

EES Batteries

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Fig. 4 (A) XPS profiles, (B) atomic ratio, and (C) SEM images of the SEIs formed on the Ca-electrode after 10 cycles in 0.5 M Ca(MSI)₂ and Ca(TFSI)₂ in DMAC electrolytes.

versus higher oxygen content for Ca(MSI)₂ – highlighting fundamentally different interfacial chemistries. Further plating experiments on Cu (Fig. S12 and S13) confirmed that Ca(TFSI)₂ forms a fluorine-rich, heavily decomposed SEI dominated by CaF₂, while Ca(MSI)₂ yields a fluorine-free, carbonate-rich, organic SEI. This chemical contrast directly affects performance: the resistive CaF₂ layer in Ca(TFSI)₂ hampers Ca²⁺ transport, leading to higher polarization, while the thinner, more uniform, CaF₂-free SEI in Ca(MSI)₂ facilitates improved ion transport and cycling stability. Morphological analysis (Fig. 4C) supports these conclusions – Ca(TFSI)₂ shows a rough, inhomogeneous surface; Ca(MSI)₂ yields a smoother Ca metal deposit, possibly the result of a more compact and homogeneous interphase favoring uniform electrodeposition.

Finally, to assess their practical applicability, the optimized electrolyte was tested in full Ca metal cells employing a 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) organic cathode (Fig. S15). The cell delivered clear reversible charge-discharge profiles in 0.5 M Ca(MSI)₂ in DMAC, demonstrating efficient calcium plating and stripping at the metal anode and reversible redox activity of PTCDA,⁴¹ while requiring further optimization for enabling efficient cycling of high voltage Ca-ion cathodes.⁴² Although a gradual capacity fading was observed upon cycling, this degradation is attributed to the partial dissolution of PTCDA in the electrolyte. These results

provide direct experimental evidence that the optimized electrolyte enables reversible Ca metal operation under realistic full-cell conditions, thereby validating its potential for integration into future calcium-based battery systems.

In summary, we introduce methanesulfonylimide (MSI⁻), a fluorine-free anions that enables the design of high-performance and environmentally benign electrolytes for calcium metal batteries. Owing to its straightforward synthetic accessibility and absence of fluorinated moieties, the hydrogen-rich analogue of TFSI⁻ offers a sustainable alternative to commercially available salts, whose degradation products often include corrosive and insulating fluorides. The Ca(MSI)₂/DMAC system exhibits stable and reversible Ca plating/stripping with lower overpotentials, and improved interfacial properties compared to its Ca(TFSI)₂-based counterpart. Spectroscopic and surface analyses reveal that the absence of fluorine prevents CaF₂ formation and instead promotes the growth of a uniform, organic-rich SEI that facilitates more efficient Ca²⁺ transport. This work highlights the importance of tuning solvation structures and interfacial chemistry through careful salt and solvent design. While a moderate increase in overpotential is observed during prolonged cycling, further enhancement of electrochemical stability and ionic conductivity is anticipated through future interfacial engineering strategies such as the integration of artificial SEI layers or



