Supporting information for

Alkoxy-functionalized Ionic Liquid Electrolytes: Understanding Ionic Coordination of Calcium Ion Speciation for the Rational Design of Calcium Electrolytes

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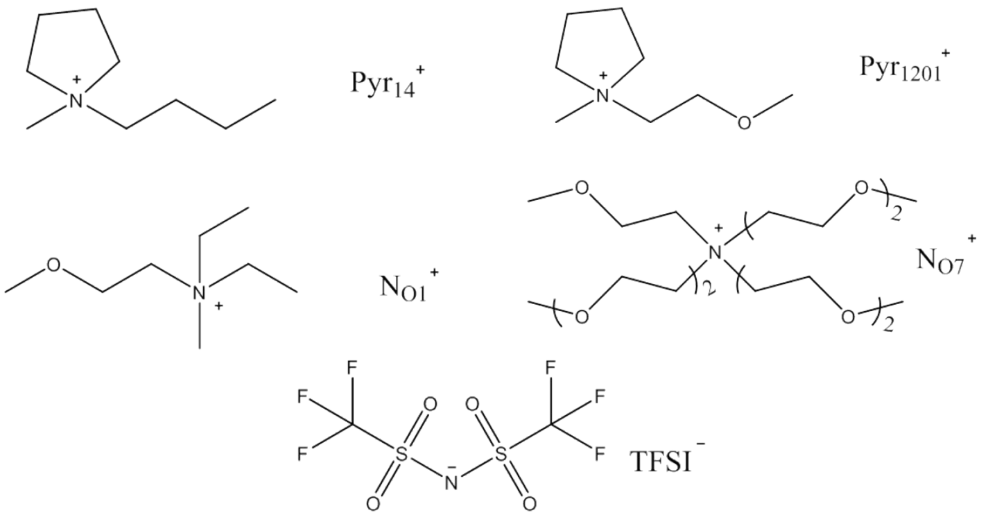


Scheme S1. Chemical structure and abbreviation of component ions of alkoxyfunctionalized ILs investigated in this study.

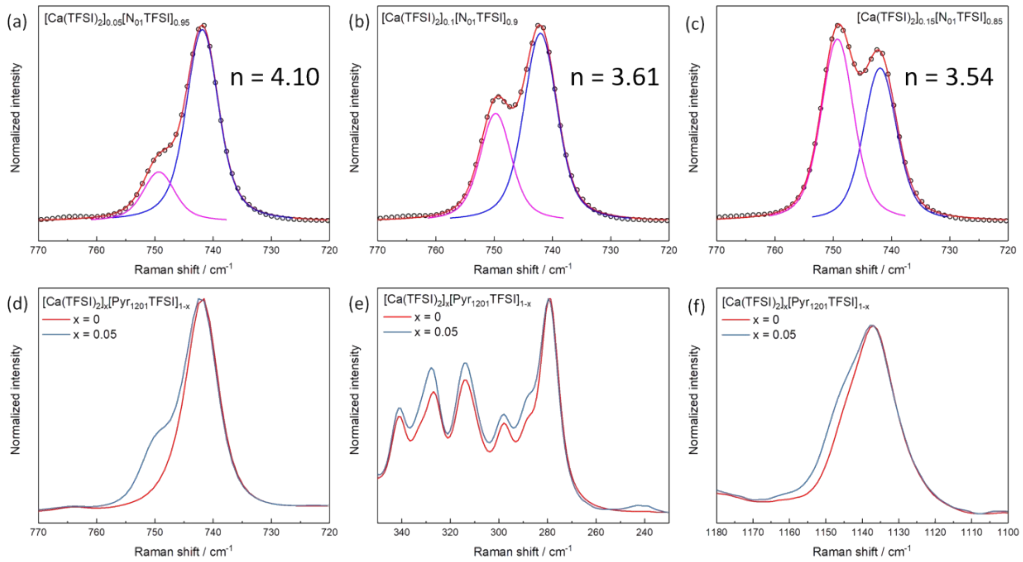


Figure S1. (a-c) Fits of the Raman spectra of $[Ca(TFSI)_2]_x[N_{01}TFSI]_{1-x}$ electrolytes in the 720-770 cm^{-1} spectral region. The circle markers correspond to the experimental data, the red lines are the fit curves while the blue and magenta lines are the fit peaks attributed to the different $TFSI^-$ species. The average number (n) of $TFSI^-$ anion coordinated per Ca^{2+} cation is shown in insets. (d-f) Raman spectra of $[Ca(TFSI)_2]_x[Pyr_{1201}TFSI]_{1-x}$.

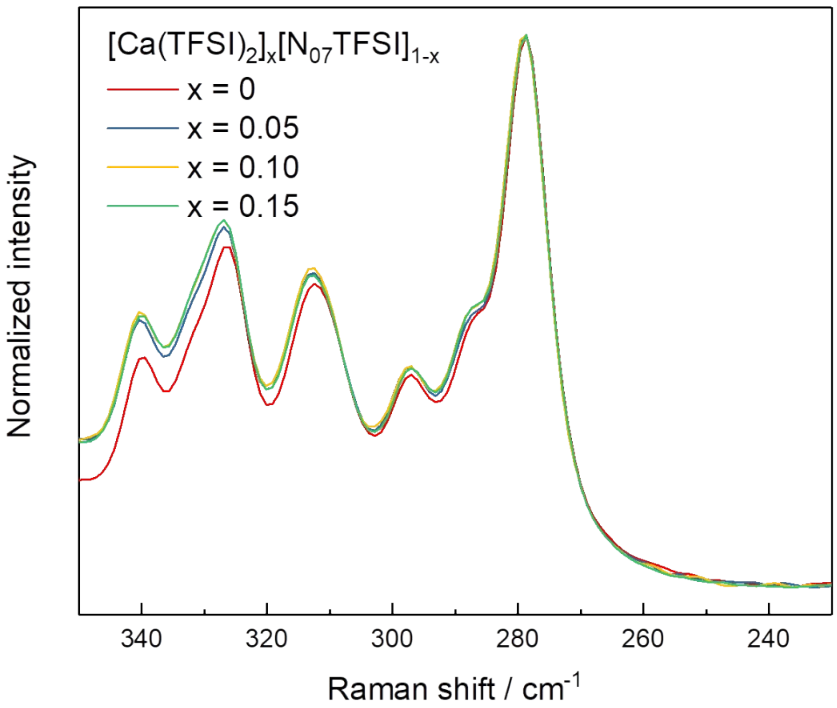


Figure S2. Raman spectra of $[Ca(TFSI)_2]_x[N_{07}TFSI]_{1-x}$ electrolytes in the 230-350 cm^{-1} spectral region.

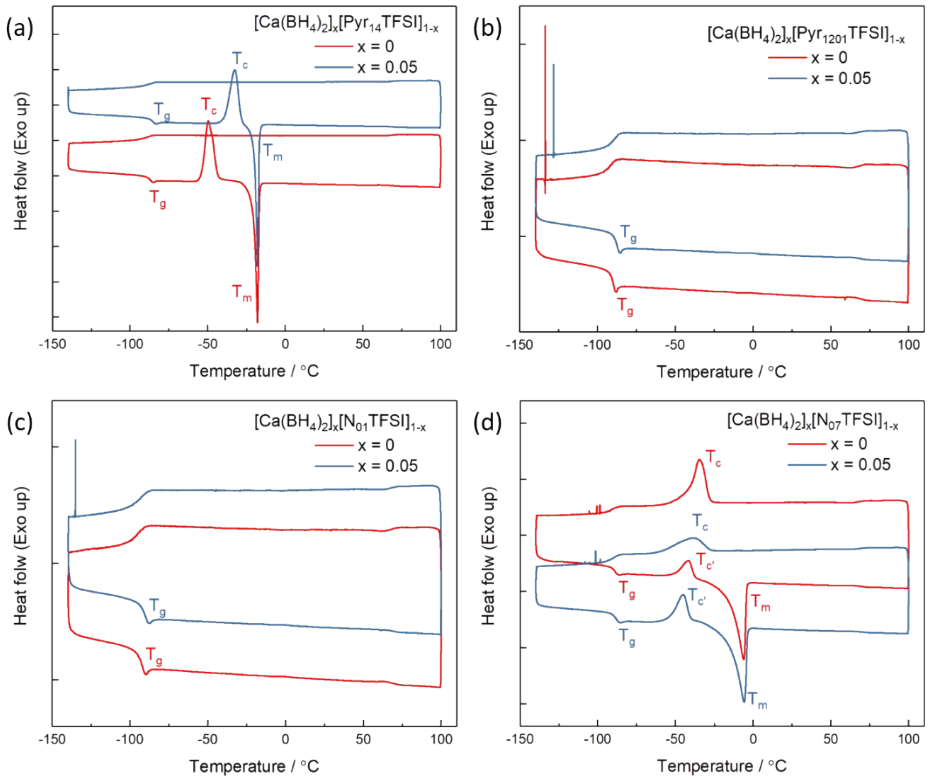


Figure S3. DSC thermograms of $[Ca(BH_4)_2]_x[Pyr_{14}TFSI]_{1-x}$ (a), $[Ca(BH_4)_2]_x[Pyr_{1201}TFSI]_{1-x}$ (b), $[Ca(BH_4)_2]_x[N_{01}TFSI]_{1-x}$ (c), and $[Ca(BH_4)_2]_x[N_{07}TFSI]_{1-x}$ (d). Scan rate: 5 °C·min^{-1}. The traces are vertically shifted for clarity, all tick marks on the left axis correspond to heat flow differences of 0.25 W·g^{-1}.

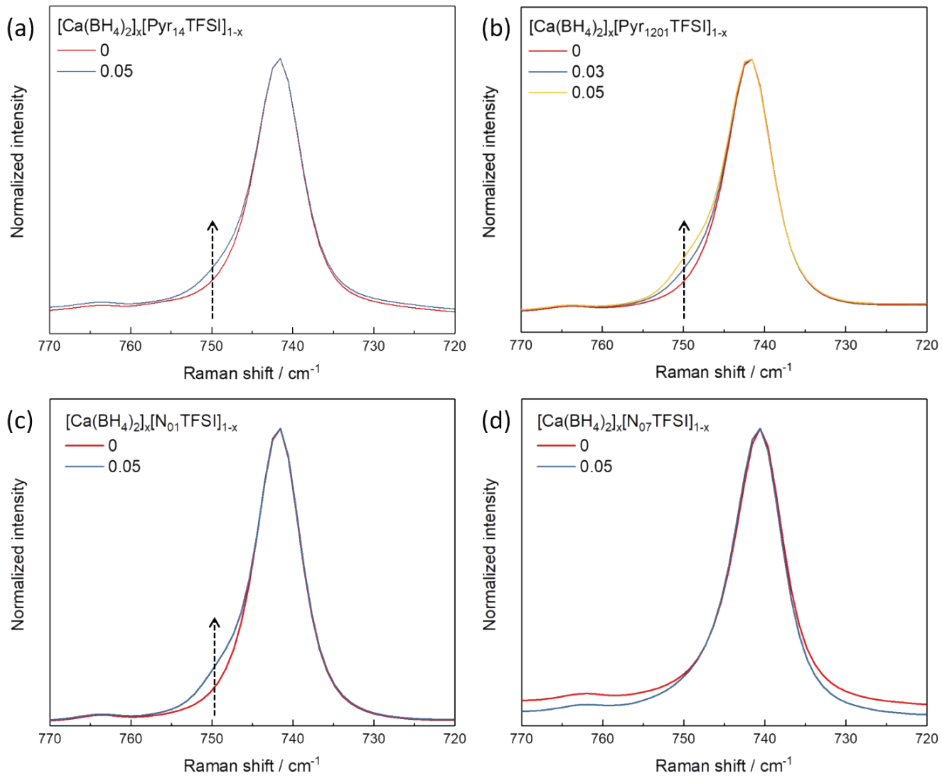
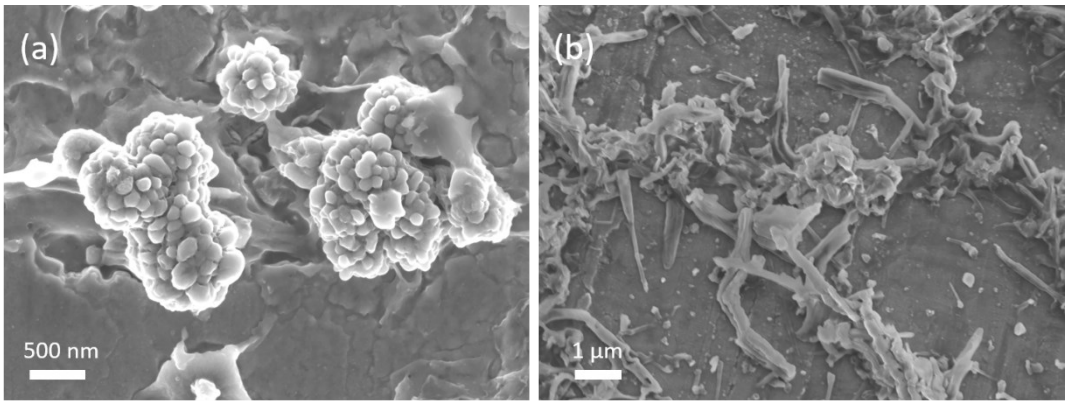


Figure S4. Raman spectra of $[Ca(BH_4)_2]_x[Pyr_{14}TFSI]_{1-x}$ (a), $[Ca(BH_4)_2]_x[Pyr_{1201}TFSI]_{1-x}$ (b), $[Ca(BH_4)_2]_x[N_{01}TFSI]_{1-x}$ (c), and $[Ca(BH_4)_2]_x[N_{07}TFSI]_{1-x}$ (d) in the 720-770 cm^{-1} spectral region.



Atomic %	$[Ca(BH_4)_2]_{0.05}[N_{01}TFSI]_{0.95}$	Atomic %	$[Ca(BH_4)_2]_{0.05}[N_{07}TFSI]_{0.95}$
O	24.9	C	57.4
Ca	22.1	O	24.0
F	21.4	Ca	15.2
S	21.1	F	2.0
C	10.4	S	1.4

Figure S5. The SEM image of the deposits obtained from $[Ca(BH_4)_2]_{0.05}[N_{01}TFSI]_{0.95}$ (a) and $[Ca(BH_4)_2]_{0.05}[N_{07}TFSI]_{0.95}$ (b) electrolytes. Element content determined by EDX are indicated. Three electrode Swagelock cells using Whatman GF/D glass fiber separators. Working electrode: Cu, counter and reference electrodes: Ca.

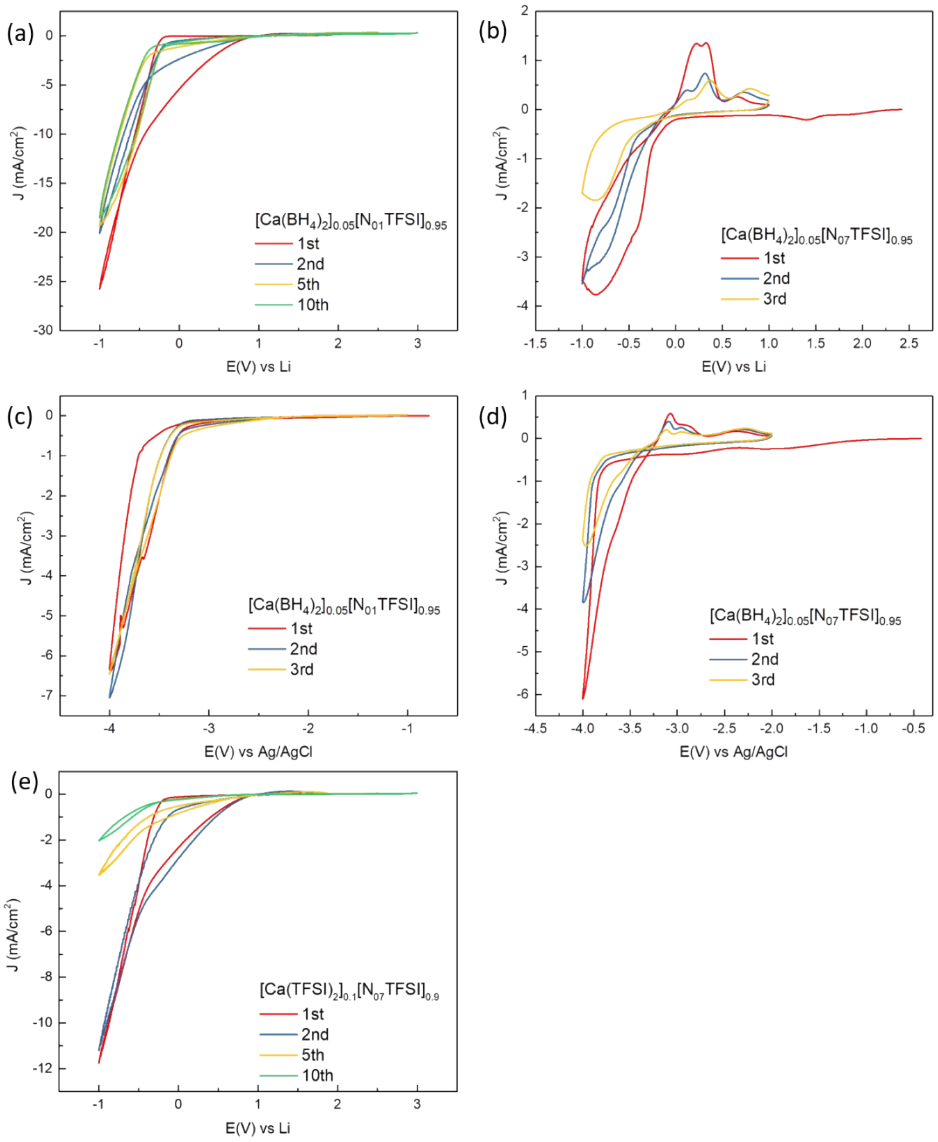


Figure S6. Cyclic voltammograms of the Ca deposition and dissolution reaction in $[Ca(BH_4)_2]_{0.05}[N_{01}TFSI]_{0.95}$ and $[Ca(BH_4)_2]_{0.05}[N_{07}TFSI]_{0.95}$ electrolytes using Li (a, b) or leakless Ag/AgCl (c, d) reference electrode. (e) Cyclic voltammograms of $[Ca(TFSI)_2]_{0.1}[N_{07}TFSI]_{0.9}$ electrolytes using Li reference electrode.

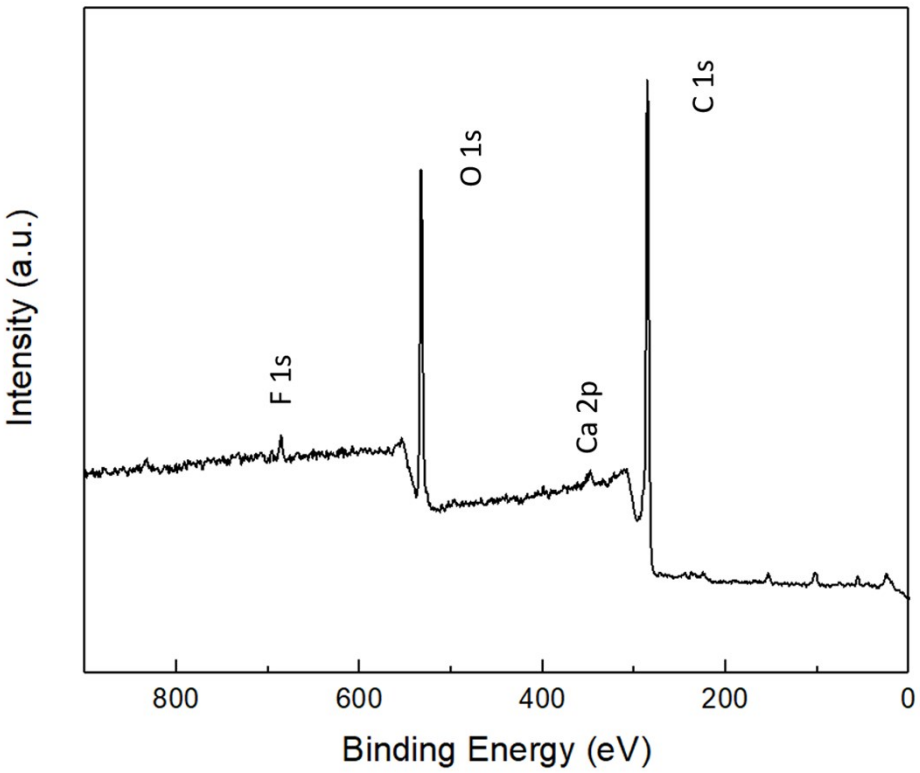


Figure S7. XPS survey spectrum of deposits obtained from $[Ca(BH_4)_2]_{0.05}[N_{07}TFSI]_{0.95}$ electrolyte.

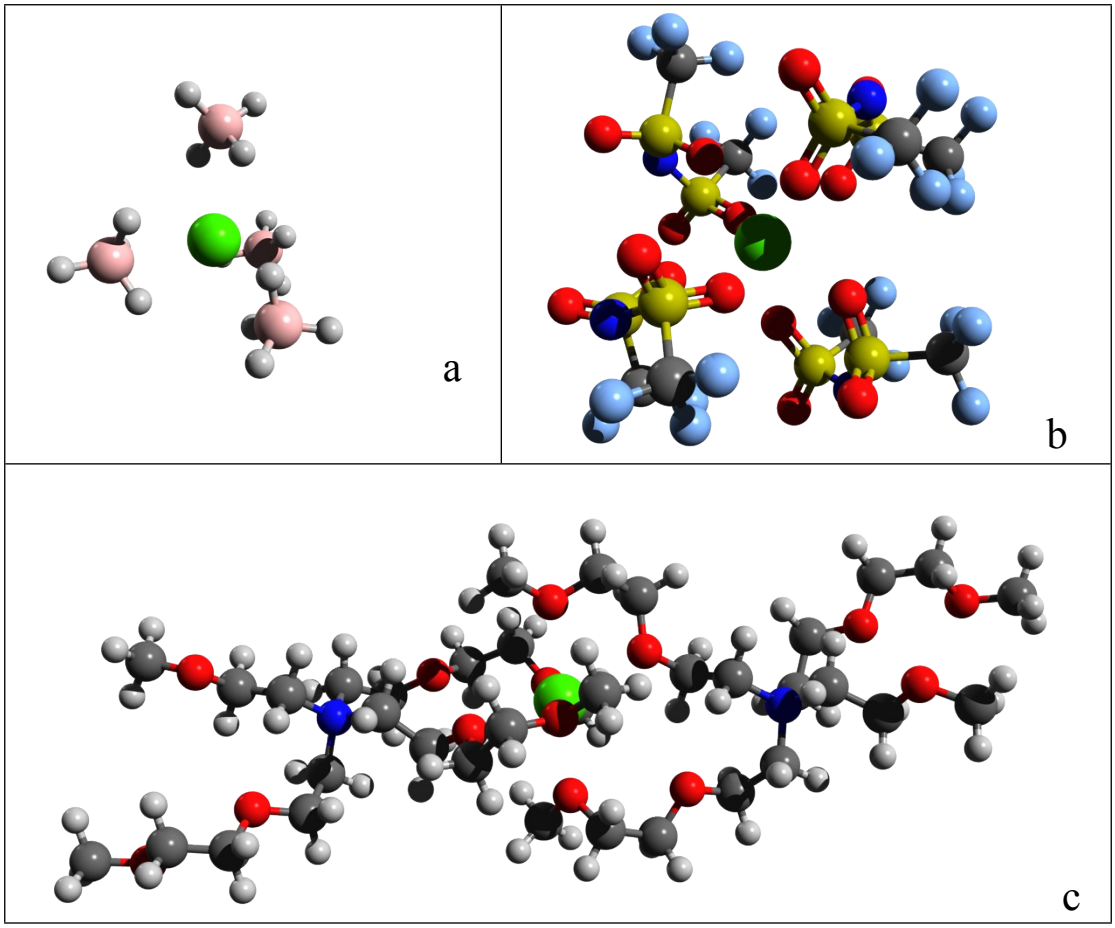


Figure S8. DFT optimized clusters. $[Ca(BH_4)_4]^{2-}$ (a), $[Ca(TFSI)_4]^{2-}$ (b), $[Ca(N_{07})_2]^{4+}$ (c). Calcium ions are represented in green, carbon in black, hydrogen in white, oxygen in red, nitrogen in blue, fluorine in cyan, sulfur in yellow, and boron in pink.

To calculate the interaction energies $\Delta_{int}G$, the following equation was used:

$$\Delta_{int}G_{298.15} = G_{298.15}^{Cluster} - (G_{298.15}^{Ca^{2+}} + n * G_{298.15}^{Other})$$

Where $G^{Cluster}$ is the energy calculated for the clusters depicted in **Figure S8**, G^{Ca2+} is the energy of a single calcium ion, and G^{Other} is the energy of a single coordination ion. The latter is multiplied by a factor n representing the number of the specific ion in the cluster. All the calculations refer to 298.15 K, and where done at the same level of theory specified in the main text. The obtained interaction energies are reported in **Table S1**.

Table S1. The interaction energy of Ca-BH_4, Ca-TFSI and Ca-N_{07} clusters.

$[Ca(BH_4)_4]^{2-}$	$[Ca(TFSI)_4]^{2-}$	$[Ca(N_{07})_2]^{4+}$
-31.85 kJ/mol	-65.47 kJ/mol	-206.39 kJ/mol

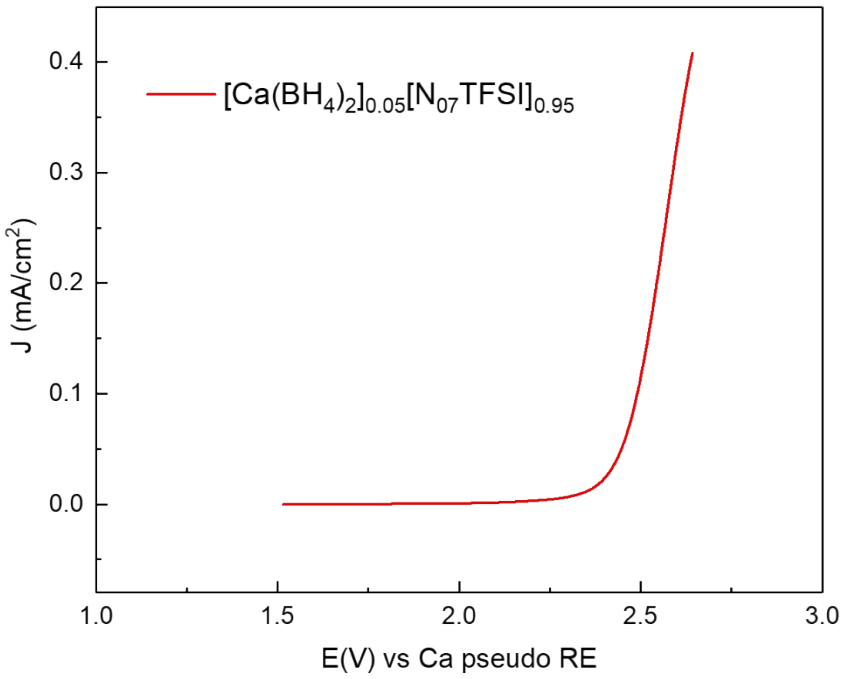


Figure S9. Linear sweep voltammograms recorded on Au substrates at a scan rate of 0.05 mV/s with Ca as both the reference and counter electrodes for $[Ca(BH_4)_2]_{0.05}[N_{07}TFSI]_{0.95}$ electrolyte.