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Towards Room Temperature Performance for Lithium-Polymer Batteries.

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Abstract

Recent work on molecular simulations of the mechanisms of lithium ion conductance has pointed towards two types of limiting process. One has involved the commonly cited segmental motion while the other is related to energy barriers in the solvation shell of polymeric ether oxygens around the lithium ions. Calculations of the barriers to lithium ion migration have provided important indicators as to the best design of the polymer. The theoretical work has coincided with and guided some recent developments on polymer synthesis for lithium batteries. Structural change of the polymer solvation shell has been pursued by introduction of trimethylene oxide l(TMO) units into the polymer. The conductivity measurements on polymers containing the PDO unit are encouraging. The architecture of the polymer networks has been varied upon which the solvating groups are attached and significant improvements in sub-ambient performance are observed as a result. However, the above-ambient temperature performance appears controlled by an Arrhenius process that is not completely consistent with the theoretical calculations described here and may indicate the operation of a different mechanism. The new polymers possess significantly lower Tg values in the presence of lithium salts which indicates weaker binding of the lithium ions by the polymers. These properties provide considerable improvement in the transport properties close to the electrode surfaces resulting in decreased impedances at the surfaces both at lithium metal and in composite electrodes. The greater flexibility of the solvation groups combined with appropriate architecture not only has applications in lithium metal polymer batteries but also in lithium ion liquid and gel systems as well as in fuel cell electrodes.

Introduction.

Interest in polymer electrolytes for the last twenty years has been largely driven by their use in rechargeable lithium batteries. The lithium metal-polymer system has been investigated as an answer to the dendrite problem which precludes the use of lithium metal electrodes in liquid systems. Polyethylene oxide (PEO) has been the most commonly studied polymer for this purpose due to its ready availability and ease of use. Unfortunately, the transport properties of lithium salts in PEO and its many variations are inadequate to allow the energy of the battery to be utilized at useful rates at ambient temperatures and elevated temperatures (>60^oC) are required to allow practical power and energy densities to be attained[1-4]. This is not necessarily a problem for electric vehicle use but certainly prevents the use of these batteries in most consumer applications and thereby impedes the development of the technology in small scale uses such as has occurred for the lithium ion batteries. It is therefore a matter of great interest to determine the nature of the barriers to higher lithium ion mobility in polymers in order to determine whether ambient temperature operation can ever be practical.

One approach to this problem is a combination of theoretical modeling with directed synthesis and characterization. Recently, quantum chemical studies have been carried out to determine the strength of the binding of Li^+ to the oxygens in polyalkyloxides[5] and to determine the height of the energy barriers to movement of the ions along the chains[6-8]. This work has coincided with synthetic efforts to prepare polymers with solvation groups that differ from the usual ethylene oxide (EO) and propylene oxide (PO) units[1, 2]. This paper provides a preliminary report on the comparison of theory and experiment.

Experimental.

Theoretical methods and calculation techniques and programs have been previously described[5, 6, 8]. Synthesis of polyepoxide ethers and the TMO and EOTMO chains have been described previously[1, 2]. Li TFSI salt was a gift from 3M. Conductivity measurements were carried out using Swagelok cells that have been previously described. A Solartron™ SI 1254 four-channel frequency response analyzer and a 1286 electrochemical interface were used to measure the impedance of electrolyte films of known thickness in constant-volume cells with blocking electrodes. The methods of preparing the films have been described. Salt diffusion coefficients were measured in the same cells with lithium metal electrodes using the method described by Ma et al[9]. Cell cycling, polarization and diffusion measurements were carried out using an Arbin (College Station, TX, USA) BT 4020 multichannel cycler. Glass transition temperatures were measured using a Perkin-Elmer DSC7 differential scanning calorimeter. Polymer samples were prepared in a glove box and transferred to the calorimeter without exposure to atmosphere.

Results and Discussion.

In Table 1 are listed the results of calculations on the binding of lithium ions to linear polymer chains containing all ethylene oxide units (PEO), all trimethylene oxide (TMO) units and a polymer containing alternating TMO and EO units. Shown are the binding constants calculated as a function of the co-ordination number around the lithium ion. The TMO polymer shows stronger binding for co-ordination numbers up to 5 but with co-ordination number 6 the binding is less due to steric crowding. Although full calculations have not been performed for the EOTMO polymer it also appears to have weaker binding at higher co-ordination number although the effect is smaller in accord with the reduced steric crowding. It is also noted that binding of the ions to two chains gives stronger binding than a single chain. A more detailed comparison of the results of calculations on EO, TMO and PO polymers has been recently published[5].

Table 2 shows the results of calculations of the energy involved in the barrier to movement of the lithium ion along the polymer chain where the transition state involves a decrease in co-ordination. The barrier to ion movement along a chain is distinctly lower for TMO than EO at higher co-ordination numbers. The TMOEO structure is calculated to also have a lower barrier than PEO. Thus, theoretical calculations predict stronger binding for lithium ions by TMO polymers unless the co-ordination numbers are high and the mobility of the lithium ions should be higher if the ionic movement follows the S_N1-type mechanism that has been the basis of the calculations.

Figure 1 shows the conductivities of a series of polyepoxide ether polymers containing different proportions of EO and TMO units in the side chains of the comb branch polymer. In this case the salt is LiTFSI which is present in a ratio of one lithium ion to ten oxygens. It can be seen that there appears to be little effect of the TMO groups upon the conductivity above room temperature but there is a large effect at lower temperatures where the impact of the glass transition temperature is strongest. Figure 2 shows the glass transition temperatures plotted as a function of the concentration of LiTFSI salt for the same set of polymers. The points for no added salt are plotted as 100:1 for convenience. The dependence of the glass transition temperature on the salt concentration is considerably stronger for the polymers that contain the most EO while the TMO-containing polymers exhibit a weaker dependence. This is consistent with less ionic cross-linking in the TMO polymers that leads to more segmental motion of the polymer chains and hence higher conductivities at low temperatures.

The conductivity of the polymer with the highest proportion of TMO (PE(TMO)$_3$) is plotted against reciprocal temperature for different concentrations of salt in Figure 3. The conductivity at 10:1 concentration (cf. Figure 1) is significantly lower below room temperature than the lower concentration electrolytes in agreement with the glass transition temperature measurements. Also noteworthy are the lower conductivities for lower salt concentrations at high temperatures which yield a flatter temperature dependence for the low concentrations. Measurements of the salt diffusion coefficients show some consistency with these trends. The salt diffusion coefficients for the PE(TMO)$_3$ are plotted against LiTFSI salt concentration in Figure 4 for four different temperatures (85, 60, 40 and 25-27^{o}C). The measured values are similar to those recently reported for linear amorphous PEO-LiTFSI solutions for 40and 60^{o}C but are about half the magnitude for 85^{o}C[2]. In particular, there appears to be a decrease in the diffusion constant at low concentrations that is not observed with the linear polymer.

These experimental observations appear to contradict the results of the theoretical calculations listed in Tables 1 and 2. The lower dependence of glass transition temperature on salt concentration for TMO polymers could be interpreted as due to weaker binding of the ions to the polymers, which is in fact predicted for high co-ordination numbers. Initial Raman spectroscopy of the polymer–salt systems indicate that the O-Li$^+$ binding is similar for TMO and EO linear polymers but that the longer range interactions are different. Thus the degree of cross-linking induced by binding of one ion to two polymer chains may be less for the TMO than for the EO systems which would explain the T_g dependence. The theoretical calculations show stronger binding with PEO when two chains are involved but similar calculations for TMO and EOTMO have not yet been completed. A further complication is the presence of the propylene oxide (PO) unit in the backbone of the comb polymer. Polypropylene oxide is known to exhibit poorer conductivity and transport properties than PEO and also a stronger dependence of the T_g upon salt concentration. Theoretical calculations show little difference in binding energies between PPO and PEO, however[5].

The conductivities shown in Figures 1 and 3 reveal that the introduction of the TMO groups has little effect upon the barrier to ionic motion above 25^{o}C. The temperature dependence appears to differ little as the proportion of TMO increases. This is in contrast to the conductivity dependence of PPO and PO containing comb polymers where the absolute values of conductivity are lower while the temperature dependence is more pronounced than for EO polymers. These observations imply that the rate determining step for lithium ion motion has not yet been identified. The theoretical calculations described above show that the barrier to lithium ion motion is distinctly lower for TMO containing polymers. Although the barrier to motion in PO units may be inferred to be higher due to the observed poorer transport properties in PPO these calculations remain to be completed. Initial conductivity measurements on linear PolyTMO do not reveal significant improvements in conductivities over those reported here, however, which indicates that the backbone PO units in the combs are not acting as coulombic traps.

An alternative limiting process might be a different mechanism where the transition state for lithium ion motion may involve an increase in co-ordination number in an S_N2-type mechanism. Such a mechanism might be more likely as the ion moves between chains, for example, and the process would be strongly affected by the nature and binding energy of the anion. Indeed, quite striking effects of the anion have been recently reported with respect to the polymer structure and this aspect needs further study[2].

Even though the introduction of TMO groups has not led to the hoped for increases in conductivity to provide room temperature performance, the observed effect on the glass transition temperature dependence on salt concentration is most encouraging. The mechanical properties of polymers are often strongly affected by the presence of a solid surface, which often leads to a decrease in segmental motion and hence a higher glass transition temperature[10]. High concentrations of salt next to an electrode surface as occurs during polarization[11-14] will likely lead to very restricted polymer motion and hence high resistivity if not actual glassification or precipitation. Thus changes in the polymer structure such as the introduction of the more flexible TMO group that keep the glass transition temperature low are likely to reduce the generation of resistive layers on the electrode. This effect can influence the interfacial impedance. Figure 5 shows the AC interfacial impedance plot at 85^{o}C for PE(TMO)$_3$-LiTFSI (20:1) in a symmetrical lithium-lithium cell (1cm^2 electrode area) before and after cycling at 0.2mA/cm^2 current density. The interfacial impedance is about half the value observed for PEO-LiTFSI under similar conditions. It has been noted that interfacial impedance of polarized cells varies as the cell relaxes after the current is turned off, indicating that a portion of the observed impedance is due to salt concentration gradients which generate phase changes next to the electrode surface. The preliminary results indicate that the introduction of the TMO group may reduce the severity of this problem, resulting in smaller losses of power due to interfacial resistances.

Another interesting observation in Figure 5 is the absence of change in the magnitude of the interfacial impedance after extensive cycling. This implies that there is little if any reaction of the polymer electrolyte with the lithium electrode, indicating the presence of a stable SEI layer. Upon increasing the current density to $0.4 mA/cm^2$ the cell polarizes in a classic transition time manner and quickly fails due to dendrite short-circuiting. Upon disassembling the cell and extracting the electrolyte for chemical analysis by gas chromatography degradation products resulting from carbon-oxygen bond cleavage are easily observed. The result of exceeding the limiting current is dendrite growth and reduction of the polymer while cycling at current densities well below the limiting current appears to cause no damage to the polymer. From the current density used to generate the transition time behavior one can also estimate a transference number of about 0.2 since the salt diffusion coefficient, concentration and cell geometry are known.

Conclusions

Quantum chemical studies of the binding of lithium ions to polyalkylalkoxide polyers such as PEO, PTMO and PPO indicate that the TMO polymers bind the lithium ion more strongly except at high co-ordination number where steric crowding is dominant. Calculations of the barrier to ionic motion along the polymer chain via an S_N1-type mechanism that involves a lower co-ordination number in the transition state indicates that the barrier is lower for TMO-containing polymers. Conductivity measurements of TMO-containing polymers show no change in the slope of the Arrhenius temperature dependence indicating the operation of a different mechanism of ion motion as the rate determining step. Low temperature conductivities and the dependence of T_g on salt concentration indicate the presence of less ionic cross-linking in the TMO system that leads to smaller interfacial resistance at both the lithium metal and within the composite electrode that will facilitate higher discharge rates. However, the nature of the limiting barrier to lithium ion motion remains to b elucidated.

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References

1. Buriez, O., Y.B. Han, J. Hou, J.B. Kerr, J. Qiao, S.E. Sloop, M.M. Tian, and S.G. Wang, *Performance limitations of polymer electrolytes based on ethylene oxide polymers.* Journal of Power Sources, 2000. **89**(2): p. 149-155.
2. Kerr, J.B., S.E. Sloop, G. Liu, Y.B. Han, J. Hou, and S. Wang, *From Molecular Models To System Analysis For Lithium Battery Electrolytes.* Journal of Power Sources, 2002. **In Press**.
3. Thomas, K.E., S.E. Sloop, J.B. Kerr, and J. Newman, *Comparison of lithium-polymer cell performance with unity and nonunity transference numbers.* Journal of Power Sources, 2000. **89**: p. 132.
4. Dees, D.W., V.S. Battaglia, L. Redey, G.L. Henriksen, R. Atanasoski, and A. Belanger, *Toward standardizing the measurement of electrochemical properties of solid-state electrolytes in lithium batteries.* Journal of Power Sources, 2000. **89**(2): p. 249-255.
5. Redfern, P.C. and L.A. Curtiss, *Quantum Chemical Studies of* Li^+ *Cation Binding to Polylalkyloxides.* Journal of Power Sources, 2002. **In Press**.
6. Baboul, A.G., P.C. Redfern, A. Sutjianto, and L.A. Curtiss, *Li+-(diglyme)(2) and LiClO4-diglyme complexes: Barriers to lithium ion migration.* Journal of the American Chemical Society, 1999. **121**(31): p. 7220-7227.
7. Curtiss, L.A. Personal Communication, October 2000.
8. Sutjianto, A. and L.A. Curtiss, *Li+-diglyme complexes: Barriers to lithium cation migration.* Journal of Physical Chemistry a, 1998. **102**(6): p. 968-974.
9. Ma, Y.P., M. Doyle, T.F. Fuller, M.M. Doeff, L.C. Dejonghe, and J. Newman, *The Measurement of a Complete Set of Transport Properties For a Concentrated Solid Polymer Electrolyte Solution.* Journal of the Electrochemical Society, 1995. **142**(6): p. 1859-1868.
10. Tsagaropoulos, G. and A. Eisenberg, *Dynamic Mechanical Study of the Factors Affecting the Two Glass Transition Behavior of Filled Polymers - Similarities and Differences With Random Ionomers.* Macromolecules, 1995. **28**(18): p. 6067-6077.
11. Doyle, M., T.F. Fuller, and J. Newman, *The Importance of the Lithium Ion Transference Number in Lithium Polymer Cells.* Electrochimica Acta, 1994. **39**(13): p. 2073-2081.
12. Doyle, M. and J. Newman, *The Use of Mathematical Modeling in the Design of Lithium Polymer Battery Systems.* Electrochimica Acta, 1995. **40**(13-1): p. 2191-2196.
13. Doyle, M. and J. Newman, *Modeling the Performance of Rechargeable Lithium-Based Cells - Design Correlations For Limiting Cases.* Journal of Power Sources, 1995. **54**(1): p. 46-51.
14. Doyle, M., J. Newman, A.S. Gozdz, C.N. Schmutz, and J.M. Tarascon, *Comparison of Modeling Predictions With Experimental Data From Plastic Lithium Ion Cells.* Journal of the Electrochemical Society, 1996. **143**(6): p. 1890-1903.

Table and Figure Captions.

Table 1. Binding Energies as a Function of Coordination Number

Binding Energy ΔE_e (kcal/mol)

Table 2. Comparison of Barriers (in kcal/mol) for Li+ migration in PEO, PTMO and mixed PTMOEO.

Figure 1. Conductivity of Polyepoxide ethers with different contents of TMO and EO units as a function of reciprocal temperature (1/K). Salt is LiTFSI at [O]:[Li^+] ratio of 10:1.

Figure 2. Glass transition temperature (T_g/°C) as a function of salt concentration (LiTFSI) for Polyepoxide ether polymers.

Figure 3. Conductivity of $PE(TMO)_3$ as a function of reciprocal temperature (1/K) for different salt concentrations (LiTFSI). Legend on figure gives concentration as the ratio [O]:[Li^+].

Figure 4. Salt diffusion coefficient (D_s/cm^2s^{-1}) as a function of salt concentration (LiTFSI) for four different temperatures (85, 60, 40 and 25-27°C). Salt concentration is the ratio [O]:[Li^+].

Figure 5. Complex plane graph of $PE(TMO)_3$-LiTFSI(20:1) in a symmetrical Li/Li cell ($1cm^2$) at 85°C. AC impedance measured potentiostatically (10mV) from 65kHz to 0.1Hz before and after galvanostatic cycling at $0.2mA/cm^2$, 1.4coulombs/cycle.

Table 1.

Coordination number	Li+ -TMO	Li+ -PEO	Li+ -PEO (2 chains)	Li+-TMOEO
1	48.6	39.4		
2	75	66		
3	98.8	87.1	94.1	
4	110.9	103	110.1	
5	115.6	110.2	115.3	113.6
6	112.7	115.4	121.5	114.1

Table 2.

	Li+ TMO	Li+ PEO	Li+TMOEO
Species	$\Delta E_e^{TS}(n+1 \rightarrow n)$	$\Delta E_e^{TS}(n+1 \rightarrow n)$	$\Delta E_e^{TS}(n+1 \rightarrow n)$
2 to 1 to 2	27.40	27.1	
3 to 2 to 3	21.50	22.9	
4 to 3 to 4	11.1	18.6	
5 to 4 to 5	5.9	9.4	
6 to 5 to 6		7.6	5.3

Figure 1.

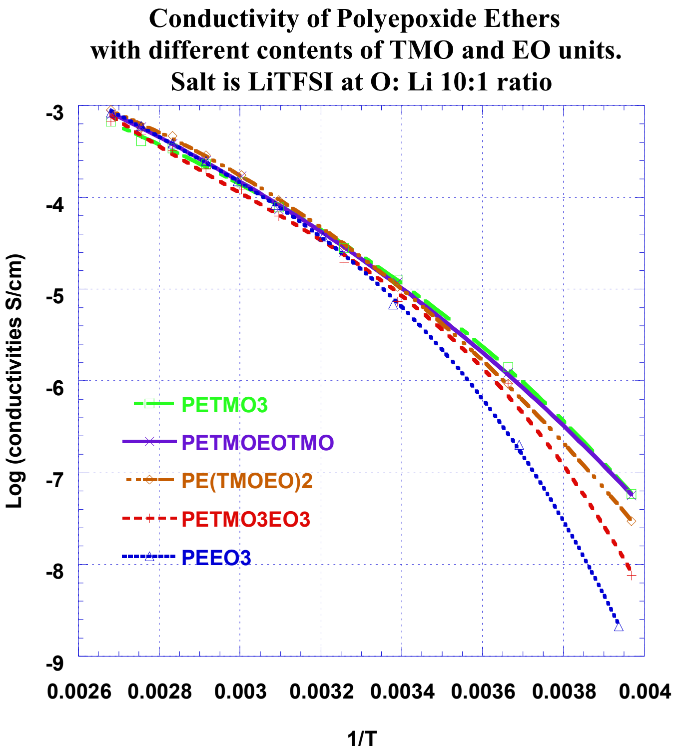
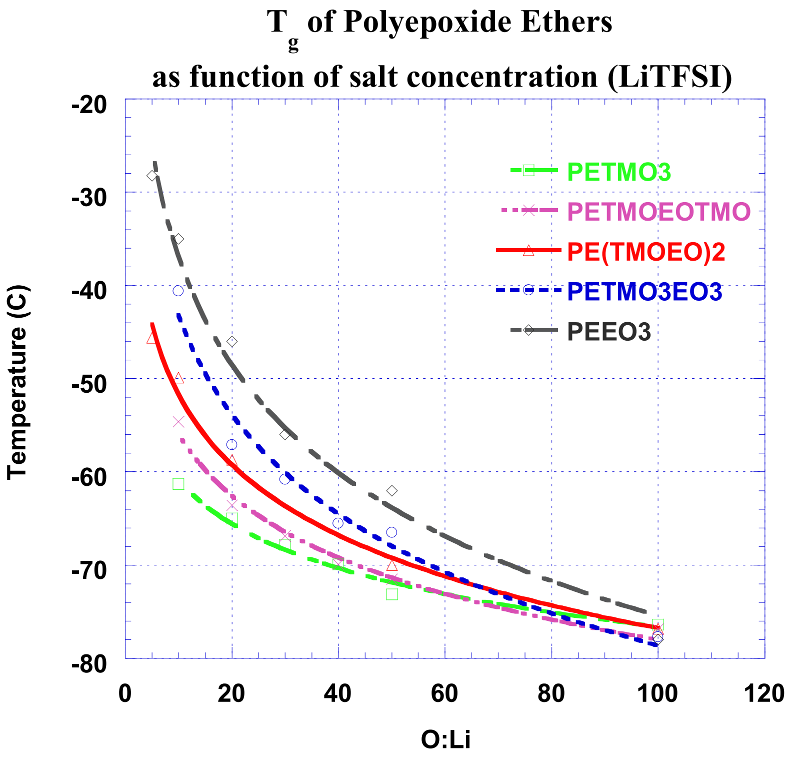
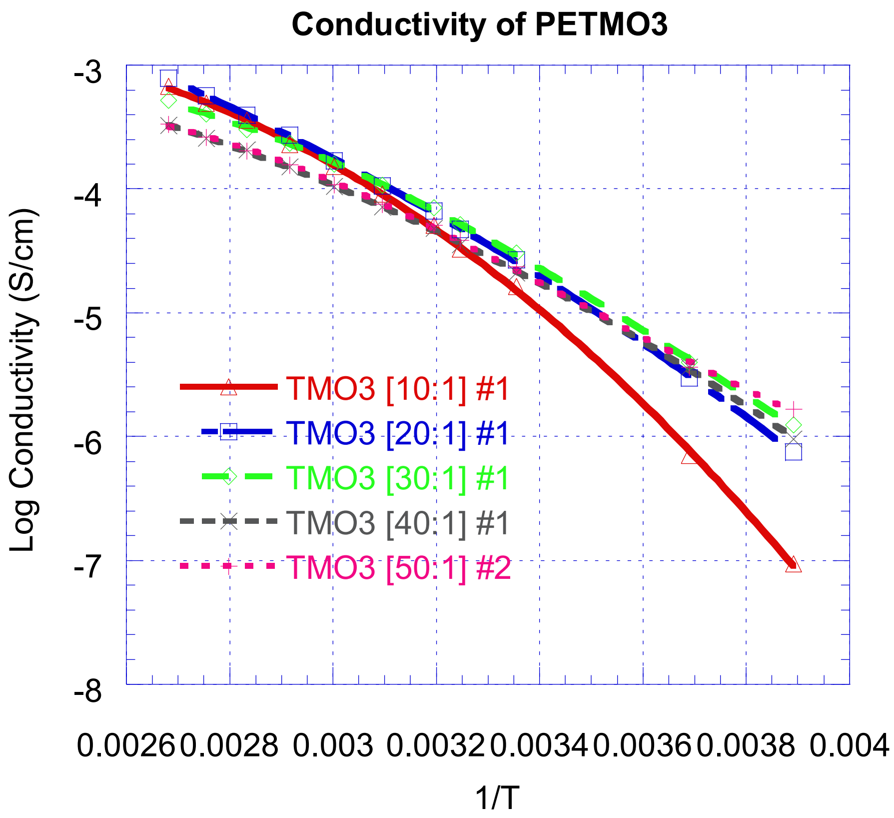

Conductivity of Polyepoxide Ethers
with different contents of TMO and EO units.
Salt is LiTFSI at O: Li 10:1 ratio
-3
-4
-5
-6
-7
-8
-9
Log (conductivities S/cm)
PETMO3
PETMOEOTMO
PE(TMOEO)2
PETMO3EO3
PEEO3
0.0026
0.0028
0.003
0.0032
0.0034
0.0036
0.0038
0.004
1/T

Figure 2.



T_g of Polyepoxide Ethers
as function of salt concentration (LiTFSI)

Figure 3.



Conductivity of PETMO3
Log Conductivity (S/cm)
-3
-4
-5
-6
-7
-8
0.0026
0.0028
0.003
0.0032
0.0034
0.0036
0.0038
0.004
1/T
TMO3 [10:1] #1
TMO3 [20:1] #1
TMO3 [30:1] #1
TMO3 [40:1] #1
TMO3 [50:1] #2

Figure 4.

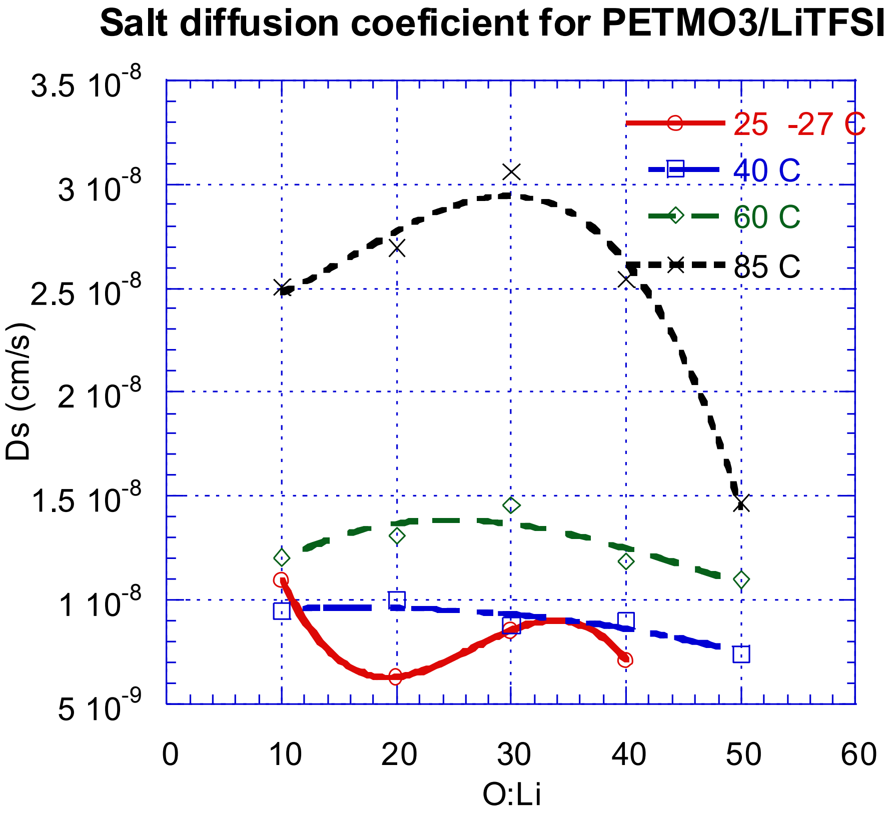
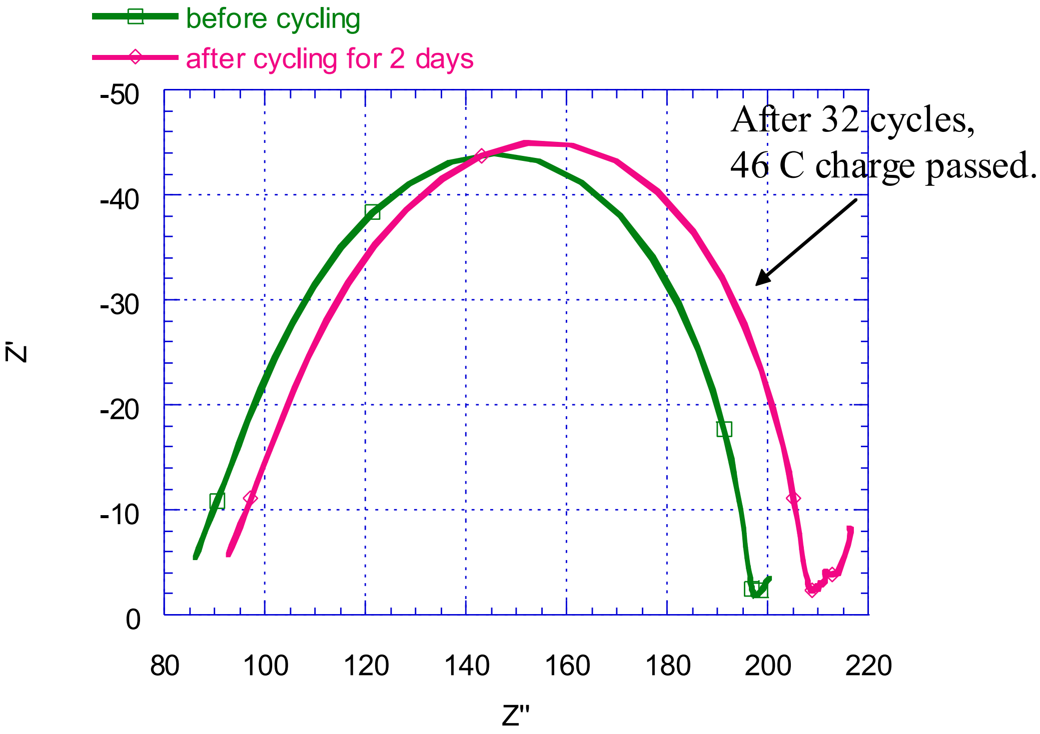

Salt diffusion coeficient for PETMO3/LiTFSI
25 -27 C
40 C
60 C
85 C
Ds (cm/s)
3.5 10^{-8}
3 10^{-8}
2.5 10^{-8}
2 10^{-8}
1.5 10^{-8}
1 10^{-8}
5 10^{-9}
0
10
20
30
40
50
60
O:Li

Figure 5.


before cycling
after cycling for 2 days
After 32 cycles,
46 C charge passed.
Z'
Z''
-50
-40
-30
-20
-10
0
80
100
120
140
160
180
200
220