

Supporting Information

A novel calcium fluorinated alkoxyaluminate salt as a next step towards Ca metal anode rechargeable batteries

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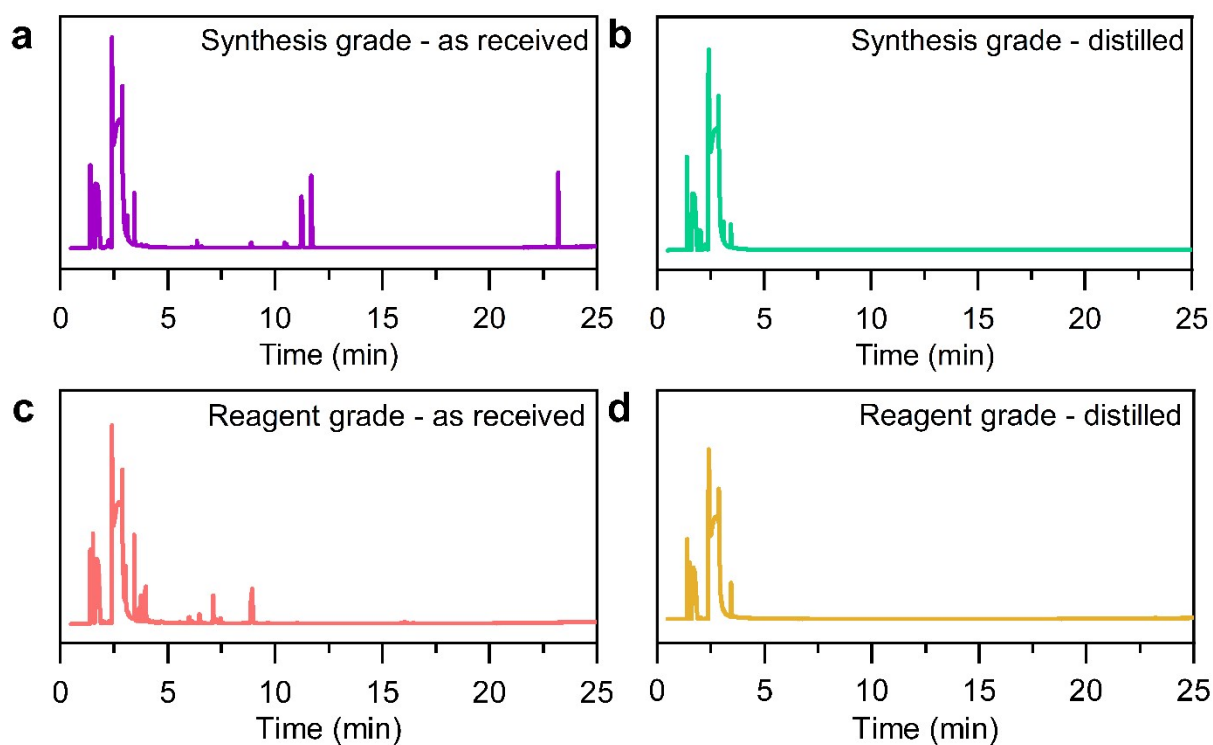


Figure S1: Chromatograms of DME solvents: synthesis grade – **a)** as received and **b)** after drying/purification procedure including fractional distillation; reagent grade – **c)** as received and **d)** after drying/purification procedure including fractional distillation.

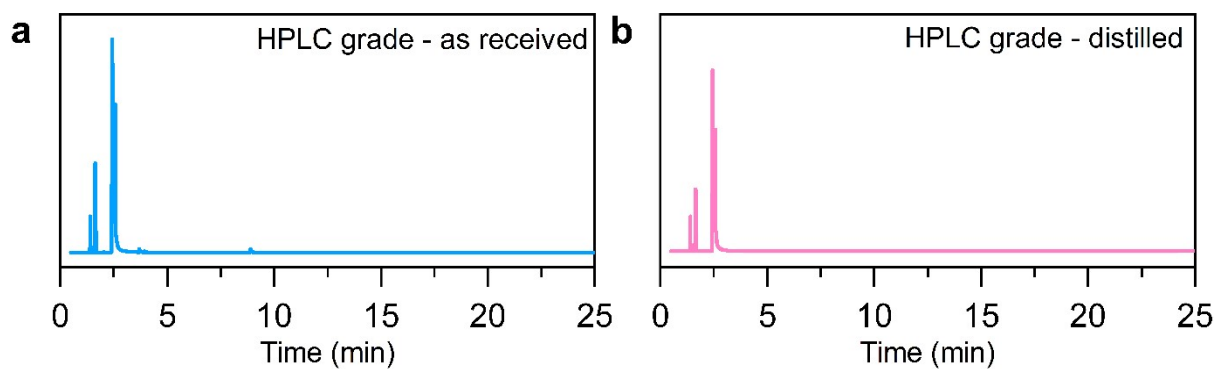


Figure S2: Chromatograms of DME solvents: chromatographic (HPLC) grade – **a)** as received and **b)** after drying/purification procedure including fractional distillation.

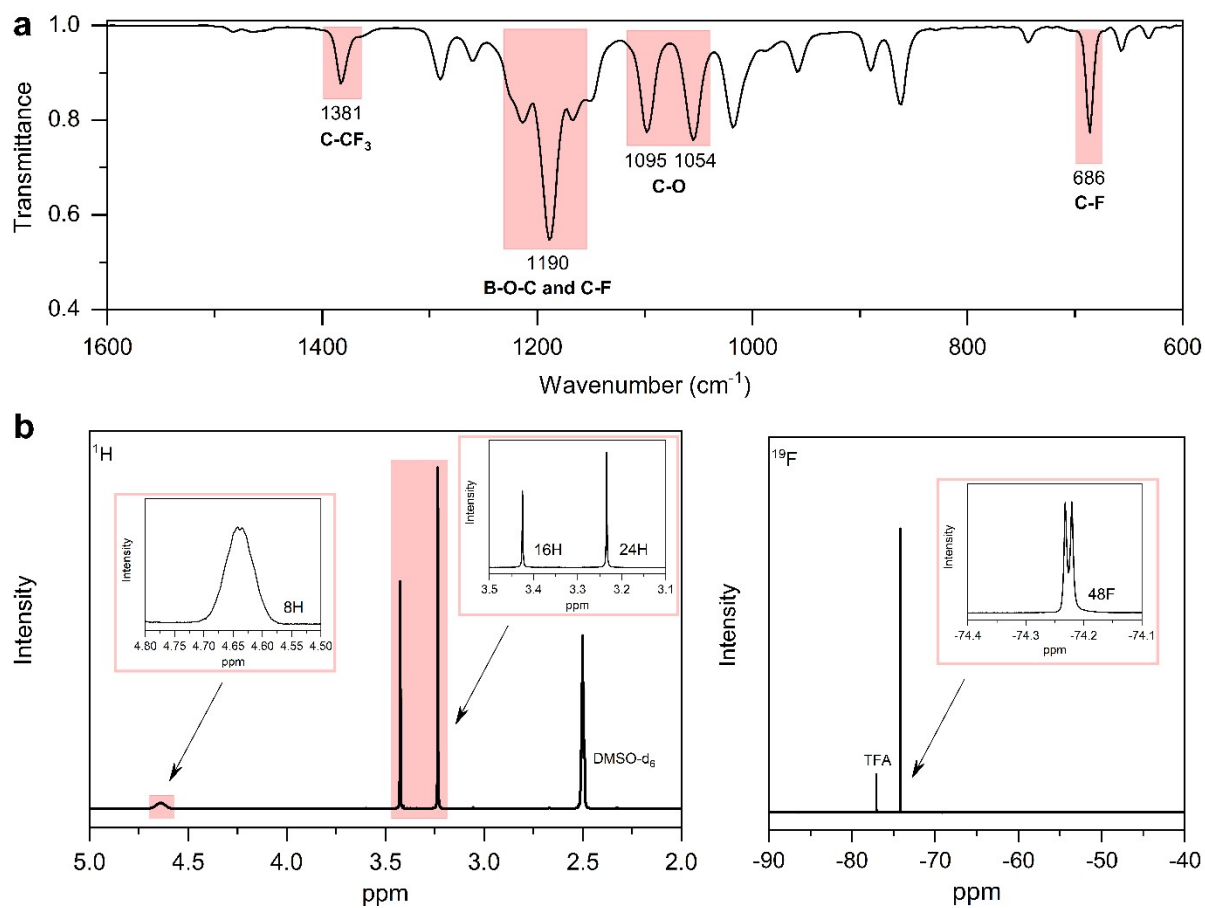


Figure S3: a) ATR-IR spectrum of CaBhfip with peak assignment. **b)** ^1H (right) and ^{19}F (left) NMR spectra of CaBhfip with peak assignment.

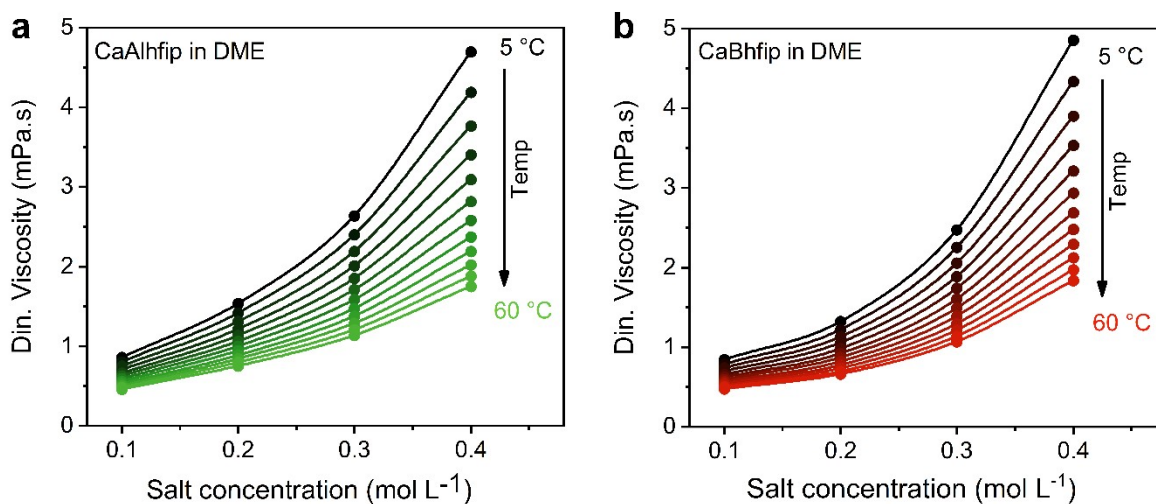


Figure S4: Viscosity of electrolytes in DME at different temperatures as function of salt concentration. **a)** CaAlhfip, **b)** CaBhfip. Lines added only as visual aid, the markers indicate experimental data points.

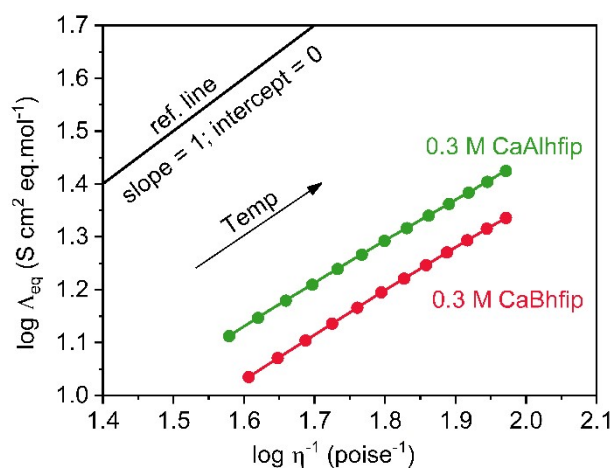


Figure S5: Walden plot of 0.3 M CaAlhfip and 0.3 M CaBhfip in DME. The plot was constructed using the viscosity and ionic conductivity of the electrolytes measured at different temperatures between 5 and 60 °C.

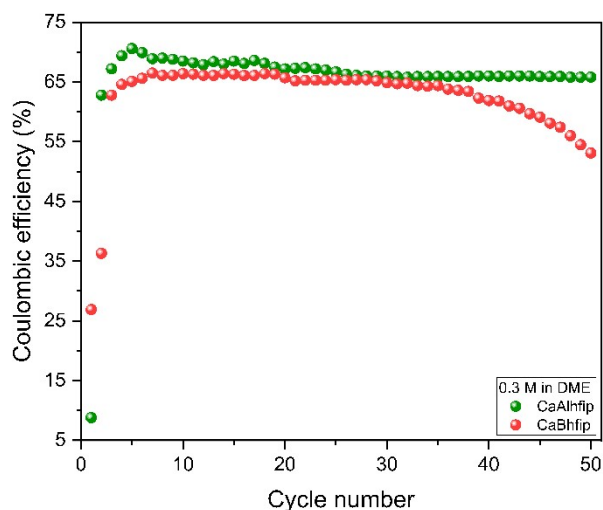


Figure S6: Coulombic efficiency for Ca plating/stripping in 0.3 M CaAlhfp and CaBhfp electrolytes in DME with a 2-electrode cell setup. The efficiencies were calculated manually from CV curves (**Figure 3, a and b**) by dividing the area under the curve for Ca stripping with the area above the curve for Ca plating.

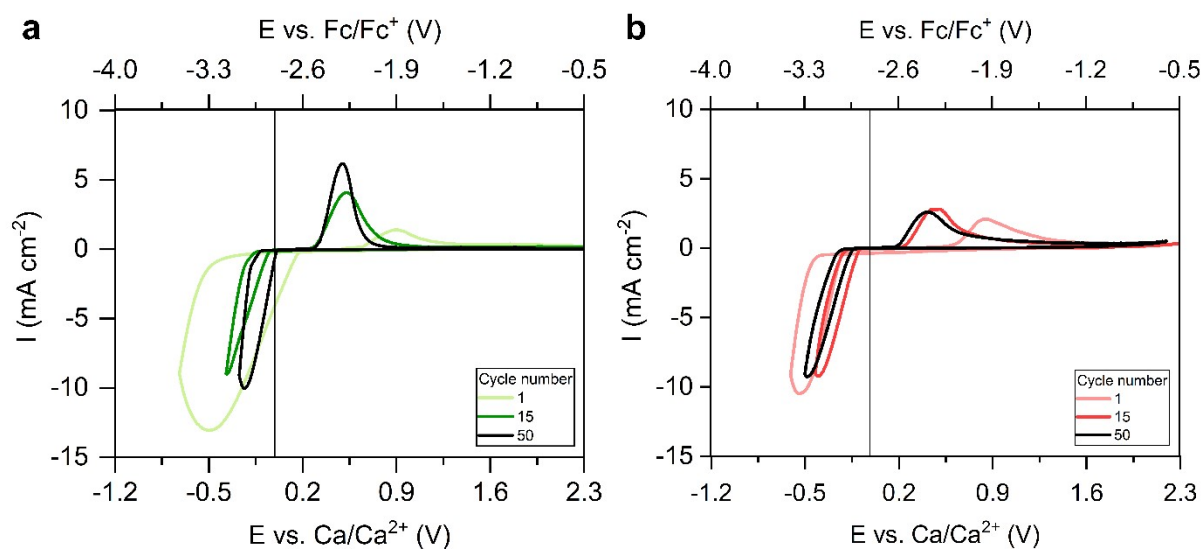


Figure S7: Selected CV cycles of Ca plating/stripping in **a)** 0.3 M CaAlhfp/DME and **b)** 0.3 M CaBhfp/DME with a 3-electrode cell setup (Ca CE, SS WE, Ag RE) at 25 mV s^{-1} . Potential of reference electrode is calibrated with respect to ferrocene redox couple.

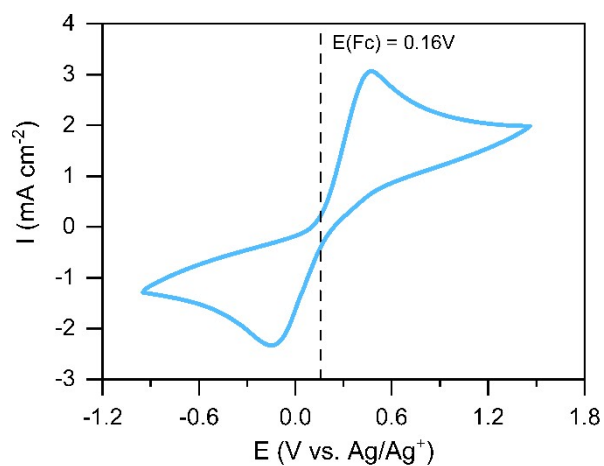


Figure S8: The redox potential of ferrocene (Fc) vs. Ag reference electrode measured in 3-electrode cell configuration using Ca as counter, SS as working and Ag as reference electrode at 25 mV s^{-1} .

Table S1: EDX analysis of deposits from 0.3 M CaAlhfip/DME electrolyte with reported average values of five measurements for each element.

No.	Ca	O	C	F	Al
1	58.2	17.9	6.7	13.7	3.5
2	50.9	20.7	8.7	5.2	2.2
3	46.4	31.8	8.6	11.9	1.3
4	47.8	30.8	8.6	11.4	1.4
5	45.5	35.1	13.7	4.9	0.8
Average	49.8	27.3	9.3	9.4	1.8

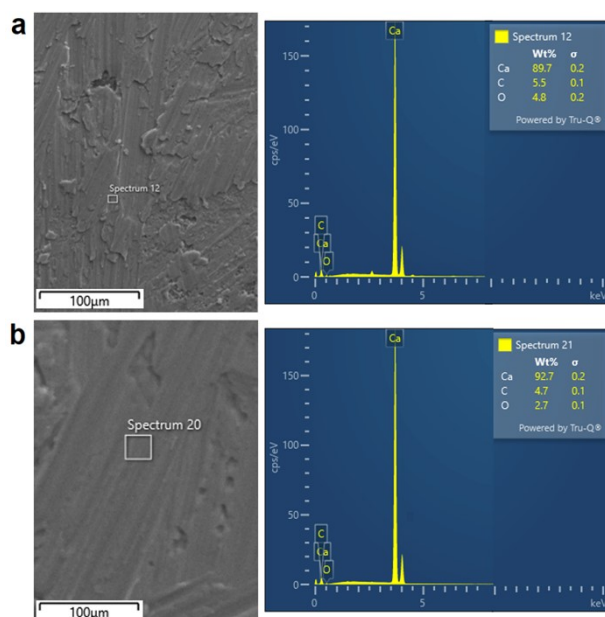


Figure S9: a) SEM image and corresponding EDX spectra of Ca metal dipped into DME and b) fresh Ca metal.

Table S2: EDX analysis of deposits from 0.3 M CaBhfp/DME electrolyte with reported average values of five measurements for each element.

No.	Ca	O	C	F
1	50.8	37.4	6.1	5.7
2	45.6	32.6	12.3	9.4
3	50.9	37.1	7.4	4.6
4	51.6	35.4	4.7	8.3
5	45.5	31.8	14.4	8.4
Average	48.9	35.3	9.2	7.3

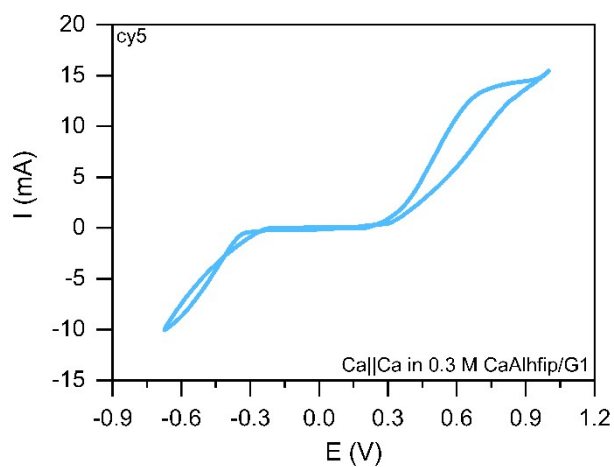


Figure S10: 5th CV cycle of Ca plating/stripping in 0.3 M CaAlhfp/DME with a 2-electrode symmetrical Ca || Ca cell (Ca CE, Ca WE) at 25 mV s⁻¹.

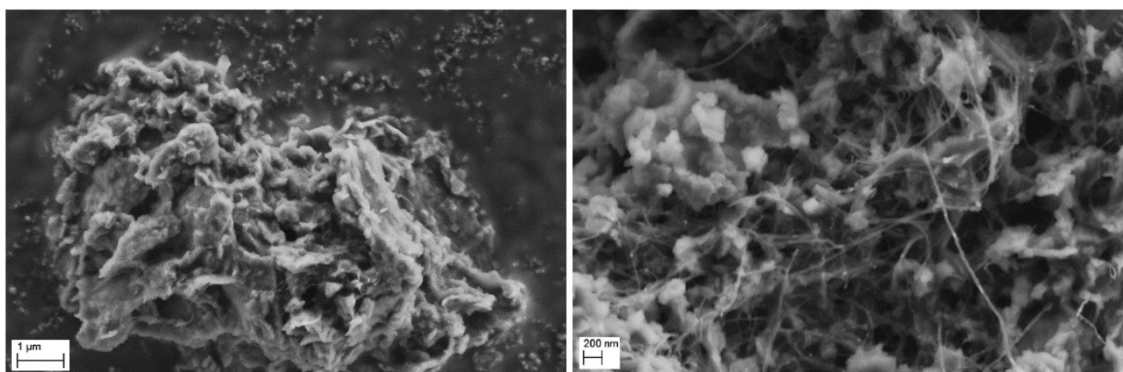


Figure S11: SEM micrographs of naphthalene-hydrazine diimide polymer nanostructured with MWCNTs.

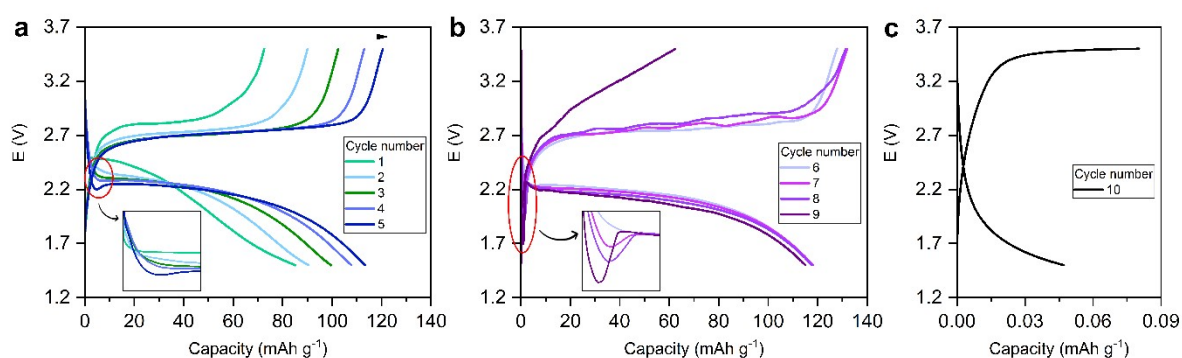


Figure S12: Discharge/charge profiles of Ca metal – NP battery in 0.3 M CaAlhfip/DME at C/4 and voltage window from 1.5 to 3.5 V: **a)** cycles 1–5; **b)** cycles 6–9; **c)** cycle 10. Inset areas represent voltage dips due to the increase of overpotential on anode.

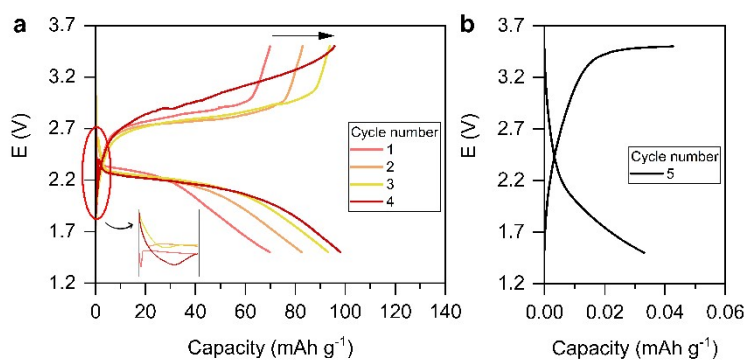


Figure S13: Discharge/charge profiles of Ca metal – NP battery in 0.3 M CaBhfip/DME at C/4 and voltage window from 1.5 to 3.5 V: **a)** cycles 1–4; **b)** cycle 5. Magnified areas represent voltage dips due to the increase of overpotential on anode.