Supplementary information

Ion coordination and transport in magnesium polymer electrolytes: polyester–polycarbonate copolymer compared to poly(ethylene oxide)

Authors

Bumjun Park,[a] Rassmus Andersson,[b] Sarah G. Pate,[a] Jiacheng Liu,[a] Casey P. O'Brien,[a] Guiomar Hernández,[b] Jonas Mindemark,[b] Jennifer L. Schaefer [a*]

[a] Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA
[b] Department of Chemistry – Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

*Email: Jennifer.L.Schaefer.43@nd.edu

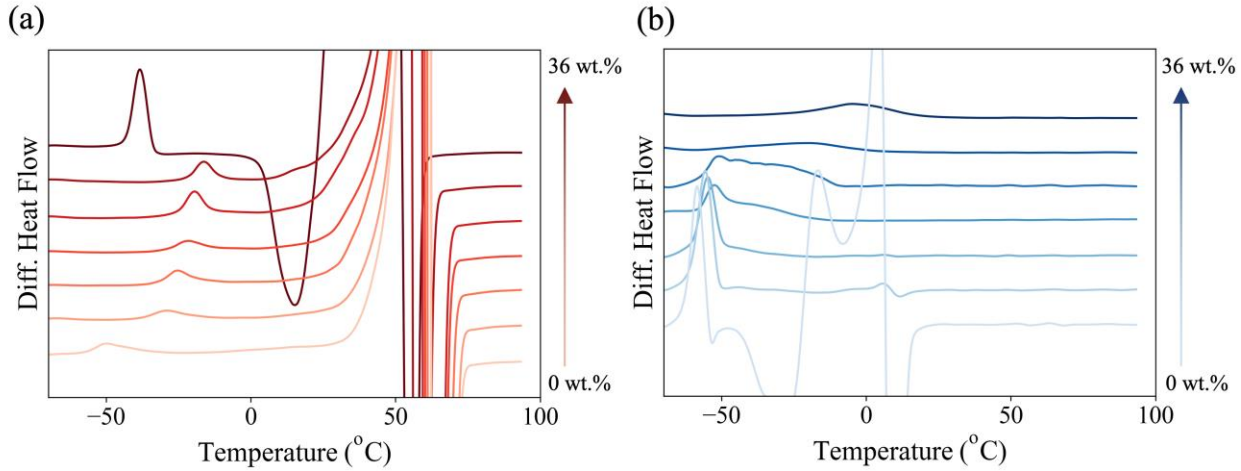

Figure S1. Differentiated heat flow curves of (a) PEO and (b) PCL-PTMC electrolytes.

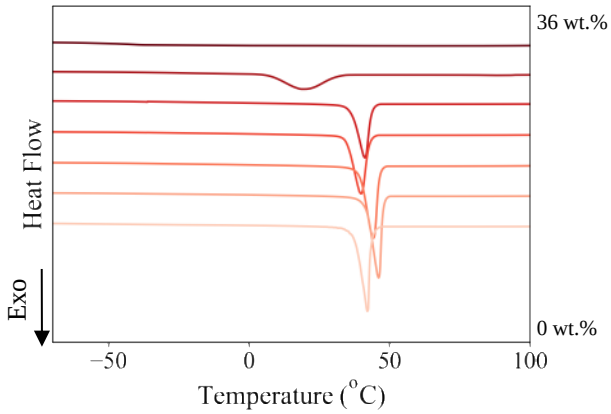

Figure S2. DSC cooling scans of 0–36 wt.% $Mg(TFSI)_2$ in PEO.

Table S1. Crystallinity and weight fraction of amorphous phase of $Mg(TFSI)_2$ in PEO.

Salt concentration (wt.%)	Fractional crystallinity (x_{cr})*			Weight fraction of amorphous phase PEO around T_g	Molar ratio of amorphous EO:Mg^{2+} **
$Mg(TFSI)_2$	Crystallization peak (cooling)	Cold crystallization peak (heating)	Melting peak (heating)		
0	0.91	-	0.92	0.09	-
8	0.97	-	0.98	0.03	5.2
12	0.88	-	0.89	0.12	11.6
16	0.84	-	0.85	0.16	11.3
20	0.94	-	0.96	0.06	3.4
28	0.55	-	0.51	0.45	15.3
36	-	0.30	0.31	1.00	23.6

* - The fractional crystallinity (x_{cr}) was calculated based on the equation ($x_{cr} = \Delta H_m/(w_{PEO}\,\Delta H_m^o)$) [1]. Here ΔH_m is the enthalpy of melting of the sample from DSC, ΔH_m^o is the ideal enthalpy of melting of a fully crystalline PEO, w_{PEO} is the weight fraction of PEO in the sample. The value of ΔH_m^o is assumed to be 206 J g^{-1} [2].
** - The molar ratio of amorphous EO:Mg^{2+} was calculated based on the weight fraction of amorphous phase PEO around T_g and EO:Mg^{2+} from **Table 2**.

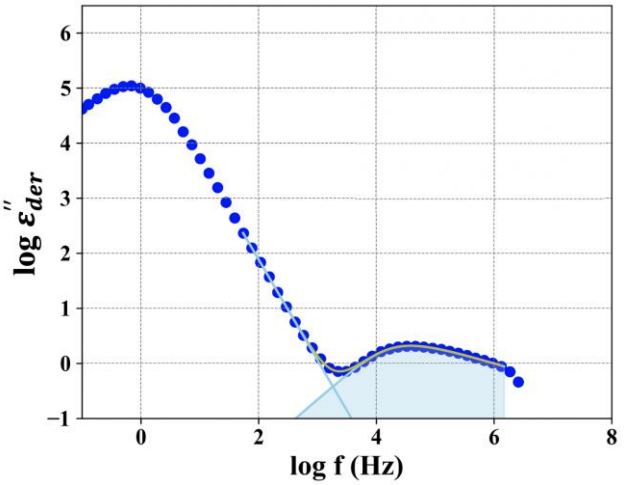

Figure S3. An example of the dielectric fitting.

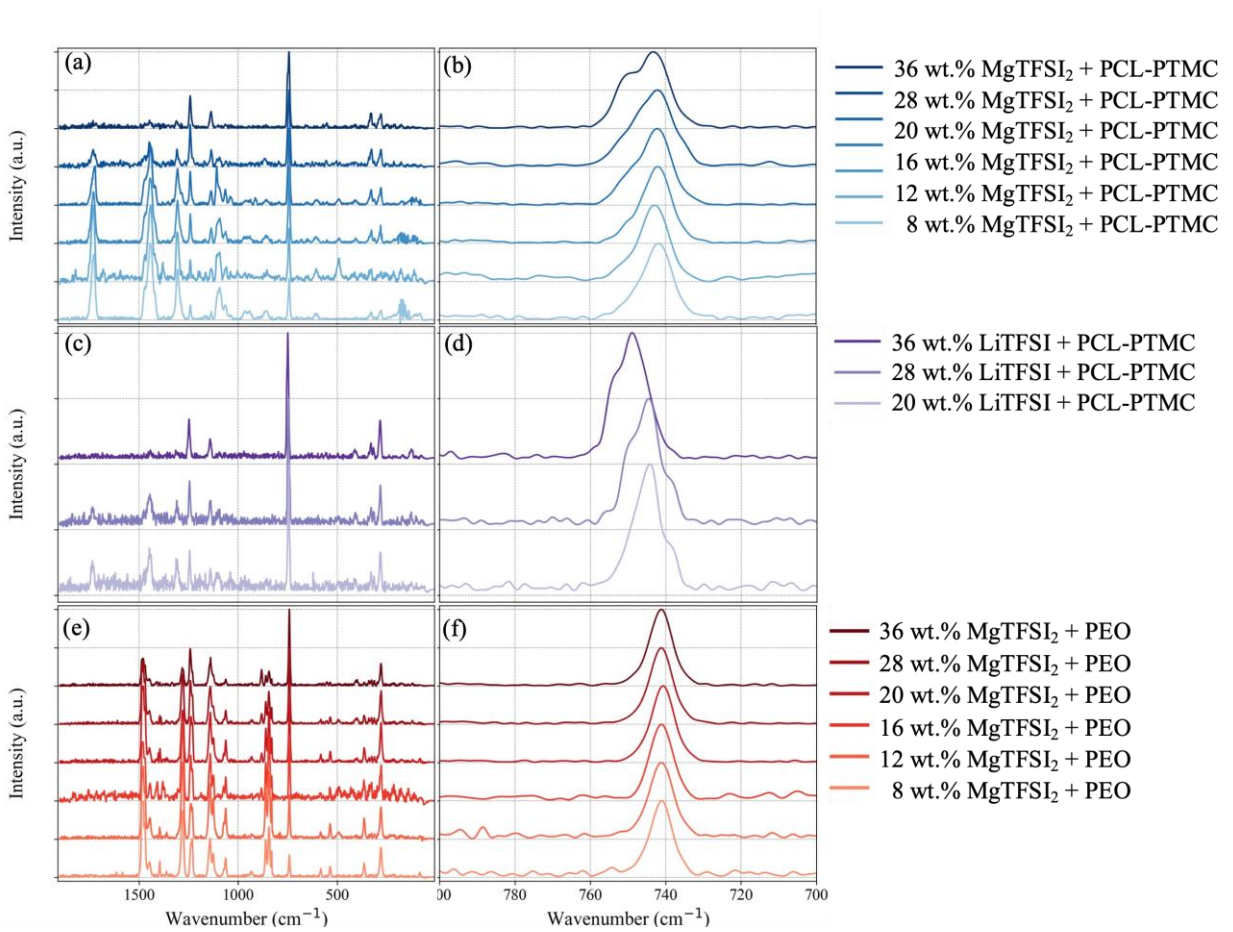

Figure S4. Raman spectra of $Mg(TFSI)_2$ in PCL-PTMC (a, b), LiTFSI in PCL-PTMC (c, d), and $Mg(TFSI)_2$ in PEO (e, f)

Table S2. Calculation of estimated shift of the C=O coordinated with Mg^{2+} using charge densities and the C=O shifts from Li^+ and Na^+.

	Effective ionic radius (nm)	volume (nm^3)	charge	charge density (nm^{-3})	Pure C=O shift*	Coordinated C=O shift	ΔC=O shift (cm^{-1})	charge density/ ΔC=O shift
Li^+	0.076 [3]	0.00184	1	544	1730	1700 [4]	30	18.13
Na^+	0.102 [3]	0.00445	1	225	1730	1720 [5]	10	22.50
Mg^{2+}	0.072 [3]	0.00156	2	1279	1730	1659**	71**	18.13***

* - The pure C=O shift is an average of C=O from both PCL (1726 cm^{-1}) and PTMC (1735 cm^{-1}) for convenience since the difference of C=O from two polymers is negligible related to the difference from coordination with metal cations

** - calculated using the charge density/ΔC=O shift of Li^+ and the charge density of Mg^{2+}

*** - used the same value as Li^+

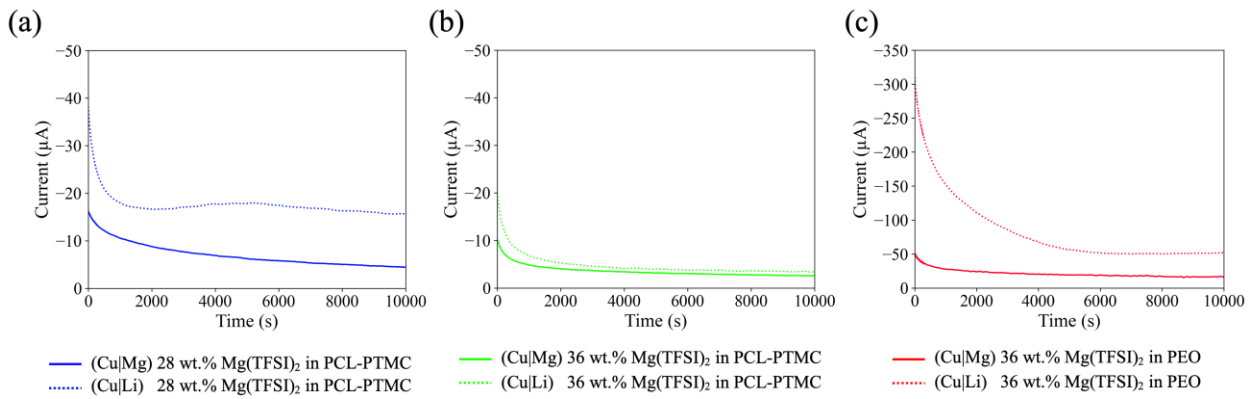

Figure S5. i vs t curves of Cu|Mg (solid lines) and Cu|Li (dotted lines) with (a) 28 wt.% $Mg(TFSI)_2$ in PCL-PTMC, (b) 36 wt.% $Mg(TFSI)_2$ in PCL-PTMC, and (c) 36 wt.% $Mg(TFSI)_2$ in PEO.

The *i* vs *t* curves of Cu|Mg and Cu|Li cells are compared in **Figure S5**. In all three electrolytes, the currents were lower with Cu|Mg cells than Cu|Li cells. Given that the potential applied on the Cu|Li cells (−0.1 V vs Li) and Cu|Mg cells (−0.8 V vs Mg) were identical versus the standard hydrogen electrode (−3.1 V vs SHE), the charging current in the beginning of the polarization is expected to be close to each other in both cells. Moreover, the overpotential to strip metal species was higher with Mg (−0.8 V) than Li (−0.1 V). However, the initial current was lower on Cu|Mg cells than Cu|Li cells, which implies the possible difficulty of Mg stripping.

Table S3. The initial current, steady state current, and the ratio from the polarization tests on Cu|Mg cells.

Electrolyte	i_o (μA)	i_{ss} (μA)	i_{ss}/i_o
28 wt.% $Mg(TFSI)_2$ in PCL-PTMC	-16.32	-0.95	0.058
36 wt.% $Mg(TFSI)_2$ in PCL-PTMC	-10.31	-0.97	0.094
36 wt.% $Mg(TFSI)_2$ in PEO	-50.36	-6.68	0.133

Table S4. Estimated bulk resistance values calculated from the ionic conductivity using the cell dimensions.

	σ_{tot} (S cm^{-1})	R from σ_{tot} (Ω)
28 wt.% $Mg(TFSI)_2$ in PCL-PTMC	4.56×10^{-6}	2792
36 wt.% $Mg(TFSI)_2$ in PCL-PTMC	1.26×10^{-6}	10105
36 wt.% $Mg(TFSI)_2$ in PEO	4.70×10^{-4}	27

The diameter and the thickness of the polymer electrolytes to estimate the R values were 1 cm and 100 µm, respectively.

Table S5. R_2 values extracted from the EIS spectra by fitting with an equivalent circuit.

	R_2 (Cu|Li before, Ω)	R_2 (Cu|Li after, Ω)	R_2 (Cu|Mg before, Ω)	R_2 (Cu|Mg after, Ω)
28 wt.% $Mg(TFSI)_2$ in PCL-PTMC	2.53×10^4	7.19×10^4	1.61×10^5	3.68×10^6
36 wt.% $Mg(TFSI)_2$ in PCL-PTMC	6.83×10^4	4.49×10^5	1.68×10^5	4.73×10^6
36 wt.% $Mg(TFSI)_2$ in PEO	2.57×10^3	8.82×10^3	-	-

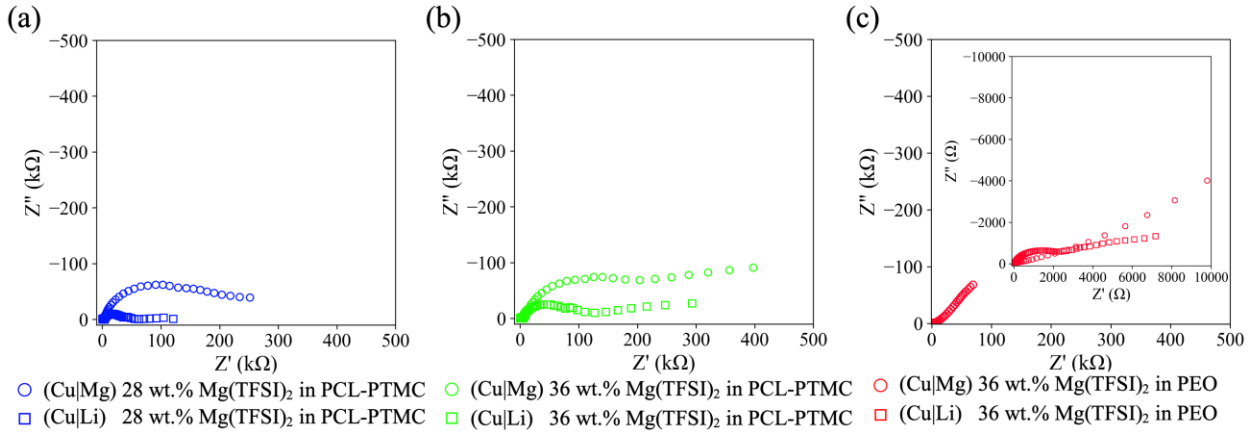

Figure S6. Impedance spectra before the polarization tests on Cu|Mg (circles) and Cu|Li (squares) cells with (a) 28 wt.% $Mg(TFSI)_2$ in PCL-PTMC, (b) 36 wt.% $Mg(TFSI)_2$ in PCL-PTMC, and (c) 36 wt.% $Mg(TFSI)_2$ in PEO.

Table S6. Atomic ratio (%) of Mg, C, O, F from SEM-EDS on Cu electrodes from Cu|Mg cells after polarization. Atomic ratios of F/Mg were calculated to compare the amount of TFSI on the Cu electrode surface to the polymer electrolytes.

	(After polarization in Cu|Mg cells) 28 wt.% $Mg(TFSI)_2$ in PCL-PTMC	28 wt.% $Mg(TFSI)_2$ in PCL-PTMC	(After polarization in Cu|Mg cells) 36 wt.% $Mg(TFSI)_2$ in PCL-PTMC	36 wt.% $Mg(TFSI)_2$ in PCL-PTMC
Mg	2.86	0.77	9.33	1.03
C	35.16	60.81	33.74	57.27
O	53.47	29.18	28.15	29.40
F	8.51	9.24	28.78	12.30
F/Mg	2.98	12.00	3.09	12.00

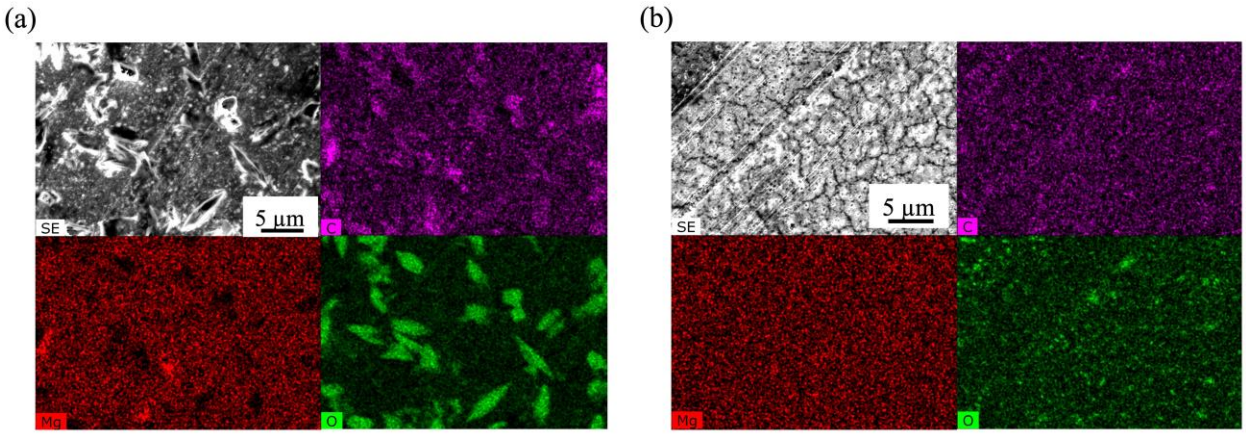

Figure S7. SEM-EDS elemental mapping from a Cu electrode from a Cu|Li cell with (a) 28 wt.% and (b) 36 wt.% $Mg(TFSI)_2$ in PCL-PTMC after polarization test.

The recovered Cu electrode from polarization testing with 28 wt.% $Mg(TFSI)_2$ in PCL-PTMC (**Figure S7a**) in Cu|Li cells showed O-rich particles without Mg, indicating Li deposition. Much less but similar spots with high O ratio without Mg were observed on Cu for 36 wt.% $Mg(TFSI)_2$ in PCL-PTMC (**Figure S7b**). The atomic ratio of each element was shown in **Table S7**.

Table S7. Atomic ratio (%) of Mg, C, O from SEM-EDS on Cu electrodes from Cu|Li cells after polarization. Atomic ratios of Mg ratio to C were calculated by $\frac{Mg}{Mg+C} \times 100$ (%) to compare the amount of Mg on the deposit to the polymer electrolytes.

	(After polarization in Cu|Li cells) 28 wt.% $Mg(TFSI)_2$ in PCL-PTMC	28 wt.% $Mg(TFSI)_2$ in PCL-PTMC	(After polarization in Cu|Li cells) 36 wt.% $Mg(TFSI)_2$ in PCL-PTMC	36 wt.% $Mg(TFSI)_2$ in PCL-PTMC
Mg	3.71	0.85	7.81	1.17
C	44.04	67.00	40.87	65.30
O	52.25	32.15	51.32	33.53
$\frac{Mg}{Mg+C} \times 100$	7.77	1.25	16.05	1.76

Mg contents were larger on Cu surface after polarization, indicating Mg deposition on the surface from the polymer electrolytes. High O may indicate that the Li deposit was oxidized when the sample was transferred into the SEM instrument.

References

[1] J.L. Thelen, X.C. Chen, S. Inceoglu, N.P. Balsara, Influence of Miscibility on Poly(ethylene oxide) Crystallization from Disordered Melts of Block Copolymers with Lithium and Magnesium Counterions, Macromolecules. 50 (2017) 4827–4839. https://doi.org/10.1021/acs.macromol.7b00735.

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