Nanoscale Organic Hybrid Electrolytes**

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Significant effort has been devoted by research groups world-wide to the development of polymer and composite polymer electrolytes for use in lithium batteries [1,2]. The best known polymer ionic conductor, polyethylene oxide (PEO), is crystalline and has low conductivity at room temperature. While short chain polyethylene glycol (PEG) oligomers exhibit good ionic conductivity at room temperature as well as chemical and thermal stability, amorphous low molecular weight electrolytes lack mechanical strength. The addition of free inorganic particles [3-7] as well as inorganic networks [8] and inorganic–organic constituents [9-11] to polymer electrolytes has been shown to improve both mechanical properties and conductivity.

In this communication, we report on a new class of solvent-free, nanoscale organic hybrid materials (NOHMs), which simultaneously manifest *superionic* conductivities, large electrochemical stability windows (-0.5V to > 5 V, vs Li), good lithium ion transference numbers (~0.45), no volatility and thermal stabilities up to 400 $^\circ$C, and which offer multiple handles through which near molecular control can be exerted on mechanical properties. All of these features provide unusual opportunities for engineering new families of high-performance, nanoscale hybrid

electrolytes for lithium batteries with markedly improved safety, enhanced tunability, and comparable electrochemical properties to currently used aprotic liquids. Created by densely grafting polyethylene glycol oligomers to the surface of inorganic nanostructures (Fig. 1(a)), these hybrids have recently been reported[12] to display liquid-like transport properties, including a well-defined Newtonian flow regime, in the absence of any suspending solvent. This last feature makes them the first example of a system of particles of any size that is able to reach equilibrium in the absence of a suspending solvent. It also means that the materials are best visualized as a collection of nanoscale building blocks, which are themselves organic/inorganic hybrids (Fig. 1b) - making them the first example of a hybrid material designed from the bottom-up, i.e. where each and every building block is a nano-sized organic/inorganic hybrid.

NOHMs were synthesized using two approaches: (i) sulfonic acid functionalization of the silica nanoparticle suspension followed by reaction with an amine terminated polyethylene glycol methyl ether (Fig. 1, pathways 1 and 2); and (ii) direct reaction of a trimethoxysilane functionalized polyethylene glycol methyl ether with nanoparticle suspensions of either silica or titania (Fig. 1, pathway 3). Unattached polymer resulting from the procedure in scheme (ii) is removed by repeated dialysis in chloroform.

By varying the nanoparticle (core) size and organic polymer (corona) molecular weight and grafting density, the volume fraction of the inorganic component can be systematically varied and mechanical properties manipulated over a broad range. Figure 2, for example, illustrates the effect of the volume fraction ϕ of SiO_2 nanoparticle cores on the dynamic shear modului. The figure compares these properties with their equivalents for the pure corona polymer ($\phi = 0$). It is immediately apparent that by tethering the PEG oligomers to nanoparticles, the

mechanical modulus measured at any frequency is dramatically increased, relative to the untethered corona ($\phi = 0$). It is also evident that both the value of the mechanical moduli and their frequency dependence can be facilely altered by changing ϕ, in this case by varying the effective oligomer grafting density (σ). At high core fractions, the real component (storage), G', of the dynamic modulus dominates the imaginary component (loss), G'', and exhibits little if any variations with shear frequency; features normally associated with ideal elastic solids. On the other hand, at low ϕ both moduli are of comparable magnitude and a transition from solid-like ($G' > G''$) to liquid-like ($G'' > G'$) behaviors is observed in the NOHMs as the shear frequency is reduced. These behaviors should be contrasted with those of the untethered corona, which is liquid-like ($G'' > G'$) and substantially softer than their NOHMs counterparts.

Figure 2(b) shows that even at the highest core fractions, NOHMs are in reality not elastic solids, but are soft glasses. Specifically, the figure shows that with increasing shear strain γ the materials rapidly soften, and at a critical strain γ_y manifest a pronounced maximum in G'', after which they behave as simple fluids (ie. $G'' > G'$). The weak frequency dependence and pronounced loss maximum apparent at γ_y are characteristic of a class of yield-stress fluids termed soft-glasses [13]. In these fluids, individual elements are thought to be trapped in cages (see left cartoon, Fig. 2(b)) with barrier energies substantially higher than the thermal energy kT, produced by interactions with their neighbors. The maximum in G'' coincides with a change in slope of the shear stress, τ, versus strain (Fig. 2(a)) and reflects enhanced dissipation of mechanical energy produced when the cages break-apart (Fib. 2(b), right cartoon) under the action of shear; the critical strain γ_y is the effective yield strain at the conditions of the measurement.

These observations imply that NOHMs are solvent-free, homogeneous soft glasses that manifest tunable mechanical properties. To determine the effect of tethering on ionic conductivity of the oligomer corona, we synthesized a series of NOHMs doped with varying amounts of lithium bis(trifluoromethylsulfonyl) imide (LiTFSI) to form a 1M electrolyte in the organic phase. To investigate the effect of core particle size and chemistry and corona molecular weight, NOHMs with a range of physical characteristics (Table 1, Supporting Information) were synthesized. Electrochemical and thermal properties of the hybrid electrolytes and the inorganic fraction were characterized by a suite of experimental techniques, including linear scan voltammetry (LSV), differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The electrochemical stability window of hybrid electrolyte S2 in a symmetric lithium metal cell was determined to be approximately 6 V by LSV.

Broadband dielectric spectroscopy was used to quantify the ionic conductivities of the materials as a function of temperature. DC ionic conductivity values were extracted from this data using a standard procedure (see supporting information). Figure 3(a) displays temperature dependent ionic conductivity data for NOHMs comprised of 8 nm. silica cores and PEG corona with varying length, electrolytes S1-S7. Figure 3(b) displays conductivity of hybrids with varying core sizes and chemistry, all with M_n = 660 g/mol molecular weight PEG corona, electrolytes S2, S8-S9. Both figures include temperature-dependent conductivity data for free, MPEG oligomers with M_n = 500 and 2000 also doped with 1 M LiTFSI, which allows the effect of tethering on conductivity to be evaluated. Lines in the figures are obtained by fitting the data to either of two theoretical forms: (i) Vogel-Fulcher-Tammann (VFT), $\mu = A\exp(-B/(T-T_0))$, where B is the effective *activation energy* barrier for coupled ion and local polymer segment motions/breathing, in units of absolute

temperature; T and T_0 are the measurement and reference (typically the equilibrium glass transition) temperatures, respectively; and A is a pre-exponential factor equivalent to the ionic conductivity in the high-temperature limit; and (ii) Arrhenius, $\mu = \Omega \exp(-\boldsymbol{E_a}/T)$, where E_a is the activation energy for ion hopping, again in units of temperature. Table 2 in the Supporting Information summarizes the parameters used for these fits. Transport properties displaying VFT temperature dependence are common in polymer systems in which local segmental motions and chain relaxations contribute significantly to the transport process. Arrhenius behavior is on the other hand typically found in systems where these motions do not play a significant role.

It is immediately noticeable from figures 3(a) & (b) that tethering PEG chains to either SiO_2 or TiO_2 produces a fractional decrease in ionic conductivity and no noticeable change in its temperature dependence above the crystallization transition, while extending VFT type conductivity into a lower temperature regime. As is the case for the pure MPEG electrolytes, however, materials S6 and S7, which exhibit both a crystalline and melting transition, manifest Arrhenius temperature-dependent ionic conductivity below the melt transition. All other samples exhibit VFT behavior throughout, implying that the ion conduction mechanism is dominated by segmental and chain motions of the tethered oligomers. Significantly, several of the hybrids are seen to attain the same conductivity, within error, at high temperatures; this conductivity value is close to that recorded for a pure high molecular weight PEO-LiTFSI system[14]; implying that polymer chains in the two systems have similar dynamics at the microscale.

It is also apparent from Figure 3(b) that an increase in the hybrid core size, results in a fractional decrease in ionic conductivity. This finding is readily explained in terms of decreased segmental motion as a result of increased chain crowding and

extension around the cores. Changing the NOHMs core chemistry from SiO_2 to TiO_2, on the other hand, has a negligible effect on ionic conductivity; confirming that the mechanism of ion transport is through local motion of the PEG chains, and that the inorganic cores have little effect - a result different from reports by others[4,6] for composite electrolytes containing inorganic particles with surface functionality.

Figure 3(c) displays the DC molar conductivity vs. the shear fluidity (inverse viscosity), the *Walden plot*, of the same electrolyte series (S2, S8, S9) with varying cores and PEG corona, M_n= 660. This approach for representing conductivity data has traditionally been used for understanding the microscopic motion of ions in molecular fluids; the standard KCl data used for comparison is for a dilute, fully dissociated solution of ions of equal mobility [15-16]. While the conduction mechanism in polymer electrolytes is normally thought to be more closely associated with free volume than viscosity, the Walden plot provides a convenient mechanism for displaying two of the most important properties of electrolytes developed for use in lithium batteries: conductivity and viscosity. It is clearly evident from the figure that the NOHMs electrolytes, even those with the shortest PEG corona, are *superionic*, ie. manifest higher ionic conductivities than anticipated from their fluidity. In comparison, untethered MPEG electrolytes (Fig. 3(d)) only display superionic properties when the chain molecular weight exceeds the entanglement value, $M_e \approx 3200$ [17]. Significantly, the superionic regime is accessible at room temperature.

In summary, we report a new class of solvent-free nanoscale organic hybrid electrolytes composed of hard nanoparticles densely grafted with oligomers. These materials flow like soft glasses and, relative to the unattached oligomers, display more than a million-fold enhancement in mechanical modulus, but show negligible changes in ionic conductivity. Because properties of the materials can be facilely tuned,

NOHMs provide a method for manipulating mechanical properties of an electrolyte, without compromising conductivity. Optimization of the NOHMs design is expected to lead to a novel family of yield-stress electrolytes in which the ion-conducting polymer phase exists as a tortuous interconnected network of corona-filled pores, constrained by an impenetrable array of inorganic core particles. By tuning the spacing and tortuosity of the conducting phase (e.g. by varying the core diameter and/or molecular weight of the corona), these materials offer unique opportunities for retarding/suppressing dendrite growth in secondary lithium metal batteries.

Experimental Section
Synthesis of Hybrids by Silane Chemistry (S2, S8-S9)

An alkaline stabilized dispersion of silica nanoparticles, Ludox SM-30 (Aldrich, 8 nm diameter) or Ludox HS-40 (Aldrich, 18 nm diameter), was diluted to 4 wt% particle fraction by addition of aqueous potassium hydroxide solution, pH ~ 10-11. [Methoxy(polyethyleneoxy)propyl] trimethoxysilane, 90% (Gelest) at a ratio of 1.5 g silane-PEG per 1.0 g silica was added dropwise, while stirring, in three aliquots each separated by heating at 100°C in an oil bath for 1 hour followed by 10-15 minutes of sonication. Following the addition of the final aliquot of silane-PEG, the reaction solution was heated for 6 hours in an oil bath at 100°C. The reaction solution was then poured into wide petri dishes and heated overnight in a convection oven at 70°C to drive off remaining water and complete the silane reaction. The following day, the product was put into dialysis tubing and dialyzed for several days in chloroform to remove any remaining free silane-PEG.

An acidic stabilized dispersion of titania nanoparticles (MKNano, 15 nm diameter) was diluted to 4 wt% particle fraction by addition of aqueous acetic acid solution, pH ~ 3. The rest of the reaction was followed identically to the above silica based procedure, though a ratio of 2.0 g silane-PEG per 1.0 g titania was employed.

Synthesis of Hybrids by Acid-Base Chemistry (S1, S3-S7)

Hybrids were prepared via procedure similar to that published in [18] with the following exceptions: the silica dispersion used was Ludox SM-30 (Aldrich) and the reaction was carried out at pH ~ 2. Following titration, amine terminated polyethylene glycol methyl ethers of varying molecular weights (Polymer Source) or tertiary amine polyethylene glycol Ethomeen C-25 (Talas) were added stoichiometrically to the acid-functionalized silica solution and allowed to stir at room temperature for 2-3 days. The resulting NOHMs were dried in a laboratory convection oven and then under vacuum overnight prior to use.

Preparation of Electrolytes

A solution oflithium bis(trifluoromethane sulfone imide) (LiTFSI, Aldrich) was prepared in dry methanol (Aldrich) in the glove box before use. The lithium salt solution was added to the NOHMs at a concentration of 1 M in PEG for all samples. After mixing, samples were dried in the convection oven at 50°C overnight and for at least 24 hours under vacuum.

Instrumentation

TEM images were taken at 120 kV with a FEI Tecnai T-12 TWIN TEM. Sample was dissolved in methanol, dropped onto a copper grid, and solvent was evaporated off prior to imaging. TGA measurements were obtained on a TA Instruments model Q5000 under N_2 flow. DSC measurements were obtained on a TA Instruments model Q2000. Dielectric measurements were taken with a Novacontrol model N40 dielectric broadband spectrometer. Rheology measurements were performed using a Rheometric Scientific Ares rheometer outfitted with 10 mm diameter, 1° cone-and-plate fixtures, and an Anton Paar Rheometer (MCR 501) outfitted with 25 mm diameter parallel plates.

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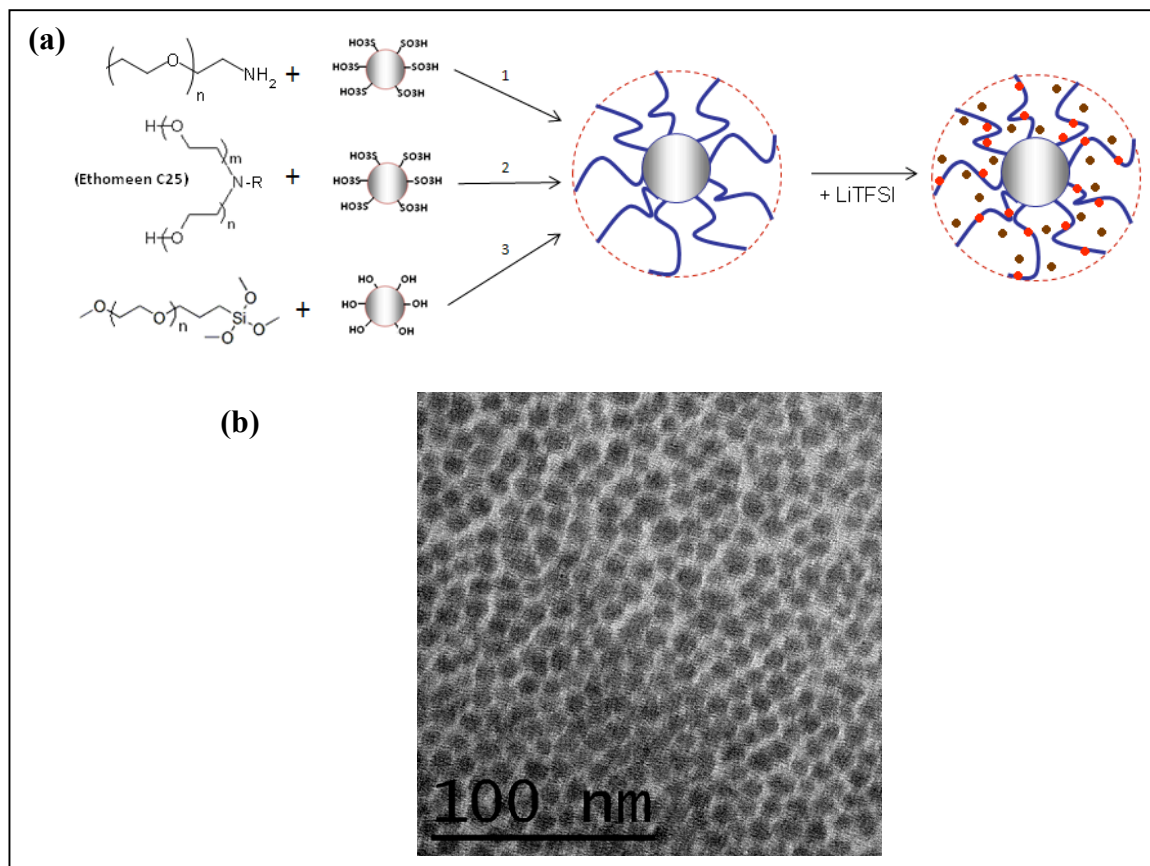
Figures

Fig. 1 (a) Schematic of NOHMs electrolyte synthesis. The red and brown dots represent Li$^+$ and TFSI$^-$ ions, respectively; **(b)** TEM of SiO$_2$-PEG NOHMs comprised of 8 nm SiO$_2$ core and PEG corona, with M_n = 660 g/mol, produced by pathway 3.
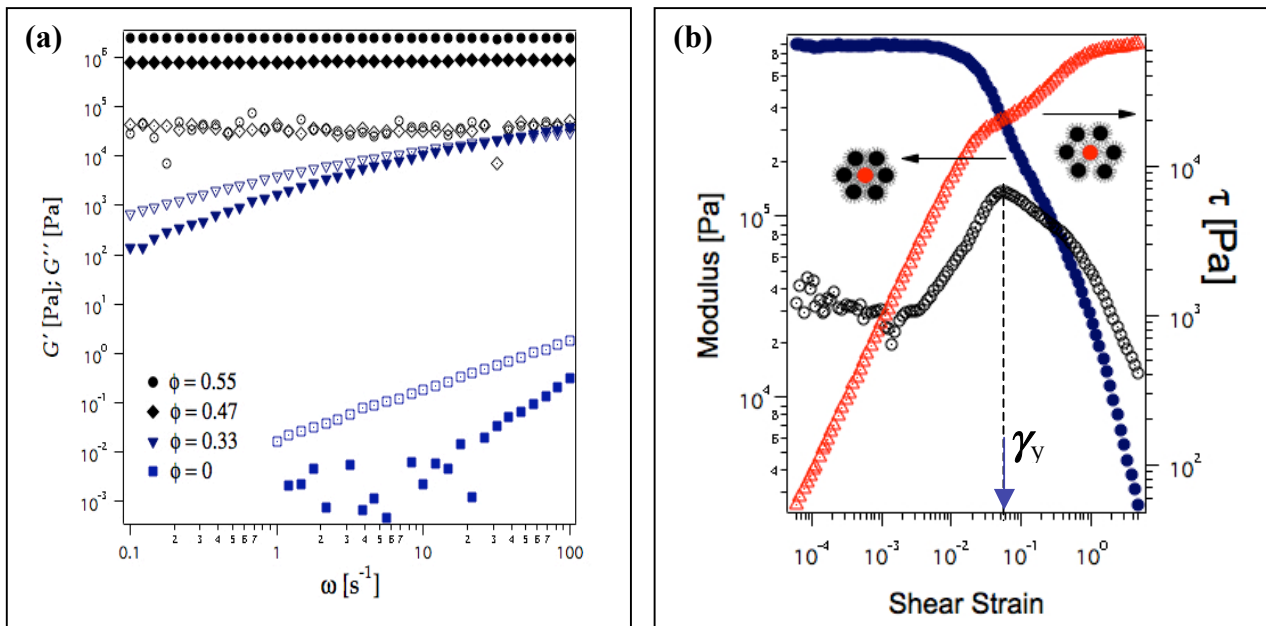
Fig. 2(a) Dynamic shear moduli versus frequency for NOHMs comprised of 18 nm SiO$_2$ core and PEG corona, with M_n = 660 g/mol produced by pathway 3, as a function of core volume fraction ϕ; **(b)** Dynamic storage G' (filled circles), loss G'' (open), and shear stress (triangles) versus strain for NOHMs in 2**(a)** with ϕ = 0.47.
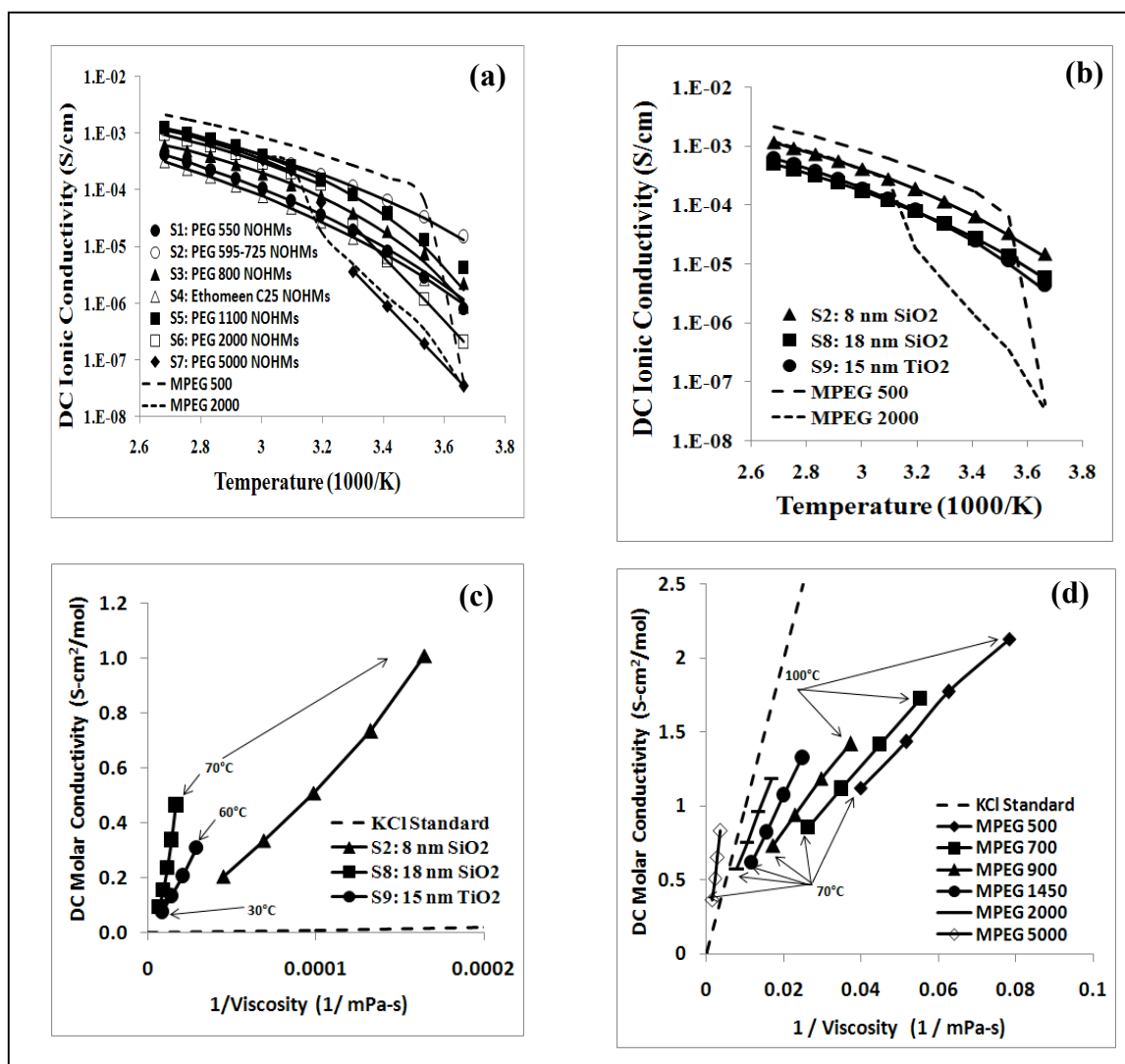
Fig. 3(a) DC ionic conductivity of un-tethered and particle-tethered PEG/hybrid electrolytes based on 8 nm SiO₂ cores and varying PEG corona molecular weights. The solid lines in the figure are fits to VFT or Arrhenius temperature dependence; **(b)** Conductivity of NOHMs electrolytes with varying core chemistry and size; **(c)** Walden plot of NOHMs electrolytes with varying cores and 660 PEG corona. The dashed line represents the standard result for dilute KCl in aqueous solution; **(d)** Walden plot of MPEG electrolytes.

Supporting Information

Table 1. NOHMs Electrolyte – Sample specifications

Sample	Synthesis Pathway # in Fig. 1	Core	Core Diameter (nm)	PEG Corona M_n (g/mol)	PEG PI	Core volume fraction, _	T_c (°C)	T_m (°C)
S1	1	SiO_2	8	550	1.15	0.35	-36	10
S2	3	SiO_2	8	660	-[2]	0.33	-39	5
S3	1	SiO_2	8	800	1.10	0.28	-35	10
S4	2	SiO_2	8	865[1]	-[3]	0.31	-	-
S5	1	SiO_2	8	1100	1.09	0.25	-	-
S6	1	SiO_2	8	2000	1.05	0.16	-12	31
S7	1	SiO_2	8	5000	1.06	0.07	23	44
S8	3	SiO_2	18	660	-[2]	0.35	-35	5
S9	3	TiO_2	15	660	-[2]	0.27	-30	9

[1] Average total molecular weight of branched poly(ethylene glycol) functionalized amine (Ethomeen C25)
[2] Commercial polymer (Gelest), molecular weight listed as 596 -725
[3] Commercial polymer (Talas), equivalent mass listed as 825 -909

Table 2. Parameters for VFT and Arrhenius fits as displayed in Fig. 3 (a) and Fig. 3 (b) at the 95% confidence interval

| Sample	VTF Fit Parameters			Arrhenius Fit Parameters	
	A (S/cm)	B (K)	T_0 (K)	Λ (S/cm)	Ea (K)
S1	0.07 ± 0.02	970 ± 80	185 ± 7	-	-
S2	0.047 ± 0.003	680 ± 20	190 ± 2	-	-
S3	0.014 ± 0.003	470 ± 60	224 ± 7	-	-
S4	0.07 ± 0.01	1050 ± 50	180 ± 4	-	-
S5	0.023 ± 0.005	420 ± 50	229 ± 6	-	-
S6	0.028 ± 0.003	540 ± 30	214 ± 4	$2E12 \pm 4E12$	12360 ± 70
S7	0.06 ± 0.02	600 ± 100	210 ± 10	$1.07E14 \pm 5E12$	13010 ± 20
S8	0.027 ± 0.001	760 ± 10	184 ± 1	-	-
S9	0.037 ± 0.008	720 ± 60	195 ± 7	-	-

Measuring T_m and T_c for NOHMs electrolytes

Differential Scanning Calorimetry, DSC, data obtained for electrolyte S7 are presented below. The melting transition temperature, T_m, and crystallization temperature, T_c are the temperatures at which the heat loss displays a local maximum and minimum, respectively.
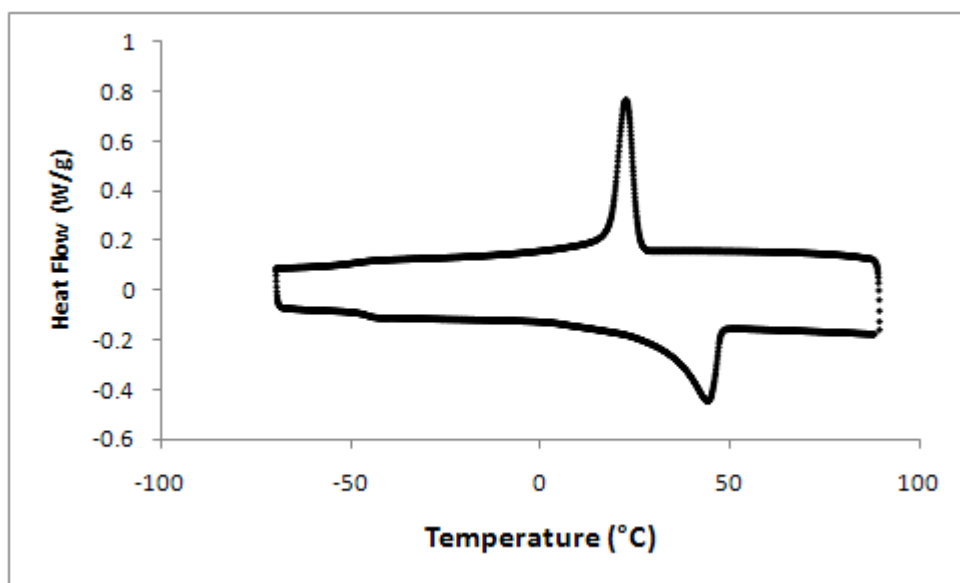
Determining the DC ionic conductivity

Frequency and temperature dependent dielectric data over a range of $0.1\text{-}3\times10^6$ Hz and 0-100°C was obtained using a Novocontrol Dielectric Broadband Spectrometer. The data was plotted as the real part of the ionic conductivity vs. frequency; data for electrolyte S7 is displayed.
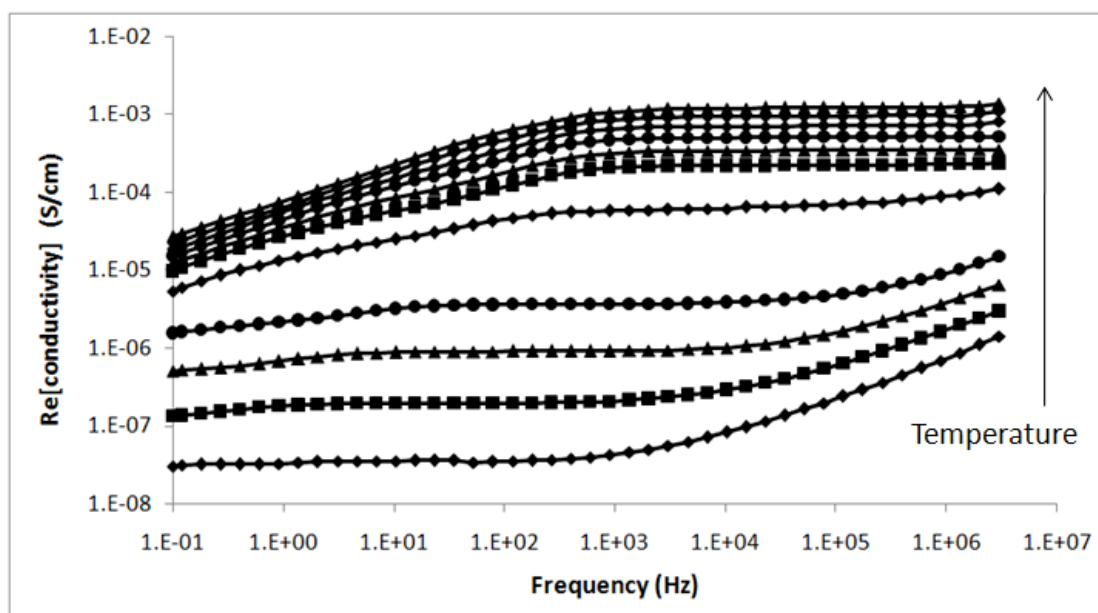

The dielectric data for all studied electrolytes is consistent with a phenomena known as universal dynamic response (UDR), noted by Jonscher [i], whereas

$\sigma'(\omega) = \sigma_{DC} + A\omega^s$. The DC conductivity may be estimated from the plateau value. Beyond a critical frequency above the plateau, a power law relationship between the real conductivity and frequency is displayed. Below the plateau, the decrease in conductivity with decreasing frequency is due to polarization of the cell.

### *Measuring the shear viscosity*

Viscosity measurements were taken on an Rheometrics Scientific, Ares rheometer and an Anton Paar Rheometer, MCR501. Temperature-dependent experiments were performed in increments of 5°C in the range 30-70°C for NOHMs electrolytes and in the range 70-100°C for MPEG electrolytes. Following temperature stabilization, NOHMs electrolyte samples were subjected to a shear rate of 10 Hz for 100 seconds; the data obtained for electrolyte S2 is displayed below. MPEG electrolytes were sheared at 100 Hz. The average steady state viscosity was taken to be the shear viscosity as displayed in the Walden plot.
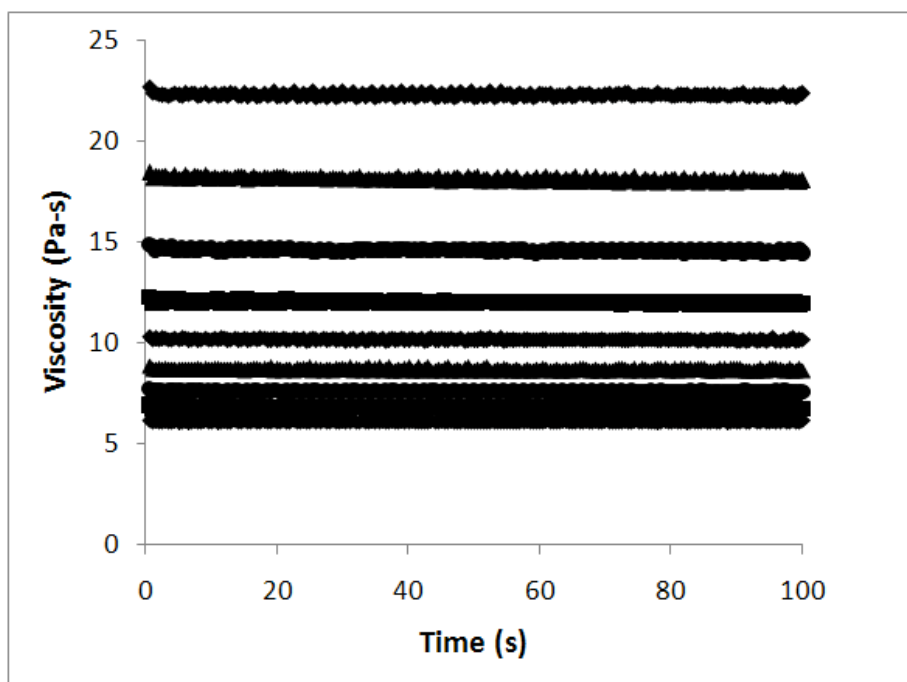
i   A. K. Jonscher, *Nature (London).* **1977,** *267,* 673.

Determining the Electrochemical window of NOHMs electrolytes

The electrochemical stability window of S2 in a two electrode symmetric lithium metal cell was measured by LSV. The discontinuity in the plot is due to the compilation of data from two scans, 1 to 7 V and 2 to -2 V.
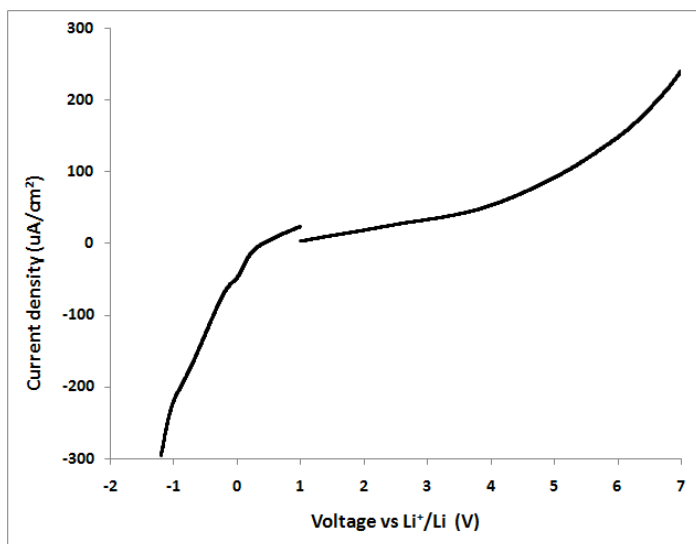
Linear scan voltammetry of a symmetric lithium cell with hybrid polymer electrolyte S2, 8 nm SiO_2 core and 660 Mn PEG corona with 1 M LiTFSI: scan rate, 1 mV/s; temperature, 20°C; electrode area, 0.32 cm^2.