Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Lithium, sodium and magnesium ion conduction in solid state mixed polymer electrolytes

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S1. Sample Preparation Scheme

Precursor Details :
Li/Na/Mg-ClO_4 (CAS Number 7791-03-9/7601-89-0/10034-81-8 respectively, Sigma- Aldrich)
ethanol (CAS Number 64-17-5, Sigma-Aldrich),
PEO(average Mw 400,000, CAS Number 25322-68-3, Sigma-Aldrich)
PDMS (viscosity 15- 40 mPa.s, CAS Number 63148-57-2)

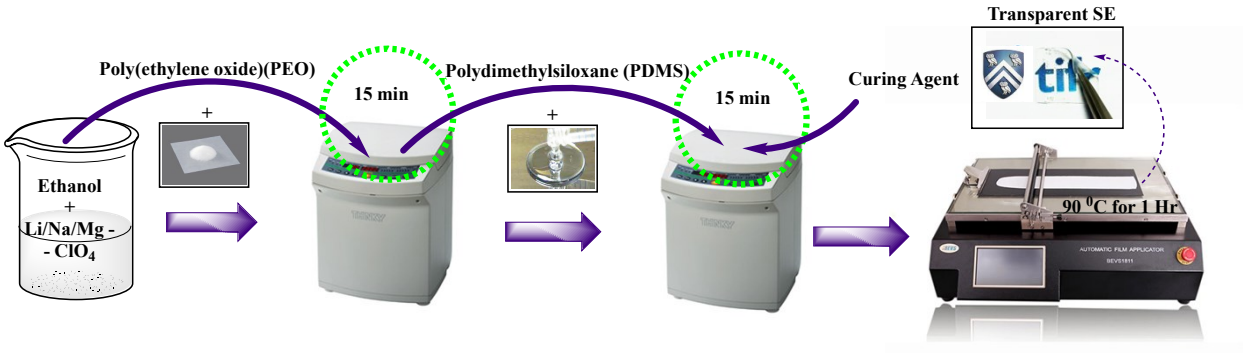
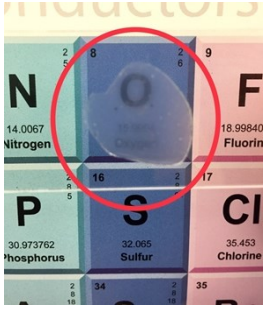


Figure 1. Making of the transparent and flexible multi cation channel (MCC). A transparent flexible MCC is shown in the last segment where the "Rice/ tifr" logos are seen underneath the MCC which is held using a tweezer.

Table 1 Composition of precursors in each sample

Sample	(mg)	Ethanol (µL)	PEO (mg)	PDMS (mL)	Curing Agent (µL)
PEO - PDMS	-	400	100	1	400
Li-TFM	$LiClO_4$ -100	400	100	1	400
Na-TFM	$NaClO_4$ -100	400	100	1	400
Mg-TFM	$MgClO_4$ -100	400	100	1	400

Membrane



Density

Diameter : 16 mm
Weight : 78.47 mg
Density : Mass/ Volume

$$\frac{0.078}{(Pi * (0.8)\text{^}2 * 0.027)} =$$

	1.44 g/cm^3

S2: Raman & FTIR Spectra

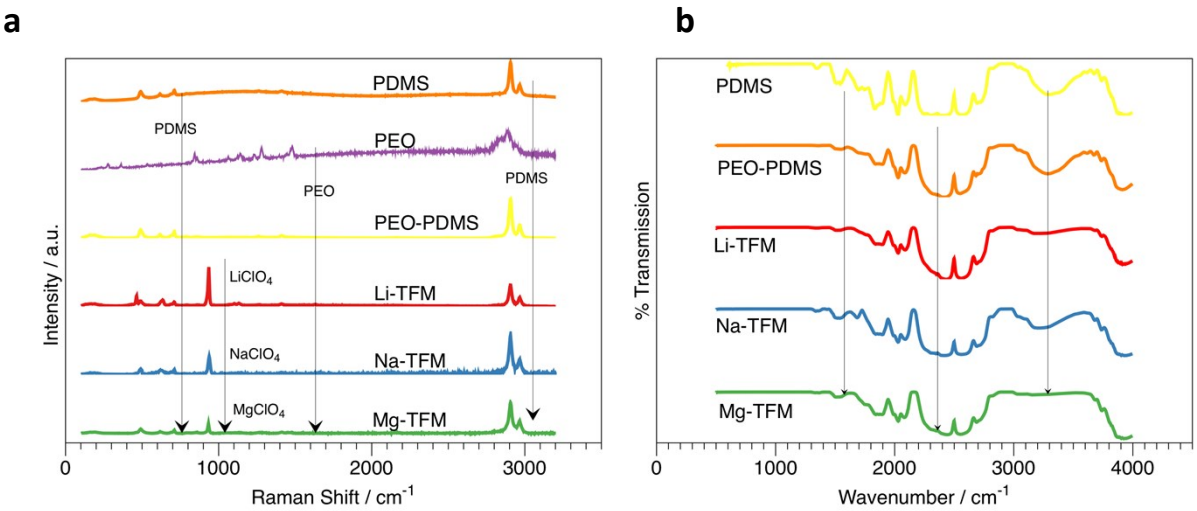


Figure 2. (a) Raman Spectra (b) FTIR Spectra

Table 2 FTIR and Raman band positions of the samples [1]

IR (ϑ/cm^{-1})	Assignment	Raman (ϑ/cm^{-1})	Assignment
3400-3600 cm^{-1}	ϑ_p(Si-OH)	2964s	ϑ_p (C-H)
3400 – 3200 cm^{-1}	ϑ_{PEO}(O-H)	2904vs	ϑ_p(C-H)
2950 cm^{-1}	ϑ_p (C-H)	709s	ϑ_p(C-Si-C)
1600 cm^{-1}	$\delta\vartheta_{PEO}$(O-H)	490s	ϑ_p (Si-O-Si)
1500 – 1300	δ_p (C-H)	1106sr, 850sr and 932sr	γ_{PEO}($C\text{-}H_2$ rock, ϑ_{LiPEO} (C-O) ϑ_{PEO}(C-C)
800, 1250 cm^{-1}	ϑ_p (Si-CH_3)	457	Disordered longitudinal acoustic mode (D-LAM)

ϑ_p :PDMS bands ϑ_{PEO} : PEO Bands ϑ :Strecting δ:Bending γ :Rocking s:Strong vs :very strong

S3 SEM Analysis

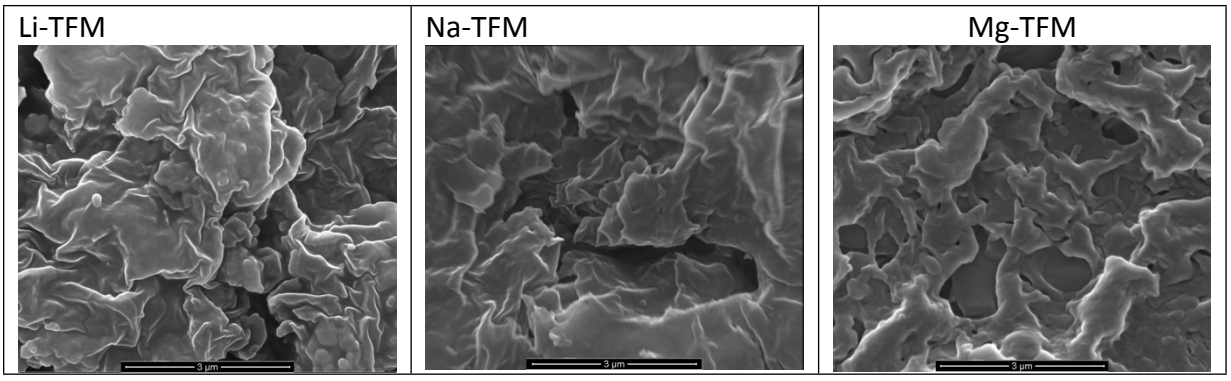


Figure 3. SEM images of Li, Na and Mg impregnated polymer matrices

S4 Contact Angle Experiment Results

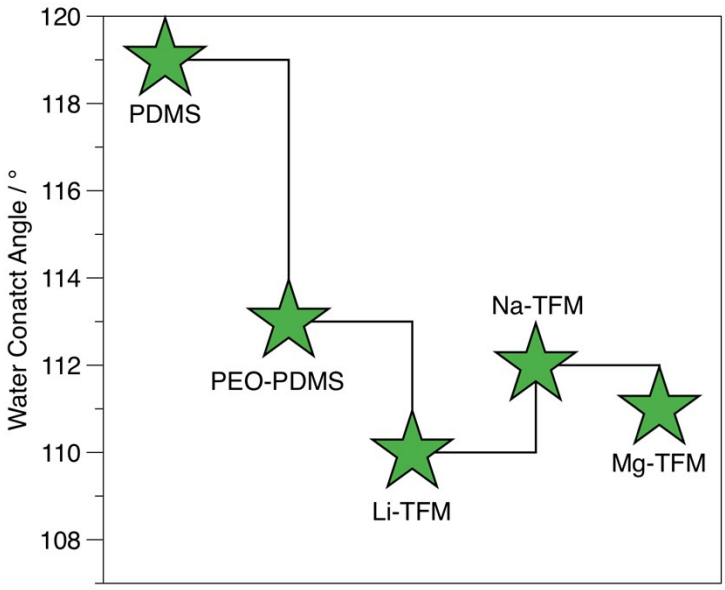


Figure 4. The variation of water contact angle from Pristine PDMS to Mg-dissolved membrane. Though the water contact angle is reduced to an extent, the samples surfaces are still hydrophobic which in turn empower the membrane to be in humidity free condition during the operation even in open cell configurations.

S5 Thermal Analysis

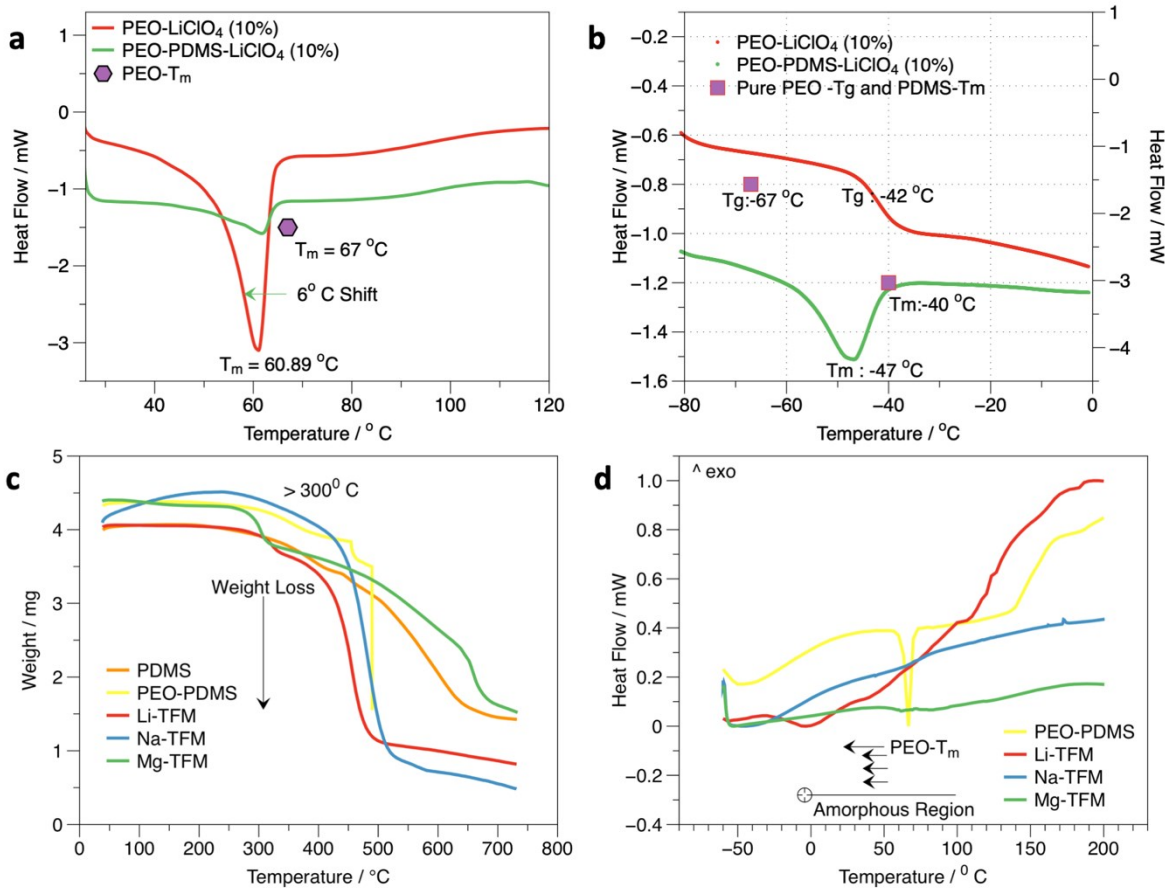


Figure 5. (a) & (b) demonstrating the shift in crystalline melting (T_m) point and glass transition temperatures (T_g) on addition of Li salts (10%, low concentration) in to the polymer matrix. (c) TGA curves of the samples show that all the samples are thermally stable up to 300 ^{0}C. Li-PE shows the lowest degradation temperature, then Na-PE and finally Mg-PE. (d) The DSC curves of the various samples validate the shift in crystalline melting temperature on addition of salts and PDMS with PEO. PEO-PDMS structure possess similar T_m as of PEO while the salted PEO-PDMS structure shows T_m near to 0^{o}C . This shift in T_m is helpful in improving the cation conductivity by reducing the chance of crystallisation at room temperature.(1)

S6 Computational

The optimized configurations converged to a selected few configurations. The most energetically favorable configurations were two charged PDMS-Lithium configurations referred to as $(HO[Si(CH_3)_2O]_nH)Li^+$ in **Figure 1a-b**, two neutral PDMS-Lithium configurations referred to as $(HO[Si(CH_3)_2O]_nH)Li$ in **Figure 1c-d**, one charged PEO-Lithium configuration referred to as $[HO(CH_2CH_2O)_2H]Li^+$ in **Figure 1e**, two neutral PEO-Lithium configurations referred to as $[HO(CH_2CH_2O)_2H]Li$ in **Figure 1f-g**, one charged PDMS-Sodium configuration referred to as $(HO[Si(CH_3)_2O]_nH)Na^+$ in **Figure 1h**, one neutral PDMS-Sodium configuration referred to as $(HO[Si(CH_3)_2O]_nH)Na$ in **Figure 1i**, one charged PEO-Sodium configuration referred to as $[HO(CH_2CH_2O)_2H]Na^+$ in **Figure 1j**, one neutral PEO-Sodium configuration referred to as $[HO(CH_2CH_2O)_2H]Na$ in **Figure 1k**, one charged PDMS-Magnesium configuration referred to as $(HO[Si(CH_3)_2O]_nH)Mg^{2+}$ in **Figure 1l**, one neutral PDMS-Magnesium configuration referred to as $(HO[Si(CH_3)_2O]_nH)Mg$ in **Figure 1m**, one charged PEO-Magnesium configuration referred to as $[HO(CH_2CH_2O)_2H]Mg^{2+}$ in **Figure 1n**, and one neutral PEO-Magnesium configuration referred to as $[HO(CH_2CH_2O)_2H]Mg$ in **Figure 1o**.

Subsequent frequency calculations were performed on all optimized configurations as well as on Li, Li^+, Na, Na^+, Mg, and Mg^{2+}. Temperature-dependent (from 100 K to 1000 K) Gibbs free energies, G, were calculated as the sum of the total electronic energies and thermal free energies. The difference between the free energy of the optimized configurations and the sum of the free energy of the polymer (PDMS or PEO) and the guest species (Li, Li^+, Na, Na^+, Mg, or Mg^{2+}) taken separately was calculated as a measure of how thermodynamically favorable the reaction between the polymer and the guest species is. In order to determine the reversibility of the reactions, the temperature-dependent equilibrium constants, κ, were calculated as $\exp(-\Delta G/RT)$, R being the universal gas constant.

References

1. Puthirath AB, Patra S, Pal S, Manoj M, Balan AP, Jayalekshmi S, et al. Transparent flexible lithium ion conducting solid polymer electrolyte. Journal of Materials Chemistry A. 2017;5(22):11152-62.