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Mg^{2+} ion-catalyzed polymerization of 1,3-dioxolane in battery electrolytes

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Electrolyte salts with Mg^{2+} and Al^{3+} Lewis acidic cations demonstrate polymerization of 1,3-dioxolane. The speed and extent of the reaction depends on coordination of the anion with the Mg^{2+} cation catalyst. Weakly coordinating anions such as $TFSI^-$ aid faster polymerization while strongly coordinating anions such as ClO_4^- hinder the polymerization.

Solid and gel polymer electrolytes have been studied for a variety of energy storage systems, particularly lithium-ion[1–4] and rechargeable magnesium batteries[5–7]. There are safety benefits in moving away from flammable liquid electrolytes, and there have been improvements to polymers' ion transport, stability, and mechanical properties which make them an attractive choice for electrolytes.[6] One solvent commonly used in Li batteries known to undergo polymerization reactions is 1,3-dioxolane (DOL). This solvent has been used widely as a component in electrolytes for lithium-sulfur batteries due to its unique ability to electropolymerize on the surface of Li metal anodes, investigated by Aurbach's group.[8] The DOL additive helped to create a protective SEI layer containing a DOL elastomer combined with commonly formed inorganic species such as Li_2O, Li_2CO_3, and $LiNO_3$ (which may differ depending on electrolyte additives) and has been utilized in a variety of ways to improve Li anode performance.[9] In addition to its application in creating a functional, protective SEI layer, recently polymerized DOL (poly-DOL) has been demonstrated as an effective solid polymer electrolyte in Li batteries.[10–12] DOL has not been used or investigated extensively in Mg batteries as an electrolyte solvent, which may be due to reports indicating instability at the Mg anode and a decreased coulombic efficiency in electrolytes containing DOL.[13] However, some Mg-S battery studies have utilized DOL as a part of their electrolytes,[14–16] and understanding the Mg anode interface properties are critical to battery design.[17] The lack of insight into DOL compatibility with Mg anodes is important to investigate.

Therefore, the findings in this work will have two-fold importance. First, it is urgent to inform the Mg battery community of certain Mg^{2+} salts ability to catalytically polymerize DOL in electrolytes, which has not previously been reported. In a broader impact to the science community, while Mg^{2+} ion catalytic activity is known in some biological systems and small organic molecule synthesis,[18] researchers have not realized its applications in polymerization reactions. Second, it is essential to investigate the electrochemical properties of DOL polymers that may form on electrode surfaces in electrolyte systems containing Mg^{2+} and DOL. Additionally, while poly-DOL was determined to be an effective polymer electrolyte for Li systems,[10–12] it has not been studied as an Mg electrolyte; if it can be utilized as a solid or gel polymer electrolyte, it could bypass possible incompatibilities of liquid DOL electrolytes.

In this study, the polymerization behavior of DOL with multivalent Mg and Al salts was investigated. While the ability of certain Lewis acids have been investigated in cationic ring-opening polymerization,[19] neither Mg triflate (OTf) nor Mg bis(trifluoromethanesulfonyl)imide (TFSI) have been demonstrated for use in the polymerization of DOL, or other polymerization reactions, to our knowledge. In this communication, we studied Mg^{2+} and Al^{3+} Lewis acid catalyzed polymerization of DOL and investigated the effect of strength of Lewis acidity, Mg^{2+} counter anions, and cosolvents on such polymerization. We briefly explored the potential application of the DOL polymer as a solid electrolyte.

To evaluate the role of the cation of the metal salt in the catalysis of DOL polymerization, different metal (Mg, Li, and Al) triflate salts were tested. The stronger Lewis acid cations (Mg^{2+} and Al^{3+}) were anticipated to induce the polymerization reaction, which is supported by the use of $Al(OTf)_3$ as a catalyst

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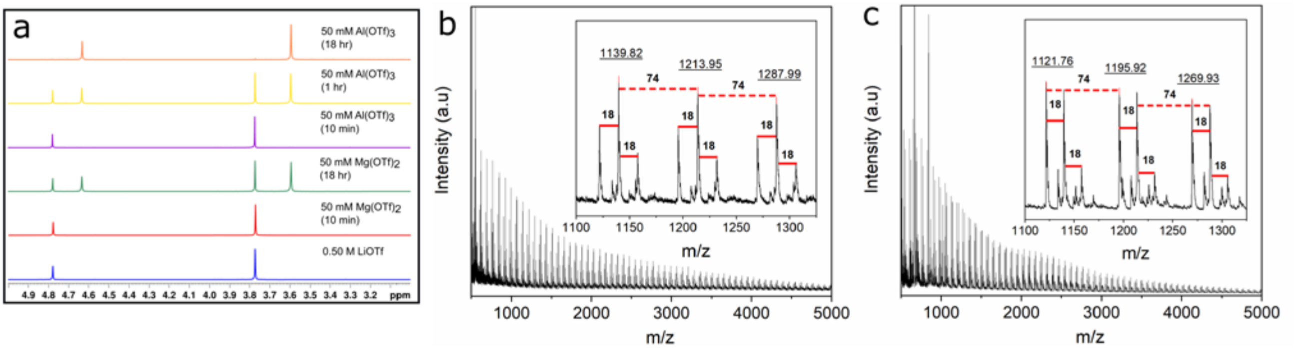

Fig. 1 H-NMR spectra of a) DOL samples with Al, Mg, and Li triflate salts after various reaction times, and MALDI-MS spectra of 50 mM b) $Mg(OTf)_2$ in DOL and c) $Al(OTf)_3$ in DOL after 18 hours.

for a variety of reactions in the literature.[20,21] However, the less Lewis acidic Li^+ cation was not expected to cause the same reaction. After adding the salts to DOL, H-NMR was conducted after the salt was fully dissolved, after about 10 minutes of mixing. The solutions were then left overnight, and H-NMR samples were run the following day after 18 hours. Matrix-assisted laser desorption/ionization – mass spectroscopy (MALDI-MS) was run on the polymerized samples after the same 18-hour reaction period. The results of H-NMR and MALDI experiments are depicted in Fig. 1. The H-NMR in Fig. 1a indicates that in the case of the LiOTf solution, no peaks indicative of DOL polymerization can be seen in the spectra – only the peaks at 3.77 and 4.78 ppm for the DOL monomer (O-CH_2-O and O-CH_2CH_2-O) are present. The same observation is true of the 50 mM Mg and Al triflate salt solutions after short time periods (10 minutes). However, after waiting for 1 hour, $Al(OTf)_3$ shows new peaks for poly-DOL at 3.59 and 4.63 ppm, whereas Mg triflate shows a similar level of polymerization after 18 hours. FTIR spectra of polymerized DOL using $Al(OTf)_2$ and $Mg(TFSI)_2$ catalysts and a sample also containing $Mg(ClO_4)_2$ are in Fig. S1 (see ESI). The percent polymer detected by H-NMR, using Equation 1 where H_p is the integral of polymer protons and H_m is the integral of monomer protons,[10] for $Mg(OTf)_2$ is 61.7% after 18 hours while $Al(OTf)_3$ is 63.6% after 1 hour. The $Al(OTf)_3$ sample has achieved 99.0% polymer composition at 18 hours and minimal monomer is present. The H-NMR spectra show only peaks from the DOL monomer, poly-DOL, and water (3.33 ppm). The DMSO solvent peak appears at 2.50 ppm but is omitted for simplicity. These observations indicate that we do not see end groups for the polymer, meaning the hydroxyl terminations may be in too low concentration to detect or some of the products may be cyclic oligomers.[22]

$$\frac{H_p}{H_p+H_m}\times 100 = \%\ \text{polymer} \qquad (1)$$

To confirm the products of the DOL polymerization, MALDI-MS was performed on all samples. Fig. 1 shows the MALDI-TOF MS result of polymerized 50 mM $Mg(OTf)_2$ and $Al(OTf)_3$ dissolved in DOL solvent. It shows a series of molecular ion peaks with molecular weights up to the scanning limit, 5000 Da. The high MW fragments indicate the formation of polymer macromolecules. Further investigating the MALDI mass spectrum, the inset of Fig. 1b shows the regional spectrum of $Mg(OTf)_2$ in DOL. For each group of peaks that represents a similar pattern, there is a main peak with the highest intensity and two satellite peaks on each side of the main peak. The molecular weight difference between the two main peaks adjacent to each other is ~74 Da, which is equivalent to the molecular weight of one DOL molecule. This pattern is representative of the entire mass spectrum which proves the molecular ion peaks are of poly-DOL molecules, formed due to Mg^{2+} catalytic polymerization of DOL monomers. Moreover, each satellite peak has a molecular weight difference of ~18 Da relative to its main peak, indicating there are likely polymers with one and two water adducts. In the cluster of three peaks, the first peak contains no water, the second (and highest) has one water, while the final peak has two water molecules.

The 50 mM $Al(OTf)_3$ in DOL was tested using MALDI-TOF MS and the result is shown in Fig. 1b. In this mass spectrum, there are significant molecular ion peaks even in the high MW region. Those peaks also show the same pattern of 74 difference in MW between the main peaks of two adjacent groups. This confirms that poly-DOL molecules were formed in $Al(OTf)_3$ in DOL solution. However, the peak distribution in mass spectrum of $Al(OTf)_3$ has changed from the one of $Mg(OTf)_2$. In the mass spectrum of $Al(OTf)_3$, there are two main peaks instead of just one with nearly identical intensity that have a 74 Da difference in MW. This indicates with stronger Lewis acid $Al(OTf)_3$ as polymerization catalyst, the reaction that generates polymer chains assumed without water is more favored. Further, a 0.35 M LiTFSI in DOL sample was tested using MALDI-TOF MS and the results can be found in Fig. S2 in the ESI. The mass spectrum of LiTFSI solution is unlike the $Mg(OTf)_2$ and $Al(OTf)_3$ samples in DOL; it does not have peaks of high molecular weight and does not show the pattern of 74 Da in MW between adjacent groups of peaks. This demonstrates that under same conditions, Li^+ cannot catalyze the polymerization of DOL, which can be attributed to its lower Lewis acidity compared to Mg^{2+} and Al^{3+}.

While there is a dependence of the DOL reaction on the cation of the metal salt, the anions of Mg^{2+} salts were also altered to determine if it influenced the polymerization. In addition to $Mg(OTf)_2$, $Mg(TFSI)_2$ and Mg perchlorate ($Mg(ClO_4)_2$) salts were tested in DOL. The 0.25 M $Mg(ClO_4)_2$/DOL solution did not visibly increase in viscosity or show peaks of a polymerized product in the H-NMR results (Fig. 2a). The $Mg(ClO_4)_2$ solutions were tested at higher concentrations and left to react for longer times, and even after 5 days no new peaks are present in the H-NMR. Interestingly, the $Mg(TFSI)_2$ salt catalyzes a much faster polymerization than the triflate, as the polymer peaks at 3.59 and 4.63 ppm are visible after only 10 minutes with a 50 mM concentration of the salt. In comparison, the $Mg(OTf)_3$ sample contains 61.7% polymer after 18 hours while $Mg(TFSI)_2$ is 49.1% polymer in the same time.

Like the mass spectrum of $Mg(OTf)_2$ in DOL, the solution with 50 mM $Mg(TFSI)_2$ also shows distinct molecular ion peaks of high molecular weights and the 74 Da difference in MW between adjacent main peaks. It indicates that $Mg(TFSI)_2$ can also catalyze the polymerization of DOL. Both $TFSI^-$ anion and triflate anion have $-SO_2CF_3$ group in their structures, which help delocalize the negative charge throughout the anion.[23] The TFSI anion has two $-SO_2CF_3$ groups, making the charge even more delocalized, enhancing its ability to be a weakly coordinating anion and increasing the Mg^{2+} cation's positive character and Lewis acidity. For the 0.25 M $Mg(ClO_4)_2$ in DOL sample (Fig. S3), while there was not significant polymer formation observed in H-NMR, some peaks also show the characteristic 74 difference in MW pattern in the MALDI mass spectrum, though the overall intensity of the peaks are smaller than those in $Mg(TFSI)_2$ and $Mg(OTf)_2$ solutions. Most importantly, there are minimal peaks at high MW region of mass spectrum. Mg and Al triflate and $Mg(TFSI)_2$ can catalyze DOL polymerization, and while $Mg(ClO_4)_2$ may catalyze the reaction we believe it is much slower due to the stronger interactions of the ClO_4^- anion with Mg^{2+}.

For electrochemical applications such as batteries, mixtures of solvents are often used to take advantage of an important property of each. For example, in lithium-sulfur batteries, DOL has been used as part of electrolytes that also contain ethers such as 1,2-dimethoxyethane (DME) and the larger ethers such as diglyme and tetraglyme. These dual solvent electrolytes are important due to the unique property of DOL to electropolymerize and help create a soft organic layer in the SEI in addition to the inorganic SEI components.[8,9] Due to the additional positive charge on Mg^{2+} as compared to Li^+, its solvation and solution behavior is very different.[24] There are not many reported instances of DOL being used in Mg battery electrolytes, and one of the few instances was electrolyte with $Mg(TFSI)_2$ and $MgCl_2$ in TEGDME/DOL (1:1 v:v).[14] This electrolyte with other solvents is known to create a metal complex with Mg,[25] meaning the Mg^{2+} ion itself is not free in the electrolyte. We propose that these complexes do not catalyze DOL polymerization, hence why other groups have not observed significant polymerization of their electrolytes. To further support the hypothesis that free Mg^{2+} ions are necessary to catalyze polymerization of DOL, this solvation behavior of Mg^{2+} was utilized. It was previously observed that Mg^{2+} ions from $Mg(TFSI)_2$ in DME electrolyte became so strongly complexed by 3 DME molecules that the complex could be crystallized and studied using XRD.[26] We propose that if the Mg^{2+} is first complexed by DME, it will not be able to polymerize DOL.

To test this hypothesis, a 1:1 v/v solution of DME/DOL was mixed to create a 0.35 M $Mg(TFSI)_2$ in DME/DOL electrolyte solution. Interestingly, this electrolyte does not polymerize in the same manner as when DME is absent. When the amount of DME is decreased to a 1:7 DME/DOL solution with 0.35 M $Mg(TFSI)_2$, a phase separation is still observed, and gelation of the top layer occurs (Fig. S4). The initial mole ratio of DOL:DME in this case is 10:1, and different ratios of the solvents were found in the new phase separated upper and lower layer when investigated using H-NMR. The lower layer contained 4 times more DOL than DME, while the upper layer contained 25 times more DOL than DME. Further, the poly-DOL peaks are only in the top layer of the solution after 24 hours. The complexation of DME with Mg may prevent Mg from acting as the catalyst for the cationic ring-opening polymerization reaction, especially if it is concentrated in the lower layer of the solution, which supports the proposed mechanism in Scheme S1 (see ESI).

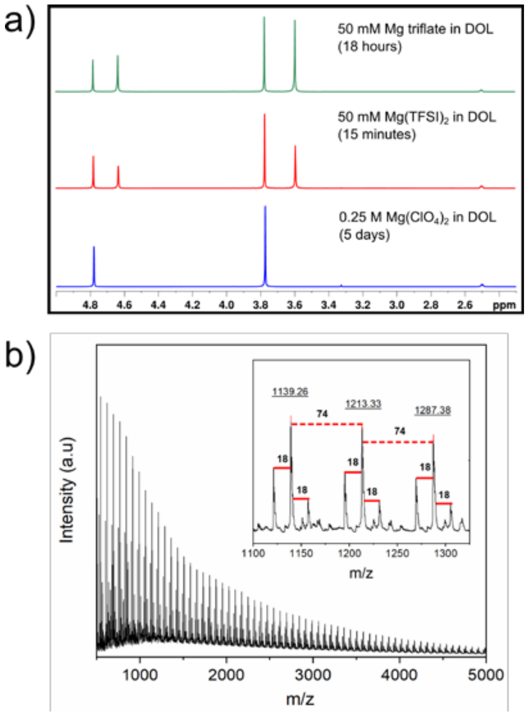

Fig. 2 H-NMR spectra of a) DOL samples Mg triflate, TFSI, and perchlorate salts after varied reaction times, b) MALDI-MS spectra of 50 mM $Mg(TFSI)_2$ in DOL.

One application for this poly-DOL synthesized using Mg salts is in polymer electrolytes, more specifically a solid electrolyte formed via in-situ polymerization.[3] This type of polymer electrolyte could help decrease interfacial contact resistance from rough or incompatible free-standing polymer gels with electrode interfaces. To test the ionic conductivity of the Mg-DOL electrolyte, an electrolyte solution with 0.125 M $Mg(TFSI)_2$ and 0.25 M $Mg(ClO_4)_2$ in DOL was mixed and drop casted onto stainless steel blocking electrodes, which were sandwiched together without a separator. This concentration of $Mg(TFSI)_2$ catalyst is high to help the polymer firm up to close in the coin cell. The electrochemical impedance spectra can be seen in Fig. 3. The ionic conductivity was 2.6×10^{-9} S/cm at a low room temperature (20 °C), and fit values for the equivalent circuit are in Table S1 in the ESI. Potential hold tests in the inset demonstrate low electronic conductivity of about 9.2×10^{-11} S/cm. It is important to note that the EIS was recorded on a completely polymerized sample with a high concentration of catalyst, which previous studies demonstrated can decrease the ionic conductivity.[10] Decreasing the $Mg(TFSI)_2$ and optimizing the composition could increase ionic conductivity. This

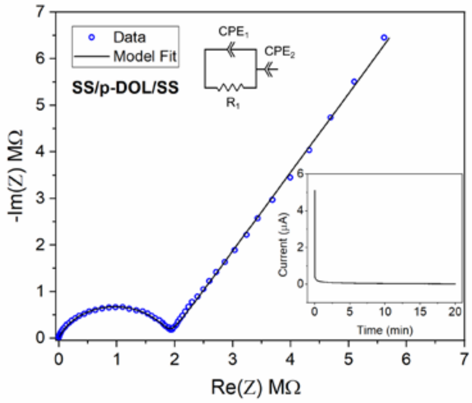

Fig. 3 Nyquist Impedance plot for Mg-DOL (0.125M Mg(TFSI)$_2$ + 0.25 M Mg(ClO$_4$)$_2$ in DOL) polymer sandwiched between two stainless steel disks. The inset displays the current vs. time plot for the same cell when a 2 V bias was applied for 20 minutes.

composition is a proof of concept for testing poly-DOL as an electrolyte and more characterization and study are underway to investigate the polymer's properties and ionic conductivity. Results for temperature-dependent conductivity studies and an Arrhenius plot used to calculate the activation energy of the polymer are included in Fig. S6 in the ESI.

In conclusion, strong Lewis acid cations such as Al^{3+} and Mg^{2+} can catalyze DOL polymerization and their Lewis acidity, and ability to catalyze the reaction, is influenced by the associated anion. It was determined that the order of reactivity for Mg salts based on the anion was $TFSI^-$ > OTf^- > ClO_4, and we propose this difference is based on the affinity of this anion to coordinate with Mg^{2+} and affect its Lewis acidity. We determined other factors that may hinder its reactivity, such as ion solvation with secondary solvents. These discoveries could help expand the applications of Lewis acid catalysts in polymerization reactions and give insight into the importance of the properties of metal salts. These insights may also be critical in deciding whether to utilize DOL as a solvent for Mg battery systems and what electrolyte compositions may be ideal. Further, poly-DOL demonstrated ionic conductivity which if improved could indicate its use as a polymer electrolyte in Mg battery systems.

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Conflicts of interest

There are no conflicts to declare.

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