SUPPLEMENTARY INFORMATION

Figure S1. MgCl₂(aq) electrolytes after galvanostatic cycling of (a) NiHCFe (b) MgNiHCFe and (c) MgₓNiᵧHCFe

Figure S2. X-ray diffraction of porous NiHCFe electrodes comprising of 80% active material, 10% carbon black and 10% PVDF binder, casted onto graphite substrate. No significant change in lattice parameter or crystal structure is seen even after degradation of the active material during galvanostatic cycling in MgCl₂(aq).
2. **Canonical ensemble analysis of a NiHCFe framework intercalated with Mg$^{2+}$ ions to determine the fraction of Ni$^{2+}$ ions that can be substituted by Mg$^{2+}$**

For a given supercell of size $n \times n \times n$, we have $N$ Ni and $N$ Mg atoms ($N = n^3/2$) in the fully intercalated configuration for NiHCFe. To calculate the fraction of Mg ions that can substitute Ni ions during intercalation, at equilibrium, we compare the pristine configuration, i.e., all Mg atoms in the interstitial sites, with swapped configurations, where $s$ Ni atoms in the host sites are exchanged with $s$ Mg atoms in the interstitials. The degree of swapping $s$ can vary from 1 to $N$. We make the following assumptions:

i) Any Ni atom can be swapped with any Mg atom with the same probability

ii) The energy difference between the pristine and swapped structure arising because of multiple swaps is an integer multiple of the energy difference between a singly swapped structure and the pristine structure: $\Delta E_{s\text{ swaps}} = s \Delta E_{1\text{ swap}}$.

The microcanonical partition function for this system is given by: $Q = \sum_{S=0}^{N} \binom{N}{s}^2 \exp \left(-\frac{s\Delta E}{kT}\right)$. The probability of a configuration with $s$ swaps can thereby be calculated as $P(s) = \binom{N}{s}^2 \exp \left(-\frac{s\Delta E}{kT}\right)/Q$. The expectation value of the number of swaps as a fraction of total number of Ni or Mg atoms finally gives the substitution or swap fraction: $X_{\text{swap}} = \sum_{s=0}^{N} sP(s)/N$.

![Figure S3. Variation of the degree of swaps with energy difference between swapped and pristine structures, calculated for difference supercell sizes.](image)

Fig. S3 shows the degree of swapping as a function of energy difference between swapped and pristine structures, for supercell sizes starting from 2×2×2 to 8×8×8. Fig. 8 in the main manuscript uses the values from 4×4×4 supercell.
Figure S4. Total density of states for (a) pristine configuration, (b) one-swap configuration and (c) $K_2MgFe(CN)_6$

Figure S5. Experimental current vs voltage characteristic for NiHCFe and MgHCFe powders pressed into pellets. NiHCFe shows an ohmic response whereas MgHCFe acts as an insulator, as predicted from the DOS plots in Fig. S4.