Electronic Supplementary Material (ESI) for Energy & Environmental Science.
This journal is © The Royal Society of Chemistry 2019

Electronic Supplementary Information

Towards stable and efficient electrolytes for room-temperature rechargeable calcium batteries

*Zhenyou Li[1], Olaf Fuhr[2,3], Maximilian Fichtner[1,2], Zhirong Zhao-Karger[1]**

[1]*Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstraße 11, D-89081 Ulm, Germany*

[2]*Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany*

[3]*Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany*

Author Information

Corresponding Authors

*Email: zhirong.zhao-karger@kit.edu

Materials and Methods

All experiments were carried out either on the bench under Ar (99.9999%) using standard Schlenk lines (with vacuum <10^{-3} mbar) or in an argon-filled glove box (MBraun) with H_2O and O_2 <0.1 ppm. The glassware was dried at 110 °C overnight prior to use. Dimethoxyethane (DME, 99.5%, Sigma-Aldrich) was distilled under Ar and stored over 3Å molecular sieves in glove box. Hexafluoroisopropanol ($(CF_3)_2CHOH$, 99%, abcr GmbH) was dried over 4 Å molecular sieves. $Ca(BH_4)_2 \cdot 2THF$ (Sigma-Aldrich), Ca crystalline dendritic pieces (99.99%, abcr GmbH), platinum (Pt) foil (99.9%, ChemPur), silver (Ag) wire (99.9%, Sigma-Aldrich), gold (Au) foil (>99%, EL-CELL), aluminum (Al) foil (>99.3%, MTI) and stainless steel (SS 316, MTI) were purchased. Pt foil was cleaned by soaking in a Piranha solution for 30 min and subsequently washed with DI water and dried. Au foil, SS spacer and Ag wire were cleaned by ethanol and DI water. Al foil was cleaned by ethanol only. All the WEs were dried at 110 °C overnight prior to use. Ferrocene (98%, Sigma-Aldrich) was purified by vacuum sublimation at 80 °C and the obtained crystals were used for the electrochemical measurements.

Synthesis of $Ca[B(hfip)_4]_2 \cdot 4DME$ (denoted as CaBhfip)

$Ca(BH_4)_2 \cdot 2THF$ powder (3.21 g, 15.0 mmol) was dissolved into 60 mL DME in a two necked Schlenk flask equipped with a reflux condenser. 20.50 g ($(CF_3)_2CHOH$ (122 mmol) were added drop by drop into the stirred solution of $Ca(BH_4)_2$. The reaction mixture was refluxed for 4 hrs. Then the solvent was removed by vacuum drying at 40 °C overnight followed by 60 °C for 24 hrs, yielding 21.8 g (83 %) of final product. ^1H-NMR (500.28 MHz, d_8-THF): $\delta = 3.26$ (s, DME-CH_3), 3.42 (s, DME-CH_2), 4.72 (m, CH). ^{19}F NMR (470.73 MHz, d_8-THF, H-decoupled): $\delta = -75.4$ (s, CF_3). ^{11}B NMR (160.51 MHz, d_8-THF, H-decoupled): $\delta = 1.67$. MS $[B(hfip)_4]^-$ 678.95; Cal. $C_{12}H_4BF_{24}O_4$ 678.98

The X-ray single crystal structure is deposited at the Cambridge Crystallographic Data Centre with the CCDC number of 1902427.

Preparation of the electrolyte solution

The solid $Ca[B(hfip)_4]_2{\cdot}4DME$ was dissolved in a volumetric flask with proper amount of DME for the desired concentration. The molar concentration of the electrolyte is based on the molar mass of $Ca[B(hfip)_4]_2{\cdot}4DME$. The saturated concentration of CaBhfip in DME is about 0.3 M.

Characterizations

^{1}H, ^{11}B, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were collected with a Bruker Advance II 500 spectrometer. The ^{13}C NMR spectra were broadband 1H decoupled. THF-d8 was used as solvents for NMR measurements and the chemical shifts were reported in ppm using the residual solvent peak as the reference.[1] X-ray single crystal diffraction was performed with a Stoe StadiVari diffractometer using Cu-Kα (λ = 1.54186 Å) radiation. Under the frame of Olex2[2] software, the structure was solved with the ShelXS[3] structure solution program using Direct Methods and refined with the ShelXL[4] refinement package using Least Squares minimization. Powder X-ray diffraction (PXRD) was conducted using a Stoe diffractometer with Cu Kα source (λ = 1.541 Å). The sample was sealed in a glass capillary in a glovebox to prevent oxidation. Scanning electron microscopy (SEM) secondary electron images and Energy-Dispersive X-ray Spectroscopy (EDX) were obtained using a ZEISS LEO 1530 with EDX detector X-maxN from Oxford instruments and operating at 15 kV. The sample was prepared by spreading the powder on a carbon tape in a glovebox. Simultaneous thermogravimetric analysis, differential scanning calorimetry and mass spectrometry (TGA-DSC-MS) were conducted with a Setaram thermal analyzer SENSYS evo TGA-DSC equipped with a Pfeiffer OmniStar mass spectrometer for the analysis of the evolved gas.

Electrochemical measurement

The fabrication of all electrodes and the construction of the electrochemical cells were carried in an argon-filled glove box. The conductivity of the electrolyte was determined with a Metrohm 917 conductometer with platinum (Pt) electrodes at ambient temperature.

Ca anode was obtained by pressing a Ca piece onto a stainless steel mesh. A borosilicate glass fiber sheet GF/C was used as separator. The CaBhfip/DME electrolyte was prepared by dissolving the CaBhfip powder into DME with a concentration of 0.25 M. The water content of the electrolyte was about 8 ppm. Cyclic voltammetry and linear sweep voltammetry were conducted with a three-electrode EL-Cell, which comprises a defined working electrode (Ø12 mm), a ring-like reference electrode (Ø20 mm) and a Ca pellet counter electrode (Ø16 mm). More details about EL-CELL can be found in the website (https://el-cell.com) and our previous report.[5] All the Ca electrodes were polished to remove possible passivation layer prior to use. In some measurements, ferrocene (Fc, 10 mM) was introduced into the electrolyte as an internal reference. Chronopotentiometry was conducted with a two-electrode setup using Au as working electrode and Ca as counter electrode. Symmetric Ca|Ca cells were assembled by using Ca pellet as both working and counter electrodes. All the electrochemical measurements were performed using a Biologic VMP-3 potentiostat, except that symmetric cell was evaluated with an Arbin BT2000 battery cycling unit. Arbin BT2000 is a 14-bit instrument. The potential resolution for symmetric cell is ~0.6 mV. The operating temperature is 25 ± 0.1 °C. Coulombic efficiency was determined from the charge balance in a complete CV scan.

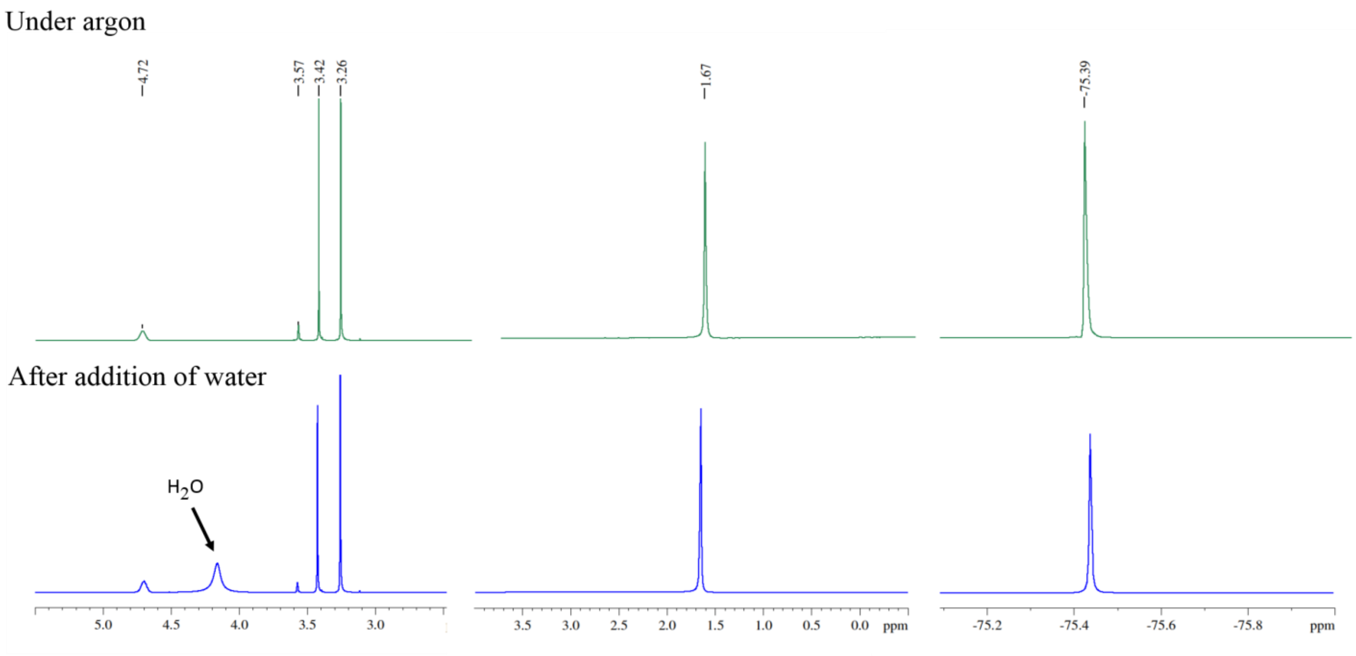

Figure S1. ^{1}H, ^{11}B and ^{19}F NMR of Ca[B(hfip)$_4$]$_2$·4DME under different conditions.

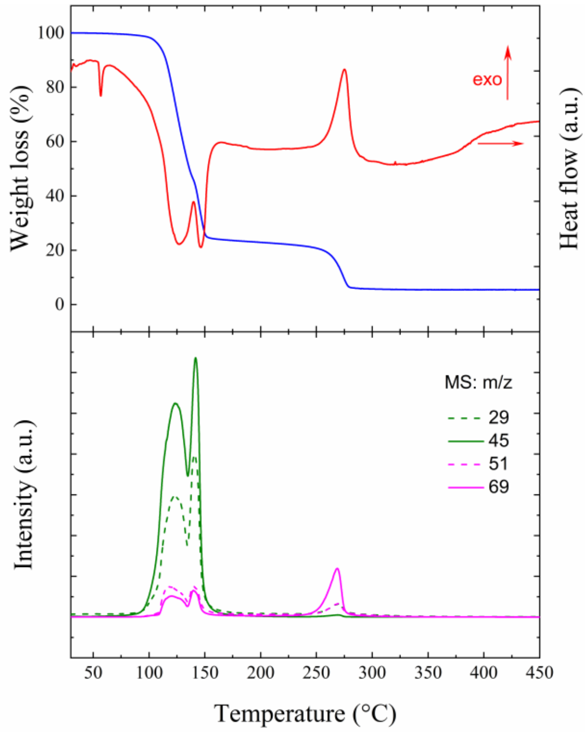

Figure S2. TGA-DSC-MS profiles measured at a heating rate of 5°C min^{-1} under helium gas flow, where the MS signals in green refer to the fragments of DME and pink to [B(hfip)$_4$]$^{-}$ ion, respectively.

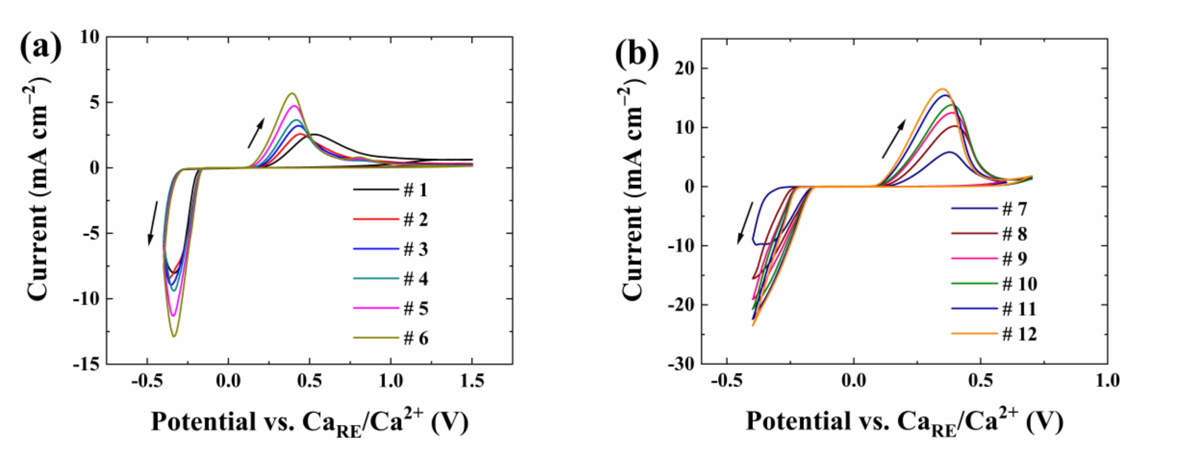

Figure S3. Initial CV scans of Ca plating/stripping in a three-electrode EL-Cell, corresponding to Figure 2a. WE: Pt, RE: Ca, CE: Ca, electrolyte: 0.25M CaBhfip/DME. Scan rate: 80 mV s^{-1}. (a) Cycle #1 - #6, (b) cycle #7 - #12.

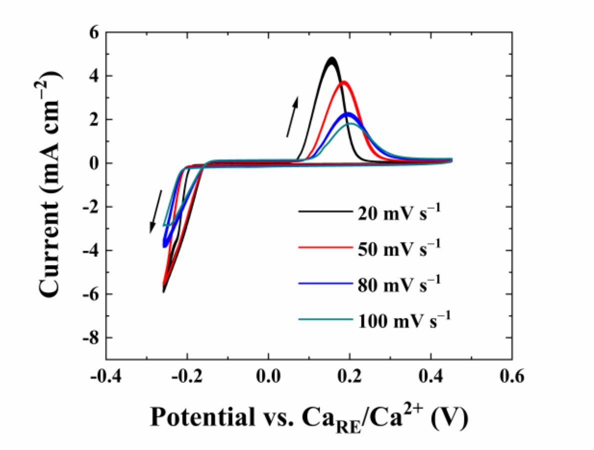

Figure S4. CVs of Ca plating/stripping in a three-electrode EL-Cell with different scan rates. WE: Pt, RE: Ca, CE: Ca, electrolyte: 0.25M CaBhfip/DME. The cell was running at each scan rate for 6 cycles after conditioning cycles.

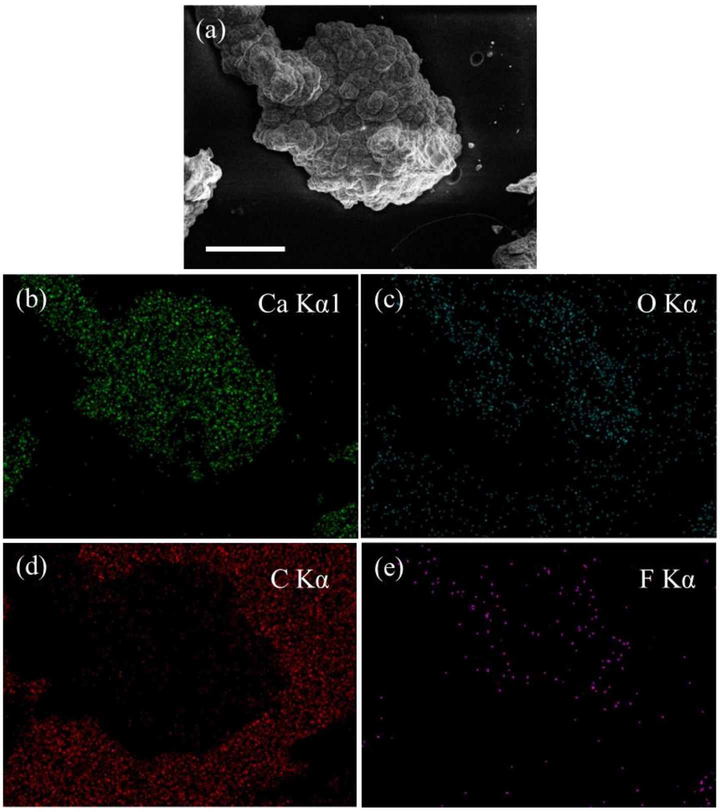

Figure S5. (a) SEM image of the deposits on the separator, the scale bar is 500 μm; (b)~(f) corresponding EDX mapping of Ca Kα1, O Kα, C Kα and F Kα lines, respectively.

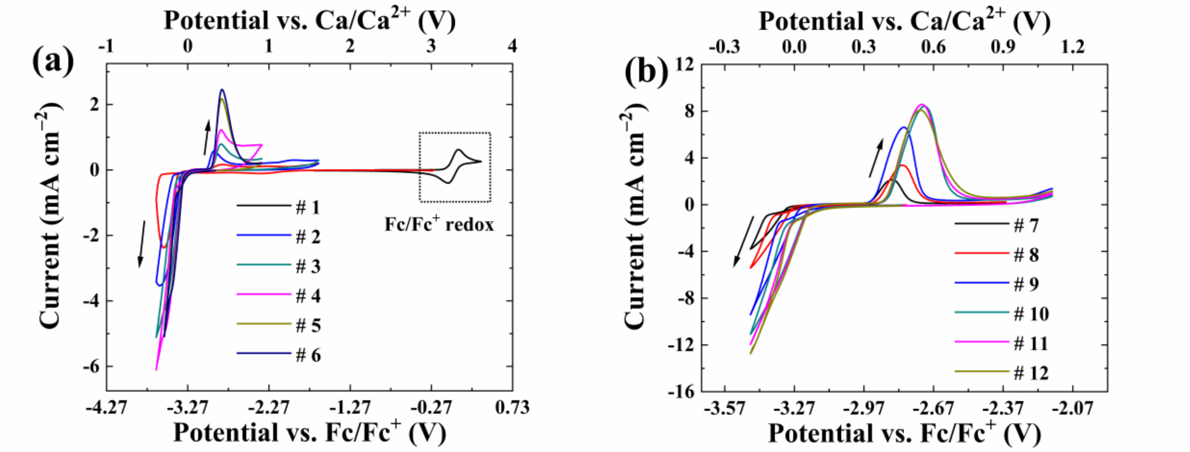

Figure S6. Initial CV scans of Ca plating/stripping in a three-electrode EL-Cell using ferrocene (Fc) as internal reference, corresponding to Figure 2b. WE: Pt, RE: Ag, CE: Ca, electrolyte: 0.25M CaBhfip/DME + 10 mM Fc. Scan rate: 80 mV s^{-1}. (a) Cycle #1 - #6, (b) cycle #7 - #12. The cell was first undergone an oxidation scan to enable a Fc^+/Fc redox before sweeping to lower voltage range. The potential *vs.* Ca/Ca^{2+} was given based on the theoretical potential difference between Fc/Fc^+ and Ca/Ca^{2+}, which is 3.27 V.

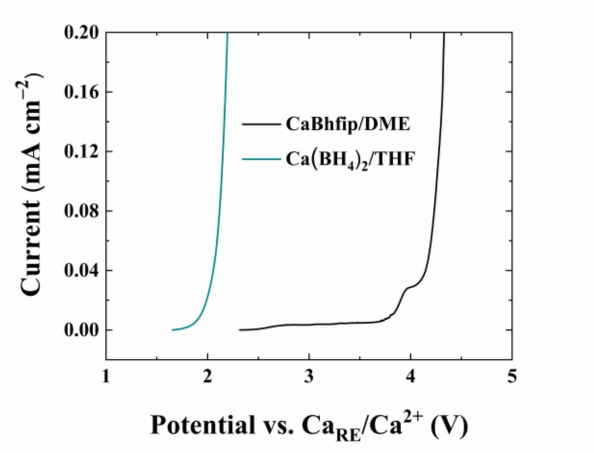

Figure S7 LSV of 1.5 M $Ca(BH_4)_2$/THF and CaBhfip/DME at 1 mV s^{-1}. The measurement was conducted with a three-electrode cell using Pt, Ca and Ca as working, reference and counter electrodes, respectively.

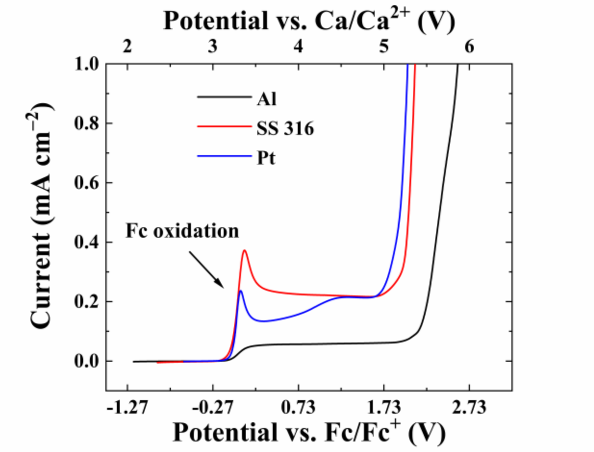

Figure S8. LSVs using Fc-contained cells on various WEs at a scan rate of 1 mV s^{-1}. The potential vs Ca/Ca^{2+} was given based on the theoretical potential difference between Fc/Fc$^+$ and Ca/Ca^{2+}, which is 3.27 V.

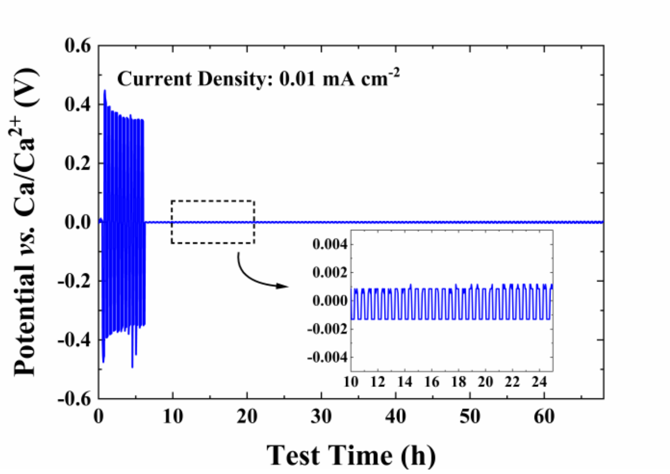

Figure S9. Voltage profile of the Ca-Ca symmetric cell at a current density of 0.01 mA cm^{-2} as conditioning cycles.

References

1. S. Bulut, P. Klose and I. Krossing, *Dalton Trans.*, 2011, **40**, 8114-8124.
2. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography*, 2009, **42**, 339-341.
3. G. Sheldrick, *Acta Crystallographica Section A*, 2008, **64**, 112-122.
4. G. Sheldrick, *Acta Crystallographica Section C*, 2015, **71**, 3-8.
5. Z. Zhao-Karger, R. Liu, W. Dai, Z. Li, T. Diemant, B. P. Vinayan, C. Bonatto Minella, X. Yu, A. Manthiram, R. J. Behm, M. Ruben and M. Fichtner, *ACS Energy Letters*, 2018, **3**, 2005-2013.