Article

Room-Temperature Calcium Plating and Stripping Using a Perfluoroalkoxyaluminate Anion Electrolyte

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Cite This: https://doi.org/10.1021/acs.jpcc.2c03272

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ABSTRACT: Multivalent ion chemistries, like Ca^{2+}, used in energy storage boast the potential to utilize solid metallic anodes and provide high volumetric energy density. The promise of such systems relies on the ability to incorporate high-voltage cathode materials while sustaining robust plating and stripping at the anode. These processes are dependent on an electrochemically stable electrolyte for ion transport and storage. Here, we report an addition to the limited pool of nonaqueous electrolytes capable of plating and stripping calcium at room temperature. The synthesis and structural properties of calcium tetrakis(perfluoro-*tert*-butoxy) aluminate ($Ca[TPFA]_2$) are described along with the electrochemical performance during plating and stripping (up to 55% Coulombic efficiency) and a proof of concept for full cell viability with a CuS cathode material. X-ray absorption spectroscopy (XAS) and density functional theory (DFT) experiments were used to study both the bulk solvation structure around calcium and possible decomposition pathways of the weakly coordinating TPFA anion.
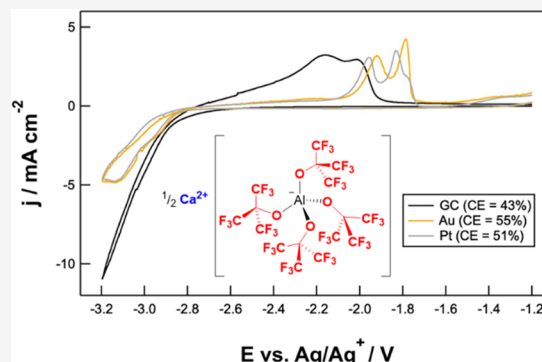
INTRODUCTION

The rise in use and scale of batteries for energy storage can benefit from more cost-effective, safer, and diverse storage systems. It stands to reason that utilizing technology based on more abundant resources and, in theory, comparable or better energy delivery will help push renewable energy sources further forward in the competition with fossil-fueled technologies. The quest for alternatives to lithium-ion batteries (LIBs) has spotlighted multivalent (MV) ion batteries. Once believed to be unfeasible technology of yesterday, studies related to calcium-ion batteries (CIB) have just taken off as research in MV-ion batteries gains momentum.[1−3] Early work reasoned that calcium deposition was impractical due to the lack of Ca-ion transport through passivating surface layers of the solid metal anode.[4]
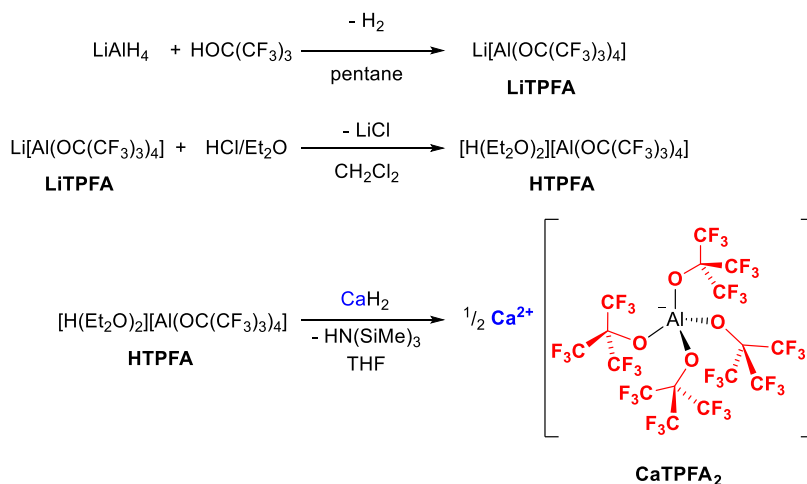
CIBs are attractive for their theoretical energy density (2060 mAh/cm^3) and relatively low reduction potential of Ca metal (−2.87 V vs standard hydrogen electrode (SHE)).[3] MV-ion technologies have the potential advantage of using solid metal anodes, as their proclivity to form dendrites is less favorable or nonexistent under operating conditions.[5] However, the development of the CIBs has been limited by the lack of suitable electrode materials, electrolytes capable of reversible deposition, and slow transport through passivating surface layers.[6] Only in the past few years have electrolytes been reported to reversibly plate and strip calcium at room temperature, beginning with the report of a reversible

$Ca(BH_4)_2$ in tetrahydrofuran (THF).[7] Commercial salts, like calcium bis (trifluoromethylsulfonimide) ($Ca[TFSI]_2$), are nonreversible due to relatively strong contact-ion pairing.[8,9] As a result, the trend toward weakly coordinating anions (WCA) paired with Ca^{2+} has been fruitful with discovery. The fluorinated calcium alkoxyborate salt, $Ca[B(hfip)_4]_2$ (hfip = hexafluoroisopropanol) in dimethoxyethane (DME), was reported twice in 2019,[10,11] followed by the report of calcium monocarbadodecaborate (in a mixed THF/DME solvent).[12] The highly reducing nature of calcium metal results in the formation of a passivating surface layer, likely due to the decomposition of electrolytes, even in the best performing electrolytes.[13]

To date, the tetrakis(perfluoro-*tert*-butoxy) aluminate (TPFA) anion is one of the most weakly coordinating anions incorporated in MV-ion electrolytes.[14] The perfluoro-*tert*-butoxide ligand lends an increased steric bulk that mitigates ion association and decomposition through [M(II)-TPFA]+ reduction or β-hydride elimination of the ligand. As a magnesium salt, the superior anodic stability has helped facilitate high-voltage cathode development for Mg-ion batteries.[15,16] As such, the TPFA anion has the necessary properties to serve as a viable candidate for a Ca-ion electrolyte

Scheme 1. Synthesis of Ca[TPFA]$_2$

$$LiAlH_4 \; + \; HOC(CF_3)_3 \xrightarrow[\text{pentane}]{- H_2} Li[Al(OC(CF_3)_3)_4]$$

LiTPFA

$$Li[Al(OC(CF_3)_3)_4] \; + \; HCl/Et_2O \xrightarrow[\text{CH}_2\text{Cl}_2]{- LiCl} [H(Et_2O)_2][Al(OC(CF_3)_3)_4]$$

LiTPFA   **HTPFA**

$$[H(Et_2O)_2][Al(OC(CF_3)_3)_4] \xrightarrow[\substack{- HN(SiMe)_3 \\ THF}]{CaH_2} \; ^{1}/_{2} \; Ca^{2+}$$

HTPFA

CaTPFA$_2$

capable of a reversible metal deposition while maintaining the high anodic stability needed to interface with high-voltage Ca cathodes. With these characteristics in mind, we report the use of Ca[TPFA]$_2$ in (DME) as an electrolyte displaying Ca-metal plating and stripping at room temperature, along with a high degree of anodic stability that enables full cell cycling. We are further able to understand the origin of electrolyte decomposition during metal deposition using knowledge of electrolyte solvation structure and reaction pathway analysis. This study further expands the multivalent electrolyte library utilizing a tetracoordinate alkoxyaluminate anion and demonstrates the versatility and accessibility of this synthetic platform.

■ RESULTS AND DISCUSSION

The target Ca[TPFA]$_2$ salt was synthesized using a three-step process similar to that of Mg[TPFA]$_2$ and Zn[TPFA]$_2$ (Scheme 1).[17,18] Li[TPFA] was synthesized by a cooled reaction between perfluoro-*tert*-butanol and a slurry of lithium aluminum hydride in pentane. Subsequently, the LiTPFA was protonated by precipitation of LiCl in a reaction with hydrogen chloride in diethyl ether. The final step was the formation of Ca[TPFA]$_2$ by the addition of CaH$_2$ to form a byproduct of hydrogen gas. The most crucial aspect of the synthesis and resulting electrochemical performance is the purification of the final salt by recrystallization of Ca[TPFA]$_2$.

Using 4,4′-difluorobenzophenone as an internal standard, the stoichiometry of the crystalline product indicates the solvated salt formula as Ca(DME)$_2$[TPFA]$_2$ (Figure S1). The absence of signal in ^{7}Li NMR in acetone-d_8 confirmed the removal of Li-containing impurities by recrystallization.

Analysis of Ca[TPFA]$_2$ compared to Mg[TPFA]$_2$ by attenuated total reflectance infrared (ATR-IR) spectroscopy displays nearly identical spectra, indicating comparable weakly coordinating behavior between Ca, Mg, and Zn systems in the solid state (Figure S2).

Cyclic voltammetry (CV) of 0.1 M Ca[TPFA]$_2$/DME electrolyte (Figure 1) demonstrates electrodeposition and dissolution of calcium metal on Au, Pt, and glassy carbon surfaces with Coulombic efficiencies calculated from CV that varied from 43 to 55%—higher in the case of the metal electrodes. Overall, Coulombic efficiency could have suffered from side reactions with residual water or overall cathodic stability of [TPFA]$^-$ toward Ca^{2+} reduction. The observed
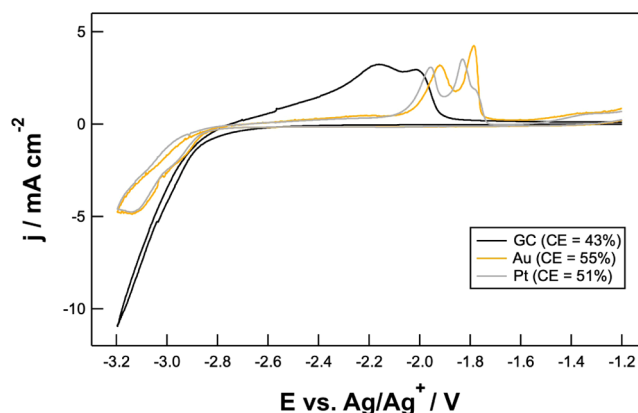

Figure 1. Cyclic voltammograms of Au, Pt, and GC in 0.1 M Ca[TPFA]$_2$/DME electrolyte. Pt was used as a counter electrode and Ag/AgNO$_3$ in DME as the reference electrode. The scan rate was 50 mV/s.

coulombic efficiencies and overpotentials hint at the presence of reductive decomposition at the interface or difficulties with Ca^{2+} desolvation during stripping. Solvation properties are known to affect electrolyte performance in plating, stripping, and intercalation.[8,13,19] The two oxidative peaks correlate with this speculation, and it is likely both types of parasitic events are to blame. To the best of our knowledge, this electrolyte system is one of two examples showing room-temperature plating and stripping with two stripping events in the oxidative sweep,[20] where others show one broad peak.[7,10−12] These observations warrant further study into bulk solvation of Ca^{2+} and interfacial composition of calcium deposition.

It is known that the Ca-ion electrolytes developed thus far often exhibit surface deposits that correlate with electrolyte decomposition. A calcium deposition product was prepared by applying a reductive current of 1.5 mA/cm^2 with Pt foil as the working electrode and a Ca rod as a counter electrode in 0.2 M Ca[TPFA]$_2$/DME electrolyte for 2.5 h. The as-prepared deposits were characterized by scanning electron microscopy (SEM). The SEM image of the deposits showed randomly dispersed globular islands (Figure S3). The energy-dispersive X-ray (EDX) spectroscopy spectrum indicates that the deposits are mainly composed of Ca, with contributions of carbon, fluorine, oxygen, and nitrogen. The O and N elements likely originated from the short period of air exposure prior to
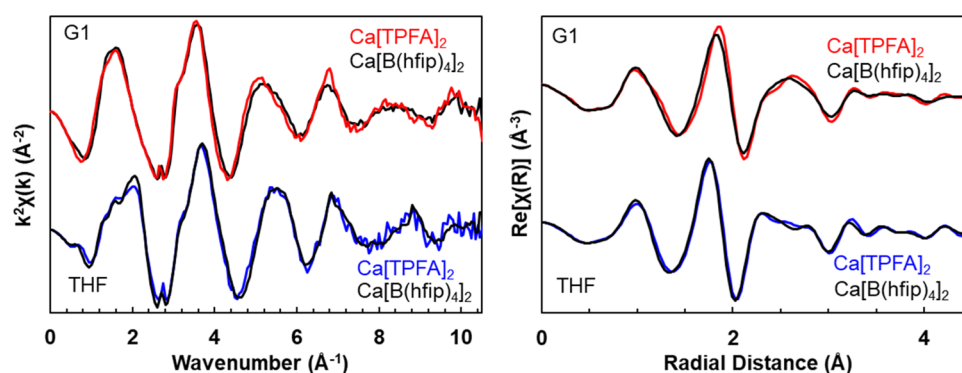
Figure 2. EXAFS of the Ca K-edge comparing $Ca[TPFA]_2$ and $Ca[BHFIP]_2$ dissolved in ethereal solvents.

sample measurement. The fluorine-containing component results from electrolyte reduction during the deposition (Figure S3). A similar reductive decomposition process of this fluorine-containing anion was noted with $Mg[TPFA]_2$, but only at higher concentrations.[18] The resulting bulk solution from chronopotentiometry left a dark gray cloudy suspension (Figure S4).

We endeavored to further understand how solvation affects the plating and stripping behavior of $Ca[TPFA]_2$ and the reductive decomposition. X-ray absorption spectroscopy (XAS) was employed to probe the local coordination environment of Ca^{2+} in ethereal solvents with $[TPFA]^-$ present. Solutions of $Ca[TPFA]_2$ were prepared in two ethereal-based solvents: tetrahydrofuran (THF) and dimethoxyethane (glyme, G1) at saturated concentrations around 0.5 M. The extended X-ray absorption fine structure (EXAFS) spectra of these Ca^{2+} solutions were then compared with $Ca[B(hfip)_4]_2$ salts dissolved within the same solvent series (Figure 2). Previous X-ray absorption near edge structure (XANES) and EXAFS measurements at the Ca K-edge of $Ca[B(hfip)_4]_2$ solutions suggested that Ca^{2+}–solvent interactions dominated the first shell solvation environment around the cation.[19,21] In contrast, anions such as trifluorosulfonimide (TFSI) have been previously shown to promote contact-ion paring with Ca^{2+}.[8,19] EXAFS oscillations for both $[TPFA]^-$-based salt solutions indicate similar first shell local structure compared with the $[B(hfip)_4]^-$-based analogues. There are slight differences in the amplitude and bond distance, particularly in the G1 solvent, that could suggest $[TPFA]$- and $[B(hfip)_4]^-$-containing electrolytes induce slightly different coordination environments around Ca^{2+}. However, we suggest the $[TPFA]^-$ anion is not present as a contact-ion pair around Ca^{2+} within the bulk solution as there are no identifiable features associated with Ca–S correlations in the EXAFS. The radial feature found at approximately 3 Å in both solvents can be fully described by multiple scattering photoelectron paths with the THF and G1 (corresponding to Ca–O–C multiple scattering).[19] The similarities between the two salts are not surprising considering their structural and weakly coordinating similarities, despite their differences electrochemically, which may indicate further nuances could be revealed at the interfaces.

To validate the role of weak coordination behavior in $Ca[TPFA]_2$, a computational investigation of reported anions with varying coordination ability was compared with the addition of Mg^{2+} and the more electropositive Ca^{2+} (Figure 3). Density functional theory (DFT) calculations determined the ion association strength between M^{2+} (M = Mg or Ca) and
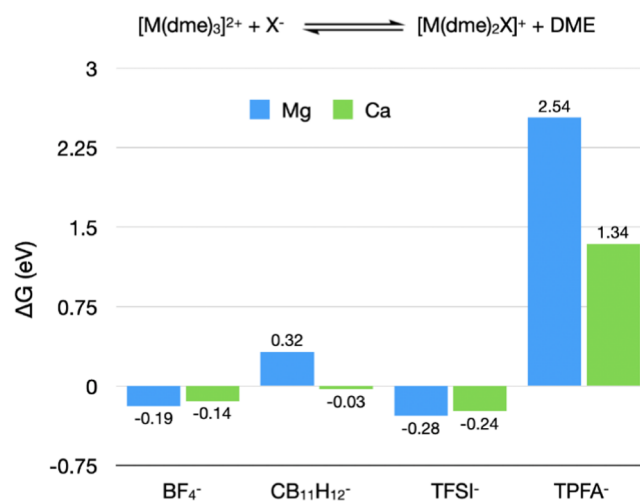

Figure 3. Free energy changes with different anions in the exchange reaction with DME. (The sign of the free energy being consistent with the right arrow direction).

anions, $[X]^-$ (where $[X]^- = [TFSI]^-$, $[BF_4]^-$, $[CB_{11}H_{12}]^-$, and $[TPFA]^-$) in DME. The negative value for $[TFSI]^-$ and near-zero value for BF_4^- suggest that coordination of these anions to Ca^{2+} (as well as Mg^{2+}) in DME is thermodynamically favored. The values for $[CB_{11}H_{12}]^-$ and $[TPFA]^-$ are positive, consistent with the classification of these anions as weakly coordinating, which may help explain, in part, their ability to plate and strip metals at room temperature. $[TPFA]^-$ shows a much more positive value compared to $[CB_{11}H_{12}]^-$, indicating $[TPFA]^-$ to be the most weakly coordinating between the two. The difference between the values for Mg^{2+} and Ca^{2+} hints toward a higher ion association with Ca^{2+} in all cases. This correlation suggests a higher likelihood of $Ca(TPFA)_2$ decomposition, despite the weak coordination ability seen in the EXAFS data.

To further probe the reductive decomposition behavior of $Ca[TPFA]_2$, DFT was used to analyze the barrier to the decomposition of the $[TPFA]^-$ anion in the presence of Ca^{2+} and Mg^{2+} (Figure 4). Based on previous computational studies on the $Mg[(TFSI)_2]$ system, where partially reduced metal ion, i.e., Mg^+, was found to enable a rapid decomposition of $TFSI^-$ through C–S bond breaking,[22] we consider the reductive decomposition should occur upon formation of the neutral $[M^+$–TPFA] complex (M = Mg or Ca). DFT analysis indicates that bond rotation of one bulky perfluoro-*tert*-butoxy group is the largest barrier to decomposition. Allowing extra
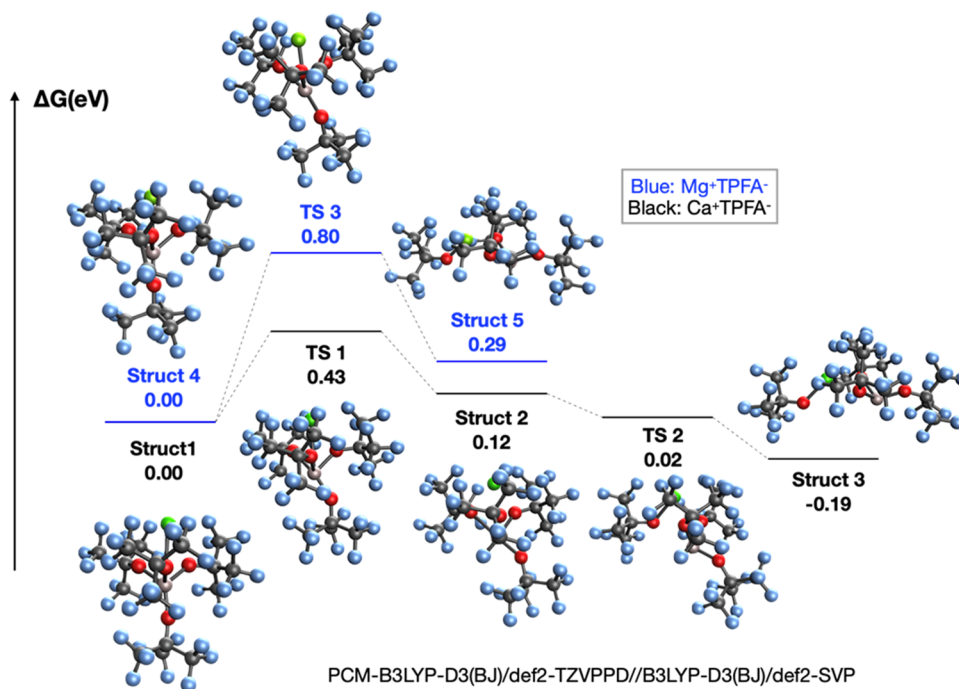
Figure 4. $[TPFA]^-$ anion decomposition analysis from DFT. The color of the atoms represents the following elements: blue—F, red—O, black—C, green—Ca or Mg, and silver—Al.

room for cation coordination to oxygen atoms paves the way toward ligand dissociation from the aluminum metal center. This finding suggests improvements can be made at the ligand through the incorporation of a more rigid ligand structure by increased steric bulk or utilizing bidentate ligands. Corollary to the calculated ion association discussed above, the barrier to anion decomposition is higher in the Mg system than Ca. With that in mind, we surmise that the $Ca[TPFA]_2$ electrolyte is more likely to experience reductive decomposition.

As an electrolyte for calcium-ion batteries, an ideal system will have to exhibit both reversible metal plating and stripping and high anodic stability to be compatible with high-voltage cathode systems. Having clearly demonstrated Ca-metal plating/stripping in this electrolyte and understood the reasons for reductive instabilities, we turn our attention to the anodic stability of the electrolyte to assess its practicality for full cell integration. Linear sweep voltammetry (LSV) of $Ca[TPFA]_2$ in DME (at 0.1 and 0.2 M) shows an onset of oxidation close to 4.5 V vs Ca/Ca^{2+} (Figure S5). There appears to be a minor oxidative event beginning near 4.0 V at 0.2 M. Since $[TPFA]^-$ has been established as one of the most anodically stable anions (paired with Mg^{2+}), it makes sense that the $Ca[TPFA]_2$ salt would also possess similar anodic stability, yet limited by the DME solvent. The practical stability limit was established using the 0.2 M solution in DME by a capacity-based method to estimate the electrochemical anodic stability.[18,23] The voltage at which a rapid increase of the R-parameters was observed was around 3.9 V (Figure S6). Although the indicated voltages do not guarantee sufficient electrolyte stability, they give an approximate estimate for the upper limit.

With an acceptably large electrochemical window, we tested a proof of concept for electrolyte compatibility with a full battery cell. For the test, 0.2 M $Ca[TPFA]_2$/DME was assembled in a Swagelok cell with a CuS cathode and Ca-metal anode. The cell was charged and discharged for four cycles showing characteristic curves for Mg-ion battery cycling with

the same cathode material.[24] At the fourth cycle (Figure 5), the increased slope during discharge correlates with the electrolyte decomposition observed during chronopotentiometry and CV.
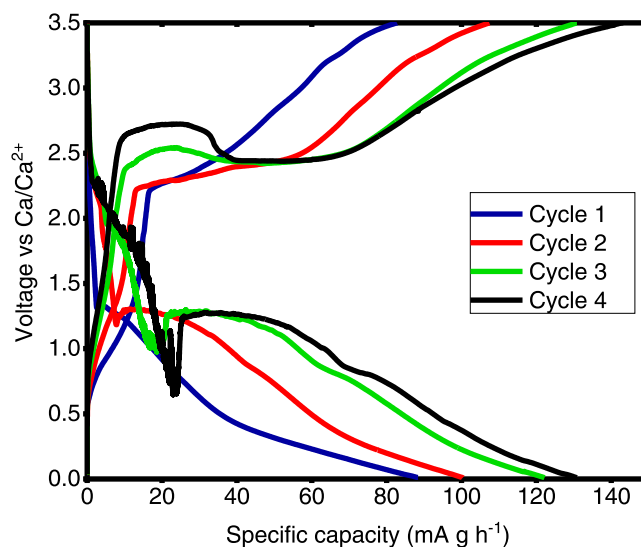

Figure 5. Charge–discharge behavior of CuS cathode material cycled at a rate of 0.1 C using 0.2 M $Ca[TPFA]_2$/DME and a calcium metal anode. Note that the first cycle is a discharge step.

■ CONCLUSIONS

We have reported a new nonaqueous Ca-ion electrolyte, $Ca[TPFA]_2$, that displays room-temperature Ca-metal electrodeposition and high anodic stability, with compatibility toward a CuS conversion cathode. Evidence of electrolyte reduction in chronopotentiometry correlates to only modest Coulombic efficiencies in CV and full cell cycling stability. DFT analysis suggests the lower overall CE of the Ca system derives from a

relatively higher likelihood of ion association and a lower barrier to $[TPFA]^-$ decomposition with Ca^{2+}. Overall, demonstration of $[TPFA]^-$ in the calcium system has shown the added hurdles multivalent electrolytes face regarding reductive decomposition and passivating interfacial byproducts. The experiment–theory combination has provided insight into future areas of improvement for the alkoxyaluminate anion design theme that, if leveraged correctly, will produce more stable electrolytes. The similarities of $[TPFA]^-$ to other WCA electrolytes help explain the ability to plate and strip calcium at room temperature. Still, the modest efficiencies hint toward differences beyond bulk solvation characteristics. Considering the highly reducing nature of calcium, current work is focused on identifying the chemistries at play at the interfaces to provide a more detailed look at the reductive stability of $Ca[TPFA]_2$ salts, their reactive byproducts, and methods for mitigating decomposition.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c03272.

Details of experimental procedures, materials, and methods (PDF)

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Notes

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■ ACKNOWLEDGMENTS

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