

Supplementary Information

Investigating the Ion Conductivity and Synthesis Conditions of Calcium Monocarborane Solid-State Electrolytes

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Material synthesis and characterisation

Calcium monocarborane (CMC, $\text{Ca}(\text{CB}_{11}\text{H}_{12})_2$) was synthesised in a manner similar to that reported in a previous study¹. To optimise the heat-treatment temperature, heat treatment was conducted at 433, 453, 473, and 513 K. To obtain powder XRD profiles, the synthesised samples were packed in capillary tubes and irradiated with $\text{CuK}\alpha$ radiation (wavelength $\lambda = 1.5406 \text{ \AA}$ for $\text{K}\alpha_1$ and 1.5444 \AA for $\text{K}\alpha_2$) in the 2θ range of $7\text{--}90^\circ$ (X'PERT PRO, PANalytical). Microscopic laser Raman spectroscopy (DXR, Thermo Scientific) was conducted to confirm the presence of $[\text{CB}_{11}\text{H}_{12}]^-$ anion peaks in the synthesised samples. A laser with a wavelength of 532 nm was used. The thermophysical properties of the heat-treated samples (3 mg) were measured via DTA (Thermo Plus TG8120, RIGAKU). The measurements were performed in a purified Ar-circulating glove box (GB; Miwa Manufacturing Co., Ltd.) to prevent exposure to air. The rate of temperature increase and decrease was 2 K min^{-1} , and the temperature ranged from 313 to 433 K. NMR spectroscopy was performed to identify the $[\text{CB}_{11}\text{H}_{12}]^-$ anion peaks in the synthesised samples. Approximately 10–20 mg of the powdered sample was dissolved in $\text{C}_3\text{D}_6\text{O}$ and used for the measurements. An NMR 400 MHz spectrometer (AVANCE III 400, Bruker) was used.

Electrochemical analysis

The synthesised sample powder was pelletised by pressing in a GB under an Ar atmosphere to fabricate an electrochemical cell. Gold powder was used as the electrode. EIS was performed using an impedance analyser (HIOKI 3532-80) in the frequency range of 4 Hz to 1 MHz at an applied voltage of 150 mV. The semicircles observed in the Nyquist plots obtained through EIS were fitted using the equivalent circuit shown in Figure S10. The ionic conductivity of the sample was determined as $\sigma = l/RS$, where R is the resistance value obtained, l is the thickness of the pellet sample, and S is the area of the electrode. This was measured every 10 K from 303 to 423 K, and an Arrhenius plot was prepared. To assess the stability of the synthesised CMC

on the electrodes, CV was conducted using Ca metal, CaSn₃ alloy (JAPAN PURE CHEMICAL Co., Ltd.), and molybdenum foil. A composite electrode was prepared by mixing CaSn₃ (Figure S11), Ketjen black, and CMC in a mass ratio of 6:2:1. The potential scanning rate was 50 mV s⁻¹, and the potential scanning range was as shown in Figure S9. For the galvanostatic test, an electrochemical cell was fabricated using a CaSn₃ alloy composite electrode and the synthesised CMC. A potentiostat (Cell Test System 1470E, Solartron Analytical) was employed for the galvanostatic test after the temperature was increased to 423 K. A constant current of $\pm 2 \mu\text{A}$ was alternately applied every 10 min, and the response voltage was measured.

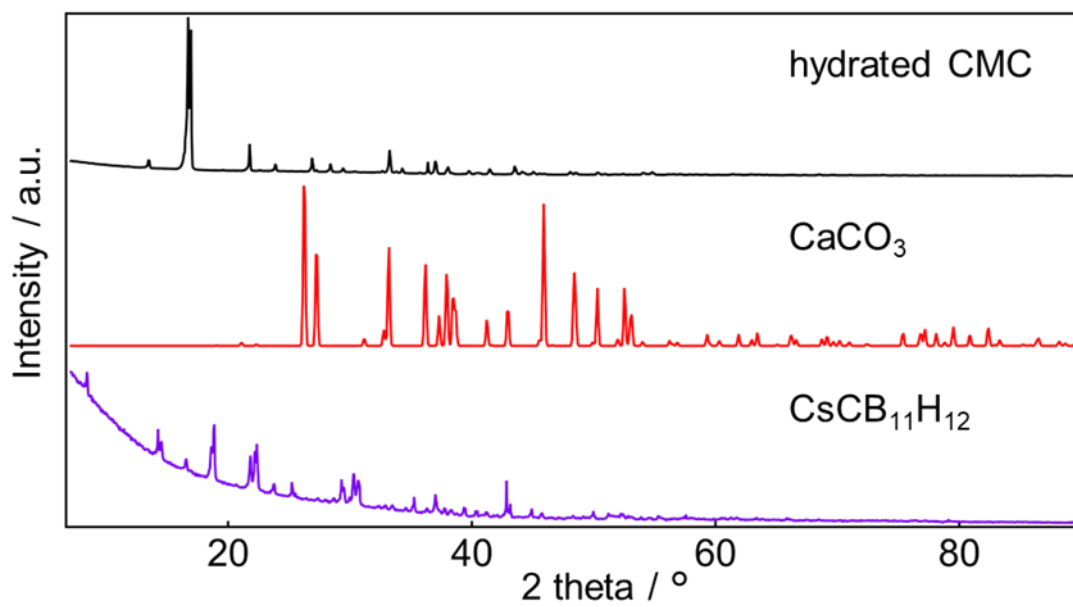


Figure S1. XRD patterns of CsCB₁₁H₁₂, CaCO₃ (ICSD#15194), and hydrated CMC before heat treatment.

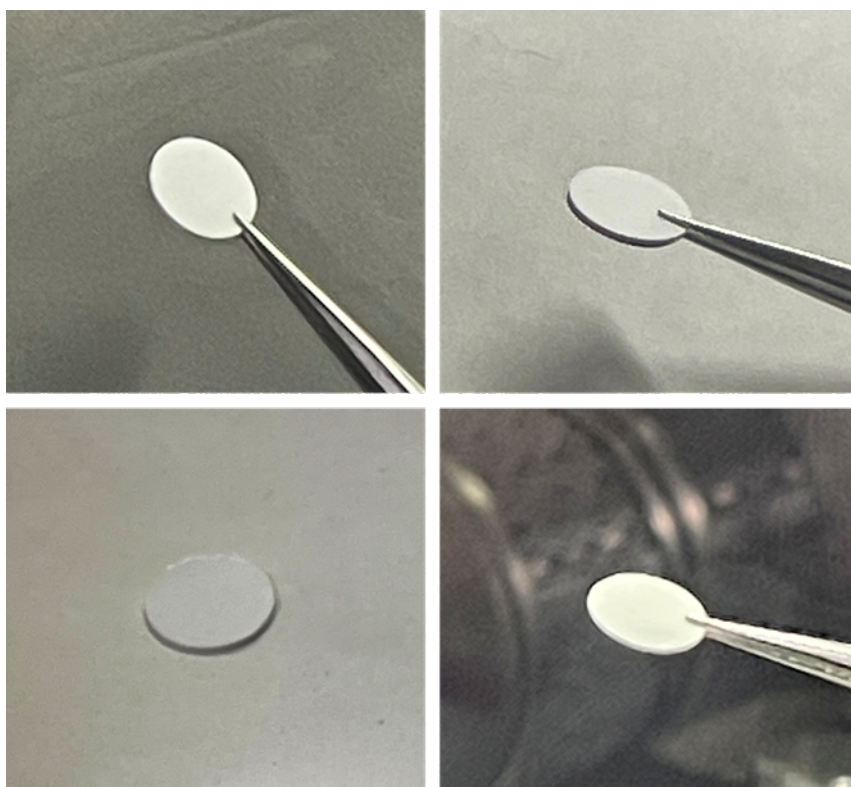


Figure S2. Photographs of a CMC electrolyte pellet (8ϕ).

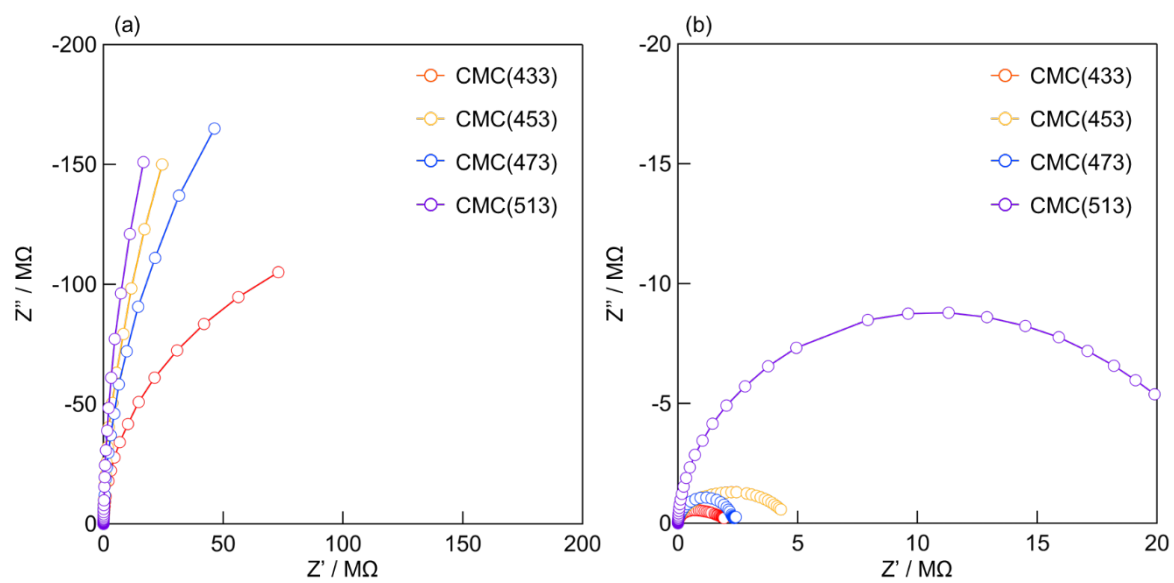


Figure S3. Nyquist plots of samples heat-treated at different temperatures ($T = 433, 453, 473, 513$ K) (a) at room temperature and (b) 373 K.

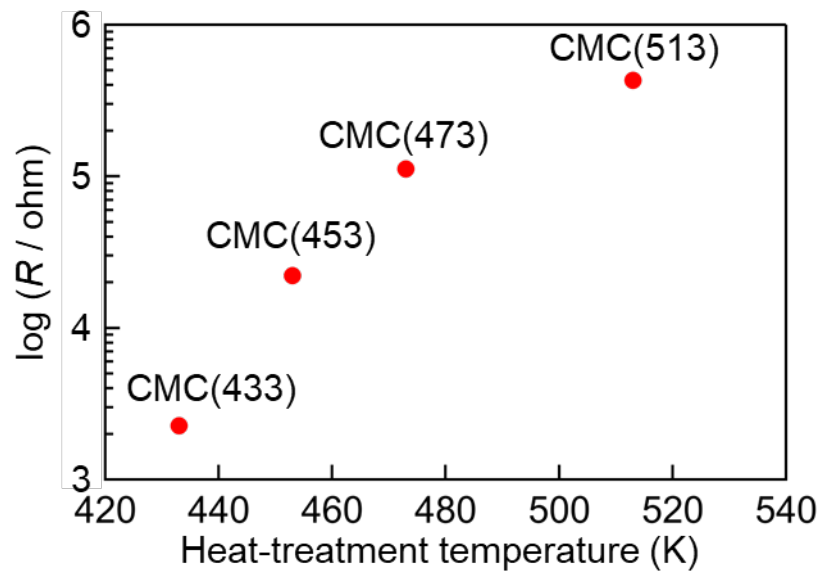


Figure S4. Relationship between the heat-treatment temperature and resistance of CMC.

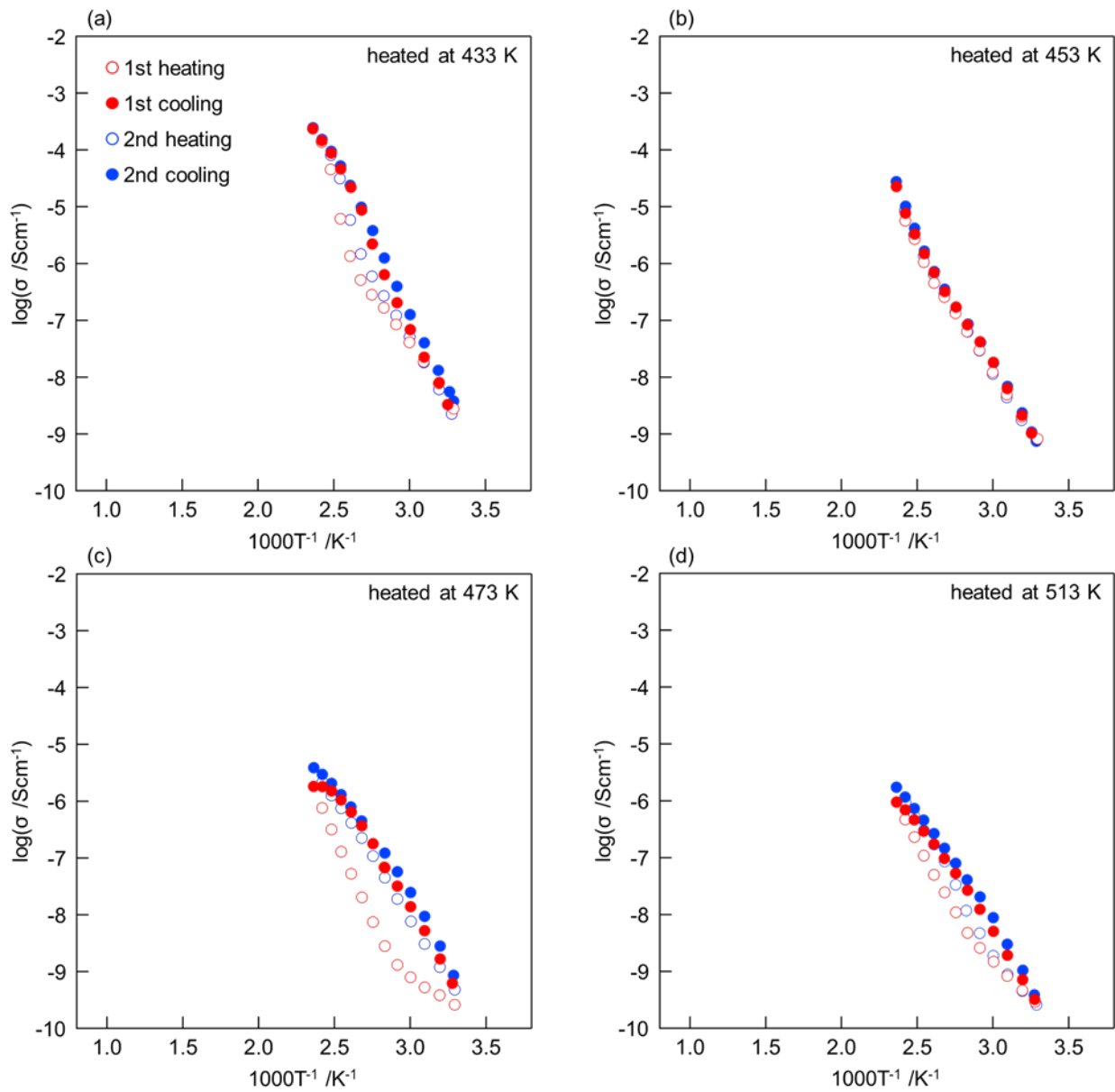


Figure S5. Arrhenius plots of samples heat-treated at (a) 433, (b) 453, (c) 473, and (d) 513 K.

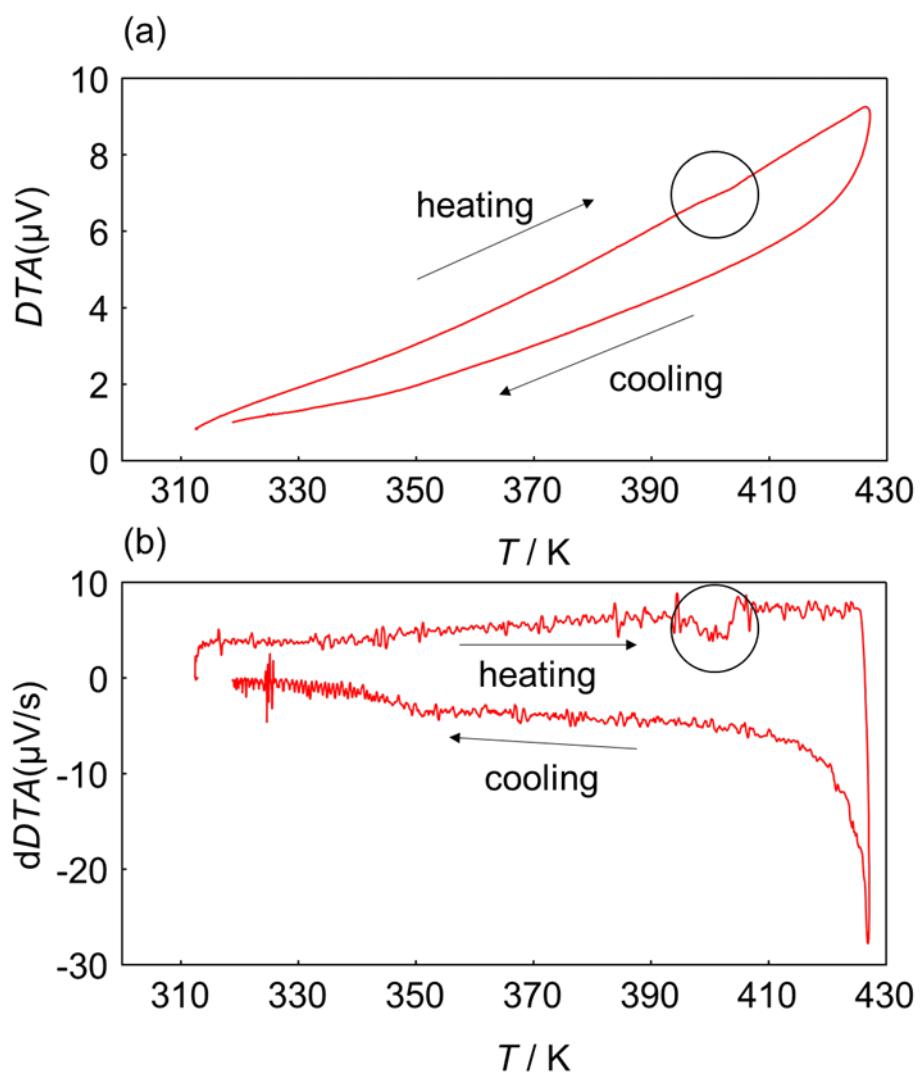


Figure S6. Thermal analysis of CMC: (a) DTA and (b) dDTA.

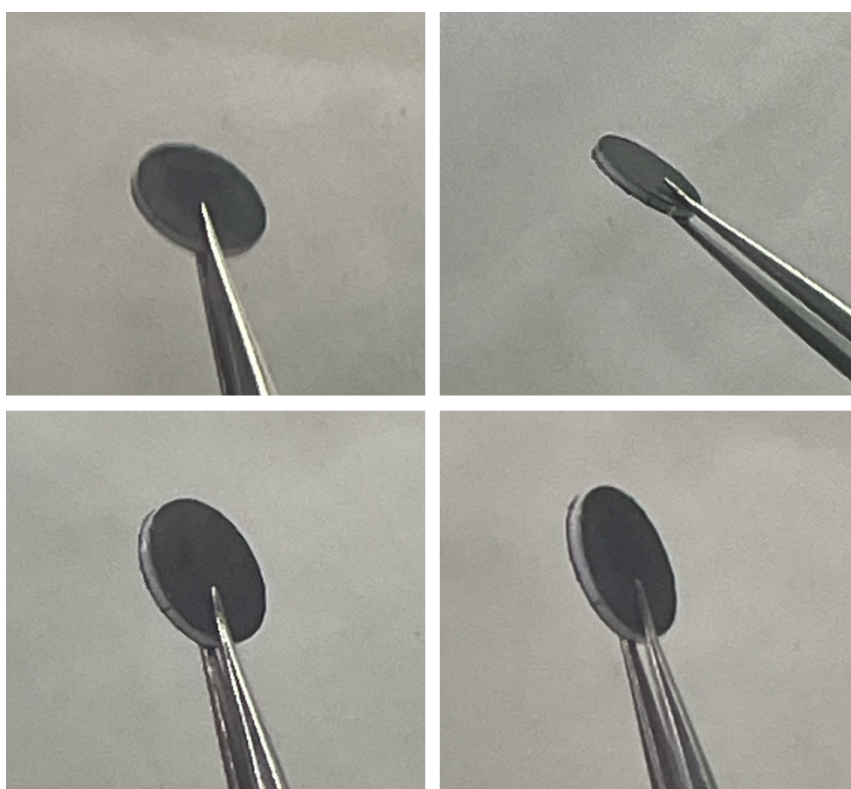


Figure S7. Photographs of a $\text{CaSn}_3|\text{CMC}|\text{CaSn}_3$ pellet.

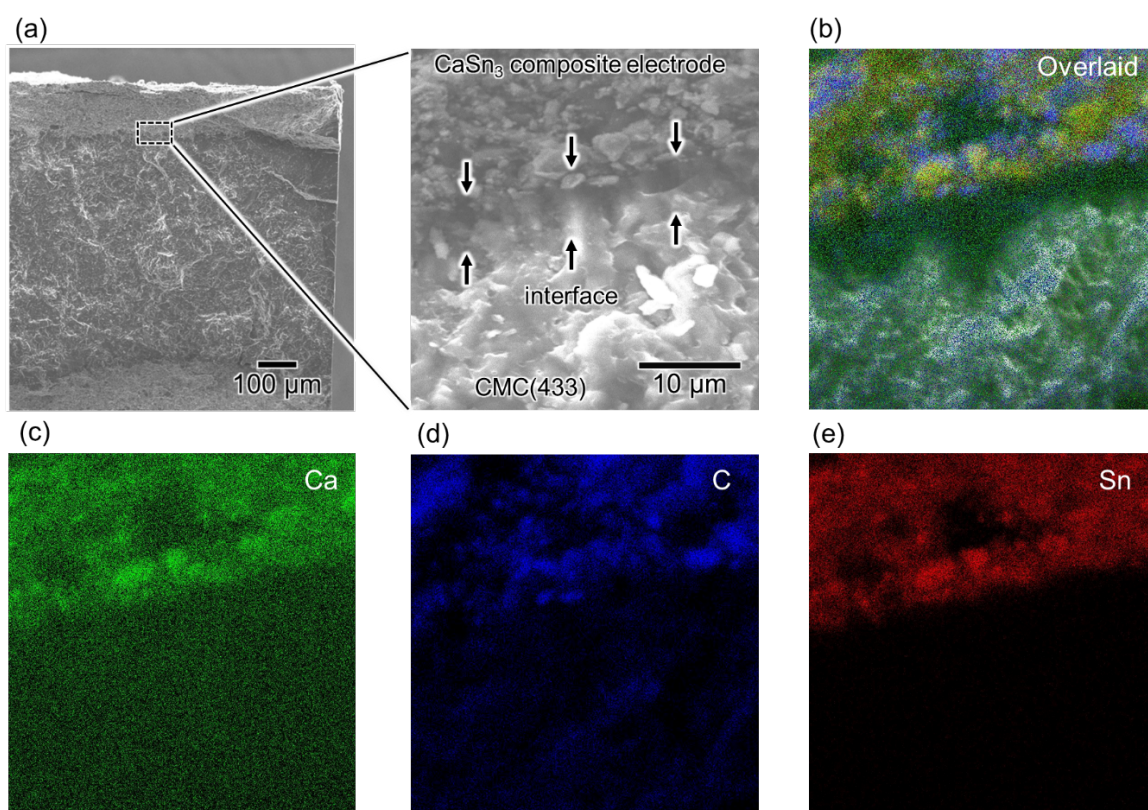


Figure S8. (a) SEM images of a CaSn₃|CMC pellet cross section and the electrode/electrolyte interface. (b) Overlaid, (c) Ca, (d) C, and (e) Sn EDS elemental maps.

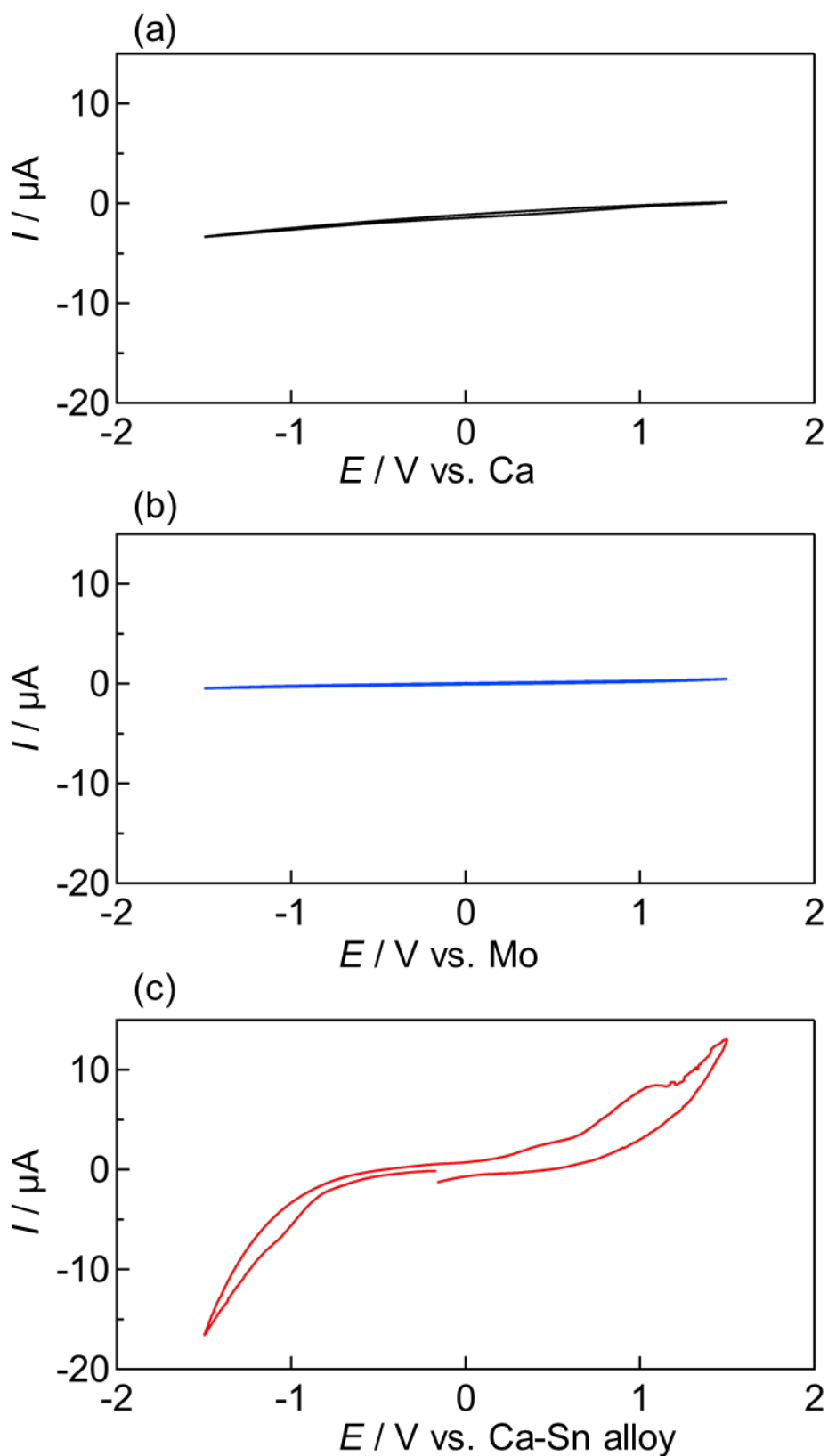


Figure S9. Cyclic voltammograms of CMC (a) using calcium metal (reference electrode) and gold foil (counter electrode), (b) using molybdenum foil electrodes (symmetric cell), and (c) using CaSn_3 composite electrodes (symmetric cell).

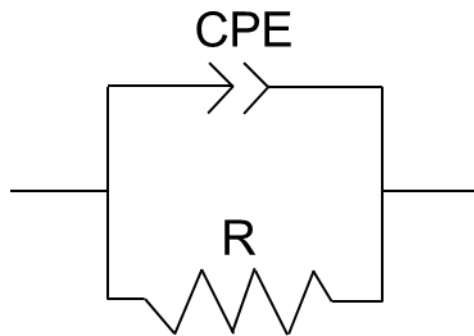


Figure S10. Equivalent circuit used for fitting.

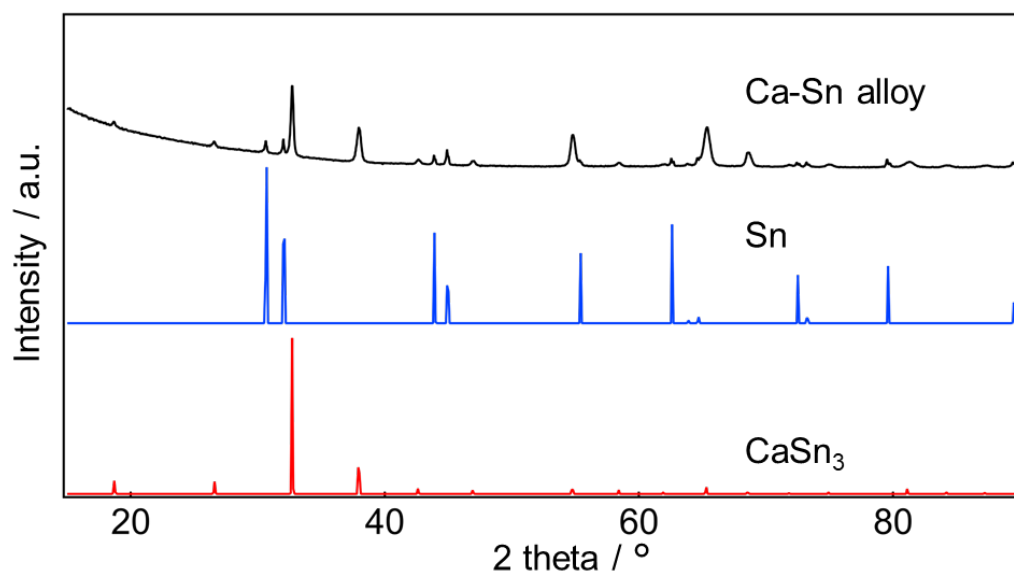


Figure S11. XRD patterns of CaSn₃ (ICSD#58934), Sn (ICSD#106072), and purchased Ca–Sn alloy powder.

Reference

1. K. Kisu, S. Kim, T. Shinohara, K. Zhao, A. Züttel and S. Orimo, *Sci. Rep.*, 2021, **11**, 7563.