

Improving Calcium–Sulfur Battery Performance Through Electrolyte Modification

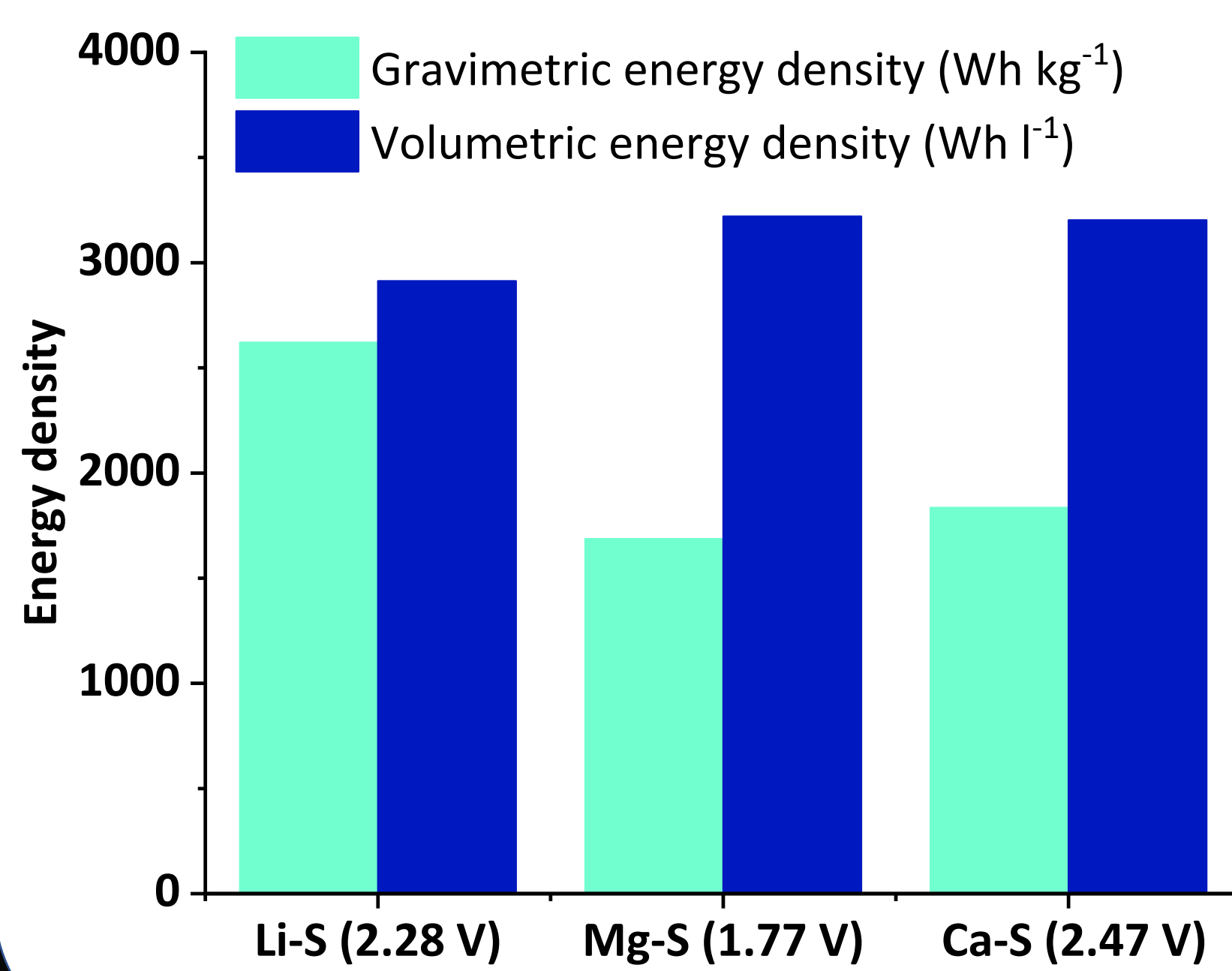
Ping Feng,¹ Sebahat Topal,¹ Sibylle Riedel,¹ Marco Kögel,² Maximilian Fichtner,^{1,3} Zhirong Zhao-Karger^{1,3}

¹Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Electrochemical Energy Storage, Helmholtzstraße 11, 89081 Ulm, Germany

²NMI Natural and Medical Sciences Institute at the University of Tübingen, Reutlingen, Germany

³Karlsruhe Institute of Technology (KIT), Institute of Nanotechnology, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

Introduction



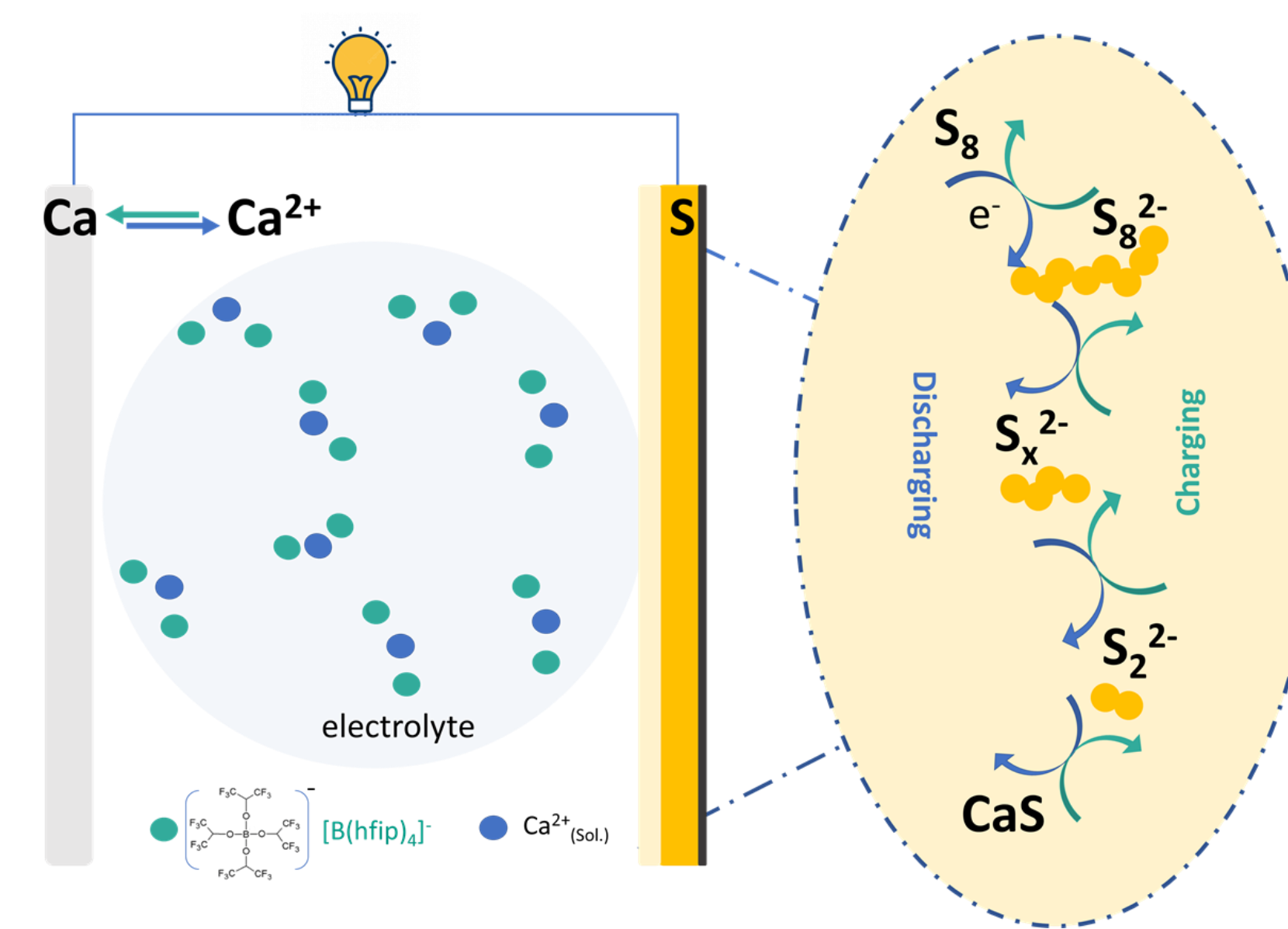
Sulfur

- Low cost, sustainable;
- high theoretical capacity (1672 mA h g⁻¹).

Calcium

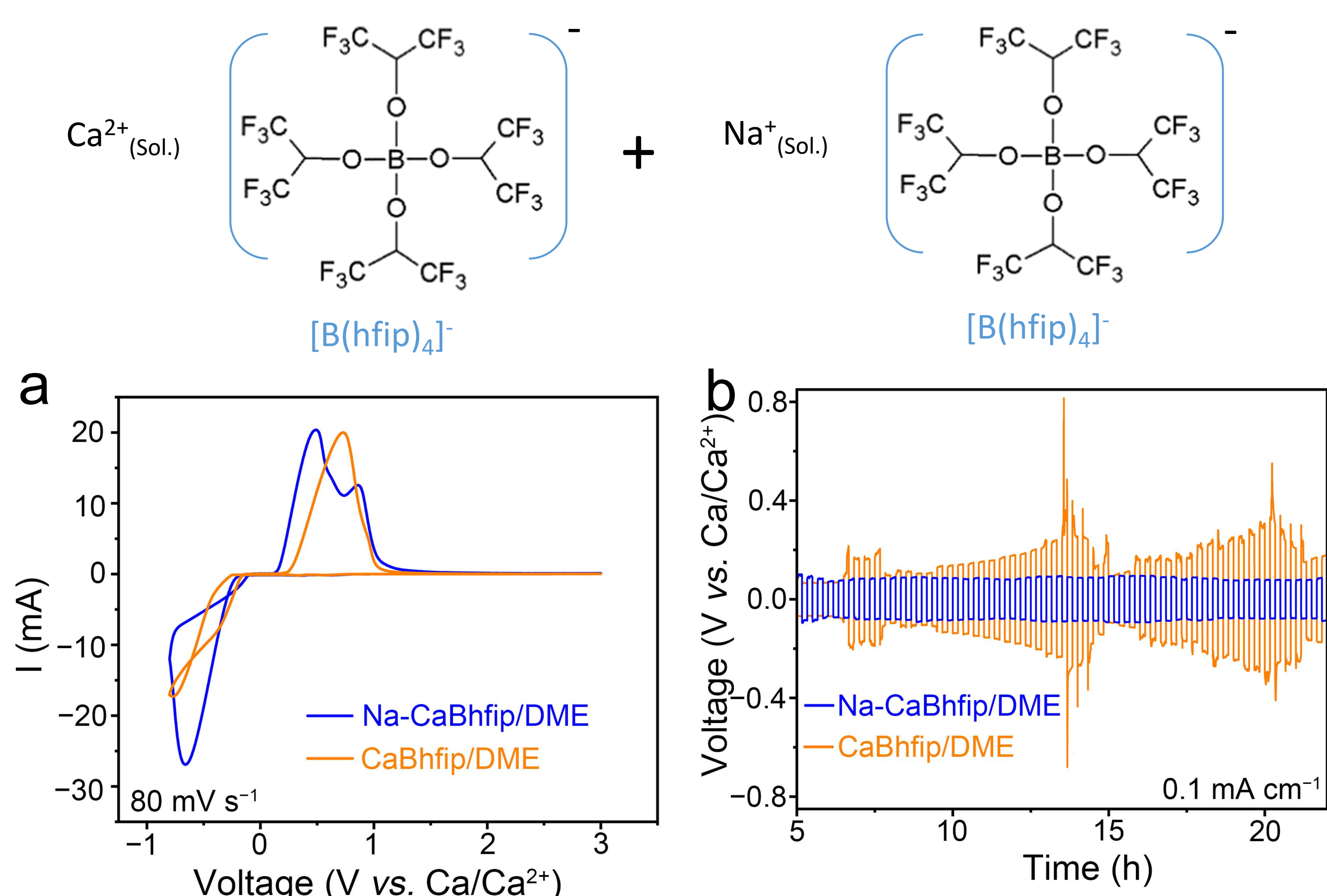
- The 5th most abundant element;
- The reduction potential of -2.87 V versus SHE, which is close to that of Li (-3.04 V vs SHE);
- Ca + S + 2e⁻ ↔ CaS (theoretical cell voltage of 2.47 V, volumetric capacity of 2073 mA h cm⁻³).

Current Challenges in Ca-S Batteries



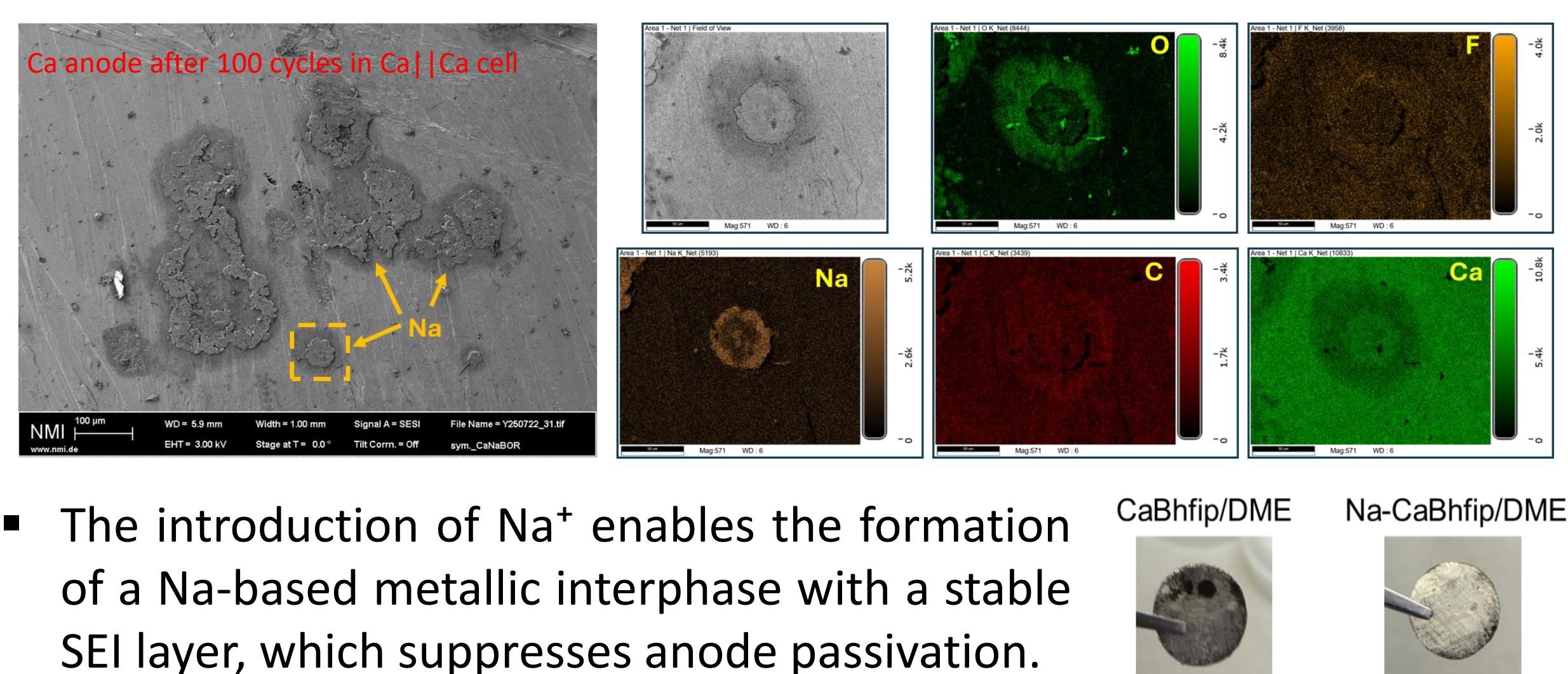
- Develop a compatible electrolyte with fast Ca ion transport;
- Suppress polysulfide shuttle and the passivation of Ca anodes;
- Understand the sulfur redox chemistry in Ca systems and achieve reversible sulfur conversion.

Electrochemical properties of modified borate electrolytes



- The modified electrolyte (Na-CaBhfp/DME) is capable of efficient Ca plating/stripping and has a high oxidation stability (>4 V).
- The Na-CaBhfp/DME electrolyte is compatible with Ca metal anode, allowing reversible Ca deposition at a low overpotential <0.1 V.

Post-SEM/EDS of the Ca anode after cycling

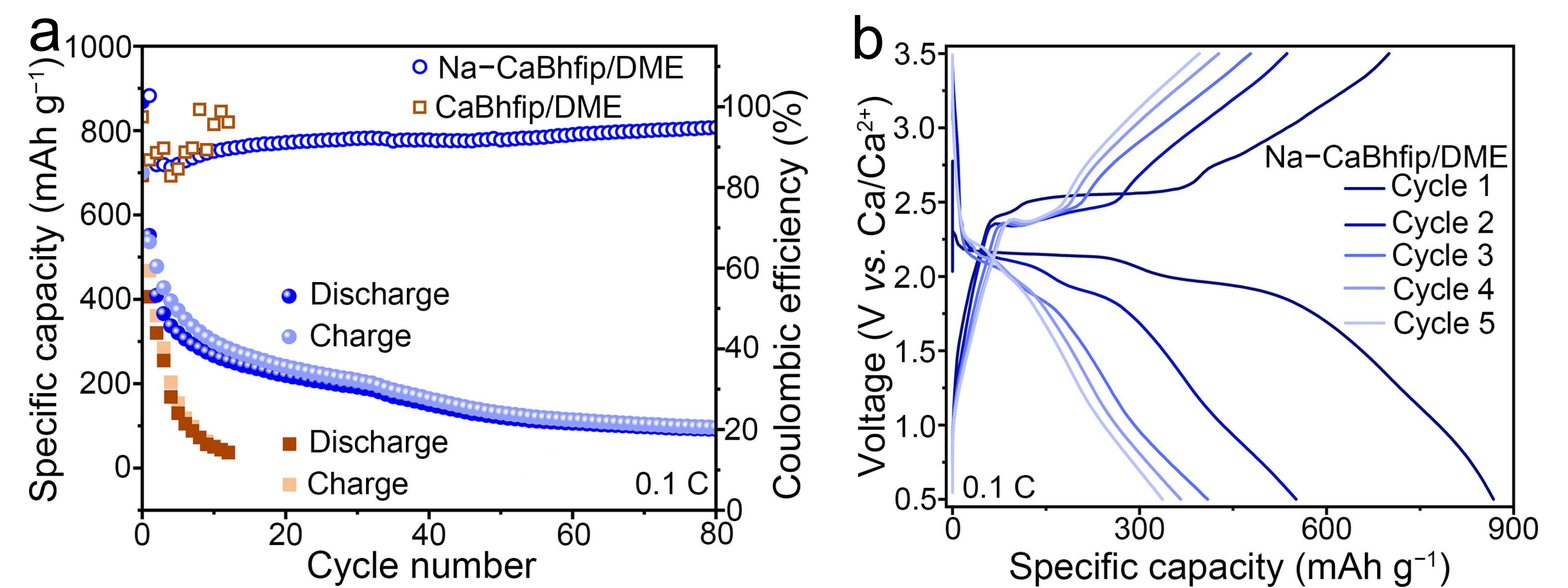


- The introduction of Na⁺ enables the formation of a Na-based metallic interphase with a stable SEI layer, which suppresses anode passivation.

References

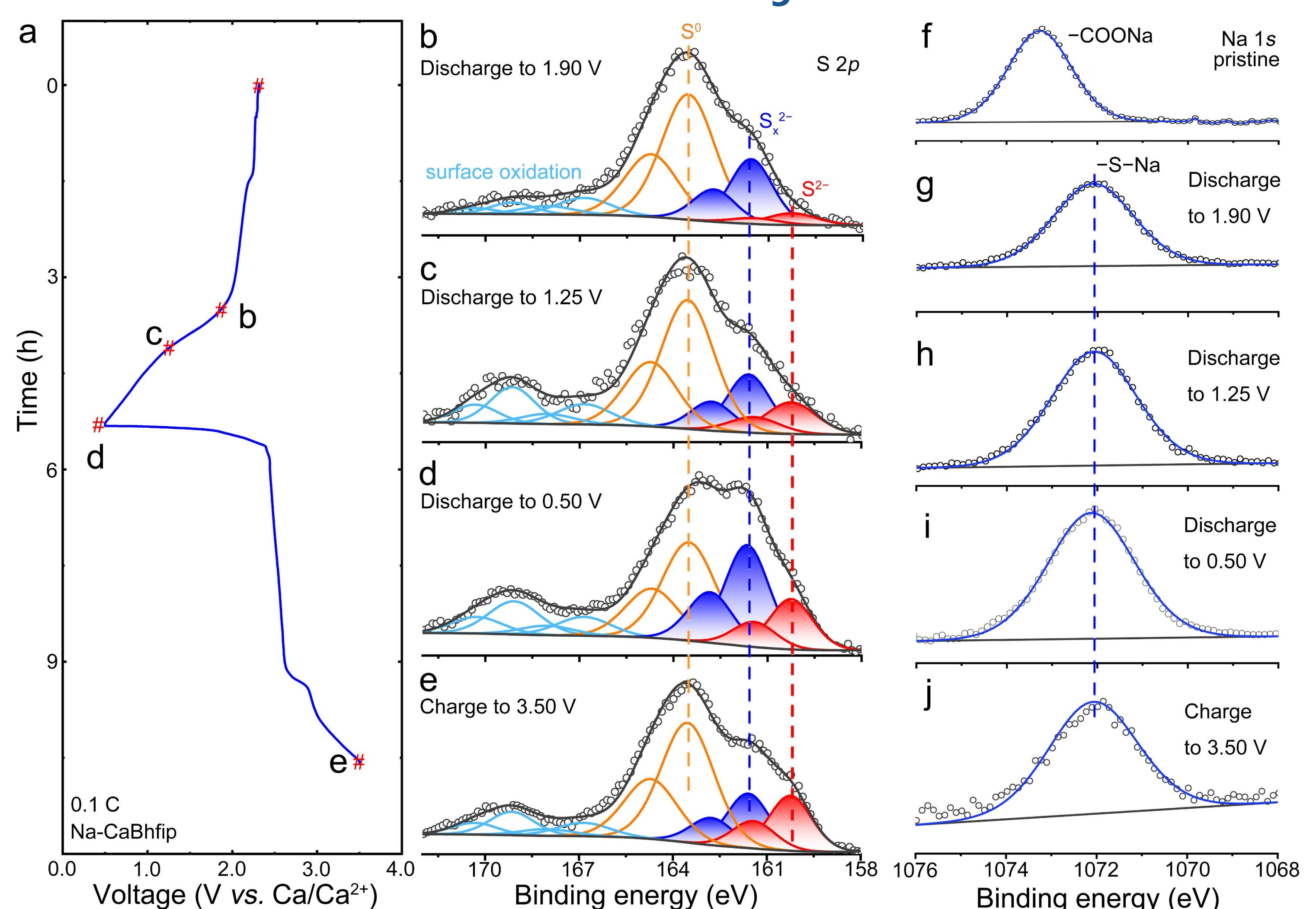
[1] M. E. Arroyo-De Dompablo, A. Ponrouch, P. Johansson, M. R. Palacín, *Chem. Rev.* 120 (2020), 6331. [2] Z. Li, B. P. Vinayan, T. Diemant, R. J. Behm, M. Fichtner, Z. Zhao-Karger, *Small* 16, (2020), 2001806. [3] Z. Li, O. Fuhr, M. Fichtner, Z. Zhao-Karger, *Energy Environ. Sci.*, 12 (2019), 3496.

Electrochemical characterization of the Ca-S batteries



- The Na-CaBhfp/DME electrolytes have been utilized for calcium-sulfur batteries, which exhibit an initial capacity 867.7 mA h g⁻¹ at a current density of 167.5 mA g⁻¹ (0.1C) and a discharge voltage plateau at ~2.2 V (close to its thermodynamic value).

Mechanistic investigation



- Na-CaBhfp/DME electrolytes enabled the effective and reversible conversion of sulfur to polysulfides and finally to sulfides.
- Na polysulfide and Na₂S were generated from the NaBhfp additive during cycling.

Acknowledgment

This project has received from the Federal Ministry of Education and Research (BMBF) of Germany within the project “CaSino” (Calcium sulfur: Innovative material development for more sustainable batteries), project ID: 03XPO487E.