

Supporting Information

Ex-situ and *operando* investigations on $(\text{FeCoCrMnZn})_3\text{O}_4$ High Entropy Oxide as Anode for Li ion battery

Sidhartha Sankar Sahoo^{1,6}, Chandrani Nayak^{1,6}, Ravi Kumar^{1,6}, Ankita Pathak², Seemita Banerjee^{3,6}, Jitendra Bahadur^{4,6}, Himanshu Srivastava^{5,6} and Dibyendu Bhattacharyya^{1,6,*}

¹Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India.

²Technical Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India.

³Radiation and Photochemistry Division, Bhabha Atomic Research Centre, Mumbai-400085, India.

⁴Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India.

⁵Accelerator Physics and Synchrotrons Utilization Division, Raja Ramanna Centre for Advanced Technology, Indore-4520135, India.

⁶Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

* Corresponding author: dibyendu@barc.gov.in

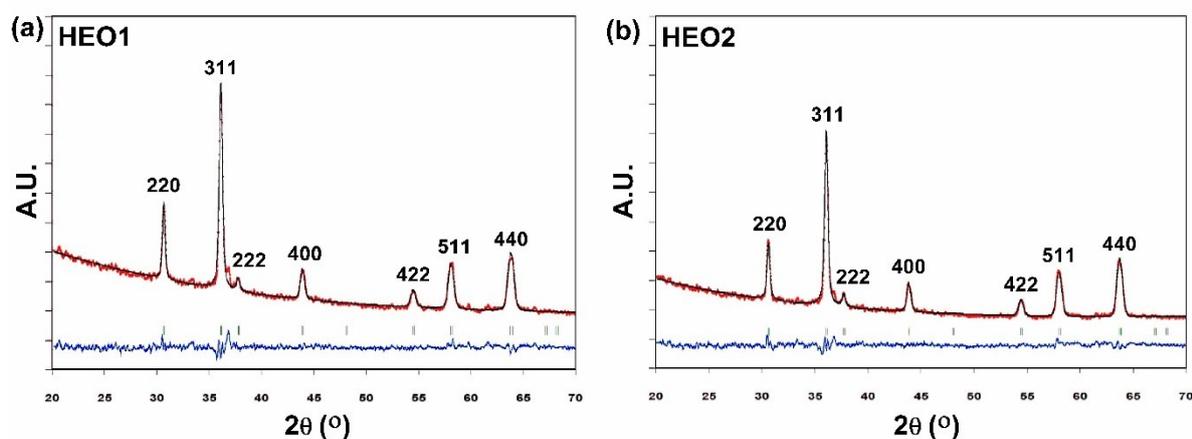


Fig. S1: Le-Bail fitting of the XRD pattern of HEO1 and HEO2

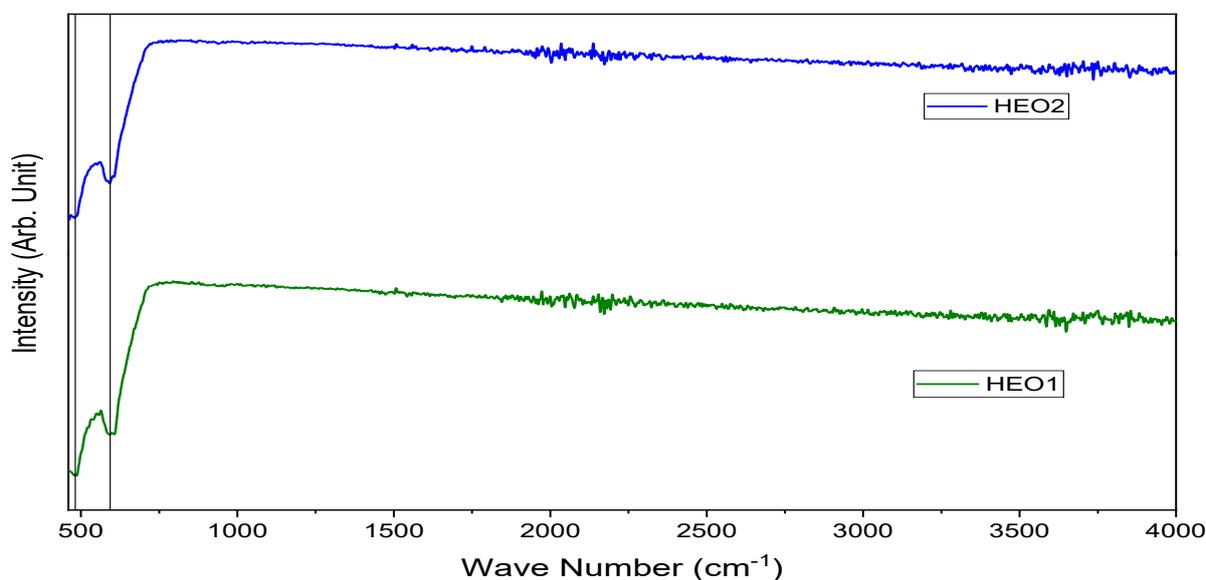


Fig. S2: FTIR spectra of the HEO1 and HEO2

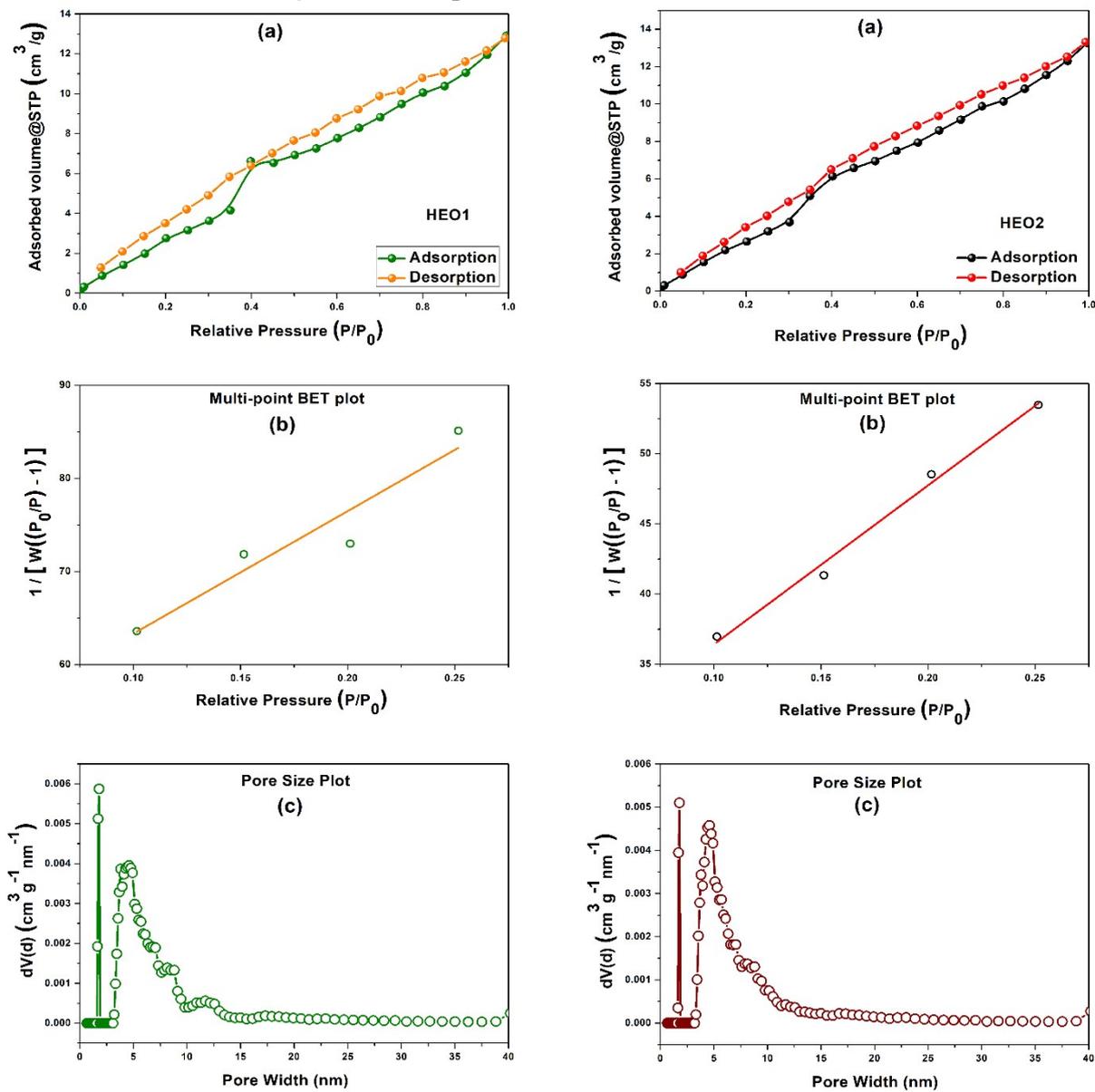


Fig. S3: BET plots of the HEO1 and HEO2.

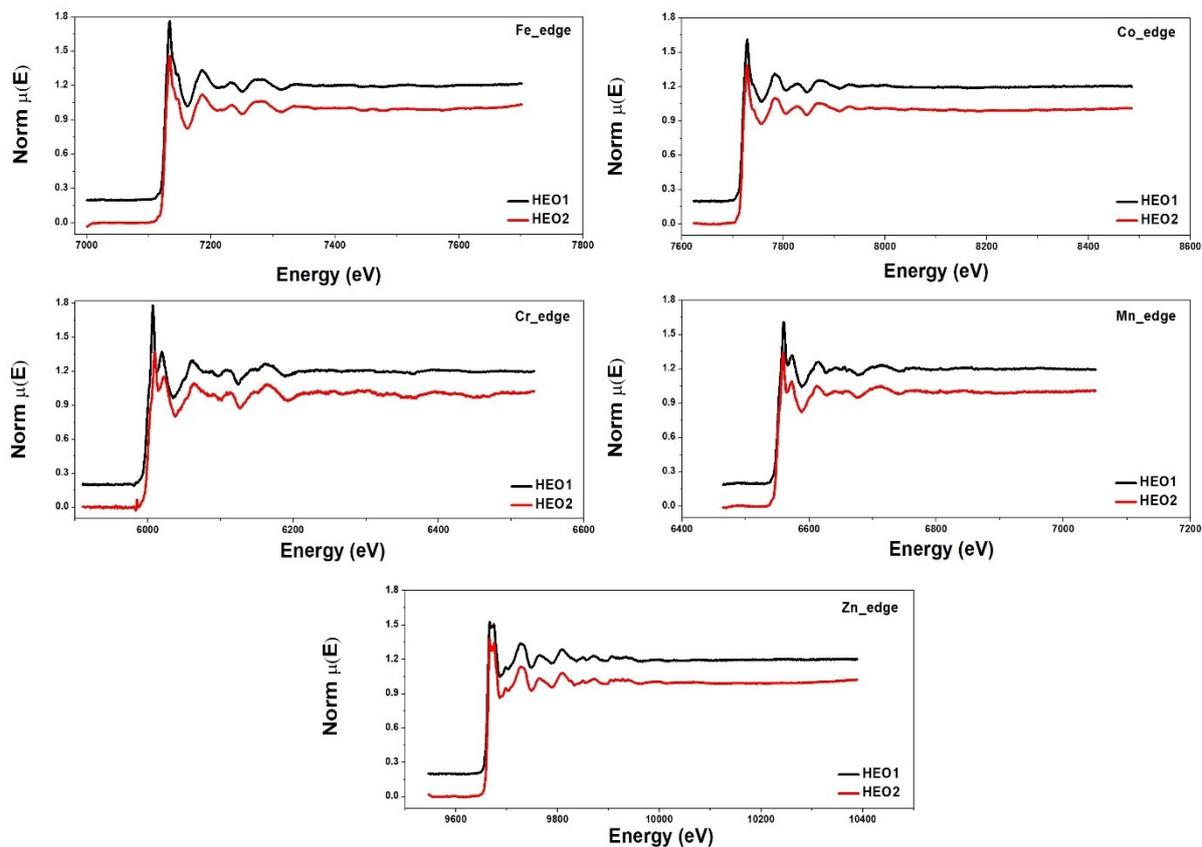


Fig. S4: EXAFS spectra of HEO1 and HEO2 samples at different element edges

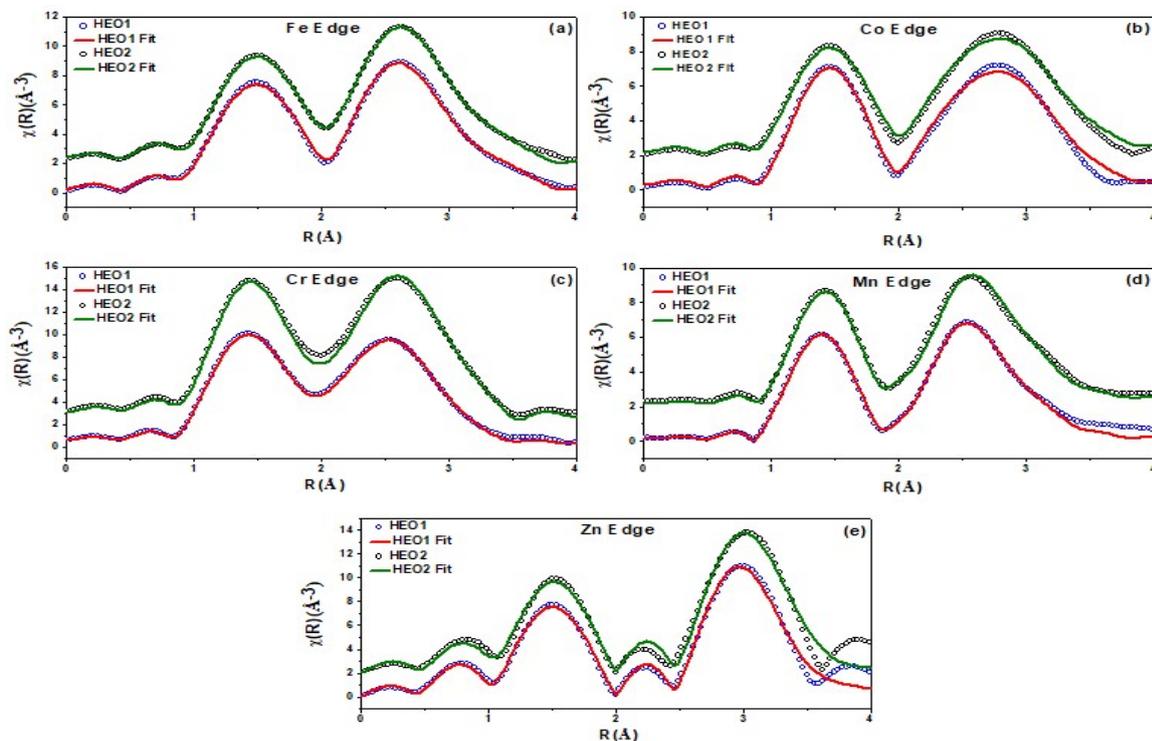


Fig. S5: Experimental $\chi(R)$ versus R plots of HEO1 and HEO2 samples at different element edges along with best fit theoretical curves.

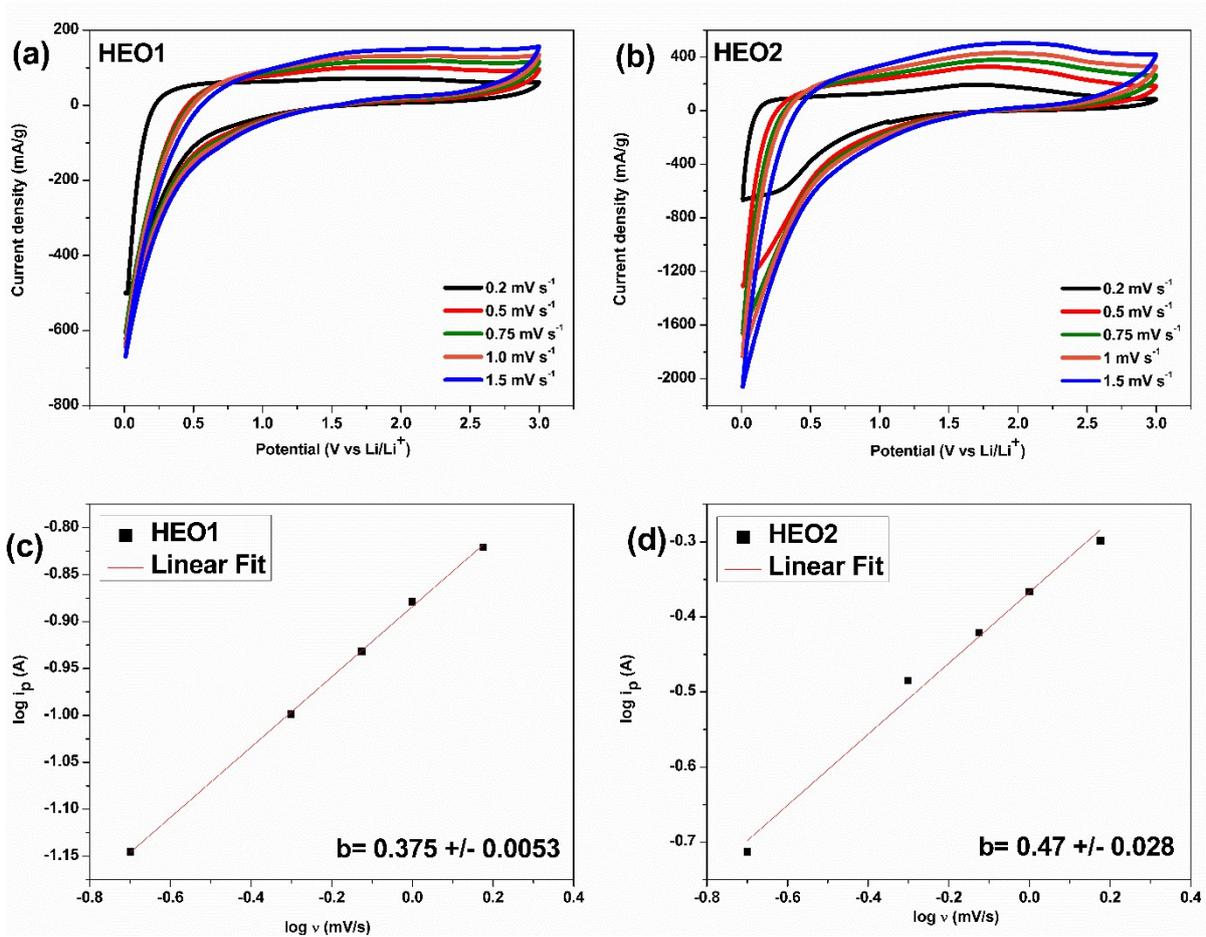


Fig. S6: CV plots of (a) HEO1 and (b) HEO2 at different scan rates. Log of anodic peak current versus log of scan rate plot for (c) HEO1 and (d) HEO2 samples

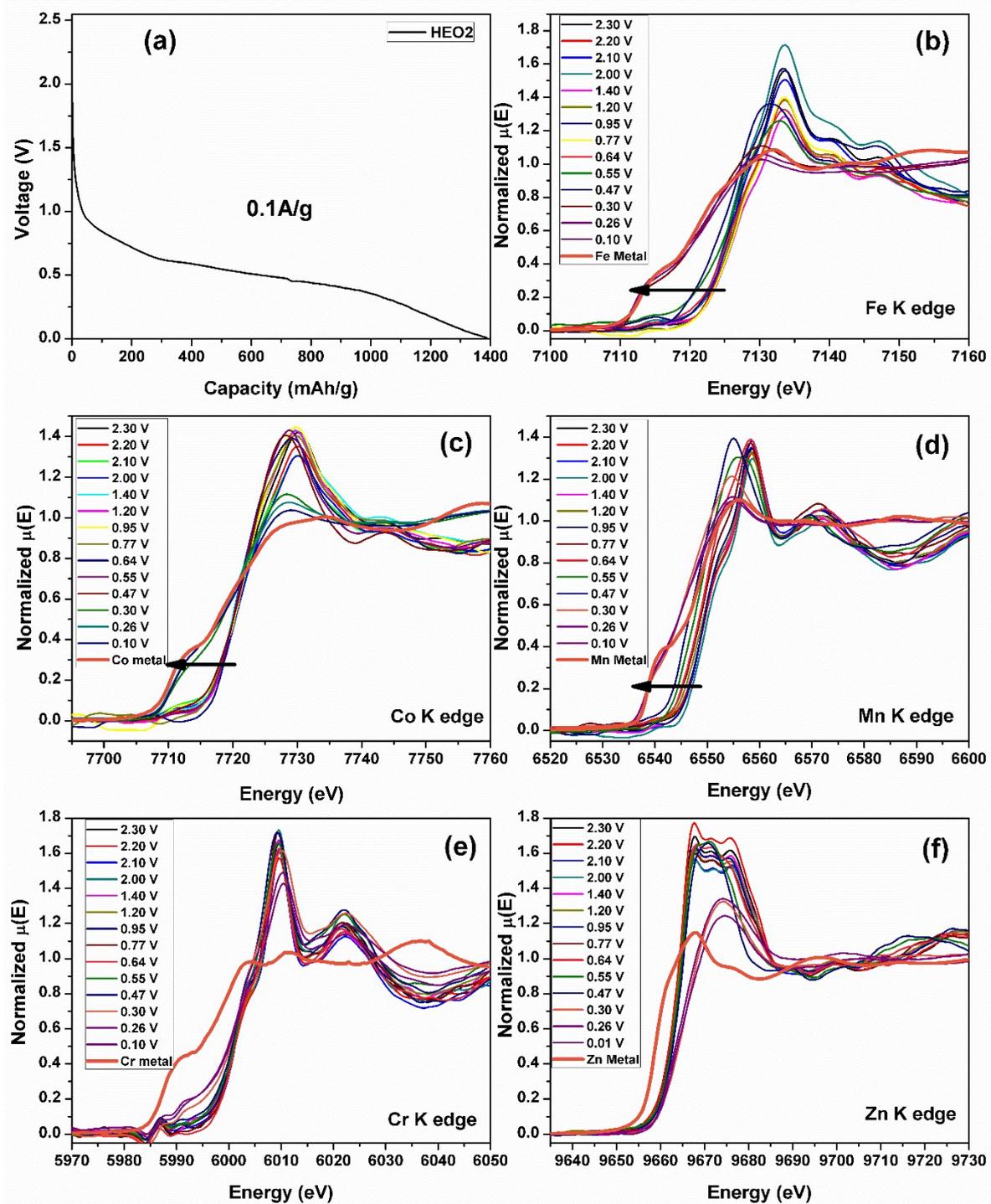


Fig. S7: (a) Voltage Profile during discharging of HEO2 anode at the rate of 0.1 A/g. (b)-(f) operando XANES plots during Lithiation of HEO2 at different element edges.

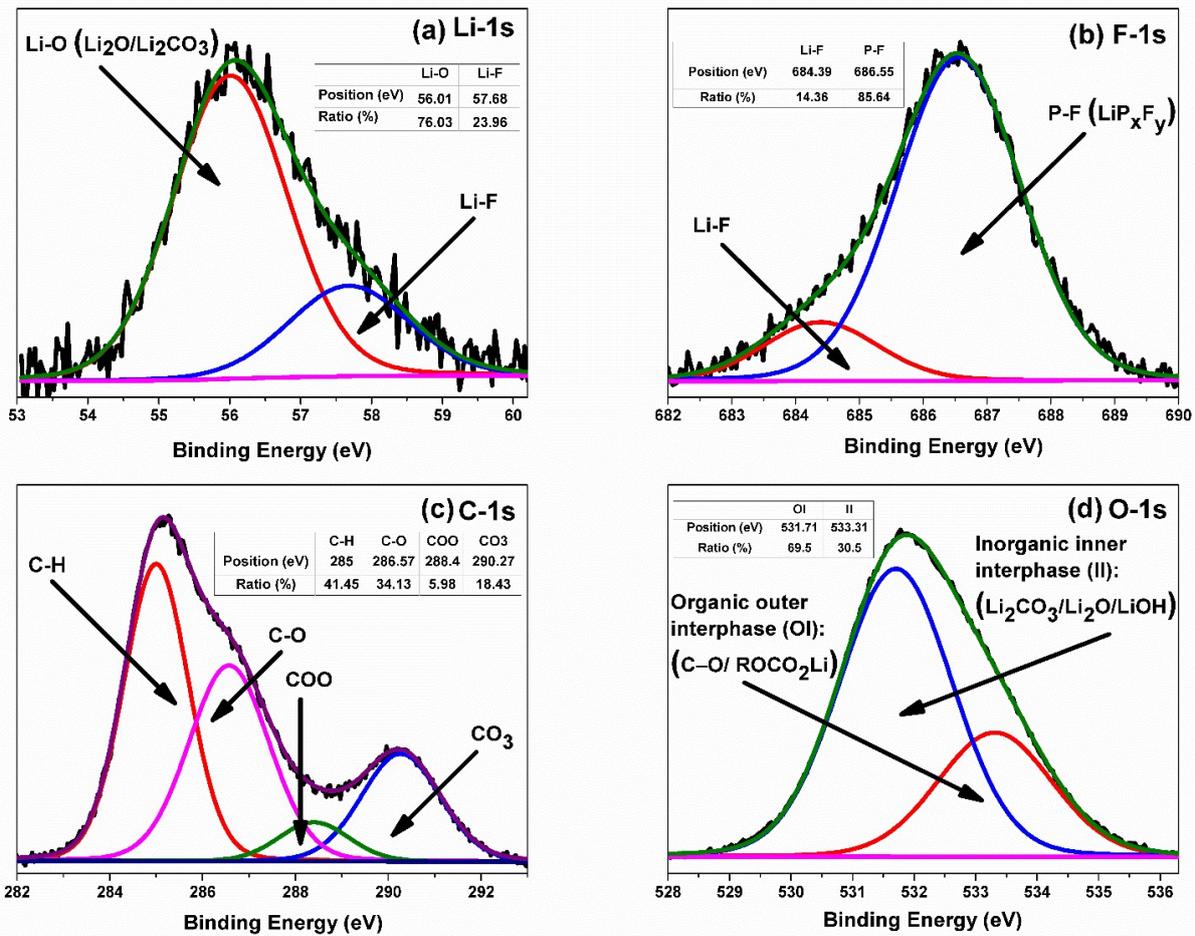


Fig. S8: Li 1s, F 1s, C 1s and O 1s XPS spectra of HEO2 anode before cycling

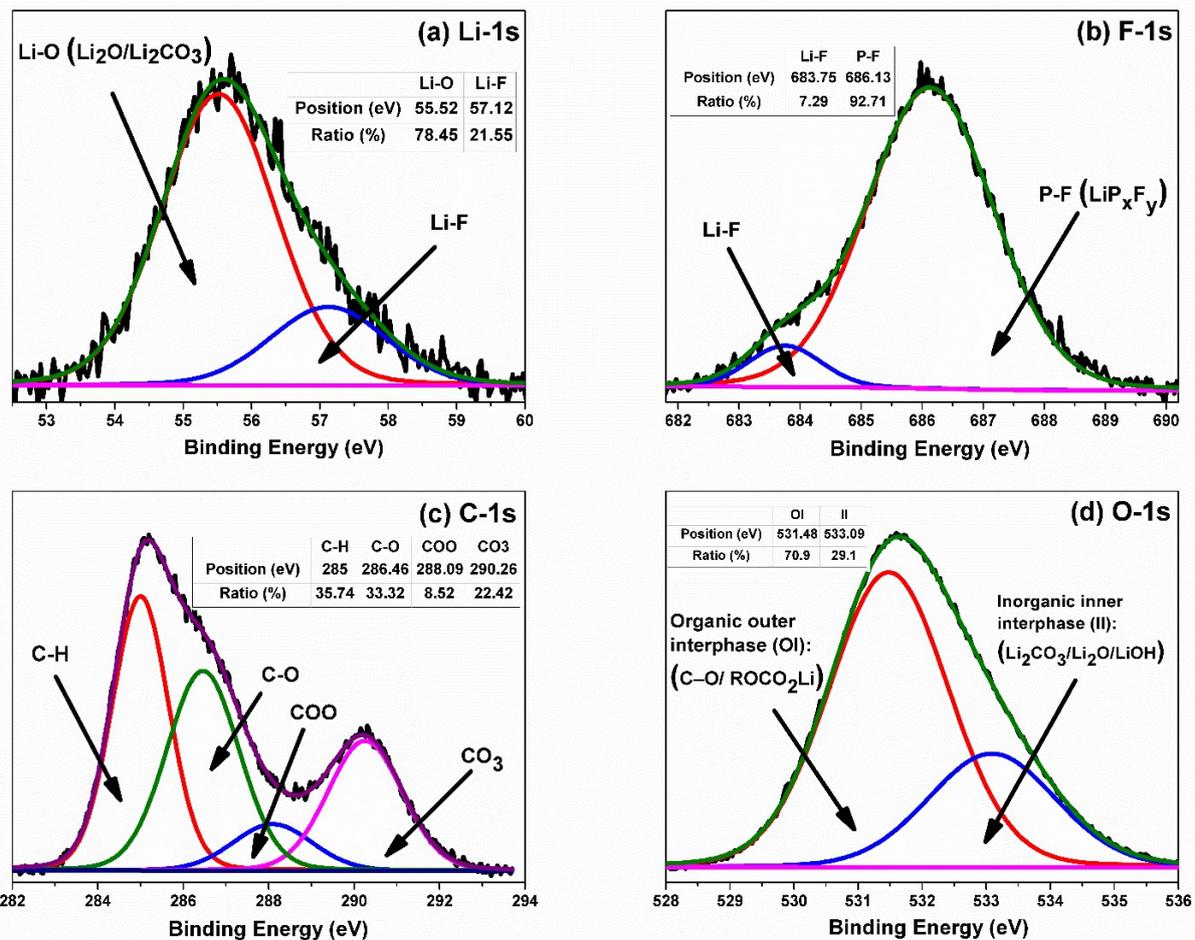


Fig. S9: Li 1s, F 1s, C 1s and O 1s XPS spectra of HEO2 anode after 100 cycles at 1 A/g current rate

Table S1: EXAFS Fitting Parameters of HEO1 and HEO2 samples at different metal K edges

Zn	HEO1			$R_{\text{factor}} = 0.0048, S_o^2 = 0.976$
Path	R (Å)	N	$\sigma^2 (\text{Å}^2)$	
Zn-O ₁	1.97±0.01	3.6±0.1	0.0041±0.0007	
Zn-TM _{oct}	3.47±0.01	12	0.0053±0.0006	
Zn-O ₂	3.41±0.05	12	0.0319±0.0061	
Zn-TM _{tet}	3.64±0.02	4	0.00013±0.0005	
Zn	HEO2			$R_{\text{factor}} = 0.0066, S_o^2 = 0.976$
Path	R (Å)	N	$\sigma^2 (\text{Å}^2)$	
Zn-O ₁	1.97±0.01	3.4±0.1	0.0034±0.0007	

Zn-TM_{oct}	3.48±0.01	12	0.0048±0.0006
Zn-O₂	3.42±0.03	12	0.0318±0.0080
Zn-TM_{tet}	3.63±0.01	4	0.00012±0.0009

Fe	HEO1			R_{factor} = 0.0016, So² =0.821
Path	R (Å)	N	σ² (Å²)	
Fe-O₁	2.00±0.01	5.9±0.3	0.0061±0.0009	
Fe-TM_{oct}	2.96±0.01	6	0.0056±0.0005	
Fe-TM_{tet}	3.49±0.01	6	0.0066±0.0006	
Fe-O₂	3.57±0.03	6	0.0274±0.0088	
Fe	HEO2			R_{factor} = 0.0021, So² =0.821
Path	R (Å)	N	σ² (Å²)	
Fe-O₁	2.00±0.01	5.1±0.3	0.0044±0.0004	
Fe-TM_{oct}	2.97±0.01	6	0.0052±0.0003	
Fe-TM_{tet}	3.49±0.02	6	0.0073±0.0007	
Fe-O₂	3.57	6	0.00274±0.0074	

Co	HEO1			R_{factor} = 0.0092, So²= 0.901
Path	R (Å)	N	σ² (Å²)	
Co-O₁	1.97±0.01	4.9±0.3	0.0071±0.0011	
Co-TM_{oct}	2.93±0.01	6	0.0105±0.0013	
Co-TM_{tet}	3.47±0.01	6	0.0063±0.0013	
Co-O₂	3.33±0.05	6	0.0306±0.0080	
Co	HEO2			R_{factor} = 0.0123, So²= 0.901
Path	R (Å)	N	σ² (Å²)	
Co-O₁	1.98±0.01	4.5±0.3	0.0072±0.0013	

Co-TM_{oct}	2.94±0.01	6	0.0105±0.0013
Co-TM_{tet}	3.48±0.01	6	0.0062±0.0013
Co-O₂	3.34±0.05	6	0.0283±0.0091

Cr	HEO1			R_{factor} = 0.0009, So² = 0.900
Path	R (Å)	N	σ² (Å²)	
Cr-O₁	1.95±0.01	5.1±0.2	0.0010±0.0005	
Cr-TM_{oct}	2.94±0.01	6	0.0040±0.0005	
Cr-TM_{tet}	3.50±0.02	6	0.0153±0.0019	
Cr-O₂	3.77±0.01	6	0.0010±0.0007	
Cr	HEO2			R_{factor} = 0.0052, So² = 0.900
Path	R (Å)	N	σ² (Å²)	
Cr-O₁	1.94±0.01	5.9±0.1	0.0010±0.0009	
Cr-TM_{oct}	2.93±0.01	6	0.0013±0.0008	
Cr-TM_{tet}	3.41±0.08	6	0.0166±0.0050	
Cr-O₂	3.77±0.05	6	0.0010±0.0009	

Mn	HEO1			R_{factor} = 0.0015, So² = 0.810
Path	R (Å)	N	σ² (Å²)	
Mn-O₁	1.90±0.01	5.7±0.4	0.0097±0.0005	
Mn-TM_{oct}	2.94±0.01	6	0.0105±0.0005	
Mn-TM_{tet}	3.32±0.01	6	0.0177±0.0014	
Mn-O₂	3.39±0.01	6	0.0011±0.0007	
Mn	HEO2			R_{factor} = 0.0070, So² = 0.810

Path	R (Å)	N	σ^2 (Å ²)
Mn-O ₁	1.90±0.01	5.9±0.3	0.0091±0.0010
Mn-TM _{oct}	2.94±0.01	6	0.0101±0.0015
Mn-TM _{tet}	3.32±0.02	6	0.0185±0.0035
Mn-O ₂	3.34±0.01	6	0.0012±0.0009

Table S2 Crystal field stabilization energy (CFSE) of the selected elements.

Ions	d _n	Tetrahedral (-Dq)	Octahedral (-Dq)
Cr ³⁺	3	3.56	12
Mn ³⁺	4	1.78	6
Fe ³⁺	5	0	0
Fe ²⁺	6	2.67	4
Co ³⁺	6	2.67	4
Co ²⁺	7	5.34	8
Zn ²⁺	10	0	0

Table S3: EIS Fitting parameters of fresh and cycled HEO1 and HEO2 electrodes

Parameters	HEO1	HEO2	HEO1 after 100 cycles at 0.1A/g	HEO2 after 100 cycles at 0.1A/g	HEO1 after 450 cycles at 1A/g	HEO2 after 450 cycles at 1A/g
R _{sol} (Ω)	4.45 ± 0.04	3.63 ± 0.06	4.06 ± 0.11	4.11 ± 0.11	4.70 ± 0.15	4.92 ± 0.12
Y ₀	(3.065 ± 1.085)×10 ⁻⁵	(2.89 ± 1.27)×10 ⁻⁵	(1.67 ± 1.15)×10 ⁻⁴	(1.63 ± 1.42)×10 ⁻⁴	(3.68 ± 0.37)×10 ⁻⁴	(2.27 ± 0.21)×10 ⁻⁴
α	0.7758 ± 0.0038	0.7574 ± 0.0067	0.5676 ± 0.0158	0.5819 ± 0.0088	0.5033 ± 0.011	0.5464 ± 0.0095
R _{ct} (Ω)	69.59 ± 0.69	294 ± 9.72	134.1 ± 25.2	47.35 ± 1.22	41.04 ± 1.53	37.25 ± 1.02
σ (Ω s ^{0.5})	36.95 ± 0.29	79.56 ± 1.33	332.27 ± 1.43	85.65 ± 1.45	18.62 ± 0.14	13.12 ± 0.07
C _{dl} (μF)	5.18 ± 0.62	6.28 ± 0.88	9.31 ± 1.54	4.91 ± 0.74	5.79 ± 0.93	4.32 ± 0.68

D (cm² s⁻¹)	(1.62 ± 0.02)×10 ⁻¹²	(3.49 ±0.12)×10 ⁻¹³	(2.00 ±0.17)×10 ⁻¹⁴	(3.01 ±0.10)×10 ⁻¹³	(6.37 ±0.09)×10 ⁻¹²	(1.28 ±0.01)×10 ⁻¹¹
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