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Citation for the original published paper (version of record):
Slim, Z., Cruz Cardona, C., Pechberty, C. et al (2025). Solvent-Mediated Electrolyte Design for Calcium Metal Batteries. ACS Materials Letters, 7(10): 3235-3242.
http://dx.doi.org/10.1021/acsmaterialslett.5c00892

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Solvent-Mediated Electrolyte Design for Calcium Metal Batteries

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Cite This: *ACS Materials Lett.* 2025, 7, 3235−3242

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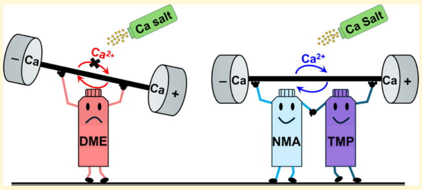


ABSTRACT: Current electrolytes for calcium batteries (CaBs) rely on cumbersome salt synthesis, hindering research and development. As a subclass of CaBs, calcium metal batteries (CMBs) could potentially offer high energy density due to their use of a calcium anode. However, realizing this advantage remains difficult, largely due to calcium's electrochemical instability. To address these challenges, we introduce a family of electrolytes made entirely from commercially accessible Ca-salts and solvent mixtures and further demonstrate stable cycling of symmetric Ca||Ca cells using only a solvent mixture, without added salt (i.e., not being an electrolyte on its own). Notably, this cycling stability extends to CMB full cells using low salt concentration electrolytes (e.g., 0.1 M Ca(OTf)$_2$ in NMA:TMP), and similar full cell performance is also achieved using other combinations of salts and solvent mixtures. Extensive electrochemical testing confirms stable cycling under diverse and challenging conditions. Overall, our findings reframe electrolyte design principles and pave the way for practically useful CMB cells.

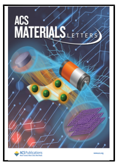
INTRODUCTION

While lithium-ion batteries remain the dominant choice in commercial applications, interest in various next-generation batteries is growing, mainly due to their promise of achieving higher energy density.[1] Among these, calcium batteries (CaBs) stand out due to calcium's high natural abundance, high theoretical volumetric capacity, low electrochemical potential, and affordability.[2] Achieving high energy densities is, however, ultimately contingent on using a Ca metal anode, i.e., making a calcium metal battery (CMB).[1] Indeed, the successful demonstration of reversible Ca plating and stripping at elevated temperatures using a Ca(BF$_4$)$_2$ in EC:PC electrolyte,[3] and later on even at room temperature using a Ca(BH$_4$)$_2$ in THF electrolyte,[4] sparked renewed interest in CMBs. However, these electrolytes have significant limitations restricting their practical applicability; the former suffers from water contamination originating from the salt and requires elevated temperature for optimal operation,[3,5] while the latter has low oxidative stability and poor ionic conductivity.[6]

This has motivated researchers to explore alternative electrolyte designs, many of which are inspired by magnesium battery chemistry. In this regard, electrolytes based on salts such as the Ca[B(hfip)$_4$)]$_2$,[7,8] its aluminate analogue,[9] and monocarborane,[10] have emerged as promising alternatives. The ability of these electrolytes to support reversible Ca plating and stripping, combined with their relatively high anodic stability, has established them as promising CMB electrolytes. Indeed, various CMB cell chemistries have since emerged, but they all remain far from practical; the salts used demand cumbersome synthesis paths and conditions and the electrolytes rely on highly flammable organic solvents.[11−13] Altogether, these obstacles further complicate the already challenging task of developing practical CMBs.

Recognizing the need for more practical electrolyte designs and strategies, the use of commercially available chemicals has become a key focus. This would eliminate the need for Ca-salt synthesis and provide a straightforward method for CMB/CaB anode and cathode screening. However, commercial salts such as Ca(TFSI)$_2$ in ethereal solvents do not support stable Ca cycling, limiting their applicability.[14,15] To overcome this, researchers have begun using strongly solvating (co)solvents, such as dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO), both of which have recently proven effective in realizing CMB full cells.[15−18] Yet, these electrolytes remain restricted to the Ca(TFSI)$_2$ salt: DMAc is highly sensitive to the Ca-salt concentration and anion type, with a reported cycling lifespan of ∼ 100 h and high polarization in symmetric Ca||Ca cells,[15,17] while DMSO-based electrolytes also rely on costly and moisture-sensitive ionic liquids in their composition.[18]

Received: June 9, 2025
Revised: August 22, 2025
Accepted: August 22, 2025
Published: August 28, 2025



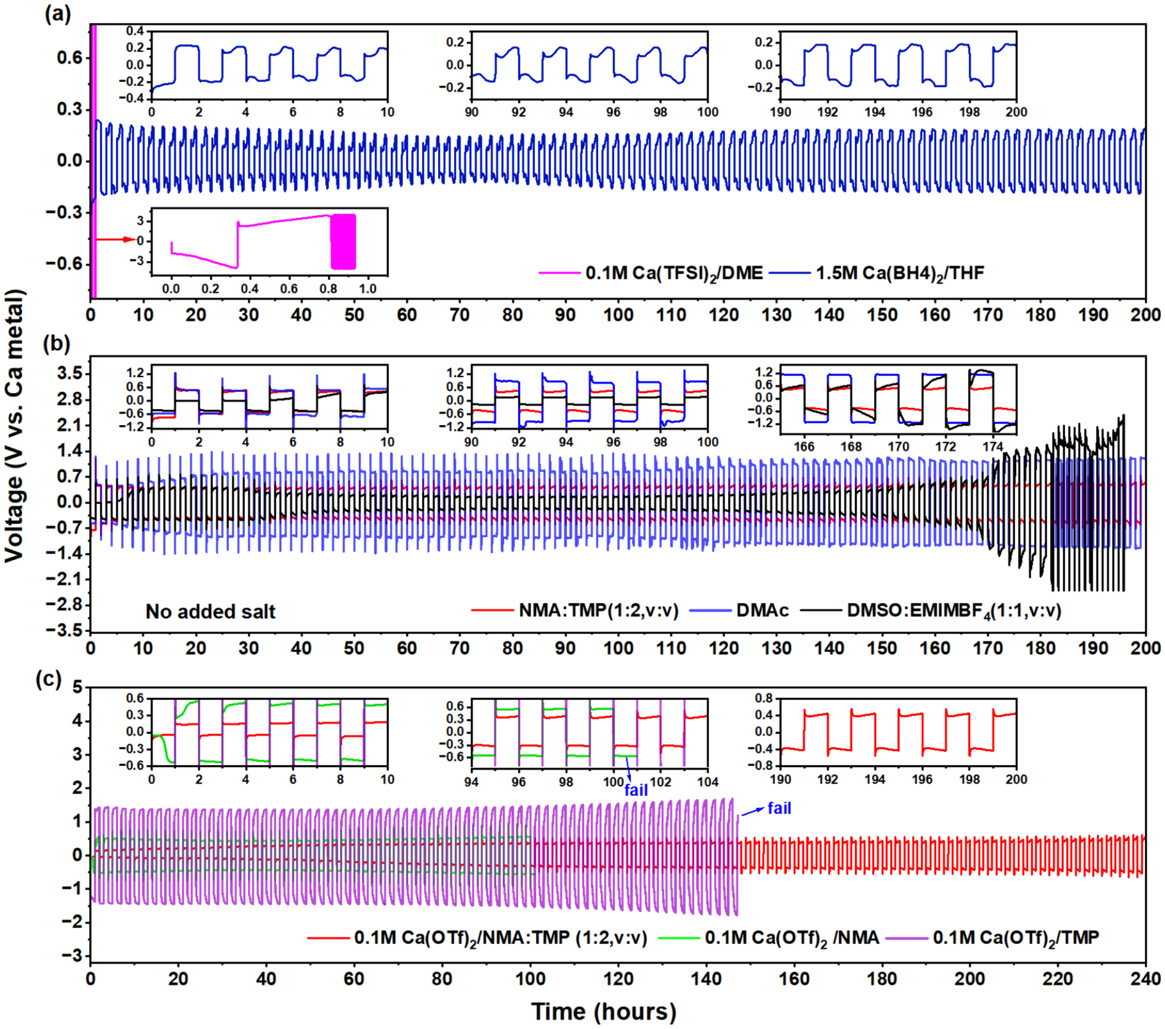


Figure 1. Electrochemical performance of Ca||Ca symmetric coin cells in various solvents, solvent mixtures and electrolytes, cycled at a current density of 0.02 mA/cm^2 and a capacity of 0.02 mAh/cm^2.

Thus, considering all the above, alternative electrolyte designs are needed. Herein, we introduce a family of electrolytes based on strongly solvating solvents. We hypothesize that such solvents can enable stable Ca cycling even without predissolved salts, laying the foundation for low-salt concentration electrolytes. While multiple electrolytes are investigated, this study primarily focuses on calcium trifluoromethanesulfonate (Ca(OTf)$_2$) dissolved in a mixture of *N*-methylacetamide (NMA) and trimethyl phosphate (TMP). Ca(OTf)$_2$ was selected as a representative commercially available Ca-salt, despite its known challenges in CMBs,[15] to demonstrate the versatility of our electrolyte design. NMA was selected for its structural similarity to DMAc. However, since NMA is solid at room temperature, a liquid primary solvent was required to create a liquid mixture; TMP was chosen not only to serve this function but also for its nonflammable nature and proven ability to facilitate reversible Mg metal battery cycling.[19,20] Building on this, we evaluate electrochemical performance, uncover redox mechanisms in the organic cathode, and probe electrolyte interactions and local structure—all to advance CMBs.

RESULTS AND DISCUSSION

To assess electrolyte performance, we first investigate cycling stability in symmetric Ca||Ca cells. We then evaluate full cell performance under various conditions using 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) as the cathode. Additionally, we analyze the Ca^{2+} redox mechanism of PTCDI via *ex situ* Fourier-transform infrared (FTIR) spectroscopy. Finally, we examine Ca^{2+}−solvent and Ca^{2+}−OTf interactions using Raman spectroscopy, density functional theory (DFT) calculations, and molecular dynamics (MD) simulations. The following sections detail these results and their implications for CMB electrolyte design.

Solvent-Mediated Cycling Stability in Symmetric Ca||Ca Cells. Initially, to establish a benchmark, we evaluated the cycling stability of Ca metal in symmetric Ca||Ca cells using a Ca(BH$_4$)$_2$ in THF electrolyte — well-known for its ability to plate and strip Ca[4,21,22] — and using Ca(TFSI)$_2$ in DME, a frequently studied electrolyte in CMB research.[14,15,23,24] The cell assembled with the Ca(BH$_4$)$_2$ in THF electrolyte cycles stably with an overpotential of ca. 0.15 V vs Ca metal, the first 200 h of cycling are presented in Figure 1a. In stark contrast, the Ca(TFSI)$_2$ in DME-based cells failed shortly after the cycling began. Although the Ca(BH$_4$)$_2$ in THF electrolyte demonstrates exceptional cycling stability (Figure S1), this

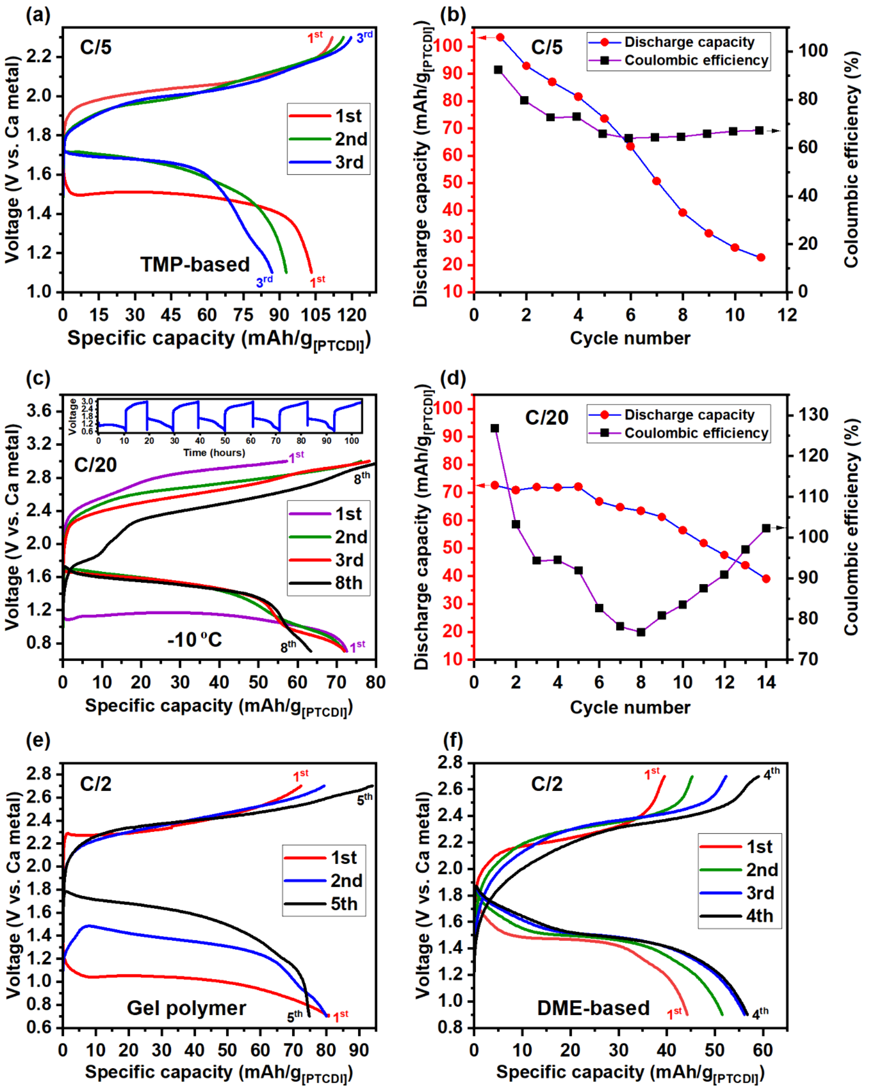


Figure 2. Discharge−charge performance of Ca||PTCDI full cells: (a) selected cycles and (b) performance using a 0.1 M Ca(OTf)$_2$ in NMA:TMP electrolyte at room temperature, (c) and (d) the same at −10 °C, and (e) same as (a) but with the electrolyte *in situ* polymerized into a GPE, and (f) using 0.1 M Ca(TFSI)$_2$ in NMA:DME (1:2, v:v).

stability alone is insufficient for constructing CMB full cells, as the application of this electrolyte in full cell configuration without Li cosalts has yet to be demonstrated.[25,26]

As a second step, we examine whether neat solvents or their mixtures, without added salt, can sustain stable Ca||Ca cycling. Conventional battery electrolytes require a dissolved salt to form an electrolyte, as stable metal anode cycling is generally assumed to be impossible without the addition of salt. However, recent studies on strongly solvating solvents, such as DMAc, have demonstrated that stable Ca cycling can be achieved even at low salt concentrations.[15,17] This stability was attributed to solvent effects, particularly the formation of a favorable solid electrolyte interphase (SEI).[15] Given their dominant role in stabilizing calcium metal, can such solvents also enable stable cycling in the complete absence of added salt?

To explore this, we tested several strongly solvating solvents and their mixtures—entirely without added salts—comparing our NMA:TMP mixture with both DMAc and DMSO:EMIMBF$_4$ (Figure 1b). The latter was selected due to its recently demonstrated success in stabilizing calcium metal anodes.[18] All cells exhibited remarkable cycling stability, although with noticeable differences in voltage profile as compared to when using a Ca(BH$_4$)$_2$ in THF electrolyte. Notably, despite the absence of any added salt, our NMA:TMP mixture enabled stable cycling for over 200 h with an overpotential of ca. 0.3 V vs Ca metal—demonstrating a significant improvement over the Ca(TFSI)$_2$ in DMAc electrolyte, which contained a dissolved salt yet showed more limited cycling performance.[15] Nonetheless, these results demonstrate that cycling stability in strongly solvating solvents is primarily governed by the interaction between the solvent and the Ca metal anode. While the cycling stability of Ca in DMAc- and EMIMBF$_4$:DMSO-based electrolytes was attributed to Ca plating and stripping in symmetric cells,[15−18] direct evidence for Ca metal deposition on inert substrates, including stable cycling in half-cell configurations, has yet to be reported. Based on our results, we propose an alternative mechanism. We hypothesize that cycling stability in strongly-solvating solvents and their mixtures arises from two simultaneous processes: the chemical/electrochemical dissolution of the Ca metal anode, mediated by the strongly solvating solvent, and a

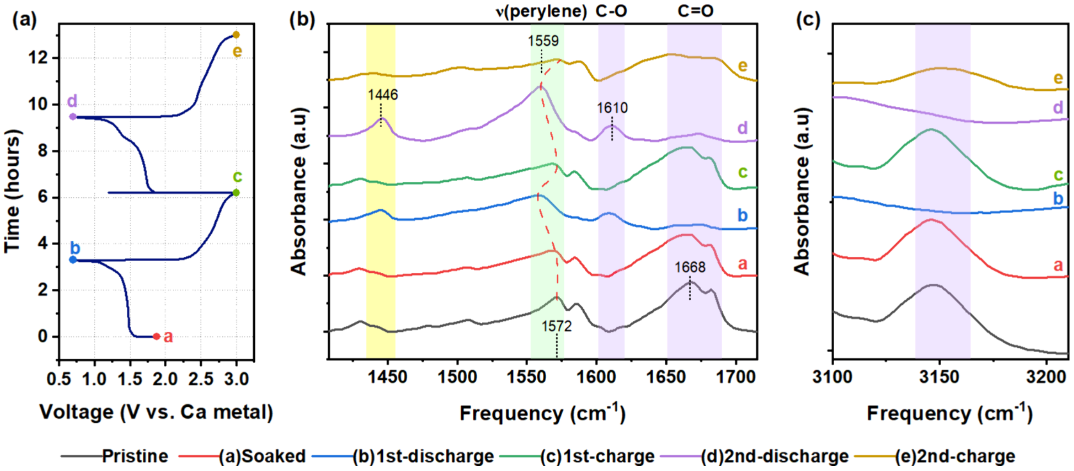


Figure 3. (a) Voltage–time profile of a Ca‖PTCDI cell cycled at C/5 rate, and (b) and (c) *ex situ* FTIR spectra illustrating the corresponding spectral changes of PTCDI at different charge–discharge stages.

solvent-dominated reductive decomposition, the latter a must for charge-neutrality. Supporting this hypothesis, electrochemical impedance spectroscopy (EIS) measurements conclusively eliminate the possibility of capacitive behavior (Figure S2). Additional evidence comes from findings that NaTFSI in NMA electrolytes can chemically dissolve Na metal,[27] while a solvent-derived SEI has been proposed as a key factor in Ca cycling stability.[15] Moreover, a very recent study on Ca(TFSI)$_2$ in DMAc proposed that Ca undergoes corrosion in these electrolytes, a process partly driven by solvent interactions with the metal surface.[28] This supports our interpretation that solvent–metal reactivity, including Ca corrosion, together with solvent decomposition, governs the electrochemistry in such electrolytes and enables galvanostatic cycling without added salt. The remarkable stability we observe in the absence of added salts is counterintuitive, given calcium's inherent tendency to passivate in conventional electrolytes,[29] yet it supports the concept of solvent-mediated stabilization.

These insights indicate that achieving stable Ca cycling requires careful solvent selection. Since the NMA:TMP mixture is the focus of this study, we sought to determine two key factors. First, we examined how salt addition influences its cycling stability, as added salt is essential for ion transport in full cells. Second, we investigated whether the mixture exhibits a synergistic effect compared to the single-solvent electrolytes. To evaluate these factors, we tested Ca‖Ca cells using Ca(OTf)$_2$ in NMA as a single solvent, in TMP as a single solvent, and in our NMA:TMP mixture (Figure 1c). The results reveal that salt addition significantly lowered the cycling overpotential. Additionally, using the Ca(OTf)$_2$ in NMA:TMP electrolyte drastically lowers the cycling overpotentials and renders longer cycling life than either the single solvent NMA or TMP electrolytes. The relatively shorter cycling life of the NMA-based electrolyte is likely due to its tendency to solidify at room temperature (Figure S3). These results suggest that the relatively low overpotential originates from the presence of NMA, while TMP contributes to improving cycling life. This interpretation is further supported by the cycling stabilities of Ca(TFSI)$_2$ in DME:NMA and Ca(TFSI)$_2$ in TMP:DMAc (Figure S4). Furthermore, unlike DMAc,[15] the stability of Ca(OTf)$_2$ in NMA:TMP is less sensitive to anion type and concentration (Figure S5). Our findings highlight the importance of solvent mixtures in stabilizing Ca cycling and demonstrate that electrolyte performance can be maintained even at low salt concentrations, regardless of the specific Ca-salt used. This lays the foundation for designing low salt concentration electrolytes for CMBs, which could significantly reduce cost (Table S1).[30] To further probe the electrochemical behavior, we conducted cyclic voltammetry using Ca‖Stainless Steel cells with either 1.5 M Ca(BH$_4$)$_2$ in THF or 0.1 M Ca(OTf)$_2$ in NMA:TMP (Figure S6). The former exhibited more reversible Ca redox behavior, whereas the latter showed quasi-reversible features. These results further suggestt that galvanostatic cycling in symmetric cells reflects mixed contributions from Ca^{2+} redox processes and solvent decomposition.

Electrochemical Performance Ca‖PTCDI Full Cells. Using the previously discussed cycling stability as the basis for our electrolyte design, we explored the application of this stability in Ca-metal full cells by incorporating a low concentration of Ca(OTf)$_2$ salt and using organic PTCDI as the cathode. The Ca‖0.1 M Ca(OTf)$_2$ in NMA:TMP ‖PTCDI cells exhibit a well-defined charge–discharge profile, delivering a discharge voltage of 1.7 V vs Ca metal and an initial discharge capacity of 105 mAh/g (~76% of the theoretical capacity of PTCDI) at a C/5 rate (Figure 2a). Stable cycling was sustained for 11 cycles, while the coulombic efficiency (CE) initially fluctuated significantly before stabilizing around ~ 67% (Figure 2b). This relatively low CE is attributed to overcharging, likely caused by PTCDI dissolution in the electrolyte, a well-reported phenomenon for PTCDI and other organic cathodes.[15,31−34] Since PTCDI dissolution contributes to capacity fade, we explored whether modifying operating conditions could further enhance stability. As lower temperatures can suppress the solubility of the discharged PTCDI product, we tested whether Ca‖PTCDI cells could operate at subzero temperatures. This approach not only improves cycle life by reducing active material loss but also expands the prospective applications of Ca‖PTCDI chemistry to include low-temperature operation. To evaluate this, we placed the Ca‖PTCDI cells in an environmental chamber and cycled them at − 10 °C. The cells exhibited stable operation for over 10 cycles at C/20 (Figure 2c-d), which, to our knowledge, marks a benchmark for CMB full cell performance at subzero temperatures. While low-temperature operation reduced PTCDI dissolution, allowing stable cycling in full cells for

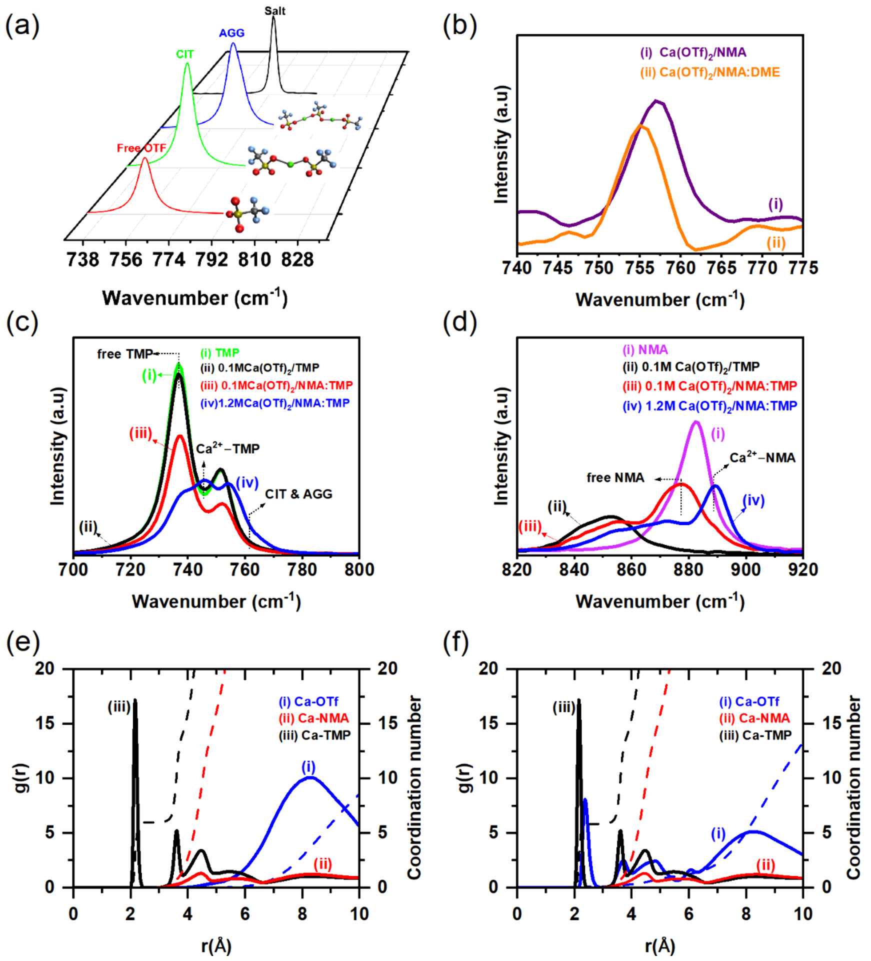


Figure 4. (a) Comparison of the DFT simulated Raman bands of free OTf, contact ion triplets (CITs), and aggregates (AGGs) and the experimental Raman spectra of the $Ca(OTf)_2$ salt, (b) Raman Spectra of $Ca(OTf)_2$ in NMA and NMA:DME electrolytes, (c) and (d) Raman spectra of $Ca(OTf)_2$ in NMA:TMP electrolytes, and (e) and (f) MD-derived radial distribution functions of 0.1 and 0.3 M $Ca(OTf)_2$ in NMA:TMP electrolytes, respectively.

over 300 h (Figure S7), it does not fully eliminate the issue. To further address this, we transformed the 0.1 M $Ca(OTf)_2$ in NMA:TMP liquid electrolyte into a gel polymer electrolyte (GPE) using *in situ* polymerization—a method successfully implemented in Mg-sulfur batteries.[35] While the GPE did not enhance performance (Figure 2e), its stable cycling confirms compatibility with Ca metal and suggests that it may help reduce leakage and improve safety.

Beyond mitigating PTCDI dissolution, we investigated another avenue for the Ca||PTCDI cell chemistry: modifying the electrolyte formulation itself. Since our results highlight NMA's effectiveness in stabilizing Ca anodes, we explored its viability as a cosolvent to $Ca(TFSI)_2$ in DME—an electrolyte that does not inherently support stable Ca cycling, as previously demonstrated (Figure 1a). While some approaches have shown promise in stabilizing the Ca interphase with this electrolyte,[24] we found that incorporating NMA as a cosolvent enabled stable Ca cycling in both full cells (Figure 2f) and Ca||Ca symmetric cells (Figure S4). Furthermore, we demonstrate that this electrolyte design is compatible with a variety of Ca-salts, including $Ca(TFSI)_2$, $Ca(FSI)_2$, $Ca(BH_4)_2$, and, most remarkably, CaF_2 (Figure S15b), highlighting the versatility and generalizability of this solvent-mediated stabilization strategy. Although these advances do not fully resolve the challenges facing CMB development, they do serve as a proof of concept, demonstrating how cosolvent modification can be leveraged to stabilize the Ca metal interphase, achieving functional CMB full cells and paving the way for practical application.

Probing the Ca^{2+}–PTCDI Redox Mechanism via *Ex Situ* FTIR spectroscopy. To gain deeper insight into the redox mechanism underlying the observed electrochemical reversibility in Ca||PTCDI cells, we performed an *ex situ* FTIR spectroscopy analysis on cycled PTCDI electrodes at different charge–discharge stages (Figure 3). During discharge, the peak at 1668 cm^{-1}, associated with the C=O group of PTCDI, is no longer observed (Figure 3b), suggesting an enolization reaction, as previously demonstrated for Li^+,[31] Mg^{2+},[32] and Ca^{2+}.[33] This loss of the C=O band is accompanied by the emergence of a new band at 1610 cm^{-1}, attributed to the formation of the $C-O^-$ group,[32] along with an additional band at 1446 cm^{-1}, previously observed for other Ca-organic batteries, indicating Ca^{2+} coordination.[33] The peak at 3150 cm^{-1} (Figure 3c), linked to hydrogen bonding within PTCDI, is also absent during discharge. Furthermore, the shift of the band from 1572 cm^{-1} to 1559 cm^{-1} suggests charge delocalization across the π-conjugated system.[32] Upon charging, these spectral features revert to their original states, confirming the electrochemical reversibility of the Ca^{2+}–PTCDI redox reaction. Altogether, these results confirm Ca^{2+}

coordination and charge delocalization, highlighting the electrochemical reversibility of the Ca^{2+}−PTCDI redox chemistry.

Probing Local Electrolyte Structure via Raman Spectroscopy, DFT Calculations and MD Simulations. Initially, we analyzed the 740−780 cm^{-1} region of the Raman spectra, which features the symmetric deformation mode $\delta_s(CF_3)$ of the OTf^- anion (Figure 4a). This region serves as a key reference for tracking electrolyte structure evolution with increasing salt concentration. A shift in the DFT-calculated $\delta_s(CF_3)$ band is observed relative to the experimental spectrum of neat $Ca(OTf)_2$ salt, reflecting changes in the coordination environment. This comparison allows us to distinguish between free anions, contact ion triplets (CITs), and aggregates (AGGs).

Furthermore, to isolate Ca−OTf interactions, we also investigated electrolytes without TMP, since its signal overlaps with $\delta_s(CF_3)$, and evaluated how NMA alone affects $Ca(OTf)_2$ speciation. To do this, we used NMA as a cosolvent with DME, where $Ca(OTf)_2$ is otherwise poorly soluble (Figure S8). In both 0.1 M $Ca(OTf)_2$ in NMA and in NMA:DME electrolytes, the $\delta s(CF_3)$ band appears at 755−758 cm^{-1} (Figure 4b), confirming that OTf primarily exists as free anions in both electrolytes. These results ascertain NMA's role in enhancing salt dissolution, increasing the availability of Ca^{2+} and thus facilitating (cat)ion transport.

Next, we examine the Ca−TMP and Ca−OTf coordination by varying the salt concentration from 0.1 to 1.2 M for the $Ca(OTf)_2$ in NMA:TMP electrolytes (Figure S9). The concentration range was chosen to observe the transition from low to higher salt concentrations, allowing us to investigate the effects of salt concentration on coordination and ion pairing.[36] As the concentration increases, the band at 737 cm^{-1} decreases in intensity, while the band at 745 cm^{-1} becomes more prominent. This trend suggests that the former corresponds to free TMP, whereas the latter is associated with coordinated TMP, in line with previous findings on $Mg(TFSI)_2$ in TMP:DME electrolytes.[20]

Moving to another region of the spectra, we observe a broad band at 882 cm^{-1}, which is attributable to neat NMA (Figure 4d). In the presence of $Ca(OTf)_2$ salt, however, this peak split into two distinct bands, one at 878 cm^{-1}, corresponding to free NMA, and another at 889 cm^{-1}, which can be assigned to Ca^{2+}−NMA interaction. This observation is consistent with the 10 cm^{-1} shift predicted by the DFT calculations, where a similar shift is observed between free NMA and Ca^{2+}−NMA (Figure S10).

To substantiate these results and determine the Ca^{2+} coordination, we turn to the MD simulations. The radial distribution functions (RDFs) for the 0.1 and 0.3 M $Ca(OTf)_2$ in NMA:TMP electrolytes both show a sharp peak at 2.1 Å, corresponding to the first cation solvation shell (Figure 4e and 4f). Ca^{2+} preferentially coordinates with TMP, with a coordination number (CN) of six, consistent with experimentally determined Ca^{2+} CNs.[36] For the 0.3 M electrolyte, however, a new peak is observed at 2.4 Å, indicative for the emergence of Ca^{2+}−OTf ion pair interactions, which is consistent with the broadening of the CIT/AGG peak at 762 cm^{-1} (Figure S9a). Despite the presence of Ca^{2+}−OTf interactions in the 0.3 M electrolyte, the Ca^{2+}−TMP coordination remains dominant, while Ca^{2+}−NMA interactions are completely absent. This suggests that NMA plays a different role, likely through hydrogen bonding (more about hydrogen bond analysis in SI).

In terms of electrochemical behavior, this transition from solvent-dominated interaction to increasing Ca^{2+}−anion association suggests a reduction in Ca^{2+} mobility. Indeed, the Ca||Ca symmetric cell performance, including cycling lifespan and polarization, declines as the salt concentration increases from 0.1 to 0.6 M (Figure S5).

In conclusion, we introduce a family of Ca electrolytes and demonstrate that strongly solvating solvents can stabilize the calcium metal interphase, enabling stable cycling in symmetric Ca||Ca cells even without added salts. This suggests that Ca metal can serve as the primary source of Ca^{2+}, but also raises important considerations for interpreting symmetric cell data. Symmetric Ca||Ca cell testing has underpinned significant advancement in CMB research, including studies that inspired this very work.[15,17,18,37−41] However, our results indicate that such cycling, particularly with strongly solvating solvents—may not, on its own, confirm reversible Ca metal plating and stripping, highlighting the need for complementary analyses. Guided by this understanding, we demonstrate that this solvent-driven stability can be leveraged by adding a small amount of Ca salt, such as $Ca(OTf)_2$, enabling stable cycling in CMB full cells, even under challenging operating conditions.

Overall, these findings establish the viability of solvent-mediated stabilization strategies and underscore the need to elucidate the mechanisms of continuous solvent decomposition that enable galvanostatic cycling without added salt. Such decomposition can cause electrolyte depletion, cell dry-out, and hindered Ca^{2+} transport at the Ca metal/electrolyte interface, as observed for lithium metal batteries.[42] Addressing these challenges in future CMB development may benefit from electrolyte innovations supported by anode modification strategies, as demonstrated for Ca,[17] Mg,[43] and Li,[44,45] which can mitigate decomposition, improve moisture tolerance, and enhance safety. Altogether, this work reframes the role of solvents in enabling Ca metal cycling and opens unexplored pathways for electrolyte design for CMBs.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.5c00892.

Experimental and computational details. Electrolytes, electrodes and coin cell preparation procedures. Electrochemical protocols. Supplementary galvanostatic cycling, LSV, CV, EIS, and low-temperature data. Additional Raman, FTIR, DFT, and molecular dynamics analyses. Photographic images of electrolytes. Estimated CMB electrolytes cost (PDF)

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Author Contributions

Z.S. conceived the idea, designed the study, conducted the experiments and DFT calculations, analyzed and interpreted the results, and wrote the first draft of the manuscript. C.C. carried out, analyzed, and interpreted the MD simulations and wrote the corresponding section of the manuscript. C.P. and T.H. provided technical assistance and valuable discussions. Z.M and V.P. acquired funding and managed the project. P.J. provided mentoring, secured funding, managed the project, and acquired computational resources. All authors thoroughly revised and edited the manuscript and approved the final version.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Z.S. is grateful to Dr. Ezio Zanghellini for technical assistance and valuable discussions. Special thanks to Dr. Patricia Huijbers for project administration, manuscript review and editing, and insightful discussions. Z.S. also thanks Prof. Erik J. Menke (Colorado School of Mines) and Lic. Josef Rizell for helpful discussions. Z.S., C.C., and P.J. acknowledge computing time and storage on Tetralith, provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS), at the National Supercomputing Center (NSC) under grants 2024/5-259 and 2024/23-451. This work was funded by the NATO Science for Peace and Security (SPS) programme under project number G5910. Z.S acknowledges the use of OpenAI's ChatGPT (accessed between February and August 2025) for language polishing.

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