Ionic liquid hybrids: Progress toward non-corrosive electrolytes with high-voltage oxidation stability for magnesium-ion based batteries

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Abstract

Magnesium – ion batteries have the potential for high energy density but require new types of electrolytes for practical application. Ionic liquid (IL) electrolytes offer the opportunity for increased safety and broader voltage windows relative to traditional electrolytes. We present here a systematic study of both the conductivity and oxidative stability of hybrid electrolytes consisting of eleven ILs mixed with dipropylene glycol dimethylether (DPGDME) or acetonitrile (ACN) cosolvents and magnesium bis(trifluoromethylsulfonyl)imide (Mg(TFSI)₂). Our study finds a correlation of higher conductivity of ILs with unsaturated rings and short carbon chain lengths, but by contrast, these ILs also exhibited lower oxidation voltage limits. For the cosolvent additive, although glymes have a demonstrated capability of coordination with Mg²⁺ ions, a decrease in conductivity compared to acetonitrile hybrid electrolytes was observed. When cycled within the appropriate voltage range, the IL-hybrid electrolytes that show the highest

conductivity provide the best cathode magnesiation current densities and lowest polarization as demonstrated with a $\text{Mg}_{0.15}\text{MnO}_2$ and $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ cathodes.

Keywords: magnesium-ion battery, ionic liquid electrolyte, electrolyte oxidation, electrolyte conductivity, high-voltage Mg-ion cathode

1. Introduction

Large-scale energy storage is needed to efficiently manage the distribution of energy produced from both renewable and nonrenewable resources. Rechargeable batteries are a viable candidate for large-scale energy storage, like the electric grid, but there is not yet a single battery technology solution which meets all needs for this application.[1-4] The grid requires large scale batteries that are affordable, safe and capable of thousands of cycles of moderate- to high-rate charging and discharging. While utilized in electronics and electric cars, lithium-ion batteries have limitations for large-scale energy storage due to cost and availability of lithium.[5] Magnesium is about 10^4 times more abundant in the Earth's crust than lithium[6] with approximately 250 times more mass produced per year than lithium at a third of the market price.[7] The availability and cost of magnesium makes it a very attractive element to utilize in diversifying the approach to large-scale energy storage. Additionally, magnesium can undergo a two electron reduction allowing for a higher theoretical volumetric capacity ($3,833 \text{ mAh/cm}^3$) than lithium ($2,060 \text{ mAh/cm}^3$).[8] For these reasons interest in Mg-ion batteries is growing and further exploration is warranted in order to progress towards practical large scale batteries.

A significant issue in the development of Mg-ion batteries is identifying suitable electrolytes with solvent and magnesium salt combinations that are compatible with magnesium anodes. Many aprotic solvents that are successful in Li-ion electrolytes cannot be applied to Mg

metal anodes.[9] These electrolytes which contain salts such as $\text{Mg}(\text{ClO}_4)_2$ or $\text{Mg}(\text{BF}_4)_2$ in carbonate solvents passivate the surface of magnesium metal forming surface compounds that are impermeable to Mg^{2+} . Preliminary success in reversible Mg dissolving and plating has been achieved by utilizing organo-haloaluminate complexes dissolved in tetrahydrofuran (THF) or glyme-based solvents as Grignard-type systems.[10] However, these systems use corrosive components and have a limited electrochemical window (~ 3 V)[11] and are thus unsuitable for higher voltage applications.

Ionic liquids (ILs), or room temperature molten salts, are possible additives for Mg-ion batteries because of their dual role as electrolyte and solvent, large windows of voltage stability, low volatility and inability to ignite.[12-14] Some of the inherent limitations of ILs are high viscosities, low transference numbers and low conductivities which can be mitigated with cosolvents like THF[15-19] and glycol ethers[20, 21]. Cosolvents with ILs have also been suggested to promote Mg^{2+} dissociation[22] because Mg electrodeposition and dissolution from pure ILs with magnesium salts has been difficult[15, 23-25] or poorly reproducible[26-28]. Glycol ether blends can improve Mg^{2+} dissociation due to their role in coordinating to and solvating Mg^{2+} . This property improves performance in electrolytes with magnesium bis(trifluoromethylsulfonyl)imide ($\text{Mg}(\text{TFSI})_2$) salt as discussed by Watkins et al.[29], since Mg^{2+} cations are coordinated with the oxygens of the glycol ethers instead of coordinating with ≥ 3 TFSI anions.[22, 29] Watkins et al. have also developed ionic liquids tailored with chelating polyether chains in substitution for alkyl chains which showed good coulombic efficiency for electrodeposition and dissolution of Mg.[30] Combining ILs with glymes is a promising system of cosolvents for Mg-ion electrolytes that could infuse the stability and safety characteristics of ILs with the Mg^{2+} solvation abilities of glycol ethers.

The voltage windows of ILs are generally believed to be wide enough for Mg-ion operation so there are only a few direct investigations of IL voltage stability in magnesium IL electrolytes. Cheek et al. determined that the window of voltage stability for 1-ethyl-3-methylimidazolium tetrafluoroborate was insufficient for reduction of magnesium triflate, but 1-butyl-1-methylpyrrolidinium bis(trifluorosulfonyl)amide could be used in the reduction of several magnesium salts.[15] Kitada et al. studied the oxidative stability of electrolytes with IL, glyme and magnesium bis[(trifluoromethyl)sulfonyl]amide salt and determined that the IL/glyme mixtures had a higher oxidative stability than IL-free electrolytes with only glyme solvent.[20] They attributed the improved stability to the lack of free glymes in solution when an IL is also present.

We sought to systematically characterize a series of ionic liquids and cosolvents to assess their relevance to magnesium ion batteries. Here, we measure conductivities and oxidative stabilities for ionic liquids blended with di(propylene glycol) dimethyl ether (DPDGME, regarded as a “green” glyme) and acetonitrile, which has found success in high voltage applications.[31, 32] Our findings indicate a cosolvent-induced conductivity enhancement as high as 12-fold with the mixing of IL with acetonitrile and oxidative stability up to an estimated 5.5 V vs Mg/Mg²⁺. Additionally, we used these electrolytes to successfully insert and remove Mg²⁺ from high-voltage cathode materials Mg_{0.07}V₂O₅ and Mg_{0.15}Na_{0.02}MnO₂·0.7H₂O. Both magnesium vanadium oxides and magnesium manganese oxides have been cited as high-voltage Mg-ion cathodes that can deliver >175 mAh/g discharge capacities.[1, 33, 34] We demonstrate that hybrid IL electrolytes with cosolvents can achieve similar current densities during cyclic voltammetry and discharge capacities from constant current discharge of Mg_{0.07}V₂O₅ cathode materials that were tested in electrolytes without ILs.[33, 34]

2. Experimental

Ionic liquids used in this study were purchased from io-li-tec Inc. **Table 1** lists the names and the respective abbreviations for each ionic liquid. The solvents di(propylene glycol) dimethyl ether (**DPDGME**) and anhydrous acetonitrile were purchased from Sigma Aldrich and Honeywell, respectively. Magnesium bis(trifluoromethylsulfonyl)imide ($\text{Mg}(\text{TFSI})_2$) salt was purchased from Strem Chemicals, Inc. Prior to any measurements, ionic liquids were dried by freeze-pump-thaw under high vacuum and **DPDGME** was dried using molecular sieves. The water content of all liquids was measured using Karl Fischer titration and all samples contained <50 ppm of H_2O .

All measurements were performed in an argon filled glovebox at room temperature. Electrolyte conductivity was measured with an Oakton CON 11 series conductivity probe. The oxidative stability was determined via cyclic voltammetry (CV) of a three electrode cell using a Biologic potentiostat. Glassy carbon was used as the working electrode, platinum wire as the counter electrode and the reference electrode was a silver wire in a solution of 0.01 M AgNO_3 in acetonitrile. CV was conducted at 100 and 20 mV/s starting at -1.0 to 1.0 V vs $\text{Ag}^0/\text{AgNO}_3$ and up to -1.0 to 2.8 V vs $\text{Ag}^0/\text{AgNO}_3$.

Electrochemical tests with cathode materials, $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ or $\text{Mg}_{0.15}\text{Na}_{0.02}\text{MnO}_2 \cdot 0.7\text{H}_2\text{O}$ (Mg-MnO_2) were performed. **Electrodes were prepared using a doctor blade with a standard tape-case method. The $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ electrodes had a formulation of 85% $\text{Mg}_{0.07}\text{V}_2\text{O}_5$, 5% graphite, 5% super P carbon, and 5% PVDF by mass. The Mg-MnO_2 electrodes had a formulation of 85% Mg-MnO_2 , 8% super P carbon, 2% graphite, and 5% PVDF by mass.** Electrochemical tests consisted of cyclic voltammetry (CV) using a three electrode teflon cell

followed by additional constant current cycling. A Ketjen black carbon coating on aluminum foil acted as the counter electrode with a reference electrode of silver wire in a solution of 0.01 M AgNO₃ in acetonitrile. CV of Mg_{0.07}V₂O₅ was performed between -1.0 and 1.2 V vs. Ag⁰/AgNO₃ at a rate of 0.5 mV/s and CV of Mg-MnO₂ was performed between -0.8 and 1.2 V vs. Ag⁰/AgNO₃ at a rate of 0.5 mV/s. After five cycles of CV, the same cells were subjected to constant current cycling between -1.0 and 1.2 V vs. Ag⁰/AgNO₃ at approximately a C/2 rate.

3. Results and Discussion

The ionic liquids chosen for this study were comprised of various cations paired with bis(trifluoromethylsulfonyl)imide anion (TFSI⁻). TFSI⁻ was chosen as the anion because ILs consisting of TFSI⁻ anions have low viscosities, high ionic conductivities and remain liquid over a large temperature range.[12, 13, 17] Cations either contained an unsaturated (pyridinium or imidazolium) or saturated (pyrrolidinium or piperidinium) organic ring which was either five (imidazolium and pyrrolidinium) or six (piperidinium and pyridinium) membered and bound to two alkyl chains ($1 \leq n \leq 4$). The names, abbreviations and structures of the 11 total ILs used in this study are given in **Table 1**.

3.1 Ionic Conductivity

Neat ILs provide an environment saturated in cations and anions, and as result, ionic conductivities are low (<6 mS/cm, **Figure 1**). This conductivity can be improved by dilution to lower concentrations via addition of a cosolvent,[12, 13, 35] Here, we compare the effects of acetonitrile (**Figure 1a**) and **DPDGME** (**Figure 2a**) where acetonitrile as a solvent is more polar, while as a glyme **DPDGME** can mediate Mg dissolution and plating. Independent of cosolvent,

conductivity correlates linearly with dilution volume to a limit of ca. 40% IL, below which there is no improvement. This trend is stronger in polar acetonitrile, which offers a higher maximum achievable conductivity (50 mS/cm vs. 8 mS/cm, DMPGE) with identical ILs.

The range of ILs studied here allow elucidation of clear conductivity vs. structure trends. Substituents with shorter chain lengths provided higher conductivities which can be attributed to smaller ions, less steric hindrance and more facile ion mobility (**Figure 1b, 2b**). Similarly, smaller five-membered rings were more conductive than six-membered rings (**Figure 1c, 2c**). Unsaturated rings displayed greater conductivities than their analogs with saturated rings. The presence of double bonds in the cation delocalizes the positive charge which may improve charge mobility in the solution and in effect improve conductivity. From these results, ionic liquids with unsaturated cation rings, less ring members and shorter substituent chain lengths produced the greatest conductivities.

In practical electrolytes for Mg-ion batteries there needs to be a presence of Mg^{2+} ions in the solution. Thus, $\text{Mg}(\text{TFSI})_2$ salt was dissolved in concentrations of 0.5 M into the mixtures with the highest conductivities. Results for solutions containing acetonitrile and **DPDGME** are given in **Figure 3**. We found a universal decrease of conductivity by approximately 50% upon Mg^{2+} addition. The differences in conductivities between the acetonitrile and **DPDGME** solutions can be attributed to the availability of free Mg^{2+} charge carriers. Acetonitrile has a relatively small desolvation energy with respect to Mg^{2+} ions[36] and glymes form stable complexes with Mg^{2+} ions.[29, 37, 38] The addition of salt typically lowers the conductivity of hybrid IL/solvent solutions.[12, 13, 35] The decrease in conductivity could be due to Mg^{2+} ions being coordinated by three or four TFSI⁻ anions which form stable clusters that reduce charge carrier transport and increase viscosity.[27] For the acetonitrile solutions reported here the mole

fractions of $\text{Mg}(\text{TFSI})_2$ salt, IL and acetonitrile are approximately 0.04, 0.11, and 0.85, respectively. The mole fractions for the **DPDGME** solutions are approximately 0.10, 0.44, and 0.46 for $\text{Mg}(\text{TFSI})_2$ salt, IL and **DPDGME**, respectively. **DPDGME** has a much higher molecular mass (162.23 g/mol) and density (0.90 g/mL) than acetonitrile (41.05 g/mol and 0.79 g/mL) which accounts for most of their differences in mole fractions. Using Raman spectroscopy Watkins et al. showed that a higher mole fraction of $\text{Mg}(\text{TFSI})_2$ in IL increased the fraction of TFSI^- anions coordinated to Mg^{2+} . [29] In consideration of the mole fractions, the acetonitrile solutions are more dilute so the Mg^{2+} ions have a smaller fraction of coordinated TFSI^- anions compared to the **DPDGME** solutions. With a lower fraction of coordinated ion pairs, the ions in the acetonitrile solutions may enhance ionic conductivity because they are more mobile.

3.2 Electrochemical Characterization

3.2.1 Oxidative Stability

Electrolyte oxidation represents the upper voltage limit of battery operation because oxidation forms products that can be harmful to battery performance or create safety concerns. [39, 40] Thus, high-voltage cathode materials require electrolytes with oxidative stabilities exceeding the discharge voltage of the battery. Cyclic voltammetry (CV) was used to determine the oxidative stability of hybrid electrolytes comprised of mixtures at the maximum conductivities with 0.5 M $\text{Mg}(\text{TFSI})_2$. CV plots of electrolytes with IL/acetonitrile are shown in **Figure 4**. Oxidation stability was determined as the potential regime through which current density is less than $\pm 0.1 \text{ mA/cm}^2$. [41-43] The oxidative stabilities for IL/acetonitrile electrolyte combinations are given in **Table 2**. For electrolytes with acetonitrile cosolvent, ILs with imidazolium cations oxidized at 0.2 to 0.3 V lower than ILs with pyrrolidinium, pyridinium, and

piperidinium cations which all displayed similar oxidative stabilities. This data shows that the imidazolium cation can influence the oxidative stability while the other three cations do not. The limitation may arise from a common component in the electrolytes, likely TFSI, which is known to oxidize at 2.3V vs. Ag/Ag⁺.^[44-46] Our findings appear to disagree with a computational study which found that the TFSI⁻ anion will oxidize at a lower voltage than the imidazolium cation^[47]

The imidazolium cation contains a tertiary amine while none of the other IL cations contain any atoms with a lone pair of electrons. The amine in the imidazolium cation is nucleophilic and could lose an electron during oxidation which could be the reason the imidazolium-containing electrolytes showed lower oxidation voltages. Imidazolium-based ILs present an interesting tradeoff where they offer the high conductivities, yet lower oxidative stability. Thus, imidazolium-based ILs provide low resistance electrolytes, but may not be compatible with all high voltage cathode materials. Cations with longer substituent chains had slightly higher oxidation voltages, but the difference was less than 0.01 V which agrees with a computational assessment of imidazolium ILs.^[47] Cation ring size and saturated bonds did not appear to influence oxidative stability.

The CV plots of electrolytes containing **DPDGME** are shown in **Figure 5**. Most electrolytes displayed similar oxidative stabilities with oxidation occurring near 1.6 V. Since the oxidation voltage is lower than those of electrolytes with acetonitrile the oxidized species is likely the **DPDGME**. **Table 3** displays the oxidative voltages for each IL tested with **DPDGME**. It appears that the type of cation or substituents does not play a role in the oxidative stability for these hybrid electrolytes.

There was a correlation of cation type with reduction currents. Electrolytes with pyridinium cations had greater reductive currents at -1.0 V than the other three cations. More positive cathodic limits for pyridinium cations has been reported.[48] The unsaturated ring structure of the pyridinium cations makes it more accommodating to gaining an electron during reduction than the other cations. Thus, pyridinium cations are not good candidates for lower operating voltages. Based on the results of the CV to determine the oxidative stability tests, hybrid electrolytes with acetonitrile are more stable at higher voltages than electrolytes with **DPDGME**, imidazolium cations have lower oxidation voltages than the other three cations and pyridinium cations will reduce at more positive voltages than the other three cations. Piperdinium and pyrrolidinium cations provided the best oxidative stabilities for higher voltages.

3.2.2 Performance with high-voltage cathodes

$\text{Mg}_{0.07}\text{V}_2\text{O}_5$ is a promising cathode in Mg batteries.[49, 50] We sought to determine the properties of this material in the presence of the best performing ionic liquids as described above. **Figure 6A** shows cyclic voltammetry data within the voltage stability range for 1M1PPi/acetonitrile. Peaks correlating to reduction and oxidation are observed at -0.38 V and 1.00 V, respectively. Cycles 2-5 were identical, suggesting good stability within this region. Other ionic liquids that were tested provided similar reduction and oxidation voltages (**Table 4**). **Figure 6B** shows the CV of $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ with 1M1PPi/**DPDGME** electrolyte. Substitution of acetonitrile with **DPDGME** allowed testing the tradeoff of a loss of conductivity with the gain of ion coordination properties reported for glymes, which are proposed to form stable complexes with Mg^{2+} ions.[51] We find a ~10 fold drop in measured mA/g, suggesting the reduced conductivity supersedes the benefit of Mg^{2+} coordination for the electrolyte with added

DPDGME. Interestingly, two oxidation and reduction peaks were observed in the CV of $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ with 1M1PPi/DPDGME electrolyte, suggesting two different vanadium center environments. This observation is similar to the prior observation of two oxidation and reduction peaks in the CV of $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ with 1.0 M LiPF_6 in ethylene carbonate (EC) / dimethyl carbonate (DMC) (v/v 30/70) electrolyte.[33] Notably, in this study, cathodes in the electrolytes with DPDGME showed less polarization with respect to the difference in oxidation and reduction potentials

A third electrolyte combination (40 vol% IL, 60 vol% acetonitrile with 0.5 M DPDGME) was tested to determine if the beneficial attributes of acetonitrile and DPDGME can be retained in a cell with both cosolvents present (**Figure 6C**). Electrolytes with both cosolvents produced a compromise of the high currents achieved with acetonitrile and low polarization accomplished from DPDGME. These blends represent an opportunity to tune the composition of cosolvents to meet the needs of a specific application.

Voltage profiles from constant current magnesiation and demagnesiation of $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ with electrolytes with 1M1PPi are displayed in **Figure 7**. Charge (demagnesiation) and discharge (magnesiation) capacities from constant current cycling after CV for the nine combinations of electrolytes are organized in **Table 4**. Solvent type affected achievable discharge and charge capacities with the most conductive electrolytes producing the highest capacities. Electrolytes with DPDGME delivered significantly less capacity than the other blends of electrolytes.

Another high-voltage Mg-ion cathode material is $\text{Mg}_{0.15}\text{Na}_{0.02}\text{MnO}_2 \cdot 0.7\text{H}_2\text{O}$ (Mg-MnO₂).[50] Voltammograms of Mg-MnO₂ cathodes in electrolytes with 40 vol% IL and 60 vol% acetonitrile are displayed in **Figure 8**. Mg-MnO₂ in the birnessite phase was tested for

electrochemical activity with 1M1PPi, 1M1PPyrr and 1M3PIIm, **Table 5**. While the birnessite phase of Mg-MnO₂ is known as a high-voltage cathode material with capacity >175 mAh/g it does show capacity fade attributed to the degradation of the cathode's crystal structure.[50, 52] Similarly, capacity fade is also observed with these hybrid IL electrolytes. Electrolyte with 1M1PPyrr displayed the largest decrease (37%) in reduction current from the first cycle to second cycle, whereas the cells with 1M1PPi and 1M3PIIm only showed decreases in reduction current between the first and second cycles of 12% and 10%, respectively.

Notably, electrolyte with 1M3PIIm generated much larger reduction currents than the other two ILs. However, 1M3PIIm did not show the largest oxidation currents; 1M1PPyrr produced the largest oxidation current. 1M3PIIm showed the least polarization with a difference in oxidation and reduction potentials of 0.85 V while 1M1PPi and 1M1PPyrr had differences of 0.89 and 1.06 V, respectively. Imidazolium-based ILs presented greater reduction currents with less polarization. Also, the oxidation potential of Mg-MnO₂ is lower than the oxidation voltage of 1M3PIIm so electrolyte oxidation should not be an issue for this system.

Previous reports have shown that the addition of water significantly improves the magnesiation and demagnesiation of MnO₂ in Mg-ion batteries.[50, 52-55] Water molecules are reported to help solvate Mg²⁺ ions and partially shield some of the charge in nonaqueous electrolytes.[52] Notably, water would react at the anode if Mg metal were used.[56-58] All of the electrolytes used in this study contained minimal water (<50 ppm H₂O) so it is interesting that these IL-hybrid electrolytes can function with Mg-MnO₂ cathodes (Mg_{0.15}Na_{0.02}MnO₂·0.7H₂O) despite their low water content.

4. Conclusions

In summary, this report investigated hybrid electrolytes based on ionic liquid (IL) and organic solvents (acetonitrile and dipropylene glycol dimethylether) and their performance as electrolytes in Mg-ion batteries. Four IL cations were studied with varying substituent chain lengths. Each IL was tested as an electrolyte in various mixtures containing acetonitrile or **DPDGME** and $\text{Mg}(\text{TFSI})_2$ salt. Higher ionic conductivities coincided with electrolytes containing ILs consisting of unsaturated cation rings and shorter substituent chain lengths. Solutions with imidazolium cations proved to be most conductive, but also showed the lowest oxidative stability. In terms of cosolvent, mixtures with acetonitrile were about 7-10 times more conductive than mixtures with **DPDGME**. The enhanced conductivity of acetonitrile solutions translated to higher reduction and oxidation currents achieved in cyclic voltammetry of high-voltage cathodes, $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ and Mg-MnO_2 . However, electrolytes with **DPDGME** showed less polarization between reduction and oxidation peak voltages by voltammetry. ILs with imidazolium cations produced the least polarization along with relatively large oxidation and reduction currents. Imidazolium-based ILs present an interesting tradeoff in which they produced high conductivities and CV currents, but low **oxidative** stability. Within the imidazolium range of voltage stability, the imidazolium-based ILs provided the best performance. This report has shown that several IL hybrid electrolytes have high oxidative voltage stability and can be used in magnesium ion based systems with high-voltage cathodes.

Key benefits of the proposed electrolyte system include use of non-corrosive materials resulting in a safe electrolyte compatible with a broad array of cell assembly materials. The focus of this work was electrolyte compatibility for implementation of high-voltage cathodes. However, a brief comment regarding anode compatibility is provided. Of the known Mg-ion anode materials, is envisioned that a bismuth based anode (Mg_3Bi_2) with a potential of +0.23 V

versus magnesium may be most appropriate.[31, 32, 59] Since acetonitrile reduces at a voltage of -0.2 V vs Mg,[60] a magnesium ion battery based on an Mg_3Bi_2 anode should be compatible with the hybrid electrolytes described herein.

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Ionic Liquid Name	Abbreviation
1-Methyl-1-Propyl-Piperidinium bis(trifluoromethylsulfonyl)imide	1M1PPi
1-Butyl-1-Methyl-Piperidinium bis(trifluoromethylsulfonyl)imide	1B1MPi
1-Ethyl-1-Methyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide	1E1MPyrr
1-Methyl-1-Propyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide	1M1PPyrr
1-Butyl-1-Methyl-Pyrrolidinium bis(trifluoromethylsulfonyl)imide	1B1MPyrr
1-Ethyl-3-Methyl-Imidazolium bis(trifluoromethylsulfonyl)imide	1E3MIm
1-Methyl-3-Propyl-Imidazolium bis(trifluoromethylsulfonyl)imide	1M3PIm
1-Butyl-3-Methyl-Imidazolium bis(trifluoromethylsulfonyl)imide	1B3MIm
1-Ethyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide	1E3MPy
1-Propyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide	1P3MPy
1-Butyl-3-Methyl-Pyridinium bis(trifluoromethylsulfonyl)imide	1B3MPy

Table 1. Names, abbreviations and structures of ionic liquids (ILs) used in this study.

Figure 1. a) Conductivity of solutions containing varied amounts of ionic liquid (IL) and acetonitrile. Horizontal axis is volume percent of the total solution. b) Conductivity of solutions with 40 vol% ionic liquid as a function of substituent chain length. c) Conductivity of solutions with 40 vol% ionic liquid separated based on ring size and saturation. Five membered rings are pyrrolidinium (saturated) and imidazolium (unsaturated). Six membered rings are pyridinium (unsaturated) and piperidinium (saturated).

Figure 2. a) Conductivity of solutions containing varied amounts of ionic liquid (IL) and di(propylene glycol) dimethyl ether (DPDGME). Horizontal axis is volume percent of the total solution. b) Conductivity of solutions with 40 vol% ionic liquid as a function of substituent chain length. c) Conductivity of solutions with 40 vol% ionic liquid separated based on ring size and saturation. Five membered rings are pyrrolidinium (saturated) and imidazolium (unsaturated). Six membered rings are pyridinium (unsaturated) and piperidinium (saturated).

Figure 3. Comparison of conductivities of solutions with and without 0.5 M magnesium bis(trifluoromethylsulfonyl)imide ($\text{Mg}(\text{TFSI})_2$) salt. Solutions contained cosolvents a) acetonitrile and b) di(propylene glycol) dimethyl ether mixed with IL in the formulations that provided the greatest conductivities (see Figure 1 and 2).

Figure 4. Cyclic voltammetry (CV) of an electrolyte with 0.5 M Magnesium bis(trifluoromethylsulfonyl)imide ($\text{Mg}(\text{TFSI})_2$) dissolved in ionic liquid (40 vol%) and acetonitrile (60 vol%). Voltage was measured with respect to a silver reference electrode in a solution of 0.01 AgNO_3 dissolved in acetonitrile. Voltage was scanned at 20 mV/s. The Mg/Mg^{2+} scale is estimated. Inset shows magnified view of voltage range from 2.55 to 2.75 V. Cations with longer chain lengths are presented as dashed lines and shorter chain lengths are displayed as solid lines.

IL	E_{ox} vs. (Mg/Mg ²⁺) / V
1E1MPyrr	5.23
1M1PPyrr	5.16
1E3MPy	5.08
1P3MPy	5.15
1E3MIm	4.94
1M3PIm	4.99
1M1PPi	5.19

Table 2. Oxidative voltage stabilities of the electrolytes containing 0.5 M Magnesium bis(trifluoromethylsulfonyl)imide (Mg(TFSI)₂) dissolved in ionic liquid (40 vol%) and acetonitrile (60 vol%). Oxidative voltages were determined as the point when the measured current exceeded 0.1 mA/cm² from the background current.

Figure 5. Cyclic voltammetry (CV) of an electrolyte with 0.5 M Magnesium bis(trifluoromethylsulfonyl)imide ($\text{Mg}(\text{TFSI})_2$) dissolved in ionic liquid (60 vol%) and di(propylene glycol) dimethyl ether (DPDGME) (40 vol%). Voltage was measured with respect to a silver reference electrode in a solution of 0.01 AgNO_3 dissolved in acetonitrile. Voltage was scanned at 20 mV/s. The Mg/Mg^{2+} scale is estimated. Inset shows magnified view of voltage range from 1.4 to 1.6 V. Cations with longer chain lengths are presented as dashed lines and shorter chain lengths are displayed as solid lines.

IL	E_{ox} vs. (Mg/Mg²⁺) / V
1E1MPyrr	4.43
1M1PPyrr	4.40
1E3MPy	4.44
1P3MPy	4.43
1E3MIm	4.44
1M3PIm	4.44
1M1PPi	4.42

Table 3. Oxidative voltage stabilities of the electrolytes containing 0.5 M Magnesium bis(trifluoromethylsulfonyl)imide (Mg(TFSI)₂) dissolved in ionic liquid (60 vol%) and di(propylene glycol) dimethyl ether (**DPDGME**) (60 vol%). Oxidative voltages were determined as the point when the measured current exceeded 0.1 mA/cm² from the background current.

Figure 6. Cyclic voltammograms of $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ in three electrolytes with 0.5 M $\text{Mg}(\text{TFSI})_2$. A) 40 vol% 1M1PPi and 60 vol% acetonitrile, B) 40 vol% 1M1PPi and 60 vol% **DPDGME**, and C) 40 vol% 1M1PPi, 60 vol% acetonitrile and 0.5 M **DPDGME**.

40% IL/60% Acetonitrile	E_{ox} vs. (Mg/Mg²⁺) / V	E_{red} vs. (Mg/Mg²⁺) / V	$\Delta(E_{ox}-E_{red})$ / V	Discharge Capacity / mAh g⁻¹	Charge Capacity / mAh g⁻¹
1M1PPi	3.90	2.52	1.38	135.9	166.4
1M1PPyrr	3.72	2.66	1.06	110.5	138.7
1M3PIIm	3.65	2.63	1.02		
40% IL/60% DPDGME	E_{ox} vs. (Mg/Mg²⁺) / V	E_{red} vs. (Mg/Mg²⁺) / V	$\Delta(E_{ox}-E_{red})$ / V	Discharge Capacity / mAh g⁻¹	Charge Capacity / mAh g⁻¹
1M1PPi	3.10; 3.64	2.90	0.20; 0.74	7.8	26.4
1M1PPyrr	3.08; 3.48	2.87	0.21; 0.61	7.2	30.7
1M3PIIm	3.06; 3.37	2.90	0.16; 0.47	4.6	15.3
40% IL/60% Acetonitrile 0.5 M DPDGME	E_{ox} vs. (Mg/Mg²⁺) / V	E_{red} vs. (Mg/Mg²⁺) / V	$\Delta(E_{ox}-E_{red})$ / V	Discharge Capacity / mAh g⁻¹	Charge Capacity / mAh g⁻¹
1M1PPi	3.50	2.63	0.87	50.1	73.7
1M1PPyrr	3.51	2.76	0.75		
1M3PIIm	3.55	2.80	0.75	56.8	83.5

Table 4. Oxidation and reduction potentials as well as corresponding peak currents observed with Mg_{0.07}V₂O₅ in each of the nine electrolytes. Discharge (magnesiumation) and charge (demagnesiumation) capacities of Mg_{0.07}V₂O₅ from constant current cycling are also displayed.

$\Delta(E_{ox}-E_{red})$ is the difference between oxidation and reduction potentials.

Figure 7. Constant current discharge and charge profiles of $\text{Mg}_{0.07}\text{V}_2\text{O}_5$ for electrolytes containing 0.5 M $\text{Mg}(\text{TFSI})_2$ dissolved in A) 40 vol% 1M1PPi and 60 vol% acetonitrile, B) 60 vol% 1M1PPi and 40 vol% **DPDGME**, and C) 40 vol% 1M1PPi, 60 vol% acetonitrile and 0.5 M **DPDGME**. Data shown in the figure represents the second constant current cycle after the first five CV cycles.

Figure 8. Cyclic voltammogram of Mg-MnO₂ in an electrolyte consisting of 0.5 M Mg(TFSI)₂ dissolved in 40 vol% IL/60 vol% acetonitrile. Each figure corresponds to the following ILs A) 1M1PPi, B) 1M1PPyrr and C) 1M3PIm.

40% IL/60% Acetonitrile	E_{ox} vs. (Mg/Mg²⁺) / V	E_{red} vs. (Mg/Mg²⁺) / V	$\Delta(E_{\text{ox}} - E_{\text{red}})$ / V	Discharge Capacity / mAh g⁻¹
1M1PPi	3.51	2.63	0.89	105.6
1M1PPyrr	3.69	2.63	1.06	149.5
1M3PIIm	3.56	2.71	0.85	136.1

Table 5. List of the oxidation and reduction potentials as well as corresponding peak currents observed with Mg-MnO₂ in electrolytes containing 0.5 M Mg(TFSI)₂ dissolved in 40 vol% IL and 60 vol% acetonitrile. $\Delta(E_{\text{ox}} - E_{\text{red}})$ is the difference between oxidation and reduction potentials. Discharge capacities represent the integrated area of the first reduction cycle during CV.