads)} \qquad (1)$$

$$O_{2(ads)} + e \rightarrow [O_{2(ads)}]^- \qquad (2)$$

$$[O_{2(ads)}]^- \rightarrow O^-_{2(ads)} \qquad (3)$$

$$O^-_{2(ads)} + H_2O \rightarrow HO_{2(ads)} + OH^- \qquad (4)$$

$$HO_{2(ads)} + e \rightarrow HO^-_{2(ads)} \qquad (5)$$

$$HO_{2(ads)}^{-} \rightarrow HO_2^{-} \quad (6)$$

Charge transfer coefficient α_a can be defined as given by Taylor and Humffray[1]

$$n\alpha_a = (\frac{n_f}{\upsilon} + n_r\beta) \quad (5)$$

Where n_f is the number of electrons transferred before rate determining step (rds), nr is the number of electrons transferred in the rds, υ is the stoichiometric number of the reaction defined as the number of times the rds occurs for one repetition of the overall reaction and β is the symmetry factor of the rds which has a value near 0.5, the subscript a stands for anodic reaction and for the cathodic reaction, slope value will be of opposite sign. nf and nr are 0 and 1 respectively for the first electron reduction step resulting in Tafel slope (b) value of -120 mV/decade. If the step followed by the first electron reduction is the rate determining step, n_f =1 and n_r = 0, resulting in a slope of -60 mV/decade, indicating a pseudo two electron transfer. Similar explanation can be applied to the OER reaction as well. [2]

4.4) Electron transfer number and Peroxide yield

Electron transfer number and peroxide yield was calculated by the equation 6 and 7 respectively.[3]

$$n = 4 * \frac{Id}{I_d + I_r/N_C} \quad (6)$$

$$p = 200 * \frac{I_r/N_C}{I_d + I_r/N_C} \quad (7)$$

where Id is the disk current, Ir is the ring current Nc is the collection efficiency, (collection efficiency in the present study is 0.37).

References

1. R.J.Taylor and A.A.Humffray, *J. Electroanal. Chem.*, 1975, **64**, 63-84.
2. X. Ge, A. Sumboja, D. Wuu, T. An, B. Li, F. W. T. Goh, T. S. A. Hor, Y. Zong and Z. Liu, *ACS Catal.*, 2015, **5**, 4643-4667.
3. R. Zhou, Y. Zheng, M. Jaroniec and S.-Z. Qiao, *ACS Catal.*, 2016, **6**, 4720-4728.