Supplementary Information (SI) for Sustainable Energy & Fuels.

High-Stability High-Capacity Aqueous Sodium-ion Battery Using High Entropy Oxide Cathode: Intercalation Vs Capacitive Sodium Charge Storage

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Supplementary Information

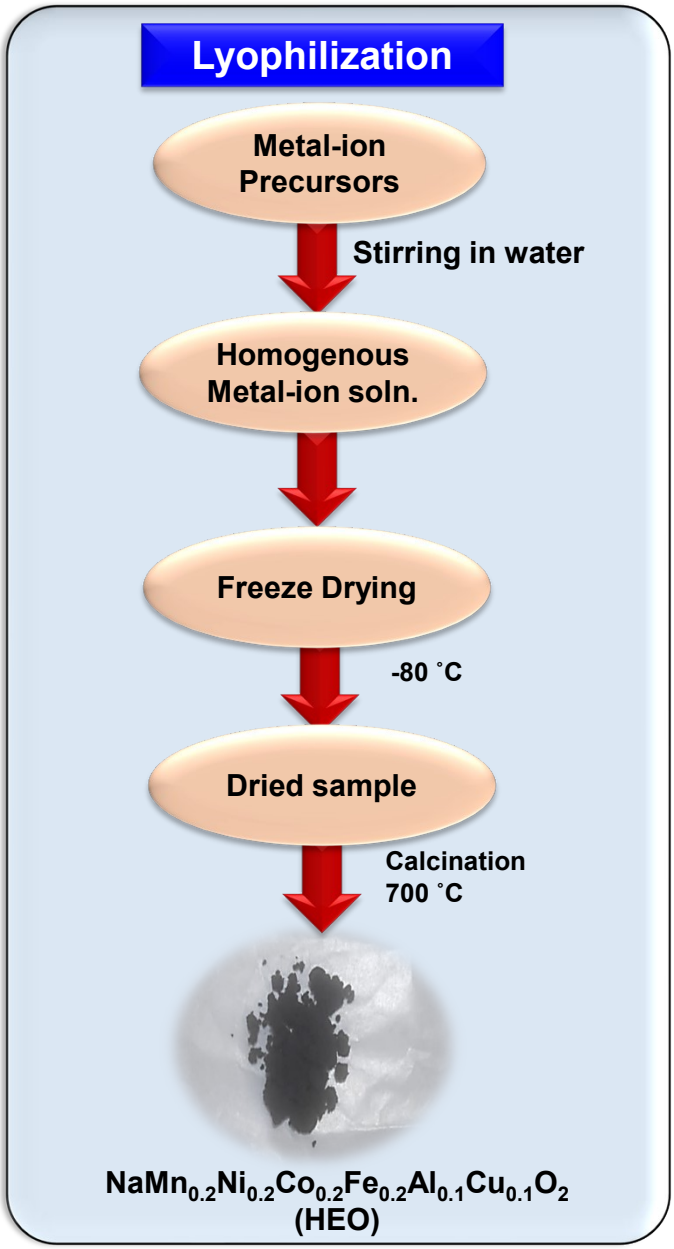

Fig. S1. Schematic representation of various steps involved in the synthesis of the HEO cathode.

Calculation of Configurational Entropy for $NaMn_{0.2}Ni_{0.2}Co_{0.2}Fe_{0.2}Al_{0.1}Cu_{0.1}O_2$:

The configurational entropy (S_{conf}) of the high entropy metal oxide is calculated as shown below using Boltzmann's equation (after applying Sterling approximation):

$$S_{conf} = -R\left(\left(\sum_i x_i \ln x_i\right)_{\text{cation site}} + \left(\sum_j x_j \ln x_j\right)_{\text{anion site}}\right)$$

	Element	Molar concentration	Mole fraction
Cation	Na	1	1/2 = 0.5
	Mn	0.2	0.2/2 = 0.1
	Fe	0.2	0.2/2 = 0.1
	Co	0.2	0.2/2 = 0.1
	Ni	0.2	0.2/2 = 0.1
	Cu	0.1	0.1/2 = 0.05
	Al	0.1	0.1/2 = 0.05
Total		2	
Anion	O	2	2/2 =1
Total		2	

S_{conf} = -R [(0.50 ln 0.50) + (0.10 ln 0.10) + (0.10 ln 0.10) + (0.10 ln 0.10) + (0.10 ln 0.10) + (0.05 ln 0.05) + (0.05 ln 0.05)] $_{\text{cation site}}$ + [(1 ln 1)] $_{\text{anion site}}$

S_{conf} = 1.57R

The estimated configurational entropy is 1.57

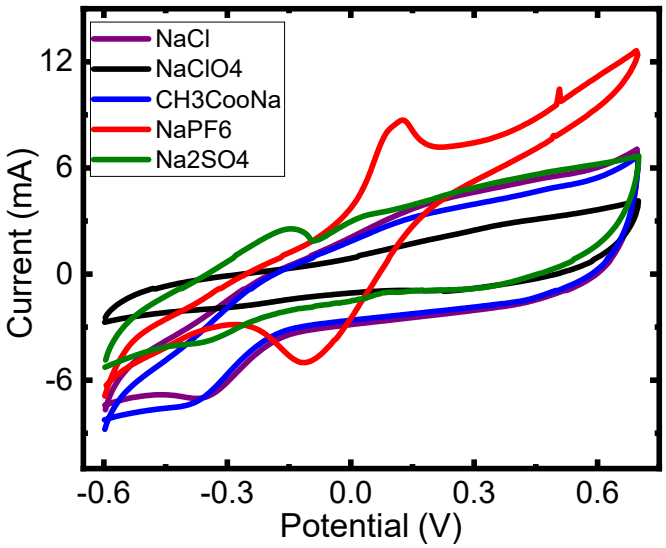

Fig. S2. Cyclic voltammograms of the HEO electrode at different scan rates recorded in (a) 1M NaCl (b) 1M $NaClO_4$ (c) 1M $NaPF_6$, (d) 1M CH_3COONa and (e) 1M Na_2SO_4 electrolytes.

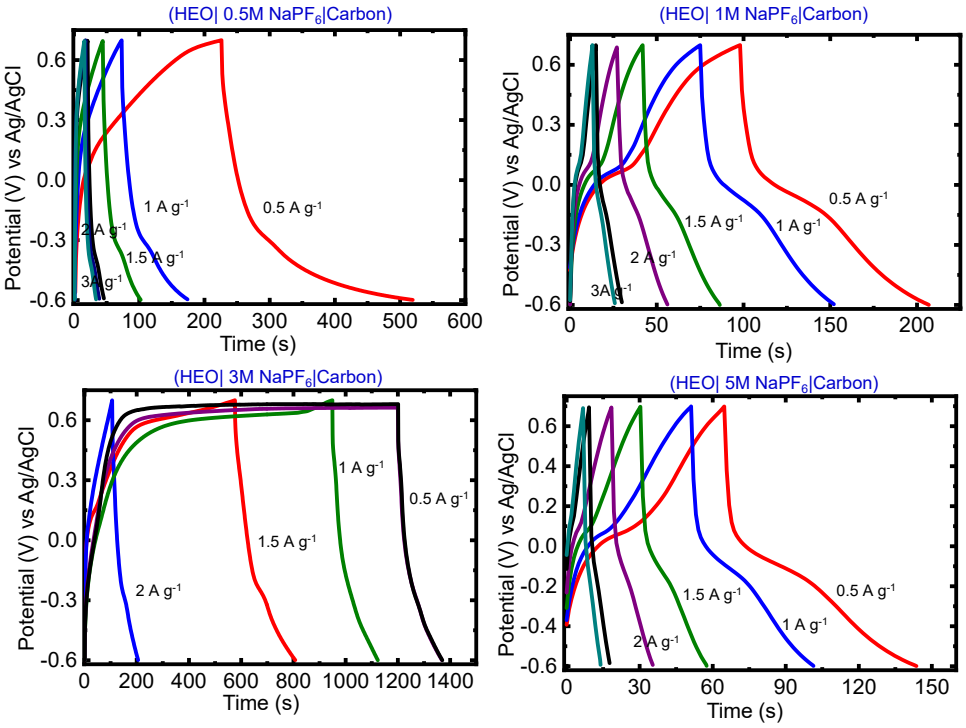

Fig. S3. GCD profiles of the HEO cathode at different scan rates recorded in different concentrations of $NaPF_6$.

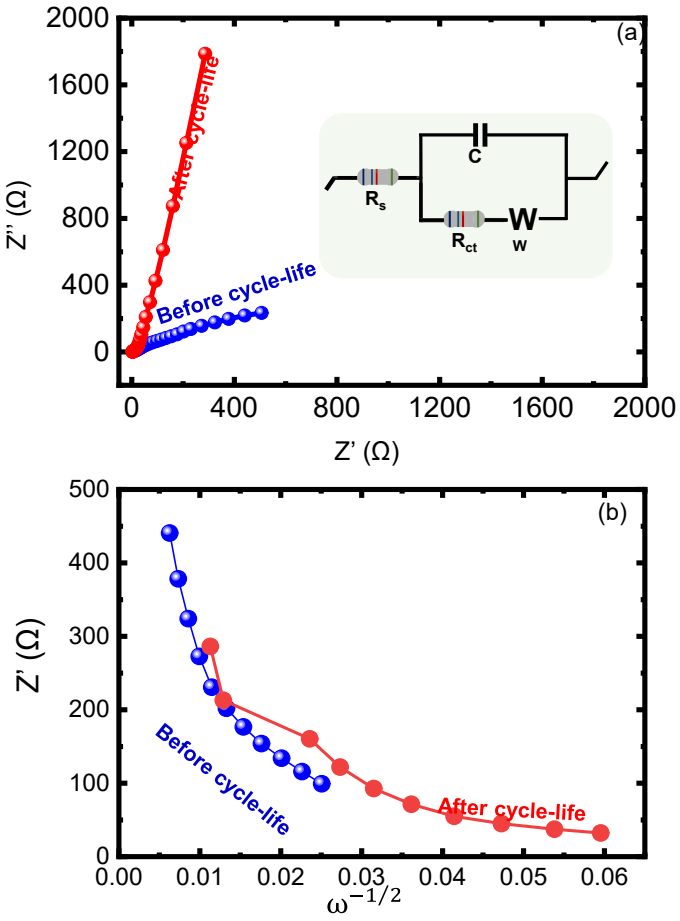

Fig. S4. (a) Nyquist plot (b) Linear plot of Z' vs $\omega^{-1/2}$ constructed for the aqueous sodium-ion battery before and after cycle

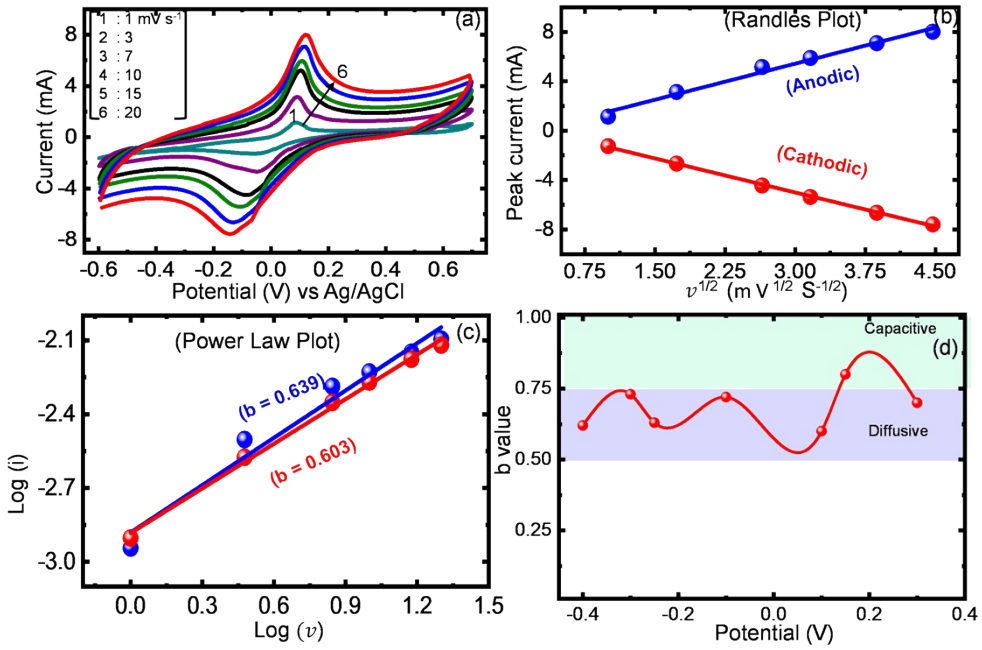

Fig. S5. (a) CV profile recorded for the HEO cathode (b) Randles plot (c) Power law plot (d) Linear plot of b-value vs. potential (v)

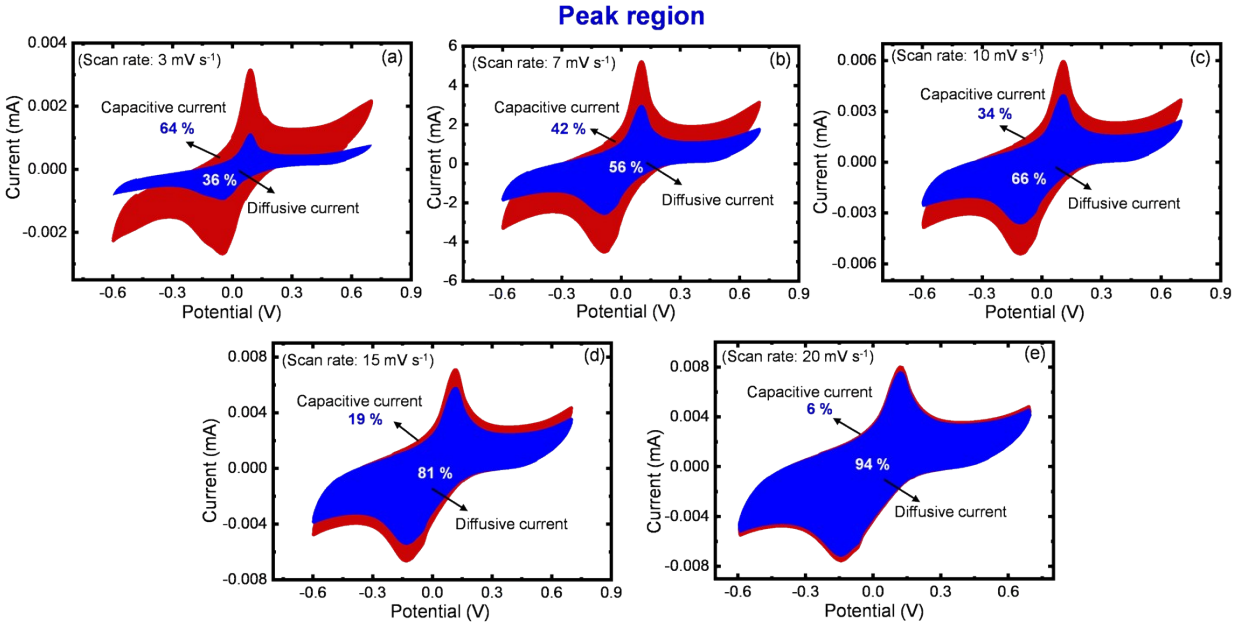

Fig. S6. Representative CV profiles at various scan rates marked with the capacitive and the diffusive contributions at peak potential region for the HEO cathodes.

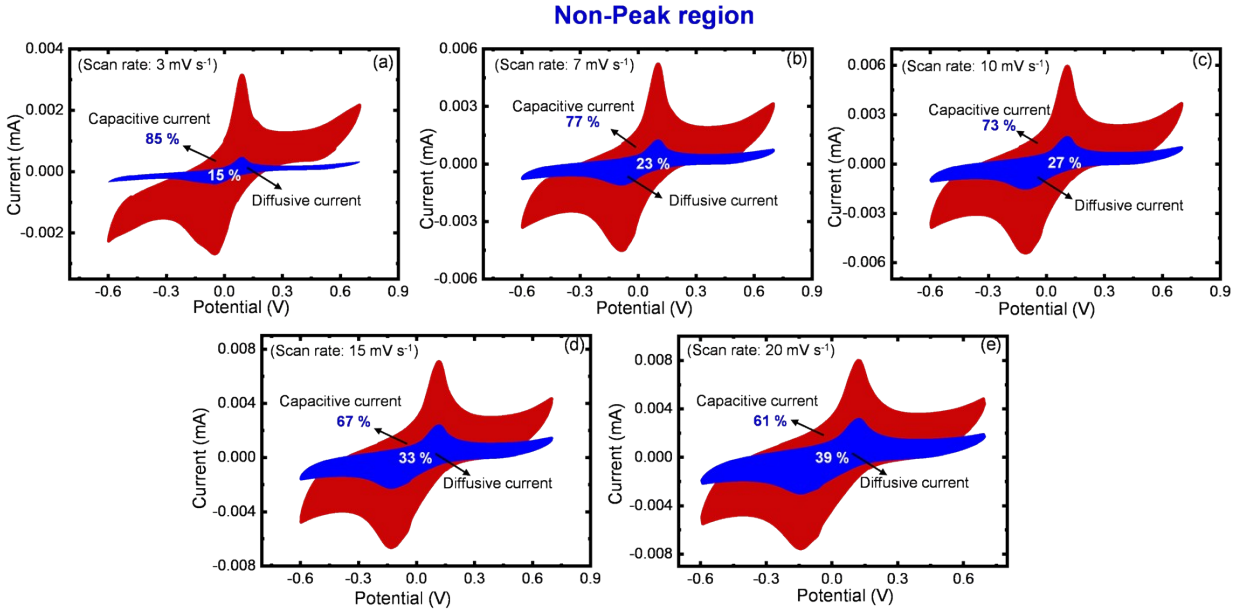

Fig. S7. Representative CV profiles at various scan rates marked with the capacitive and the diffusive contributions at non-peak potential region for the HEO cathodes.

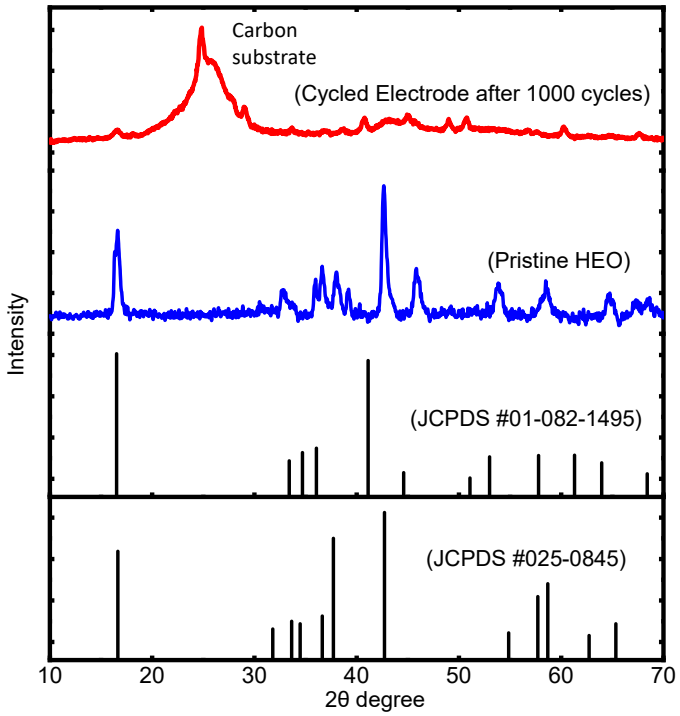

Fig. S8. Post-mortem XRD pattern of the cycled electrode after 1000 cycles.

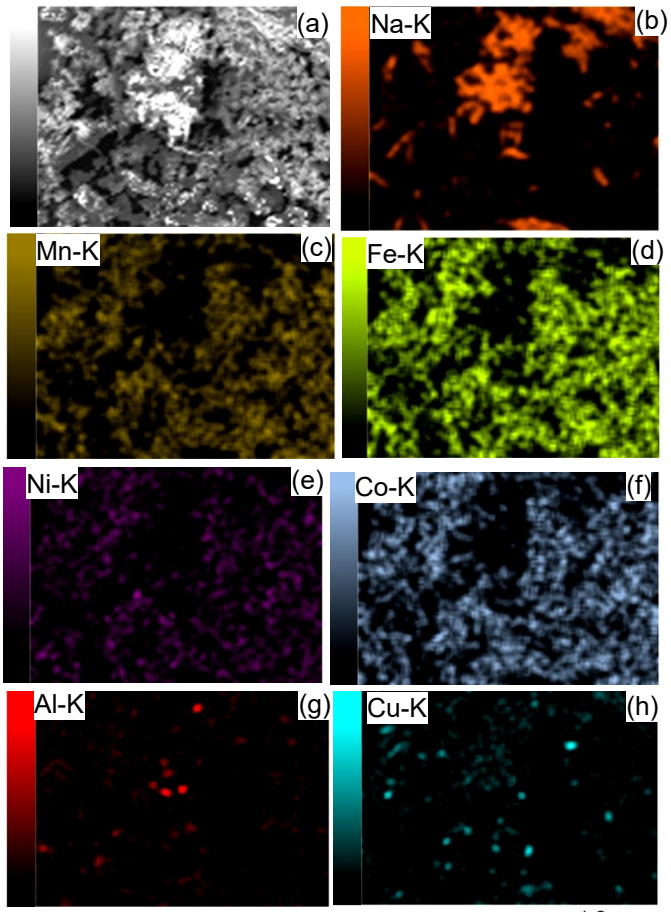

Fig. S9. (a) Representative area examined for the elemental mapping of (b) Na-K, (c) Mn-K, (d) Fe-K, (e) Ni-K, (f) Co-K, (g) Ni-K and (h) Cu-K.

Calculation of the charge compensation for the HEO cathode

Cathode: $NaMn_{0.2}Ni_{0.2}Co_{0.2}Fe_{0.2}Al_{0.1}Cu_{0.1}O_2$

$$x(+1) + \sum_i x_i(V_i) + 2(-2) = 0$$

$$1+((0.2*4)+(0.2*2)+(0.2*3)+(0.2*3)+(0.1*2)+(0.1*3))-4 = 0$$

where V_i are TM oxidation states and the oxygen are assumed to be +2 and −2, respectively. Based on the calculation, the overall charge of the HEO cathode is consistent with charge neutrality.