Phosphonium-Based Binary and Ternary Super-Concentrated Liquid Electrolytes for Magnesium Batteries

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ABSTRACT

Here, we report binary and ternary concentrated liquid electrolytes comprised of Mg(TFSI)$_2$, phosphonium-based trifluoromethanesulfonimide organo ionic salts, and acetonitrile that substantially increase both magnesium solubility and reductive stability of the electrolyte against magnesium electrodes. While acetonitrile in dilute Mg(TFSI)$_2$ undergoes spontaneous and continuous reduction while reversibly cycling magnesium electrodes, super-concentrated binary and ternary electrolytes are stable, in some cases, up to $-1.7$ V vs. Mg/Mg$^+$. Furthermore, these higher concentrations enable stable cycling for over 500 h with minimal increase in (de)plating overpotential. Through detailed spectroscopic and computational investigations, the origin of this behavior is attributed to dramatic changes in solvation structure for all species present across the phase diagram. These results suggest the utility of phosphonium TFSI additives, or similar components, for expanding the electrochemical stability window and solubility regimes of multivalent salts.
Organic solvents (e.g., ethers, carbonates, nitriles, etc.) used in liquid electrolytes for magnesium batteries have limited chemical stability against the magnesium anode.\textsuperscript{1–5} Moreover, electrolytes constituted from them and various magnesium salts (MgCl\textsubscript{2}, Mg(HMDS), Mg(OTf), Mg(TFSI), etc.) have narrow electrochemical stability windows.\textsuperscript{6–9} As a result, Mg anodes quickly become passivated with surface films.\textsuperscript{10–12} In some cases, these surface films are highly insulating or grow continuously, which ultimately limits rate, capacity, and cycle-life.\textsuperscript{13,14} Needed are electrolytes for rechargeable magnesium batteries that offer stable cycling while also possessing a wide window of electrochemical stability such that they can be used with high voltage cathodes.\textsuperscript{15–24}

Here, we show that the intrinsically high reactivity of organic solvents in magnesium electrolytes can be substantially mitigated using a solvent-in-salt approach, which makes use of organo ionic phosphonium salts to increase the solubility of Mg salts in binary and ternary electrolyte formulations to concentrated, and super-concentrated regimes—which has been difficult to achieve in conventional electrolytes comprised of either Grignards or aprotic solvents.\textsuperscript{25–29} Within the liquidous phase space mapped, we increase the electrochemical stability
window by over 3.5 V to inhibit any significant reduction or oxidation from –1.7 to 3.6 V vs. Mg/Mg²⁺. The origin of this observed stability can be attributed to the lack of “free” solvent molecules available for reduction and the increase in average TFSI coordination to magnesium. Our results demonstrate that solvent-in-salt principles now extend to non-aqueous multivalent electrolytes within binary and ternary systems, which can be explored broadly to tailor the properties of multivalent electrolytes through fine-control over solvation structure, reactivity, dynamics, and transport properties.

We explored ternary phase diagrams for electrolytes comprised of Mg(TFSI)₂, acetonitrile, and two types of phosphonium bis(trifluoromethylsulfonyl)imide (TFSI) organo ionic salts: either triisobutylmethylphosphonium (P_{14}44) TFSI or tributylethylphosphonium (P_{24}44) TFSI (Figure 1). Notably, Mg(TFSI)₂ is soluble within both P_{14}44 TFSI (Figure 1a) and P_{24}44 TFSI (Figure 1b) to yield homogeneous liquid solutions across a broad range, despite the fact that all three salts are solids at room temperature. While the higher melting point P_{14}44 TFSI remains a solid until above 10 mol% Mg(TFSI)₂, P_{24}44 TFSI binary electrolytes are liquidous from dilute concentrations of Mg(TFSI)₂ until ~50 mol%. Contrarily, magnesium concentration in conventional solvents is extremely limited (e.g. ~18 mol% Mg(TFSI)₂ in acetonitrile). Furthermore, while phosphonium TFSI is not completely miscible with acetonitrile, the presence of a small quantity of Mg(TFSI)₂ (~2 mol% Mg) yields a homogenous solution. These results indicate an expansive ternary phase space from which to examine electrochemical behavior at much higher concentrations of magnesium than have previously been utilized.
Figure 1. Ternary phase diagram for electrolytes containing acetonitrile, Mg(TFSI)$_2$, and either P$_{1444}$TFSI (a) or P$_{2444}$TFSI (b), collected at $T = 30$ °C. The liquidous regime has homogenous mixtures across dilute (teal) and concentrated (light purple) regions, as well as a biphasic region (dark purple). The remainder of the phase diagram is a solid solution (pink). Linear sweep voltammetry of dilute conventional, concentrated binary salt, and concentrated ternary electrolytes (c).

To probe the electrochemical behavior of these electrolytes, linear sweep voltammetry (LSV) was utilized (Figure 1c). For the case of dilute Mg(TFSI)$_2$ in acetonitrile, multiple reduction peaks occur starting close to 0 V vs. Mg/Mg$^{2+}$. This result is consistent with recent reports of instantaneous reduction of solvent molecules in conventional aprotic magnesium electrolytes. Following reduction of the solvent molecule, a large reduction peak corresponding to reduction of Mg(TFSI)$_2$ is seen at $-1.35$ V vs. Mg/Mg$^{2+}$. The reduction profile for binary Mg(TFSI)$_2$ in P$_{1444}$TFSI features the same reduction peak for Mg(TFSI)$_2$, but, unsurprisingly, does
not feature any reduction events at higher potentials, due to the lack of acetonitrile. Notably, the super-concentrated ternary electrolyte comprised of 35.8 mol% Mg(TFSI)_2, 37.8 mol% acetonitrile, and 26.4 mol% P_2444TFSI closely resembles the reduction curve of the binary salt electrolyte, despite the presence of a large quantity of acetonitrile. These results are reminiscent of prior work on the benefits of super-concentrated electrolytes derived from monovalent salt constituents, such as LiTFSI; here, we achieve these extremes in concentrations without introducing an alloying or preferentially intercalating working ion (i.e., Li^+). Along with avoiding reductive decomposition of the acetonitrile, the first evidence of reductive instability does not occur until -1.7 V vs Mg, indicating a 350 mV increase in reductive stability from the binary electrolyte.

While acetonitrile is generally stable towards oxidation, further increases in the electrochemical stability window are now possible with ternary (super-)concentrated electrolyte formulations made possible using P_2444TFSI. For dilute Mg(TFSI)_2 in acetonitrile, initial oxidation of the solvent molecules occurs at 1.85 V vs. Mg/Mg^2+, followed by a large oxidation peak starting at 3.93 V vs. Mg/Mg^2+. Similar to the reduction case, binary Mg(TFSI)_2 in P_2444TFSI has a much wider oxidative stability window than dilute acetonitrile electrolytes with initial oxidation not occurring until 3.13 V vs. Mg/Mg^2+. Additionally, super-concentrated ternary electrolytes are more stable towards oxidation than the other two electrolytes and once again does not show any features reminiscent of acetonitrile. Overall, the super-concentrated ternary electrolyte expands the electrochemical stability window by over 3.5 V. Such large differences between the electrochemical stability of dilute and super-concentrated electrolytes are likely concomitant with a significant change to the local coordination environment of acetonitrile.
Figure 2. (a) Raman spectra of dilute conventional (200 mM Mg(TFSI)$_2$ in ACN), concentrated binary salt (20 mol% Mg(TFSI)$_2$ in P$_{2444}$TFSI), and concentrated ternary electrolyte (37.8 mol% ACN, 35.8 mol% Mg(TFSI)$_2$, and 26.4 mol% P$_{2444}$TFSI). (b) Reversible Mg electrodeposition and stripping for each electrolyte in symmetric Mg–Mg cells, where each plate or strip cycle lasts for 1 h at a current density of 0.01 mA cm$^{-2}$.

We turned to Raman spectroscopy to elucidate the structure of acetonitrile and TFSI anions within these electrolytes, which gives rise to large increases in reductive and oxidative stability (Figure 2a). The most intense peak within the Raman spectra for dilute Mg(TFSI)$_2$ in acetonitrile occurs at 908.7 cm$^{-1}$. This feature can be assigned to C-C stretching mode of “free” acetonitrile that lacks any direct coordination. As expected, this peak is completely absent for
binary Mg(TFSI) with P$_{2444}$TFSI, due to the lack of acetonitrile molecules. However, the super-concentrated ternary electrolyte with close to 40 mol% acetonitrile (SCE2) also does not show this peak. The Raman spectral signatures displaying the free and complexed forms of acetonitrile are more clearly shown for the CN stretch between 2200 cm$^{-1}$ and 2300 cm$^{-1}$ (Figure S1), and these data also confirm that free acetonitrile is not observable in SCE2. As such, the expansion in electrochemical stability window (Figure 1c) can be attributed to the formation of an explicit Mg–acetonitrile solvate.

By protecting the acetonitrile molecules from reduction, the interphase generated during cycling will no longer originate from solvent molecules and should instead be generated from the TFSI anion.$^*$ Cycling data for symmetric Mg–Mg cells constructed with various electrolytes (Figure 2b) confirm this hypothesis. Cycling of dilute Mg(TFSI)$_2$ in acetonitrile yields a comparably small overpotential that increases rapidly after 100 h, before evidencing large spikes in the plating overpotential after 400 h; runaway growth in cell impedance led to cell failure thereafter. While long term stability in plating and stripping of Mg electrodes is not possible using dilute Mg(TFSI)$_2$ electrolytes in acetonitrile, it is possible to do so using binary and ternary (super-)concentrated electrolytes containing P$_{2444}$TFSI, even though the plating overpotentials are comparably high, which may be due to increased electrolyte viscosity, latent differences in the interphases generated, or differentiated energetics required to desolvate (or uncluster) Mg$^+$ ions on plating. Nevertheless, cells assembled with either binary or ternary P$_{2444}$TFSI-based electrolytes were stable for over 500 cycles with limited increase in overpotential (<20%). These results suggest that in these electrolytes, a stable self-limited interphase is generated immediately upon cycling. Furthermore, the properties of various interphases generated from the binary and ternary electrolytes appear to be insensitive to the electrolyte’s composition, provided that the concentration of Mg(TFSI)$_2$ and P$_{2444}$TFSI is high enough to avoid “free” acetonitrile.
Figure 3. Raman spectra of binary electrolytes comprised of Mg(TFSI)$_2$ with P$_{2444}$TFSI (a), ternary concentrated electrolytes (b), and ternary super-concentrated electrolytes (c). Binary 1, Binary 2, Binary 3, Binary 4, CLE 1, CLE 2, CLE 3, CLE 4, SCE 1, and SCE 2 electrolytes are displayed (Table S1 and Figure S2). Voltage hysteresis for symmetric cell cycling over time (d). More information about electrolyte preparation and cycling data can be found in the Supporting Information.

To better understand this observation, we analyzed the Raman shifts associated with the chemical environment of TFSI (Figure 3). Pure P$_{2444}$TFSI and Mg(TFSI)$_2$ display single peaks for TFSI at 729.8 cm$^{-1}$ and 741.8 cm$^{-1}$, respectively. Interestingly, dilute Mg(TFSI)$_2$ in acetonitrile displays the same peak position as that observed for neat P$_{2444}$TFSI (Figure S1). As such, this peak corresponds to completely dissociated (i.e., “free”) TFSI anions, which lack any appreciable electrostatic interactions with the cations in the system. Between these two peaks observable for
each salt, there are three unique peaks indicating differing degrees of TFSI coordination. Peaks at 733.1 cm⁻¹, 735.0 cm⁻¹, and 740.0 cm⁻¹ can be attributed to solvent-separated ion pairs, contact ion pairs and aggregates having monodentate coordination, and contact ion pairs and aggregates having bidentate coordination, respectively. In the case of electrolytes comprised of binary mixtures of Mg(TFSI)₂ and P₄TFSI (Figure 3a), there appears to be ideal mixing with a decrease in prevalence of “free” TFSI with decreasing P₄TFSI concentration. Similarly, the increasing Mg(TFSI)₂ concentration results in an increase in bidentate coordination as well as Mg(TFSI)₂ aggregates (Figure 3b).

Contrarily, saturated Mg(TFSI)₂ in acetonitrile (18 mol%, CLE 1) is dominated by solvent-separated ion pair interactions due to the large molar excess of solvent molecules. Moving laterally across the phase diagram along the 18 mol% Mg line, a series of ternary electrolytes were generated to explore the impact of phosphonium concentration on TFSI coordination (Table S1 and Figure S2). These electrolytes had ratios of Mg(TFSI)₂ to P₄TFSI of 3:1, 1:1, and 1:3, for CLE 2, CLE 3, and CLE 4, respectively. For the lower P₄TFSI concentration electrolytes (CLE 1 and CLE 2), solvent-separated ion pairs and monodentate coordination dominate which indicates the presence of excess solvent molecules (Figure 3b). However, increasing the concentration of P₄TFSI to be equal to that of Mg(TFSI)₂ (CLE 3) leads to the primary species being bidentate coordination and a decrease in solvent-separated ion pairs. Additionally, an increase in the peak corresponding to “free” TFSI suggests the presence of a P₄TFSI microphase. After further increasing the P₄TFSI concentration (CLE 4), the only significant peaks are from bidentate coordination and “free” TFSI. This result further supports the formation of microphase separated P₄TFSI after all “free” acetonitrile has been coordinated.

Building upon this observation, magnesium concentration can be adjusted in parallel with P₄TFSI and acetonitrile to design electrolytes with specific TFSI environments. Increasing the magnesium concentration of CLE 4 yields SCE 1 (28.5 mol% Mg(TFSI)₂, 19.1 mol% acetonitrile, 52.4 mol% P₄TFSI) and SCE 2 (35.8 mol% Mg, 37.8 mol% acetonitrile, 26.4 mol% acetonitrile, 52.4 mol% P₄TFSI).
High magnesium concentrations yield TFSI environments that have increasingly high electrostatic interactions and less abundant “free” TFSI species (Figure 3c). Additionally, as SCE 2 demonstrates, decreasing the concentration of P₉,TFSI inhibits microphase separation, while having equivalent molar ratios of magnesium and acetonitrile further mitigates low coordination and “free” TFSI. These factors result in SCE 2 having insignificant quantities of either “free” acetonitrile or “free” TFSI despite the relatively high concentration of acetonitrile (37.8 mol%). As such, SCE 2 is able to undergo stable cycling without the continuous depletion of solvent molecules to form an insulating interphase.

Figure 4. Snapshot of MD simulation cells for dilute (a), concentrated binary (d), and super-concentrated ternary (g) electrolytes. Prominent solvation structures in the various regimes obtained from MD simulations: (b) free solvated Mg-ion in the dilute regime; (c) solvent
Molecular dynamics (MD) simulations further confirm the assignment of Raman features and aid in probing the specific coordination environments within dilute, concentrated binary, and super-concentrated ternary electrolytes (Figure 4). Within the dilute regime, magnesium is fully coordinated by acetonitrile, with no direct coordination to TFSI. Instead, most TFSI is “free” with a limited fraction being involved in solvent-separated ion pair interactions (Figure 4a-c). Additionally, the large excess of solvent molecules causes the presence of “free” acetonitrile. In the case of concentrated Mg(TFSI) in P$_{2444}$ TFSI, magnesium is almost exclusively (99.6 % of Mg) involved in 6-coordinate interactions with TFSI (Figure 4e, ratio of monodentate to bidentate is 3.7). The remaining excess TFSI from the abundance of P$_{2444}$ TFSI exists as “free” TFSI (Figure 4f), in agreement with the above description provided from Raman (Figure 3a).

Within super-concentrated ternary electrolytes, there are no discernable “free” acetonitrile or “free” TFSI species. Instead, despite the large molar fraction of acetonitrile, each solvent molecule is coordinated to magnesium, with 51% of magnesium ions having either one or two acetonitrile coordination, and 38% being exclusively solvated by TFSI. Likewise, the additional TFSI units that were added to the electrolyte through the presence of P$_{2444}$ TFSI cause an increase in the average coordination of TFSI to magnesium. Notably, over 37% of magnesium is coordinated by six TFSI anions and 51% of magnesium has either four or five coordination sites occupied by TFSI. These coordination environments lead to the formation of aggregate type solvation structures for magnesium within super-concentrated ternary electrolytes (Figure 4h). Aggregates of multiple magnesium ions are formed by bridging TFSI units, with acetonitrile coordination and either monodendate or bidentate coordination to TFSI (monodentate-to-bidentate ratio = 6.3). The identification of these species further confirms the utility in P$_{2444}$ TFSI...
to design particular TFSI environments, while mitigating the presence of “free” solvent or anions. Additionally, the shift in Raman features to higher wavenumbers (e.g., SCE 2 in Figure 3c) can be attributed to the increased electrostatic shielding and coordination of the TFSI within these super concentrated electrolytes.

The above results have important ramifications on electrolyte performance and stability during cycling (Figure 3d). In the absence of “free” acetonitrile, the overpotential for cycling between compositions is comparable and is stable for extended cycling times (over 500 h). Plating-activated instability of ion-paired anions in Mg liquid electrolytes was first elucidated by Rajput et al.; and, indeed, as TFSI coordination increases, this instability is predicted to worsen: recent theory suggests that TFSI coordination numbers in excess of 3.2 promote reductive instability. Therefore, the high coordination numbers within binary and super-concentrated electrolytes, as observed through Raman and simulations, can be attributed to the success in preferential reduction of TFSI. However, in the dilute regime where “free” acetonitrile is the dominate species, the overpotential increases rapidly and results in the cell dying before 500 h (Figure 2b). Furthermore, the presence of acetonitrile in SCE 2 results in a decrease in overpotential relative to where it would be expected to fall between the concentrations of Binary 3 and Binary 4. This result is likely due to the presence of the solvent molecule decreasing viscosity and increasing conductivity.

In summary, we report that phosphonium-based TFSI organo ionic salts increase the solubility of Mg(TFSI)₂ in acetonitrile, which enables concentrated and super-concentrated binary and ternary magnesium electrolytes. Through systematic design of the ternary super-concentrated electrolytes, the oxidative and reductive stability of the electrolytes can be increased to expand the electrochemical window by over 3.5 V. Utilizing Raman, these results can be linked to the change in solvation structure with increasing magnesium concentration. Furthermore, the prevalence of TFSI solvation environments with strong electrostatic interactions produces a self-limiting interphase that is stable for over 500 h of cycling with
negligible increase in (de)plating overpotential. These results suggest the efficacy of a ternary design component to augment the solubility regime of multivalent electrolytes that have traditionally struggled with poor solubility. Additionally, adjusting the identity of the phosphonium salt to span varying cations or functionalization presents another design space to control electrolyte properties. We hope that this report sparks further research into the electrochemical behavior and transport properties of super-concentrated multivalent electrolytes.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Materials and methods, electrolyte compositions, Raman spectroscopy, and cycling data for dilute, concentrated binary, and super-concentrated ternary electrolytes.

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Notes

The authors declare no competing financial interest.
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Ion Battery Utilizing a Copper Hexacyanoferrate Cathode in an Organic Electrolyte.


Supporting Information

For

Phosphonium-Based Binary and Ternary Super-Concentrated Liquid Electrolytes for Magnesium Batteries

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Materials

Polyacrylonitrile (PAN, $M_w = 150$ kg mol$^{-1}$), acetonitrile (ACN, anhydrous 99.8%), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 99.95%) were purchased from Sigma-Aldrich. Magnesium bis(trifluoromethanesulfonyl)imide (Mg(TFSI)$_2$, 97%) and triisobutylmethylphosphonium tosylate ($P_{1444}$OTs, 95%) were purchased from Strem. Tributylethylphosphonium bromide ($P_{2444}$Br, 50% w/w in water) was purchased from Cytec Industries. Magnesium powder (325 mesh) was purchased from Alfa Aesar. Vulcan XC 72 carbon black was purchased from Fuel Cell Earth and dimethylformamide (DMF, anhydrous 99.8%) was purchased from Acros. All materials were used as received with no further purification.

Synthesis of Tributylethylphosphonium bis(trifluoromethanesulfonyl)imide

$P_{2444}$TFSI was synthesized with a modified literature preparation.$^1$ $P_{2444}$Br (50% w/w in water) (15.410 g, 24.8 mmol) and LiTFSI (5.712 g, 19.9 mmol) were combined in water (20 mL) and stirred overnight at room temperature. The mixture was cooled in an ice bath to aid in precipitation of the $P_{2444}$TFSI, which was subsequently isolated through filtration and washed repeatedly with water. The final product was dried under vacuum at 80 °C overnight to remove trace water. $^1$H NMR was consistent with the previously published procedure.$^2$ $^1$H NMR ($d_6$-DMSO, 500 MHz) $\delta = 0.91$ (9H, t, $J = 7.1$ Hz), 1.12 (3H, dt, $J = 18.2$ Hz, 7.7 Hz), 1.36–1.50 (12H, m), 2.13–2.25 (8H, m) ppm.

Synthesis of Triisobutylmethylphosphonium bis(trifluoromethanesulfonyl)imide

$P_{1444}$TFSI was synthesized consistent with the preparation for $P_{2444}$TFSI. Briefly, $P_{1444}$Ts (5.632 g, 14.5 mmol) and LiTFSI (4.183 g, 14.6 mmol) were combined in water (40 mL) and stirred overnight at room temperature. The mixture was subsequently isolated through filtration and washed repeatedly with water. The final product was dried under vacuum at 80 °C overnight to remove trace water. $^1$H NMR was consistent with previously published results.$^2$ $^1$H NMR ($d_6$-DMSO, 500 MHz) $\delta = 1.03$ (18H, d, $J = 6.7$ Hz), 1.91 (3H, d, $J = 13.9$ Hz), 1.97–2.08 (3H, m), 2.18 (6H, dd, $J = 13.8$, 6.5 Hz) ppm.
Electrolyte Preparation

All electrolytes were prepared by mixing the specified molar ratios (Table S1) of acetonitrile, Mg(TFSI)$_2$, and P$_{244}$TFSI at 50 °C overnight to ensure complete and homogeneous mixing. In the case of the binary electrolyte series (Binary 1–4), mixing was performed at 80 °C. While Mg(TFSI)$_2$ and P$_{244}$TFSI exist as solids at room temperature, all reported binary electrolytes remain liquid at room temperature after cooling.

Fabrication of Composite Magnesium Electrodes

Magnesium electrodes with a final composition of 77:10:10:3 (Mg powder, PAN, carbon black, and Mg(TFSI)$_2$, respectively) were prepared by first stirring a PAN in DMF (10% w/w) with carbon black and Mg(TFSI)$_2$ for 1 h. Magnesium powder was then added to the slurry and mechanically mixed before magnetically stirring overnight. The slurry was cast on Ni foil and allowed to dry under inert conditions before finishing drying at 80 °C under vacuum for 3 h. Mg electrodes were punched in a diameter of 12.5 mm with all handling performed in an Ar-filled glove box.

Electrochemical Testing

Mg–Mg symmetric cells were evaluated using CR2032 coin cells on an Arbin LBT electrochemical station controlled using MITS Pro software. Celgard 2535 was used as a separator. Various electrolytes tested (30 µL) were dispensed on each side of the separator to ensure proper wetting in the cells. All electrochemical testing was conducted at 20 °C.

Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were carried out under Ar, using a BioLogic VMP3 potentiostat and EC-Labs software. Glassy carbon working electrodes were acquired from CH instruments and magnesium rods were acquired from ESPI Metals. All experiments were conducted utilizing a three-electrode cell system with glassy carbon as the working electrode and magnesium as both counter and reference electrodes.
**Raman Microscopy**

Electrolytes for Raman analysis were transferred to a stainless-steel well-plate within an Ar-filled glove box, and the well-plate was then sealed against a quartz window using kalrez o-ring to prevent air exposure and contamination from oxygen and moisture during Raman measurements. Raman spectra were acquired with a Renishaw InVia confocal Raman microscope using a 785 nm laser at 100% power. 30 acquisitions of 1 s each were averaged together to obtain each spectrum. Curve fitting was performed using Renishaw Wire4 software. For curve fitting of the TFSI$^-$ stretching peaks, peak positions were fixed at 729.9, 733, 735, 740, and 741.8 based on reference spectra from pure P$_{2444}$TFSI (729.9), pure (dried) Mg(TFSI)$_2$ (741.8), and literature references for the peaks corresponding to monodentate CIP (713), bidentate CIP (735), and aggregates (740) for Mg(TFSI)$_2$ in an ionic liquid.³

**Molecular Dynamics**

Molecular dynamics simulations were carried out with the GROMACS software.⁴ Initial configurations were prepared using PACKMOL.⁵ Forcefield parameters for ACN and P$_{2444}$ were from the OPLS forcefield,⁶,⁷ extracted using Schrodinger’s MacroModel software.⁸ TFSI force field parameters were taken from Lopes and Padua.⁹ All charges were scaled by 0.8 as has been previously recommended due to the overestimation of interionic interactions in non-polarizable forcefields.¹⁰,¹¹ Initially, a steepest descent minimization was used, followed by a Berendsen barostat equilibration¹² for at least 10 ns in the NPT ensemble, with a velocity rescaling thermostat.¹³ Subsequently, systems were heated to 600 K and cooled down to room temperature. This was followed by the NVT ensemble production run, which was at least 10 ns using the velocity rescaling thermostat.¹³

Three different concentrations were studied: dilute (995 ACN, 5 Mg$^{2+}$, and 10 TFSI$^-$ (box size = 4.48 nm$^3$), concentrated binary (Binary 2, 40 Mg$^{2+}$, 180 P$_{2444}^-$, and 260 TFSI$^-$ (box size = 5.14 nm$^3$), and
super-concentrated ternary (SCE 2, 189 ACN, 179 Mg$^{2+}$, 132 P$_{2444}^-$, and 490 TFSI$^-$ (box size = 5.14 nm$^3$)).
**Supporting Tables**

**Table S1.** Selected electrolyte compositions used in systematic screening of ternary phase diagram (Figure S1).

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<th>P$_{2444}$TFSI (mol%)</th>
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</table>
Figure S1. Raman spectra for pure Mg(TFSI)$_2$, P$_{244}$TFSI, and dilute Mg(TFSI)$_2$ in acetonitrile for Raman shift corresponding to TFSI coordination (a). Raman spectra showing the CN stretch for free ($v_2$) and complexed ($v_2'$) acetonitrile concentrated (b) and super-concentrated (c) ternary electrolytes.
Figure S2. Ternary phase diagram for electrolytes containing acetonitrile, Mg(TFSI)$_2$, and P$_{244}$TFSI collected at 30 °C. The liquidous regime has homogenous mixtures across dilute (teal) and concentrated (light purple) regions, as well as a biphasic region (dark purple). The remainder of the phase diagram is a solid solution (pink). Colored circles correspond to specific electrolytes involved in the reported systematic Raman screening with the numerical molar composition reported in Table S1.
**Figure S3.** Reversible Mg deposition/stripping in symmetric Mg–Mg cells, where each cycle lasted for 1 h at a current density of 0.01 mA cm$^{-2}$. All cycling data was collected at room temperature. Dilute, SCE2, Binary 1, Binary 2, Binary 3, and Binary 4 electrolytes are displayed.
**Figure S4.** Early- (left), mid- (middle), and late- (right) stage cycling for the reversible Mg deposition/stripping in symmetric Mg–Mg cells, where each cycle lasted for 1 h at a current density of 0.01 mA cm$^{-2}$. All cycling data was collected at room temperature. Binary 2 (top), SCE 2 (middle), and dilute (bottom) electrolytes are displayed.
**Figure S5.** Reversible Mg deposition/stripping in symmetric Mg–Mg cells, where each cycle lasted for 20 h at a current density of 0.02 mA cm\(^{-2}\) to show equilibration of voltage after extended duration. Cycling data was collected at room temperature. Binary 2 electrolyte is displayed.
Figure S6. Linear sweep voltammetry of dilute conventional (teal), concentrated binary salt (pink), and concentrated ternary electrolytes (light purple) showing onset of initial reduction (a) and oxidation (b).
Figure S7. Radial distribution function (RDF) and coordination number for Mg-O(TFSI) (top) and Mg-N(ACN) (bottom) in dilute, concentrated binary (Binary 2), and super-concentrated ternary (SCE 2)
Supporting References


(8) Schrodinger, LLC. *MacroModel 2018*. 


