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Widening Electrochemical Window of Mg Salt by Weakly Coordinating Perfluoroalkoxyaluminate Anion for Mg Battery Electrolyte

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Energy storage concepts based on multivalent ion chemistries, such as Mg^{2+} , promise very high volumetric energy density, however require improvements in electrolyte (Mg salt and solvent) electrochemical window to reach their full potential. Hypothetically the window of Mg salt could be widened by disfavoring the cathodic decomposition pathway of a thermodynamically and anodically stable anion, rendering it kinetically inert toward Mg⁺-mediated reduction. Computational and electrochemical analyses on Mg[TPFA]₂ ([TPFA]⁻ = [Al{OC(CF₃)₃}]⁻) support this hypothesis, and showcase a widened electrochemical window as a result of mitigated cathodic decomposition as well as enhanced anodic stability from electron-withdrawing CF₃ groups. Detailed NMR and IR spectroscopy and scanning electron microscopy/energy-dispersive X-ray spectroscopy further support that the weak coordination to Mg²⁺ in solution is important for maintaining the wide electrochemical window of Mg salt. © 2019 The Electrochemical Society. [DOI: 10.1149/2.0751908jes]

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Li-ion batteries power a wide variety of electronics ranging from portable devices to electric vehicles. However, as safety concerns and demands for higher capacity and energy density grow, new types of rechargeable batteries beyond the prototypical Li-ion batteries need to be developed. Mg batteries are an attractive technological alternative due to the high abundance of Mg, approximately 2 to 5-fold higher theoretical volumetric anode capacity (Mg: 3832 mAh/cm³, cf. Li: 2061 mAh/cm³, graphite: 777 mAh/cm³), and enhanced safety established by electroplating of non-pyrophoric or dendrite-free Mg metal.^{1–3}

Future commercialization of a Mg-ion energy storage system requires an electrolyte with a wide voltage window. Success of such an electrolyte requires not only reversible Mg electrodeposition and dissolution, and reversible insertion/deinsertion of Mg^{2+} cations in intercalation or conversion-type cathodes, but also stability against the breakdown of solvent and solvated ion complexes in the electrolyte.^{4–6} A major fundamental roadblock to these requirements arises from the need of a thermodynamically stable Mg electrolyte (Mg salt and solvent) across a wide enough electrochemical window (>5 V), i.e. the electrolyte needs to be stable both toward Mg (cathodically stable) as well as toward high-voltage cathodes (anodically stable) during operating conditions.⁷

In particular, tuning thermodynamic stability of Mg salts has been challenging. Electron-rich anions have been shown to be cathodically stable during Mg plating and stripping; however, their experimentally observed anodic stability is limited to < 3.3 V vs. Mg/Mg²⁺ (this reference couple is used henceforth unless otherwise specified) on inert electrodes such as platinum or 2.2 V on stainless steel as a result of Cl-promoted corrosion.⁸ Examples of such electrolyte systems are LiBH₄/Mg(BH₄)₂,⁹ and [Mg₂-(μ -Cl)₃·6THF]⁺[MCl_mR_{4-m}]⁻ (M = Al, Mg; R = alkyl, aryl, HMDS, where HMDS = N{Si(CH₃)₃}₂⁻; m = 0 - 4),¹⁰⁻¹⁵ which are mixtures of Grignard reagents or Mg(HMDS)₂ with AlCl_mR_{3-m} or MgCl₂ in THF.¹⁶⁻¹⁷ Lower experimental anodic stability when utilizing porous carbon electrodes on graphite foil or stainless steel electrodes further decreases the practical operational voltage of many of these electrolytes.¹⁸ Improvement of anodic stability was experimentally achieved through designing

electrolytes without Cl⁻ and utilizing less electron-rich anions such as $[B{OCH(CF_3)_2}_4]^{-}$,¹⁹ [Al{OCH(CF_3)_2}_4]^{-},²⁰ and $[CB_{11}H_{12}]^{-}$,²¹⁻²² In particular, Mg(CB₁₁H₁₂)₂ has demonstrated excellent cathodic stability through highly reversible Mg electrodeposition and dissolution as well as experimental anodic stability of up to 3.8 V in glymes and 4.6 V in sulfolane, yet the oxidation of $[CB_{11}H_{12}]^{-}$ anions leads to passivation of electrodes.²³ Thus far, these cathodically stable electrolyte salts are limited to electrochemical windows of <4.6 V as indicated by simple voltammetry techniques.

In cases where anodic stability can be achieved, salts consisting of electron-deficient anions such as Mg(TFSI)₂, Mg(PF₆)₂, Mg(BF₄)₂, Mg(ClO₄)₂ have experimentally demonstrated superior anodic stability (>5 V in glutaronitrile with quaternary ammonium cations),^{24–27} yet these anions also strongly coordinate to Mg²⁺ to form [Mg²⁺X⁻]⁺ ion-pairs in solution (X⁻ = monoanionic ligands). As illustrated in a theoretical study with Mg(TFSI)₂, the coordination of [TFSI]⁻ anions to Lewis acidic Mg²⁺ cations provides a decomposition pathway for anions through metal-centered reduction of [Mg²⁺(TFSI)⁻]⁺ to [Mg⁺⁺(TFSI)⁻] and rapid charge transfer from the HOMO of Mg⁺⁺ to the LUMO of [TFSI]⁻ to regenerate Mg²⁺ and reduce [TFSI]⁻.²⁸ The reduced species form a passivation layer that prohibits subsequent effective Mg electrodeposition and dissolution. To date, no Mg salts exhibit wide enough electrochemical windows with *both* cathodic and anodic stability.

Fundamentally, chemical intuition suggests that incorporating electron-withdrawing groups into anions will theoretically enhance their anodic stability by lowering the electron density and HOMO level, but also in turn could impart a deleterious effect on the cathodic stability by lowering the LUMO, hence hampering most synthetic attempts to expand the thermodynamic electrochemical window. Previous work shows that derivatization of [CB₁₁H₁₂]to [CB₁₁H₁₁F]⁻ indeed increases the experimental anion oxidation potential by 300 mV.²³ Alternatively, instead of pursuing thermodynamic stability of anions at both cathodic and anodic conditions, the solvation structure of thermodynamically and anodically stable anions can be designed to disfavor kinetically facile decomposition pathways of Mg salts. One strategy is to weaken coordination of anions to Mg^{2+} to mitigate the key step in the Mg⁺-mediated reductive decomposition. Weakly coordinating anions have been widely used in catalysis,²⁹⁻³² polymerization,³³⁻³⁴ and the development of electrolytes in batteries35-37 to stabilize

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highly electrophilic, "naked" metal cations. This property typically infers higher catalytic activities to molecular transitionmetal catalysts, higher ionic conductivity, increased cation solubility in electrolytes, and potentially enhanced intercalation/ de-intercalation kinetics with electrodes.³⁸ To the best of our knowledge, mitigating kinetically facile decomposition to expand electrochemical windows of salts via rational structural design has not been explored.³⁹

Therefore, as a proof of concept, a Mg salt with a highly electrondeficient, generally weakly coordinating anion tetrakis(perfluoro-tertbutoxy)aluminate ([TPFA]⁻ = [Al{OC(CF₃)₃}]⁻) was designed. Each [TPFA]⁻ anion possesses 12 CF₃ groups surrounding the coordinating O atoms, providing steric protection and withdrawing electron density from O atoms to render the anion weakly coordinating. Electron deficiency by these CF₃ groups may also offer high anodic stability to the anion. Analogous compounds with various monovalent cations have been synthesized, characterized, and demonstrated experimentally and theoretically to be chemically robust and among most weakly coordinating anions toward monovalent cations.³⁰ Recently, similar Mg compounds with less weakly coordinating, less electron-deficient $[B{OCH(CF_3)_2}_4]^{-19}$ and $[Al{OCH(CF_3)_2}_4]^{-20}$ anions have been reported to possess decent chemical stability and \sim 4 V electrochemical window in DME, with instability attributed to the H atom abstraction from the anion.²⁰ And during the preparation of this manuscript, this compound Mg[TPFA]2 was also independently synthesized with 0.05 wt% Cl present, and the mixture in DME solution was reported to plate/strip Mg as well as allow galvanostatic cycling with Mg-Mo₆S₈ cells at modest coulombic efficiency, albeit lacking reliable Cl-free synthesis.⁴¹ Despite these recent developments, these studies failed to provide fundamental understanding in the solvation of Mg complexes and its link with electrochemical properties. In the context of this knowledge gap, this manuscript serves to first provide an alternative synthesis of Mg[TPFA]2 with negligible Cl⁻ content. With the help of this pure material, the theoretical and experimental investigation of the effect of the coordination behavior, or kinetic inertness of [TPFA]⁻ anion, on widening the electrochemical window of the Mg salt are then reported.

Results and Discussion

The coordination behavior of Mg[TPFA]₂ was computationally investigated and compared with reported anions [TFSI]⁻, BF₄⁻ and $[CB_{11}H_{12}]^{-}$ that exhibit either, but not both, cathodic or anodic stability (see above). Density functional theory (DFT) calculations determined the ion association strength between Mg^{2+} and anions (X^{-}) in triethylene glycol dimethyl ether (triglyme, G3). While the absolute ion association values only compare qualitatively to experimental results, the trend in energies is useful to gain an understanding of relative ion association strength. The free energy change for a model substitution reaction of the $Mg(G3)_2^{2+}$ complex, the most thermodynamically favored species in G3 (see Supporting Information), by anions follows the increasing order of $[TFSI]^- < BF_4^- < [CB_{11}H_{12}]^- < [TPFA]^-$ (Figure 1). The negative values for $[TFSI]^-$ and BF_4^- suggest that coordination of these anions to Mg²⁺ in triglyme is thermodynamically favored, which is unsurprising in light of the known tendency of these anions toward ion-pairing and aggregate formation in non-aqueous electrolytes.²⁸ The values for $[CB_{11}H_{12}]^{-}$ and $[TPFA]^{-}$ are positive, consistent with the generally accepted view of these anions as weakly coordinating.²⁹⁻³⁰ Notably, [TPFA]⁻ exhibits a value far above that of $[CB_{11}H_{12}]^-$, which establishes a profoundly weak ion association tendency for this anion in accordance with the design goal.

To compare the electrochemical stability of [TPFA]⁻ with other anions, the theoretical electrochemical window is determined from the calculated ionization potentials (IPs) and electron affinities (EAs) as measures of anodic and cathodic stability, respectively. DFT calculations on IPs of bare anions [TPFA]⁻, BF₄⁻, [TFSI]⁻ and [CB₁₁H₁₂]⁻ showed anodic stability ranging from 5.07 to 7.25 V, increasing in the order of [CB₁₁H₁₂]⁻ < [TFSI]⁻ < [TPFA]⁻ < BF₄⁻ (Figure 2, the blue bars). These trends are consistent with experimental studies reported of various anions (\bar{X}) with $[Mg(\bar{G})_2]^{2+}$. A negative ΔG indicates favorable ion association and a positive ΔG indicates unfavorable ion association in G3.

Figure 1. The computed free energy change in triglyme (G3) of ion association

′CF₃

-0.07

BF₄

elsewhere.^{23–24} EAs indicated that the cathodic stability increase in the order of $[CB_{11}H_{12}]^- < [TFSI]^- < BF_4^- < [TPFA]^-$, ranging from -2.03 V for $[CB_{11}H_{12}]^-$ to -3.13 V for $[TPFA]^-$. The calculated electrochemical windows range from 7.10 V for $[CB_{11}H_{12}]^-$ to 10.14 V for BF_4^- in the absence of coordination to Mg^{2+} .

As discussed previously, in the presence of Mg2+, ion-pair formation due to coordination of anions to Mg²⁺ reduces the electron density of the anions thereby shifting the stability window in favor of reduction relative to oxidation. The calculated reduction potentials of corresponding ion-pairs showed that the electrochemical windows are indeed notably shifted such that both the IP and EA are raised (red bars in Figure 2). The shift is similar for all examined pairs, and hence the relative order of anodic stability and electrochemical window remains the same. Notably, all ion-pairs exhibit EA > 0 V, indicating that these complexes are reduced above Mg metal potentials, corresponding to the first step $(Mg^{2+} \rightarrow Mg^+)$ during plating operations. The reduction potential of Mg^{2+} in the ion-pair complex increases in the order of $[TPFA]^- < [CB_{11}H_{12}]^- < BF_4^- < [TFSI]^-$. The fate of the reduced ion-pair complex can follow different routes depending on the stability of the anion. If the anion exhibits strong resistance against reduction (such as $[CB_{11}H_{12}]^{-}$), the partially reduced Mg⁺ may receive another electron and complete the plating process.²³ However, if the anion is thermodynamically and kinetically susceptible to reduction (such



Anion (X⁻) 📕 [Mg²⁺X⁻]⁺ pair

Figure 2. Calculated electrochemical windows (vs Mg/Mg^{2+}) for various anions (X⁻; blue bars) and corresponding [$Mg^{2+}X^{-}$]⁺ ion-pairs (red bars).

[Mg(G3)₂]²⁺

TPFA =

-0.41

TFSI

2.4

2.0

1.6

1.2

0.8

0.4

0.0

-0.4

-0.8

10

∆G (eV)

+ X⁻

[Mg(G3)X]⁺

0.39

+ G3

1.85

TPFA

9.66





as $[TFSI]^{-}$) the anion may decompose before the plating process is completed.²⁸ Indeed, previous work report that Mg(CB₁₁H₁₂)₂ supports reversible Mg electrodeposition and dissolution at a higher coulombic efficiency than Mg(TFSI)₂ and Mg(BF₄)₂.^{21,22,25,28} Like the previous calculations on ion association strength, we note here that the calculated EA and IP values only serve as qualitative comparison for understanding *relative* electrochemical stability. While designing cathodically stable anions provides one route for improved electrolyte performance, weakly coordinating anions are less exposed to the reactive, transient Mg⁺ and may establish kinetic inertness for increased cathodic stability. Based on Figures 1 and 2, [TPFA]⁻ is a primary candidate to expand the electrochemical window by possessing extraordinarily high thermodynamic anodic stability and very weak coordination to Mg²⁺.

Mg[TPFA]₂ was synthesized in three steps (Scheme 1). The lithium analog Li[TPFA] was first synthesized from alcoholysis of LiAlH₄ by (CF₃)₃COH in a quantitative yield. Li⁺/H⁺ cation metathesis of Li[TPFA] with HCl in a mixture of CH₂Cl₂ and Et₂O afforded [H(OEt₂)₂][TPFA] in 93% yield and side-product LiCl, which could be mostly yet incompletely removed via filtration through Celite. Finally, protonolysis of Mg(HMDS)₂ by 2 equiv [H(OEt₂)₂][TPFA] in THF and subsequent recrystallization from diffusion of Et₂O to the THF solution yielded the THF adduct [Mg(THF)₇][TPFA]₂ ([Mg][TPFA]₂) in 96% yield. The number of coordinated THF molecules per Mg[TPFA]₂ unit was established from ¹H NMR analysis using ferrocene as an internal standard (Figure S3b). Recrystallization is critical to achieving high purity and low Cl- content of this compound, since trace amount of Li[TPFA] or LiCl could pass through Celite. Elemental analysis on the recrystallized compound supported the proposed stoichiometry, and furthermore indicated complete removal of Li⁺ (<25 ppm) and Cl⁻ (<98 ppm), as well as high purity of the compound. The recrystallized compound was characterized by attenuated total reflectance infrared spectroscopy (ATR-IR), and the characteristic C-C, C-O, C-F and Al-O stretches for [TPFA]- anion were observed in the range from 700 to 1400 cm⁻¹ (See Experimental Section and the following discussion). ¹⁹F, ²⁵Mg and ²⁷Al NMR spectroscopy showed one single resonance, supporting the formation of [Mg][TPFA]₂. ¹³C NMR spectroscopy showed only one quartet for CF3 carbon, and the resonance for quaternary carbon was not observed (Figure S4a). Attempts to obtain a crystal structure from single-crystal X-ray diffraction failed.



Figure 3. A plot of ionic conductivity of solutions of [Mg][TPFA]₂ in triglyme versus concentration.

Ion association was experimentally demonstrated by conductivity analysis. Ionic conductivities of solutions of [Mg][TPFA]₂ in triglyme at various concentration were calculated from impedance values that were measured from AC impedance spectroscopy (Figure 3). In all cases, triglyme is in large excess compared to coordinated THF; hence, the effect of THF on ion association and electrochemistry could be neglected. This analysis showed that the ionic conductivity initially increased with concentration, but the trend exhibited increasingly nonlinear behavior. The ionic conductivity peaked at 0.3 M and then decreased thereafter. The maximum solubility of the compound in triglyme was 0.4 M. These results suggest that increasing concentration in triglyme increases ion association which reduces the amount of free ions in the solution.

To spectroscopically probe Mg_{2+} —[TPFA]. interactions, ATR-IR was performed on crystalline and solutions of [Mg][TPFA]₂ in triglyme. ATR-IR analysis on the crystalline [Mg][TPFA]₂ revealed the presence of five vibrational bands between 1200 and 1300 cm⁻¹ and one band at 970 cm⁻¹, which were assigned to mixed C–C and C–F stretches in [TPFA]⁻ (Figure 4). Comparison between solution IR spectra of [Mg][TPFA]₂ in triglyme at various concentration indicates concentration-dependent solution behavior of [TPFA]⁻ in the presence of Mg²⁺. Increasing the concentration of [Mg][TPFA]₂ in triglyme from 0.05 M to 0.4 M caused mixed C–C and C–F stretching bands in [TPFA]⁻ to redshift toward those in neat [Mg][TPFA]₂ by up to 10.8 cm⁻¹ (Table S1).⁴² For example, the highlighted bands in Figure 4 at 1222.5 cm⁻¹ and 974.5 cm⁻¹ for a 0.05 M solution were



Figure 4. Representative IR spectra for solutions of $[Mg][TPFA]_2$ in triglyme at concentration ranging from 0.05 M to 0.4 M and neat $[Mg][TPFA]_2$ between 1350–1150 cm⁻¹ and 1000–900 cm⁻¹. Highlighted bands correspond to mixed C–C and C–F stretches for $[TPFA]^-$. Dotted red arrows indicate the direction of changes of IR bands with increasing concentration.



Figure 5. Stacked (a) ¹⁹F NMR and (b) ²⁷Al NMR spectra of solutions of $[Mg][TPFA]_2$ in triglyme at concentration ranging from 0.1 M to 0.4 M and a solution of 0.2 M $[Bu_4N][TPFA]$ in triglyme.

shifted to 1211.7 cm^{-1} and 970.1 cm^{-1} upon increasing concentration to 0.4 M, and these bands appeared at 1210 cm^{-1} and 969.8 cm^{-1} in the crystalline [Mg][TPFA]₂.

To elucidate the effect of Mg²⁺ on these IR shifts, [Bu₄N][TPFA], of which the [Bu₄N]⁺ cation possesses no vacant coordination site, was synthesized from cation exchange between Li[TPFA] and [Bu₄N]Br. Mixed C-C and C-F stretching bands for [TPFA]⁻ of a solution of 0.4 M [Bu₄N][TPFA] in triglyme appeared at similar wavenumbers (e.g. 1221.2 and 974 cm^{-1} for the highlighted bands) compared to 0.05 M [Mg][TPFA]₂ solutions rather than the 0.2 M [Mg][TPFA]₂ solution containing 0.4 M [TPFA]⁻ (e.g. 1218.9 and 972.9 cm⁻¹; Figures S5-10). Furthermore, the addition of 10 equiv HMPA $({(CH_3)_2N}_3P = 0)$, a strong donor (donor number = 39) known to coordinate to Li⁺ and dissociate tightly bound ion-pairs of alkyllithium,43-44 to [Mg][TPFA]2 in triglyme while keeping the concentration of [Mg][TPFA]2 at 0.4 M shifted the mixed C-C and C-F stretching bands for [TPFA]⁻ (e.g. 1218.9 and 971.2 cm⁻¹) toward those at 0.2 M (Figures S5-10).⁴⁵ These results collectively attribute the concentration-dependent IR band shifts for [TPFA]⁻ to the presence of Mg²⁺, presumably through the coordination of [TPFA]⁻ to Mg²⁺, rather than the differences in the dielectric medium or viscosity of solutions.

In addition to ATR-IR analysis, Mg2+-[TPFA]. interactions in [Mg][TPFA]₂ were further investigated using NMR spectroscopy. [Mg][TPFA]₂ was only sparingly dissolved in the noncoordinating solvent CD₂Cl₂, but the ¹H NMR spectra taken in CD₂Cl₂ showed only one set of THF resonances and these chemical shift values corresponded to those of free THF. These results strongly indicate that the coordinated THF molecules were labile under NMR timescale via substitution by either the noncoordinating solvent CD₂Cl₂ or the weakly coordinating [TPFA]- anion. ¹⁹F and ²⁷Al NMR spectra taken in CD_2Cl_2 showed a single resonance at δ -77.7 and 32.3 respectively (Figures S11-12). Compared with the corresponding resonances in [Bu₄N][TPFA], those in [Mg][TPFA]₂ were shifted upfield by >1 ppm, further suggesting coordination of $[TPFA]^-$ to Mg^{2+} and rapid exchange between coordinated and free $[TPFA]^-$ anions in CD2Cl2 under the NMR timescale. Similarly, in a coordinating solvent such as triglyme, ²⁷Al and ¹⁹F NMR resonances for [TPFA]⁻ at 0.1 M appeared at δ 34.7 and -75.3 respectively, whereas those for [TPFA]⁻ in $[Bu_4N]$ [TPFA] appeared by >1 ppm downfield (Figure 5). These

discrepancies in chemical shift values indicate that some [TPFA]⁻ anions were coordinated to Mg²⁺ cations even in triglyme.

In addition, NMR analysis of solutions of [Mg][TPFA]2 in triglyme at various concentration showed concentration-dependent changes in chemical shift values in a similar fashion as IR spectra, albeit in a much smaller magnitude owing presumably to a lower sensitivity of NMR spectroscopy compared to IR spectroscopy. ²⁷Al and ¹⁹F NMR resonances for [TPFA]⁻ were shifted rather insignificantly by 0.2 to 0.3 ppm and away from those in [Bu₄N][TPFA] upon increasing concentration to 0.4 M. Despite inherently low NMR sensitivity of ²⁵Mg nuclei that precludes reliable comparison, ²⁵Mg NMR resonance of 0.1 M in triglyme appeared as a single broad resonance at δ -2.6 (Figure S13), and was shifted by >2 ppm downfield at 0.4 M. These shifts further corroborate promoted [TPFA]⁻ coordination to Mg²⁺ at higher concentration.⁴⁶ Collectively, the NMR and IR spectroscopic analyses suggest that the coordination of [TPFA]⁻ anion to form [Mg(TPFA)]⁺ ion-pairs is promoted by increasing the concentration of the bulk solution. Furthermore, these analyses imply that the generally accepted view that [TPFA]⁻ is weakly coordinating to monovalent cations could not be necessarily extended to multivalent cations, and highlight the importance in understanding more how the coordination of solvents/anions to multivalent cations influences electrochemical windows of electrolytes.

The electrochemical window of Mg[TPFA]2 was interrogated using cyclic voltammetry (CV). In order to gauge the anodic stability of Mg[TPFA]₂, the free and coordinated solvent molecules need to exhibit an anodic stability exceeding that of the salt itself to avoid the anodic degradation of the solvent molecules that limits the electrochemical window. The anodic stability of ethers coordinated to cations is around 4.5 V vs Li/Li⁺,⁴⁷ or around 3.8 V vs Mg/Mg²⁺. This implies possible interference from coordinated THF in [Mg][TPFA]₂ in the interpretation of the CV results. This anodic degradation was indeed observed in a recent study from the DME solvent.⁴¹ Unfortunately, to the best of our knowledge, no single solvent exists yet that is both cathodically and anodically stable, and ethereal solvents are the only reported, cathodically stable solvents.²⁵ Therefore, the compound was first dissolved in 3-methylsulfolane (3-MS), a solvent with superior anodic stability, prior to electrochemical testing. The residual THF was then removed under vacuum at 55 °C overnight, and ¹H NMR and GC-MS analysis of the solution indicated removal of THF to an undetectable level.

The anodic stability of a 0.1 M solution of Mg[TPFA]₂ in 3-MS was then investigated with CV using glassy carbon (GC), Au, and Pt electrodes. The electrodes were immersed in the solution at 2.0 V (0 V vs reference electrode) and cycled between 2.0 and 5.7 V at a rate of 20 mV/s for 3 consecutive cycles. The first cycle is depicted in Figure 6. Broadly speaking, bulk oxidation (defined as J $>0.1 \text{ mA/cm}^2$) occurred at potentials above 5.4 V on all three electrode materials. Similarly, bulk oxidation >5 V was also observed for Al and stainless steel electrodes when these were immersed at their opencircuit potential (Figure S14). These electrochemical processes were fast and independent of scan rates, as demonstrated with Au electrode (Figure S15). These data suggested high anodic stability of Mg[TPFA]₂ in 3-MS. It is as yet unclear whether the observed anodic stability is limited by that of 3-MS. Additionally, the inset depicts a zoomed-in view of the current profiles leading up to the bulk oxidation for each electrode material. Rather than featureless non-faradaic (capacitive) currents, reproducible redox features of varying shapes and intensities were observed at potentials preceding bulk oxidation. We consider these features indicative of early-stage interfacial instability attributed to adsorption of the electrolyte, impurities, or side reactions involving changes in bonding at the electrode-electrolyte interface.⁴⁸ Notably, these features were also distinctly different on each electrode material, which again suggest that the early-state interfacial instability features are surface-dependent. Additionally, the high anodic stability was corroborated with reversibility parameter, defined as the ratio of charges in faradaic process to charges in non-faradaic process (Figure S16).¹⁸ This analysis typically affords a lower anodic limit compared

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Figure 6. CVs of Pt, Au and GC in 0.1 M Mg[TPFA]₂ in 3-MS. A Mg foil served as the counter electrode, and Ag/AgCl as the reference electrode. The data were recorded at a scan rate of 20 mV/s.

to that obtained from conventional voltammetric methods, and suggested an onset of bulk oxidation at 4.8 V on Au electrode. Together with CV analysis, these results strongly showcase the high anodic stability of Mg[TPFA]₂.

Following bulk oxidation, an electroreduction feature was observed at potentials negative of 2.5 V on the reverse sweep. Control studies indicate that this electroreduction feature occurred only after the bulk oxidation of Mg[TPFA]₂ in 3-MS at potentials >5.4 V. The potential of this electroreduction feature depended on the electrode material, with GC at 1.1 V (Figure S17a), Au at 2.1 V (Figure S17b) and Pt at 2.2 V (Figure S17c). The observed surface dependence of faradaic processes of the degradation product, characterization of the degradation product and origin of the early-stage interfacial instability will be investigated in detail and reported in the future.

Figure 7 shows CV data for a Pt electrode cycled in 0.1 M (black line) and 0.4 M (red line) solution of [Mg][TPFA]₂ in triglyme. Both electrodeposition and dissolution of Mg were clearly observed. For the first cycle in 0.1 M [Mg][TPFA]₂, the nucleation overpotential, defined as the potential at which electrodeposition begins in the cathodic sweep, was 370 mV (Figure 7a). The dissolution of deposited Mg into the solution, was 260 mV. These improved to 270 mV and 60 mV respectively at 10th cycle (Figure 7b). These observed improvements suggest that a conditioning process of the Pt electrode occurred during the first 10 cycles. Conversely, the coulombic efficiency for the first cycle was 96% and decreased slightly to 90% at 10th cycle (Figure 7c). Nonetheless, these results show that the 0.1 M solution of [Mg][TPFA]₂ in triglyme possesses sufficient cathodic stability for supporting electrodeposition/dissolution of Mg.

At a higher concentration of 0.4 M in triglyme, where we argue for the formation of $[Mg(TPFA)]^+$ ion-pairs, Mg deposition/dissolution was also observed, but the electrochemical behavior of this solution was drastically different from that of a 0.1 M solution. The nucleation overpotential started and stayed at 260 mV throughout cycling, in sharp contrast with that of 0.1 M solution (see above), and dissolution overpotential started at 170 mV at the first cycle but dropped to 25 mV at the end of 10th cycle. The nucleation overpotential reported for other electrolytes stored at open-circuit potential before cycling has been attributed to the accumulation of adsorbed Mg²⁺ species on electrodes,⁴⁹ and is expected to increase with increasing concentration of Mg²⁺ species. The constant, yet lower nucleation overpotential observed for concentrated [Mg][TPFA]₂/triglyme electrolyte is evidence against adsorbed Mg²⁺ species as the origin of conditioning of Pt electrode observed for the 0.1 M solution. It is consistent, however,



Figure 7. Cyclic voltammograms of solutions of 0.1 M (black) and 0.4 M $[Mg][TPFA]_2$ (red) in triglyme at (a) 1st cycle and (b) 10th cycle. (c) A plot of coulombic efficiency vs cycle number is shown. Pt was used as the working electrode, Mg as the counter electrode and Ag/AgCl as the reference electrode, and a scan rate of 100 mV/s was used.

with formation of a solid-electrolyte interphase (SEI) on the Pt electrode, presumably due to the increased decomposition of ion-paired [Mg(TPFA)]⁺ that is favored at higher concentrations, leading to a SEI and decreased overpotentials. Indeed, supporting the increase in anion



Figure 8. SEM images of deposits obtained from 0.1 M (a, b; top) and 0.4 M (c, d; bottom) solutions of $[Mg][TPFA]_2$ in triglyme at various magnification: (a) ×239, (b) ×1000, (c) ×250, and (d) ×1000.

decomposition, we find the coulombic efficiency of the first cycle of the 0.4 M electrolyte to be 54%, significantly lower than that for the 0.1 M solution, and increased to 85% after 10 cycles. These results collectively suggest that reductive decomposition of the electrolyte was promoted by increasing concentration of [Mg][TPFA]₂, resulting in a gradually decreasing and an initially lower coulombic efficiency with the 0.1 M and 0.4 M solutions respectively.

The cathodic stability of Mg[TPFA]₂ is tuned by varying the concentration. This is established by characterizing the speciation of deposits during constant-current electrodeposition. Images of the deposits obtained from the 0.1 M solution via scanning electron microscopy (SEM) showed randomly dispersed globular islands (Figure 8a), which were composed of densely packed, crystalline platelets of $20 \times 100 \,\mu\text{m}$ in size (Figure 8b). The morphology of these deposits is different from the commonly observed smooth and continuous film, but this morphology is not unprecedented. Prior XRD, SEM and STM studies on Mg deposition from solutions of R_{2-m}MgCl_m (R = Et, Bu; m = 0, 1) and $R'_{3-n}AlCl_n$ in ethereal solvents (R' = Me, Et; n = 1, 2) suggest that nucleation of Mg⁰ starts randomly with similar island formation as observed here according to a local concentration gradient of active species.⁵⁰ Such a nucleation process is strongly dependent on the applied current density as a result of competitive kinetics between charge transfer and mass transfer, as well as the structure of adsorbed Mg²⁺ species.⁵¹ Energy-dispersive X-ray spectroscopy (EDS) on these crystalline aggregates revealed undetectable Al or F atoms (<0.1 wt%), whereas Mg was detected as the sole element in the deposit (Figure 9). These results are consistent with CV data that Mg could be electrodeposited from [Mg][TPFA]₂ in triglyme, and minimal decomposition of the [TPFA]⁻ anion on Mg surface during constant-current electrodeposition at the concentration of 0.1 M.

Interestingly, SEM images of the deposits obtained from the 0.4 M solution showed similar globular macrostructures (Figure 8c). However, these aggregates were highly amorphous (Figure 8d). EDS analysis of these structures still showed Mg as the major element

(Figure 10). Contrary to the deposits obtained from the 0.1 M solution, these structures also contained significant deposits of F and Al atoms, indicative of increased decomposition of the [TPFA]⁻ anion. These results strongly suggest that galvanostatic deposition of Mg in a more concentrated solution of Mg[TPFA]₂ leads to electrodeposition of Mg that was accompanied by increased decomposition of [TPFA]⁻ anion to form the observed amorphous mixtures. These comparative SEM/EDS results are also consistent with CV results, where a lower initial coulombic efficiency of Mg deposition/dissolution in the 0.4 M solution was observed. Together with CV studies, these results strongly indicate that at 0.4 M, where more ion-pairs are formed, increased reductive decomposition of the complexed anion occurred.

We note that the decomposition of $[TPFA]^-$ anion gave rise to amorphous mixtures that were rich in C, F and Al atoms. While the function of such deposit, if any, was outside the scope of this investigation, this observation is consistent with the proposed formation of an SEI under a negative bias as observed in CV studies. The formation of beneficial SEI in Mg-ion batteries via controlled decomposition of the electrolyte will be explored further in a future study.

To understand mechanistically how the decomposition of [TPFA]⁻ contributed to the observed surface deposits, the decomposition pathway of a model species $[Mg(G3)TPFA]^-$ was examined from first-principles computations. After exploring possible decomposition pathways of the $[Mg(G3)TPFA]^-$ ion-pair, a decomposition pathway was found to be thermodynamically favorable by 1.08 eV, involving cleavage of a C–O bond in [TPFA]⁻ and a subsequent dissociation of a $(CF_3)_3C^-$ radical (Figure 11). These decomposed species could potentially lead to the observed formation of Al_xF_y -rich surface deposits or SEI. Collectively, these theoretical and experimental results further support that weakening coordination to Mg^{2+} via the use of [TPFA]⁻ anion and tuning its bulk concentration minimizes subsequent Mg^+ -mediated decomposition despite its observed thermodynamic cathodic instability, consistent with the initial design principle. Overall, the electrochemical window of Mg salt was widened by weak-



Figure 9. EDS mapping of deposits obtained from 0.1 M solution of [Mg][TPFA]₂ in triglyme. The SEM image of deposits is shown on top left, and EDS maps for Al, F and Mg are shown on the top right, bottom left and bottom right respectively.

ening coordination to Mg²⁺ while maintaining desirable, high anodic stability particular to [TPFA]⁻ anions.

Experimental

General information.—All experiments were performed using dry box under an argon atmosphere. Perfluoro-*tert*-butanol was purchased from Oakwood Chemical and dried over 3 Å molecular sieves. THF, diethyl ether, CH₂Cl₂, CD₂Cl₂, heptane and pentane were purchased from Sigma Aldrich and dried over 3 Å molecular sieves. Triethylene glycol dimethyl ether was purchased from Sigma Aldrich and distilled under vacuum from NaH. 3-methylsulfolane was purchased from TCI America and distilled under vacuum from 3 Å molecular sieves. THF-*d*₈ was purchased from Acros Organics and dried over 3 Å molecular sieves. CD₂Cl₂ and HMPA were purchased from Sigma Aldrich and dried over 3 Å molecular sieves. LiAlH₄ was purchased from Sigma Aldrich and purified according to literature.⁵² HCl/Et₂O (1 M), [Bu₄N]Br and Mg(HMDS)₂ were purchased from Sigma Aldrich and used as received. Li[TPFA],⁵² [H(OEt₂)₂][TPFA],⁵³ and [Bu₄N][TPFA]⁵⁴ were synthesized according to literature.

NMR spectra were recorded on a 300 MHz Bruker Avance spectrometer at ambient temperature. ¹H NMR chemical shifts are reported relative to SiMe₄ and were determined by reference to the residual ¹H solvent resonances. ¹⁹F{¹H} NMR spectra were referenced externally to BF₃·Et₂O (δ -153). ²⁷Al{¹H} NMR spectra were referenced externally to 1 M Al(NO₃)₃/D₂O (δ 0). ²⁵Mg{¹H} NMR spectra were

referenced externally to 1 M MgCl₂/D₂O (δ 0). Coupling constants are given in Hz. IR spectra were recorded on a laminated diamond crystal in iD5 ATR Accessory mounted on Thermo Scientific Nicolet iS5 Infra-red spectrometer at ambient temperature. Elemental analysis was performed by Galbraith Laboratories, Inc.

Voltammetry and chronopotentiometry were performed on 3electrode cells comprising Pt, Au or glassy carbon (GC) as the working electrode, Mg as the counter electrode and leak-free Ag/AgCl as the reference electrode using Princeton Applied Research PMG 1000 Potentiostat. Pt, Au and GC electrodes were purchased from CH Instruments, Inc. Mg metals were purchased from Galliumsource, LLC. Leak-free Ag/AgCl electrodes were purchased from Innovative Instruments, Inc. Molybdenum foil was purchased from Sigma Aldrich. Potential values measured with Ag/AgCl reference electrodes were referenced to Mg/Mg²⁺ by $E(Mg/Mg^{2+}) = E(Ag/AgCl) + 1.96$ V, as determined from ferrocene redox couple measurement in triglyme using separately Ag/AgCl and Mg reference electrodes. A current density of 1.5 mA/cm² was applied for 2.5 h in chronopotentiometry. The ionic conductivity of the electrolyte was measured by an AC impedance technique in a two-electrode cell using Princeton Applied Research PMG 1000 Potentiostat in the frequency range from 3 \times 10⁵ Hz to 0.1 Hz with perturbation amplitude of 10 mV at 25 °C, and Pt as working, counter and reference electrodes.

Scanning electron microscopy images were obtained using Hitachi S4700 II scanning electron microscope with a field emission electron source. Energy-dispersive X-ray spectroscopy was performed using



Figure 10. EDS mapping of deposits obtained from 0.4 M solution of [Mg][TPFA]₂ in triglyme. The SEM image of deposits is shown on top left, and EDS maps for Al, F and Mg are shown on the top right, bottom left and bottom right respectively.

Bruker Quantax. The samples were very briefly exposed to air before insertion into the analysis chamber.

DFT calculations were carried out with Gaussian 16.5^5 Anodic and cathodic stabilities were modelled from ionization potentials and electron affinities computed under the adiabatic approximation^{56–57} with energies from the PCM-wB97X-D/6-311+G(d,p)//wB97X-D/6-31+G(d)^{58–60} level of theory. The same model chemistry was used to compute free energy changes for the ion association process of Figure 1 and the free energy to dissociate the C-O bond in the Mg(triglyme)⁺/TPFA⁻ except the 6–31G(d) basis set was used in the optimization level.

Synthesis of $[Mg(THF)_7][TPFA]_2$ ($[Mg][TPFA]_2$).—1 equiv [H(OEt₂)₂][TPFA] (1.06 g, 0.95 mmol) and 0.52 equiv Mg(HMDS)₂ (168 mg, 0.49 mmol) were charged in a 20 mL scintillation vial, and THF (5 mL) was added to the mixture (200 mg [H(OEt₂)₂][TPFA]/1 mL THF). After 5 min, a clear solution was formed. Recrystallization by diffusion of Et₂O into the THF solution (v/v = 1/1) at room temperature afforded colorless crystals. The crystals were collected by filtration, washed with minimal amount of Et₂O and dried at 100 mTorr at room temperature for 2.5 h to afford [Mg][TPFA]₂ as a white solid (1.10 g, 0.46 mmol, 96%). NMR analysis using ferrocene as an internal standard and elemental analysis collectively identified the stoichiometry of the compound as [Mg(THF)₇][TPFA]₂. ¹H NMR (CD₂Cl₂): 3.70 (m, THF), δ 1.85 (m, THF). ¹³C NMR (triglyme): δ 122.1 (q, ¹J_{C-F} = 290 Hz, *CF*₃), 68.2 (THF), 26.2 (THF). The signal for quaternary carbon was not detected. ¹⁹F NMR: δ –77.7 (CD₂Cl₂); δ –75.3 (triglyme, 0.1 M); δ –75.6 (triglyme, 0.4 M). ²⁵Mg NMR (triglyme): δ –2.6 (0.1 M); δ –0.5 (0.4 M). ²⁷Al NMR: δ 32.3 (CD₂Cl₂); δ 34.7 (triglyme, 0.1 M); δ 34.5 (triglyme, 0.4 M). Anal. Calcd. for C₆₀H₅₆Al₂F₇₂MgO₁₅: C, 29.26; H, 2.29; Mg, 0.99. Found: C, 29.17; H, 2.26; Mg, 0.99. Li and Cl contents were determined to be <25 ppm and <98 ppm respectively. ATR-IR: $v_{C-C, C-F}$: 1296.1, 1274.8, 1265.1, 1239.1, 1210, 969.8; $v_{C-C, AI-O}$: 858.8, 831.7; $v_{C-C, C-O}$: 725.9 cm⁻¹. IR assignments were made by comparison of the IR spectra of Li[TPFA], Ag[TPFA], [Ag(CH₂Cl₂)][TPFA] and [Bu₄N][TPFA] in the literature (See Supporting Information).⁵⁴

Conclusions

An expansion of electrochemical window of the Mg salt was accomplished through the rationally designed, weakly coordinating nature of the highly electron-deficient anion. Computational and electrochemical studies reveal that perfluorinated, highly electron-deficient [Al{OC(CF₃)₃}₄]⁻ anions ([TPFA]⁻) possesses high thermodynamic oxidative stability on glassy carbon, Au and Pt electrodes. Although this electron deficiency compromises the thermodynamic reductive stability of the anion, as established by electrochemical measurements, scanning electron microscopy/energy-dispersive X-ray spectroscopy and DFT calculations, the coordinating ability of the anion to Mg²⁺ is greatly diminished due to sterics and electron deficiency from CF₃ groups, consistent with widely reported literatures of such anions. This significantly limits the plating-induced reductive decomposition



Figure 11. A schematic of the $[Mg(G3)_2]^{2+}/[Mg(G3)TPFA]^-$ equilibrium and possible species following reduction. Upon reduction, the $[Mg(G3)TPFA]^-$ complex is predicted to undergo thermodynamically favorable cleavage of a C–O bond in the $[TPFA]^-$ anion. The equilibrium favors the $[Mg(G3)TPFA]^-$ complex, minimizing the decomposition of $[TPFA]^-$ anions.

pathway that proceeds through coordination of anions to Mg^{2+} , and thus widens the electrochemical window. This study further suggests that disabling kinetically facile decomposition via weak coordination can be a critical element in expansion of electrochemical windows for Mg salts in battery applications, and provides an alternative avenue for future rational design of multivalent electrolyte salts in advanced battery technologies. A practical high-voltage Mg-ion battery is only feasible with thermodynamically stable Mg salts, solvents and cathodes. With one puzzle addressed, designing thermodynamically stable solvents and high-voltage cathodes to be used with this salt, as well as battery cycling will be reported in the near future.

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References

- 1. N. Nitta, F. Wu, J. T. Lee, and G Yushin, *Mater. Today*, 18, 252 (2015).
- J. Song, E. Sahadeo, M. Noked, and S. B. Lee, J. Phys. Chem. Lett., 7, 1736 (2016).
 P. Canepa, G. Sai Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher,
- K. A. Persson, and G. Ceder, *Chem. Rev.*, **117**, 4287 (2017).
 J. Muldoon, C. B. Bucur, A. G. Oliver, T. Sugimoto, M. Matsui, H. S. Kim,
- G. D. Allred, J. Zajicek, and Y. Kotani, *Energy. Environ. Sci.*, 5, 5941 (2012).
 H. D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, and D. Aurbach, *Energy Environ. Sci.*, 6, 2265 (2013).
- J. Muldoon, C. B. Bucur, and T. Gregory, *Angew. Chem. Int. Ed.*, 56, 12064 (2017).
- M. Liu, Z. Rong, R. Malik, P. Canepa, A. Jain, G. Ceder, and K. A. Persson, *Energy Environ. Sci.*, 8, 964 (2015).
- J. Muldoon, C. B. Bucur, A. G. Oliver, J. Zajicek, G. D. Allred, and W. C. Boggess, *Energy Environ. Sci.*, 6, 482 (2013).
- R. Mohtadi, M. Matsui, T. S. Arthur, and S.-J. Hwang, *Angew. Chem. Int. Ed.*, 51, 9780 (2012).
- D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, and E. Levi, *Nature*, 407, 724 (2000).
- Y. Vestfried, O. Chusid, Y. Goffer, P. Aped, and D. Aurbach, *Organometallics*, 26, 3130 (2007).
- 12. N. Pour, Y. Gofer, D. T. Major, and D. Aurbach, J. Am. Chem. Soc., 133, 6270 (2011).
- R. E. Doe, R. Han, J. Hwang, A. J. Gmitter, I. Shterenberg, H. D. Yoo, N. Pour, and D. Aurbach, *Chem. Commun.*, 50, 243, (2014).
- T. Liu, Y. Shao, G. Li, M. Gu, J. Hu, S. Xu, Z. Nie, X. Chen, C. Wang, and J. Liu, J. Mater. Chem. A, 2, 3430, (2014).
- 15. J. Luo, S. He, and T. L. Liu, ACS Energy Lett., 2, 1197, (2017).
- H. S. Kim, T. S. Arthur, G. D. Allred, J. Zajicek, J. G. Newman, A. E. Rodnyansky, A. G. Oliver, W. C. Boggess, and J. Muldoon, *Nature Commun.*, 2, 427 (2011).
- C. Liao, N. Sa, B. Key, A. K. Burrell, L. Cheng, L. A. Curtiss, J. T. Vaughey, J.-J. Woo, L. Hu, B. Pan, and Z. Zhang, *J. Mater. Chem. A.*, 3, 6082 (2015).
- A. L. Lipson, S.-D. Han, B. Pan, K. A. See, A. A. Gewirth, C. Liao, J. T. Vaughey, and B. J. Ingram, *J. Electrochem. Soc.*, **163**, A2253 (2016).
- Z. Zhao-Karger, M. E. G. Bardaji, O. Fuhr, and M. Fichtner, J. Mater. Chem. A., 5, 10815 (2017).
- J. T. Herb, C. A. Nist-Lund, and C. B. Arnold, ACS Energy Lett., 1, 1227 (2016).
 O. Tutusaus, R. Mohtadi, T. S. Arthur, F. Mizuno, E. G. Nelson, and Y. V. Sevryugina,
- Angew. Chem. Int. Ed., 54, 7900 (2015).
 S. G. McArthur, L. Geng, J. Guo, and V. Lavallo, Inorg. Chem. Front., 2, 1101 (2015).
- N. T. Hahn, T. J. Seguin, K.-C. Lau, C. Liao, B. J. Ingram, K. A. Persson, and K. R. Zavadil, J. Am. Chem. Soc., 140, 11076 (2018).
- 24. M. Ue, M. Takeda, M. Takehara, and S. Mori, J. Electrochem. Soc., 144, 2684 (1997).
- Z. Lu, A. Schechter, M. Moshkovich, and D. Aurbach, *J. Electroanal. Chem.*, 466, 203 (1999).
- 26. E. N. Keyzer, H. F. J. Glass, Z. Liu, P. M. Bayley, S. E. Dutton, C. P. Grey, and
- D. S. Wright, *J. Am. Chem. Soc.*, **138**, 8682 (2016).
 27. I. Shterenberg, M. Salama, Y. Gofer, and D. Aurbach, *Langmuir*, **33**, 9472 (2017).
- N. N. Rajput, X. Qu, N. Sa, A. K. Burrell, and K. A. Persson, J. Am. Chem. Soc., 137, 3411 (2015).
- 29. C. A. Reed, Acc. Chem. Res., 31, 133 (1998).
- 30. I. Krossing and I. Raabe, Angew. Chem. Int. Ed., 43, 2066 (2004).
- 31. Y.-M. Wang, A. D. Lackner, and F. D. Toste, Acc. Chem. Res., 47, 889 (2014).
- J. A. Johnson, B. M. Petersen, A. Kormos, E. Echeverría, Y.-S. Chen, and J. Zhang, J. Am. Chem. Soc., 138, 10293 (2016).
- 33. R. F. Jordan, Adv. Organomet. Chem., 32, 325 (1991).
- 34. V. C. Gibson and S. K. Spitzmesser, Chem. Rev., 103, 283 (2003).
- 35. W. Xu and C. A. Angell, *Electrochem. Solid-State Lett.*, 3, 366 (2000).
- 36. A. B. A. Rupp and I. Krossing, *Acc. Chem. Res.*, **48**, 2537 (2015).
- 37. M. Zhong, H. Fang, and P. Jena, *J. Phys. Chem.* C, **122**, 13371 (2018).
- L. F. Wan, B. R. Perdue, C. A. Apblett, and D. Prendergast, *Chem. Mater.*, 27, 5932 (2015).
- Another study on imparting high thermodynamic stability was recently accepted after this manuscript was submitted: J. Luo, Y. Bi, L. Zhang, X. Zhang, and T. L. Liu, *Angew. Chem. Int. Ed.* Just accepted.
- [TPFA]⁻ was in situ generated and characterized in a previous study involving transmetallation with AlCl₃: A. J. Crowe, K. K. Stringham, and B. M. Bartlett, ACS Appl. Mater. Interfaces, 8, 23060, (2016).
- E. N. Keyzer, J. Lee, Z. Liu, A. D. Bond, D. S. Wright, and C. P. Grey, J. Mater. Chem. A., 7, 2677 (2019).
- 42. Increasing the concentration of [Mg][TPFA]₂ in triglyme also caused mixed C–C and C–O stretches to redshift and mixed C–C and Al–O stretches to blueshift, the latter indicating strengthened bonds presumably due to enhanced electrostatic interactions between Mg²⁺—O–Al. See Supporting Information.

- 43. H. J. Reich, J. P. Borst, R. R. Dykstra, and D. P. Green, J. Am. Chem. Soc., 115, 8728 (1993).
- C. Laurence and J. F. Gal, Lewis Basicity and Affinity Scales: Data and Measurements, 44. Chapter 2 and 3, Wiley, New York (2010). The exception is the band at 1295.6 cm^{-1} which overlapped with a band of free
- 45. HMPA.
- 46. Broadening of Al signals upon increasing concentration was indicative of slowed exchange between coordinated and free [TPFA]- in triglyme, presumably caused by increased viscosity as concentration increased.
- 47. K. Xu, Chem. Rev., 104, 4303 (2004). 48. E. V. Carino, D. J. Newman, J. G. Connell, C. Kim, and F. R. Brushett, Langmuir,
- 33, 11911 (2017). 49. O. Tutusaus, R. Mohtadi, N. Singh, T. S. Arthur, and F. Mizuno, ACS Energy Lett.,
- 2, 224 (2017).
- 50. D. Aurbach, A. Schechter, M. Moshkovich, and Y. Cohen, J. Electrochem. Soc., 148, A1004 (2001).
- 51. M. Matsui, J. Power Sources, 196, 7048 (2011).
- 52. I Krossing and A. Reisinger, Coord. Chem. Rev., 250, 2721 (2006).
- 53. I. Krossing and A. Reisinger, Eur. J. Inorg. Chem., 1979 (2005).
- 54. I. Raabe, K. Wagner, K. Guttsche, M. Wang, M. Grätzel, G. Santiso-Quiñones, and I. Krossing, Chem. Eur. J., 15, 1966 (2009).
- 55. Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.
- 56. S. P. Ong and G. Ceder, *Electrochim. Acta*, 55, 3804 (2010).
- 57. X. Qu, A. Jain, N. N. Rajput, L. Cheng, Y. Zhang, S. P. Ong, M. Brafman, E. Maginn, L. A. Curtiss, and K. A. Persson, Comput. Mater. Sci., 103, 56 (2015).
- 58. J.-D. Chai and M. Head-Gordon, J. Chem. Phys., 128, 084106 (2008).
- 59. J. Tomasi, B. Mennucci, and R. Cammi, Chem. Rev., 105, 2999 (2005).
- 60. S. Miertuš, E. Scrocco, and J. Tomasi, Chem. Phys., 55, 117 (1981).