Supplementary Information for:

## Enabling Ca plating and stripping by electrolyte manipulation in low-volatility solvents for Ca metal batteries

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## Experimental

Air-sensitive materials were prepared and handled in a dry Ar atmosphere using a glovebox and Schlenk techniques.

**Materials:** CsCB<sub>11</sub>H<sub>12</sub> (Katchem Ltd.) and CaCO<sub>3</sub> (FUJIFILM Wako Pure Chemical Co., Ltd.) were used to prepare Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub>, while Ambarlite IR120B (DuPont Water Solutions) was used for ion exchange. G2 (Sigma-Aldrich) and CaBr<sub>2</sub> (Thermo Scientific) were used as received.

**Electrolyte preparation:** Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> electrolytes were synthesised via ion exchange and heat treatment. CsCB<sub>11</sub>H<sub>12</sub> (2.759 g, 10 mmol) was converted to the corresponding acid (H<sub>3</sub>OCB<sub>11</sub>H<sub>12</sub>) via ion exchange using Ambarlite IR120B (20 mL). Aqueous Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> was prepared by neutralising H<sub>3</sub>OCB<sub>11</sub>H<sub>12</sub> with excess CaCO<sub>3</sub> (1.5013 g, 1.5 equiv). Solvent removal yielded hydrated Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub>, which was further dried in vacuum ( $<8 \times 10^{-4}$  Pa) at 160 °C for 10 h to obtain anhydrous Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub>. To prepare Ca electrolytes, Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> and CaBr<sub>2</sub> were dissolved in appropriate amounts of G2 in volumetric flasks to achieve the desired concentrations. The molar concentration of the electrolyte was based on the molar mass of Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub>.

**S/C electrode preparation:** Sulphur/carbon (S/C) composites were prepared by weighing elemental sulphur (Sigma-Aldrich), Ketjen Black (KB, ECP600JD, Lion Corp.), and Maxsorb (MSC-30, Kansai Coke and Chemicals Co., Ltd) in a weight ratio of 50:25:25. The mixture was ball-milled at 400 rpm for 20 h in an Ar atmosphere. S/C electrodes were fabricated by mixing 80 wt% of the composite with 20 wt% of polyvinylidene difluoride dissolved in *N*-methyl-2-pyrrolidone. The resulting slurry was coated onto etched aluminium foil (serving as the current collector) and subsequently dried in a vacuum at 80 °C for 12 h.

**Characterisation:** <sup>43</sup>Ca, <sup>1</sup>H, and <sup>11</sup>B NMR spectra were recorded for samples loaded in 5 mg glass tubes at ambient temperature and frequencies of 33.659, 160.45, and 500.13 MHz, respectively, using a Bruker Avance 500 MHz spectrometer. <sup>43</sup>Ca, <sup>1</sup>H, and <sup>11</sup>B shifts were referenced to 1 M Ca(NO<sub>3</sub>)<sub>2</sub> in D<sub>2</sub>O ( $\delta_{iso} = 0.0$  ppm), 2 vol% tetramethylsilane in CDCl<sub>3</sub> ( $\delta_{iso} = 0.0$  ppm), and H<sub>3</sub>BO<sub>3</sub> ( $\delta_{iso} = 19.5$  ppm) as external standards. <sup>43</sup>Ca NMR spectra were acquired using a spin echo pulse sequence with 2k acquisitions. The vibrational modes of solvation were characterised by Raman spectroscopy (DXR, Thermo Scientific). The XPS analysis of the Ca metal surface was performed before and after galvanostatic cycling for the pristine electrode and after discharge at the 0.5 V S/C electrode (PHI5000 VersaProbe II, ULVAC PHI, Inc.). Precycled

Ca metal was prepared by immersing the Ca electrode in the electrolyte for 30 min. After cell disassembly in an Ar-filled glovebox, all samples were washed three times with G2 and subsequently dried in vacuum. The dried samples were transferred to the XPS vacuum chamber without air exposure.

Electrochemical analyses and battery tests: Disk-shaped Au working electrodes with diameters of 8.0 mm and counter and reference Ca electrodes with diameters of 8.0 and 5.0 mm, respectively, were extensively polished until metallic lustre was achieved before each use. All electrochemical analyses were performed at room temperature using a stainless-steel electrochemical cell holder (EC Frontier). Electrolyte conductivities were measured using the alternating-current impedance method for Au/electrolyte/Au samples at room temperature, with the applied frequencies ranging from 4 Hz to 1 MHz produced using a frequency response analyser (3532-80, HIOKI). CV measurements were conducted at a scan rate of 50 mV s<sup>-1</sup> and voltages g between -0.5 and 2.5 V vs. Ca<sup>2+</sup>/Ca using multichannel potentiostats (Cell Test System 1470E, Solectron Analytical). Long-term cycling performance was evaluated by galvanostatic measurements using Ca/electrolyte/Ca symmetric cells. A constant current density ( $\pm 5 \ \mu A \ cm^{-2}$ ) was applied to the cells every 10 min, and the voltage change was recorded. Battery tests were conducted using stainless-steel electrochemical cell holders, where S/C electrodes, separators, electrolytes, and Ca metal anodes were assembled. Each cell contained 80 µL of the electrolyte. Electrochemical measurements were conducted at a current density of 167.2 mA g<sup>-1</sup> (0.1 C) and room temperature in the voltage range of 3.0-0.5 V using a battery test system (580 Battery Test System, Scribner Associates, Inc.). The capacity of each battery was presented on the basis of the weight of sulphur.



**Figure S1.** Cyclic voltammograms of Ca plating/stripping recorded for initial three conditioning processes and a fourth cycle at 50 mV s<sup>-1</sup> in a three-electrode setup with Au as the working electrode and Ca as the reference and counter electrodes at room temperature.



**Figure S2.** Cyclic voltammograms for Ca plating/stripping recorded over 1-50 cycles using 0.4 M Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> in diglyme (G2) with (a) 0.01, (b) 0.03, and (c) 0.05 M CaBr<sub>2</sub> as electrolytes. (d) Coulombic efficiency at each CaBr<sub>2</sub> concentration calculated from cyclic voltammetry (CV) data. (e) Image of Au electrode after 50 CV cycles in the electrolyte with 0.05 M CaBr<sub>2</sub>. (f) Image of separator after 50 CV cycles in the electrolyte with 0.05 M CaBr<sub>2</sub>. Black deposits were observed on the Au film and separator. Although only data for the 0.05 M concentration are presented here, similar observations were made for 0.01 and 0.03 M. These deposits were identified as 'dead Ca,' which remains after Ca deposition because of electrical contact loss. The formation of 'dead Ca' deposits probably contributes to a low coulombic efficiency.



**Figure S3.** (a) Nyquist plots recorded for the Au/Au symmetric cell at different concentrations of CaBr<sub>2</sub> in 0.4 M Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> in G2. The cell constant was calibrated using 0.08% aqueous KCl as the electrolyte. (b) Calculated conductivity as a function of CaBr<sub>2</sub> concentration.



Figure S4. (a) <sup>1</sup>H and (b) <sup>11</sup>B nuclear magnetic resonance spectra of 0.4 M Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> + 0, 0.01, 0.03, and 0.05 M CaBr<sub>2</sub> in G2.



Figure S5. Raman spectra of pure G2 and 0.4 M  $Ca(CB_{11}H_{12})_2 + 0, 0.01, 0.03, and 0.05$  M  $CaBr_2$  in G2.



**Figure S6.** (a) C 1s, O 1s, Ca 2p, B 1s, and Br 3d spectra of Ca metal soaked for 30 min in 0.4 M Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> with 0.01 and 0.05 M CaBr<sub>2</sub> in G2. (b) Corresponding atomic concentrations (atom %) of the passivation layer components on the Ca metal surface. (c) X-ray photoelectron spectra of Ca metal recorded after galvanostatic Ca plating/stripping cycling using the conditions used in Fig. 1c and the same electrolyte. (d) Atomic concentrations (atom %) of the passivation layer components after cycling.

**Note:** Although the O 1s signal attributed to O–C=O minimally gained intensity at 0.05 M CaBr<sub>2</sub>, this does not necessarily evidence the enhanced formation of CO<sub>3</sub> species, such as CaCO<sub>3</sub>. This conclusion is supported by the suppressed CaCO<sub>3</sub>-related signals in the Ca 2p spectrum and absence of a corresponding increase in the COO component in the C 1s spectrum. The O–C=O signal enhancement is instead attributed to organic carboxylates or polymeric species formed after prolonged cycling. In addition, the minimally enhanced B 1s signal at 0.05 M suggests that more CB<sub>11</sub>H<sub>12</sub><sup>-</sup> anions were incorporated into a more developed polymeric SEI layer formed under the Br<sup>-</sup>-induced solvation structure modulation.



**Figure S7.** (a) C 1s, O 1s, Ca 2p, B 1s, and Br 3d spectra of Ca metal recorded after five CV cycles in 0.4 M  $Ca(CB_{11}H_{12})_2$  with 0 M  $CaBr_2$  in G2. (b) Corresponding atomic concentration (atom %) of the passivation layer components on the Ca metal surface.

**Note:** After CV cycling under the 0 M CaBr<sub>2</sub> condition, the C 1s spectrum showed a decrease in C–O and an increase in C=O species, while the O 1s spectrum revealed a notable weakening of O–C=O and intensification of Ca–O signals. The Ca 2p indicated a CaO content increase. Minimal increases in Ca and O contents and decreases in C and B contents were observed. These results suggest that the applied electrochemical potential promoted the decomposition of the initially formed organic components even in the absence of observable Ca plating/stripping. In contrast to the 0.05 M condition after cycling (Fig. S6), in which case the SEI retained its polymeric features, polymer loss and conversion to CaCO<sub>3</sub> and CaO were observed at 0 M. This contrast underscores the role of Br<sup>-</sup> in stabilising the SEI.



**Figure S8.** Linear sweep voltammetry curves of Ca/Au cells with 0.4 M Ca(CB<sub>11</sub>H<sub>12</sub>)<sub>2</sub> in G2 containing 0, 0.01, and 0.05 M CaBr<sub>2</sub>. The anodic scan was performed at 1 mV s<sup>-1</sup> from the open-circuit voltage to 4.0 V vs. Ca<sup>2+</sup>/Ca. The oxidation onset potential was defined as the voltage at which the anodic current density reached 10  $\mu$ A cm<sup>-2</sup>, as indicated by the dashed line.



**Figure S9.** Voltage profiles of a prototype Ca metal battery recorded across the initial 10 cycles using 0.4 M Ca( $CB_{11}H_{12}$ )<sub>2</sub> with 0.05 M CaBr<sub>2</sub> in G2 as an electrolyte.