

## Supporting Information for “Materials for Aqueous Sodium Ion Batteries: Cation Mobility in Zinc Hexacyanoferrate Electrode”, by

Miguel A. Oliver-Tolentino, Juvencio Vazquez-Samperio, Roman Cabrera-Sierra, Edilso Reguera

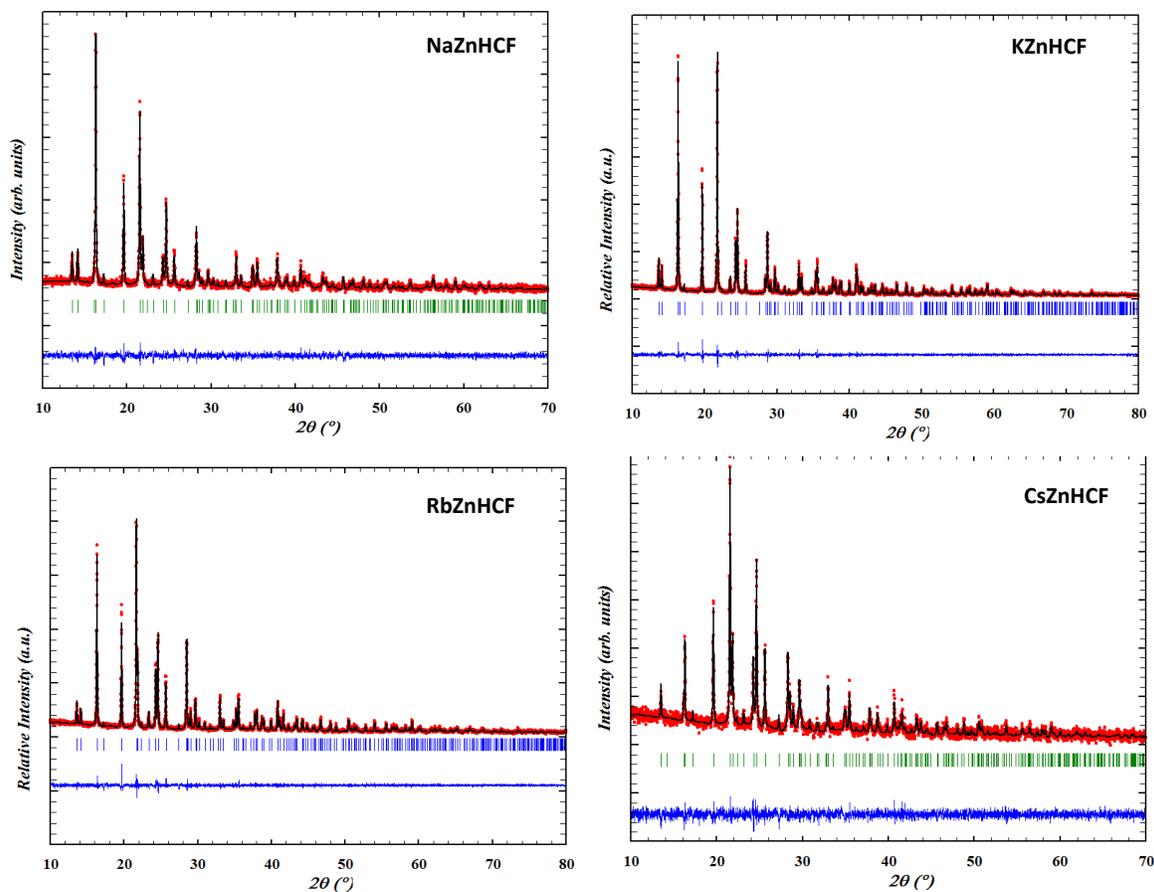


Figure S1. Powder X-ray Diffraction, with a Le Bail profile fitting for the materials under study, the index pattern is in agreement with: NaZnHCF (#PDF 01-074-1430), KZnHCF (#PDF 01-086-2067), RbZnHCF (#ICSD 157851) and CsZnHCF (#PDF 01-077-0077).

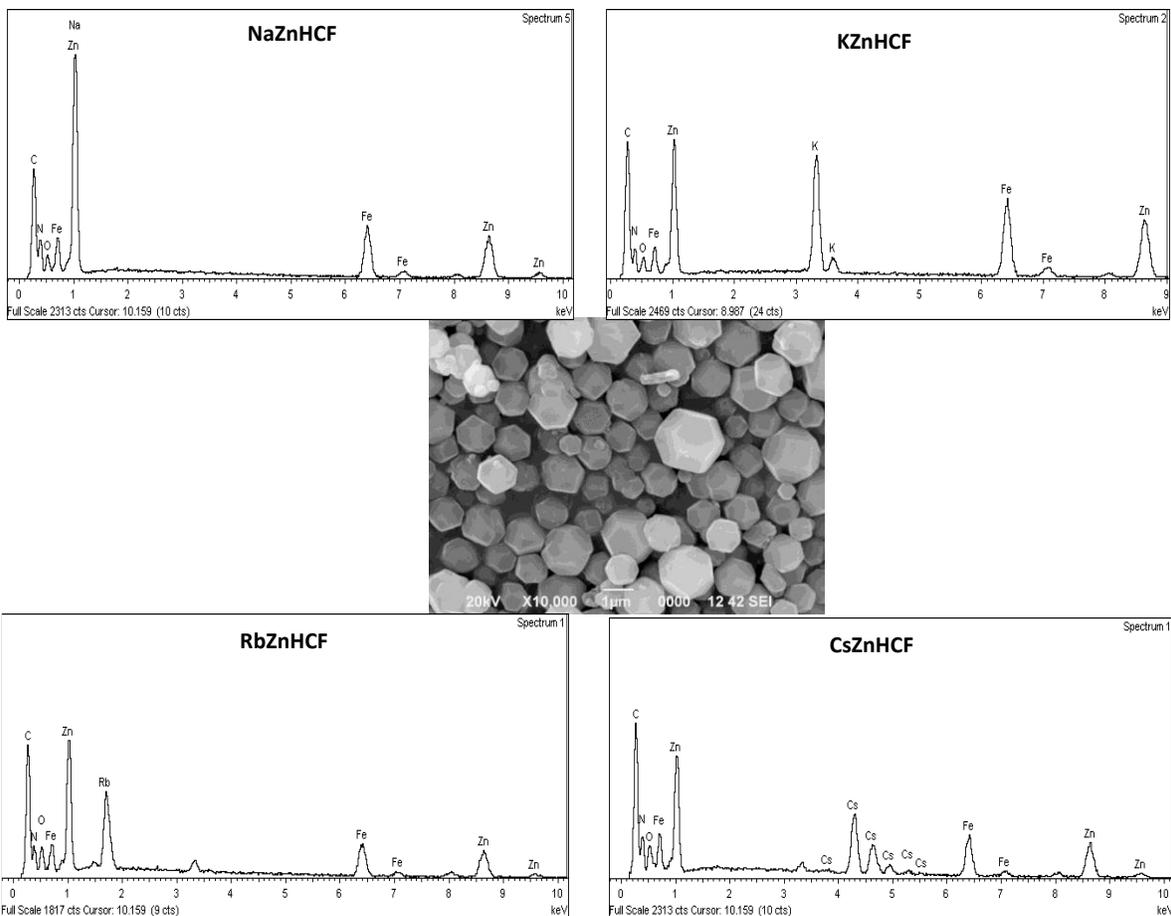


Figure S2. EDS spectra for the four considered compositions of zinc hexacyanoferrate, and a typical SEM micrography. These materials crystallize with a rhombohedral unit cell with the Zn atom coordinated to four N ends from CN ligands while the iron atom has an octahedral coordination to the C end, which is typical of hexacyanoferrates.

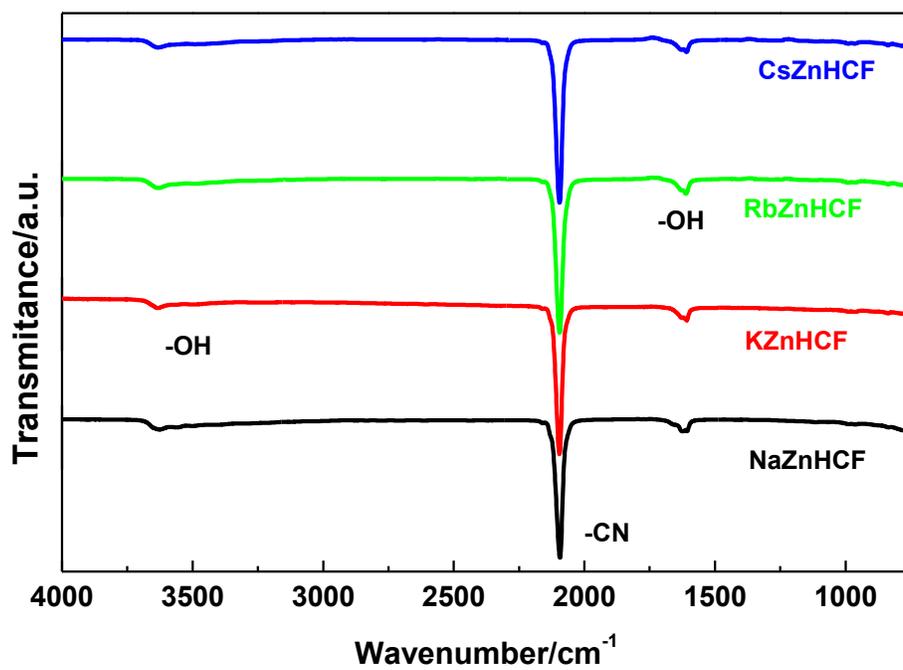


Figure S3. Typical IR spectra for the series of Zinc Hexacyanoferrates under study in this contribution.

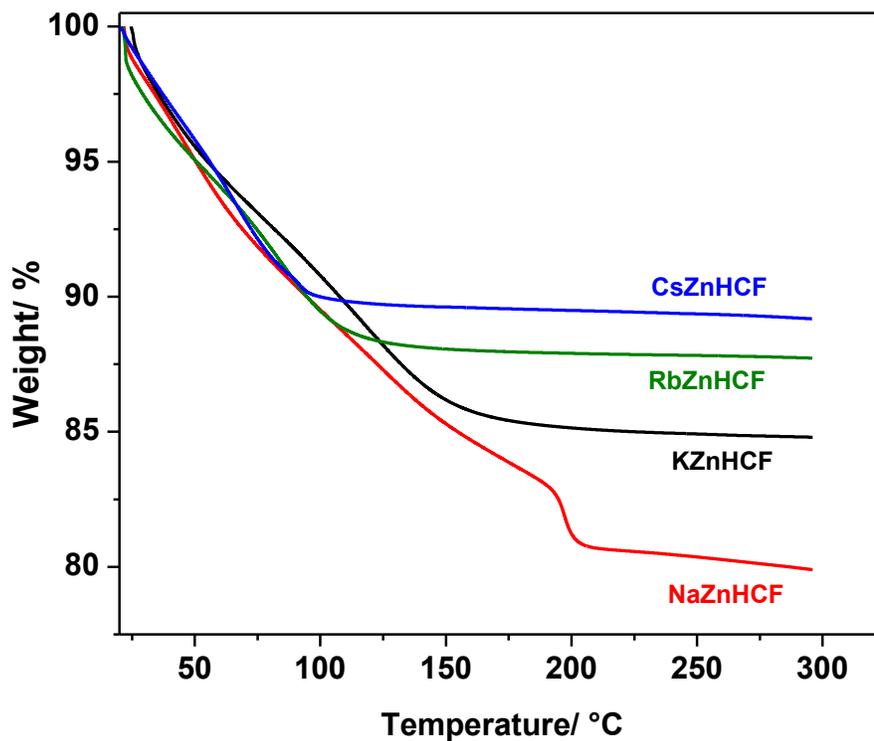


Figure S4. Thermogravimetric curves for the series of Zinc Hexacyanoferrates. The exchangeable cation (Na, K, Rb, Cs) polarizing power determines the temperature of dehydration. The TGA shows the temperature necessary for the evolution of weakly bonded and coordinated water molecules, which depend on the polarizing power for the cation inside the structure, modulating the distance between the water molecule dipole moment and charge center in cation. These temperature, in Kelvin, follows the order: Na(473) > K(436) > Rb(390) > Cs(370).

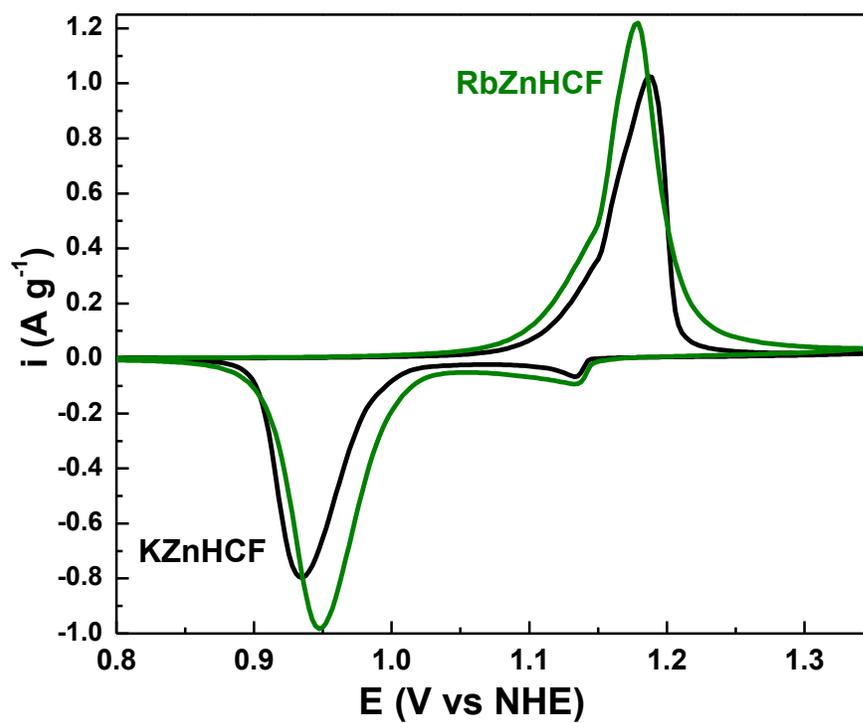
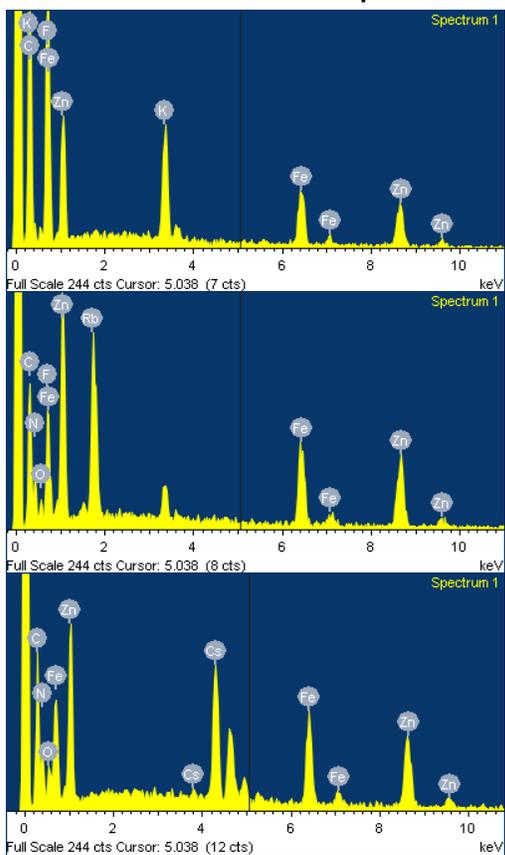


Figure S5. Cyclic Voltammetry after 6 cycles of KZnHCF and RbZnHCF  $\text{NaNO}_3$  ( $1 \text{ mol L}^{-1}$ ) at  $1 \text{ mV s}^{-1}$ .

Before to electrochemical experiments



After 6 CV cycles in NaNO<sub>3</sub> as electrolyte

KZnHCF

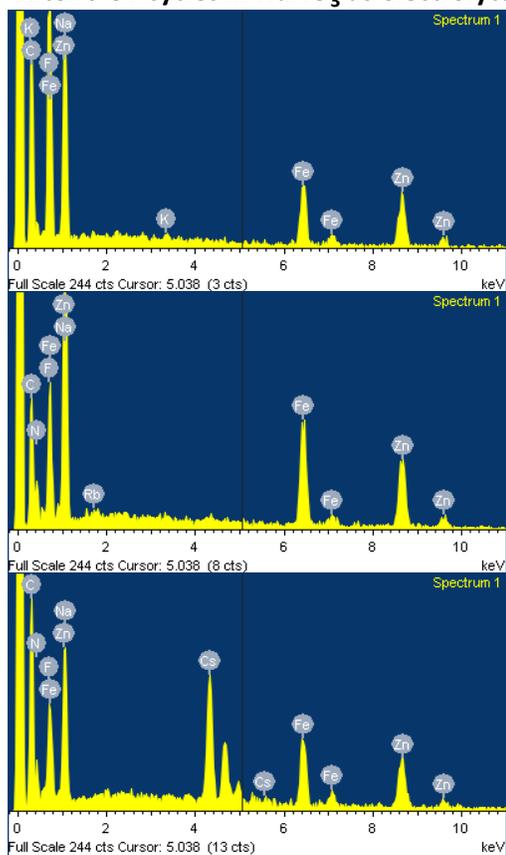


Figure S6. EDS spectra recorded before and after electrochemical process.

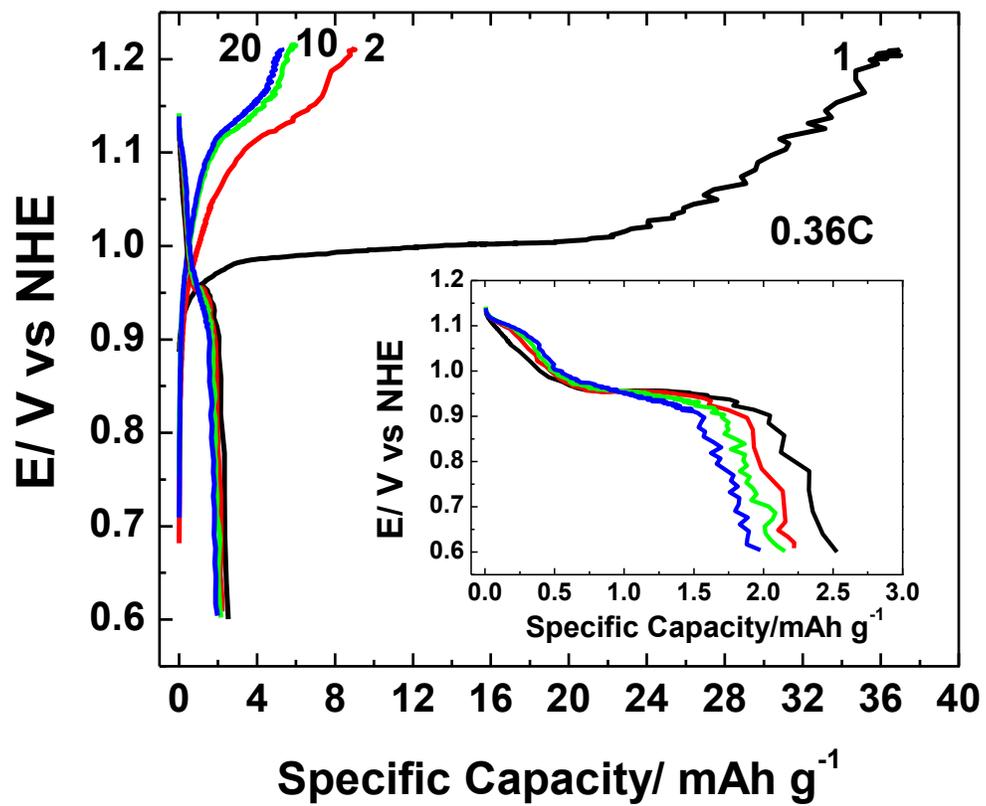


Figure S7. Galvanostatic charge/discharge profile for NaZnHCF in NaNO<sub>3</sub> solution at 0.36 C

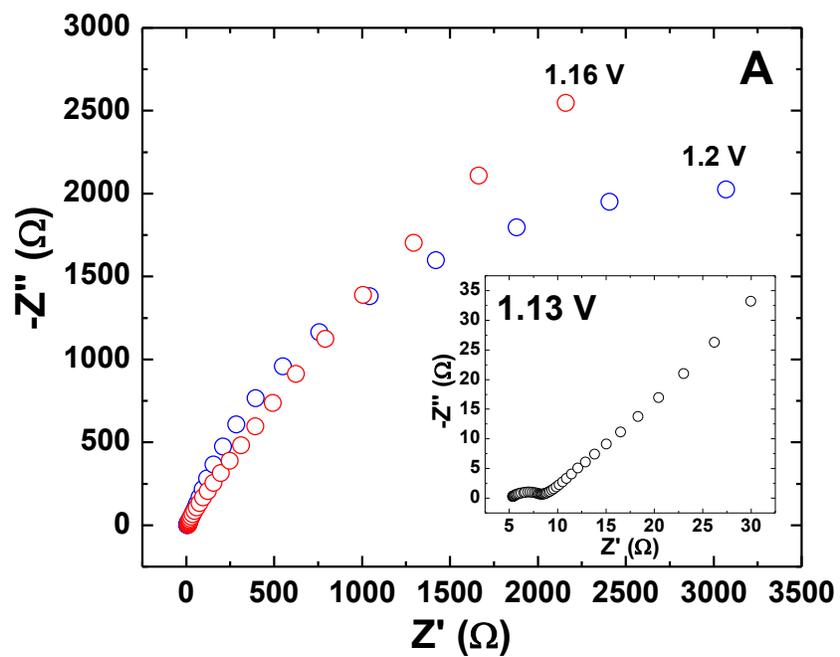


Figure S8. Nyquist plot of NaZnHCF in NaNO<sub>3</sub> at different potential during oxidation process.

Table S1. Parameters obtained by fitting the EIS diagrams of CsZnHCF in NaNO<sub>3</sub> using the equivalent circuit shown in Figure 5c and Boukamp program.

E (V)	R <sub>S</sub>	CPE <sub>F</sub>		R <sub>CT</sub>	CPE <sub>IO</sub>		R <sub>IO</sub>	T	
		Y <sub>o</sub> x 10 <sup>3</sup>	n		Y <sub>o</sub> x 10 <sup>3</sup>	n		Y <sub>o</sub> x 10 <sup>3</sup>	B
0.7	6.33	0.586	0.722	2.47	57.1	0.69	5.14	27.3	1.96
0.81	6.08	1.44	0.603	2.65	73.16	0.74	1.04	104.3	1.89
0.95	5.98	3.542	0.519	2.84	31.92	0.88	0.35	63.37	1.13
0.93	6.02	3.225	0.558	3.61	29.72	0.86	0.66	48.9	1.16
0.8	5.97	1.98	0.596	3.28	31.52	0.76	2.08	38.81	1.51