

# Study of novel lithium salt-based, plasticized polymer electrolytes

Maria Manuela Silva<sup>a</sup>, Sandra Cerqueira Barros<sup>a</sup>, Michael J. Smith<sup>a,\*</sup>,  
James R. MacCallum<sup>b</sup>

<sup>a</sup>*IBQF, Campus de Gualtar, Universidade do Minho, 4710-057 Braga, Portugal*

<sup>b</sup>*School of Chemistry, University of St. Andrews, St. Andrews, UK*

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## Abstract

The results of a preliminary investigation of a series of polymer electrolytes based on a novel polymer host, poly(trimethylene carbonate) (p(TMC)), with lithium triflate or lithium perchlorate and various plasticizing additives, are described in this presentation. Electrolytes with lithium salt compositions of about  $n = 10$  (where  $n$  represents the molar ratio of (O=COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>O) units per lithium ion) and additive compositions between 5 and 15 wt.% (with respect to p(TMC)), were prepared by co-dissolution of salt and polymer in anhydrous solvent with a controlled amount of additive. The homogeneous solutions obtained were evaporated within a preparative glovebox and under a dry argon atmosphere to form thin films of electrolyte.

The solvent-free electrolyte films produced were characterized by measurements of total ionic conductivity, differential scanning calorimetry and thermogravimetry. In general the triflate-based electrolytes were found to show moderate ionic conductivity and good thermal stability while perchlorate-based electrolytes showed higher levels of conductivity but lower thermal stability. Electrolytes based on this host polymer, with both lithium salts, were obtained as very flexible, transparent, completely amorphous films.

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## 1. Introduction

Since the recognition of the potential application of thin film polymer electrolytes in primary and secondary lithium batteries [1], a remarkable research effort has been dedicated to this relatively new sub-domain of solid electrolytes. While initial interest was stimulated by various factors including the processibility of the polymer, the advantageous mechanical properties of solid polymer electrolytes (SPEs), excellent stability (thermal and electrochemical) and the elimination of electrolyte leakage problems, the moderate total ionic conductivity observed with the first generation of these novel materials delayed immediate commercial application.

Attempts to increase the ionic conductivity of second generation SPEs involved the application of various strategies [2–6], including the study of a wide variety of elastomeric host polymers, alternative lithium salts and the use of a range of conductivity-enhancing additives. The conductivity of the so-called “dry” polymer electrolytes is limited by the chain segment mobility which forms the basis of ionic

transport, and consequently the enhancement of conductivity by the addition of low molecular weight compounds to produce “plasticized” electrolytes is a strategy which has been explored by various authors. The use of moderate or large quantities of additives results in the production of gel electrolytes [7–12]. Unfortunately these latter systems often suffer from the same tendency to lose electrolyte, or interfacial and mechanical problems associated with the use of conventional liquid electrolytes [13]. In some examples of the gel electrolyte class, the role of the polymer becomes that of immobilizer rather than the medium through which ionic transport occurs. The choice of the liquid phase for gel electrolyte compositions is critical and must take into account the effect which poor solvent retention by the polymeric immobilizer may have on the level of conductivity and at the electrode/electrolyte interface [14]. The presence of certain plasticizers may also give rise to problems caused by their reaction with the lithium anode. Clearly the advantages of superior ionic conductivity of the plasticized or gel electrolytes are also attenuated by characteristic problems.

The preparation of a dimensionally stable electrolyte with high levels of total ionic conductivity and moderate amounts of low molecular weight additives remains an elusive goal in

\* Corresponding author. Fax: +351-253-678-983.

E-mail address: mjsmith@quimica (M.J. Smith).

SPE development. In this scenario the use of poly(trimethylene carbonate) (p(TMC)) as a host polymer represents an interesting new development as it has a proven capacity to dissolve lithium salts [15], suitable mechanical properties and acceptable thermal stability. The objective of this study was to characterize the effect of relatively low quantities of a variety of plasticizing additives on the ionic conductivity and thermal stability of electrolytes with acceptable mechanical properties.

## 2. Experimental section

### 2.1. Materials

High molar mass p(TMC) ( $3 \times 10^5 \text{ g mol}^{-1}$ ), prepared by catalyzed bulk polymerization and characterized by gel permeation chromatography, was provided by Shell Chemicals, Houston, TX, USA. The elastomeric host polymer was dried before use at  $70^\circ\text{C}$ , under vacuum, for a period of about 7 days. No further purification of the polymer matrix was carried out. Lithium triflate (Aldrich, 95%) and lithium perchlorate (Aldrich, 99.99%) were dried under vacuum at 180 and  $190^\circ\text{C}$ , respectively, for 7 days and then stored in a high integrity, dry argon-filled glovebox. The structures of the selected additives are illustrated in Scheme 1. Trimethylene carbonate (Shell Chemicals, 99%), diethyl phthalate (Lancaster, 99%), propylene carbonate (Aldrich, 99.7%) and dioctyl sebacate (Acros, 95%) were supplied as high purity solids and liquids and were used without further purification.

All subsequent manipulations of salt, electrolyte sample preparations and measurements were carried out under a dry argon atmosphere.

### 2.2. Sample preparation

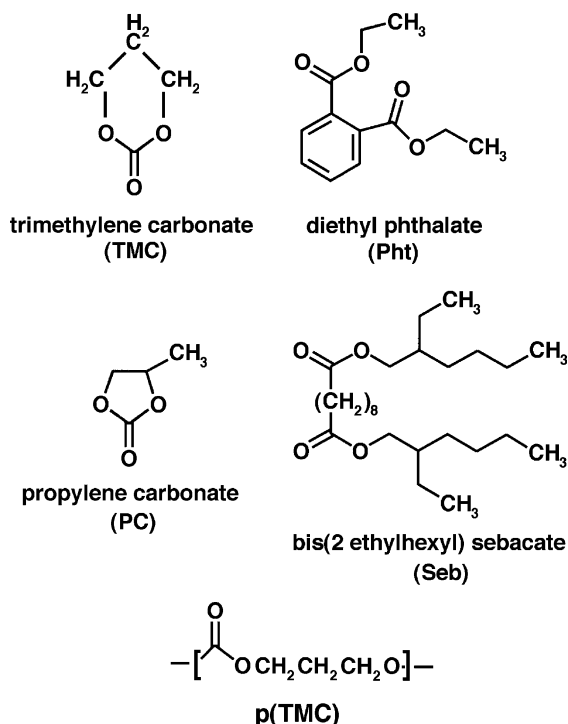
Homogeneous solutions of p(TMC), plasticizing additive and lithium salts in THF (Aldrich, anhydrous 99.9%, inhibitor-free) were prepared by adding known masses of polymer and lithium salt to a small conical flask containing an appropriate mass of additive. A convenient volume of THF was transferred to the flask and the components were stirred for a period of at least 48 h within a dry argon-filled preparative glovebox. The resulting homogeneous solutions were cast into glass rings on glass plates and the solvent was then removed slowly by locating the samples in an isolated chamber within the preparative glovebox. The atmosphere of the chamber was recirculated through a column of molecular sieves to effect a slow evaporation of the solvent and form films of about  $150 \mu\text{m}$  thickness. These films were subjected to a drying procedure in which the temperature was raised from 30 to  $60^\circ\text{C}$  over a period of 3 days. During this period the tube oven was periodically evacuated and purged with dry argon.

### 2.3. Measurements

Total ionic conductivities of electrolyte samples were determined using a constant volume support [16] with gold blocking electrodes located within a Buchi TO 50 oven. The sample temperature was measured with a type K thermocouple placed close to the electrolyte film and impedance measurements were carried out at frequencies between 96 kHz and 500 mHz with a Solartron 1250 FRA and 1286 ECI, between 20 and  $90^\circ\text{C}$ . Measurements of conductivity were effected during heating cycles and at temperature intervals of about  $7^\circ\text{C}$ . The reproducibility of recorded conductivities was demonstrated by cooling the sample and repeating the measurement in a subsequent heating cycle. This procedure confirmed the efficiency of the support operation and mechanical stability of the samples.

Polymer electrolyte film sections were subjected to thermal analysis under a flowing argon atmosphere between  $-40$  and  $350^\circ\text{C}$  and at a heating rate of  $5^\circ\text{C min}^{-1}$  using a Mettler DSC 821e. Sample sections were cut from polymer films and presented for analysis in  $40 \mu\text{l}$  aluminum cans with perforated lids to permit the release of decomposition products.

Samples for thermogravimetric studies were also prepared by cutting sections of suitable dimensions from electrolyte films. These sections were transferred to open platinum crucibles and analyzed using a Rheometric Scientific TG 1000 thermobalance operating under a flowing argon atmosphere. A heating rate of  $10^\circ\text{C min}^{-1}$  was used to analyze all the electrolyte samples.



Scheme 1. Structures of plasticizing additives and host polymer.

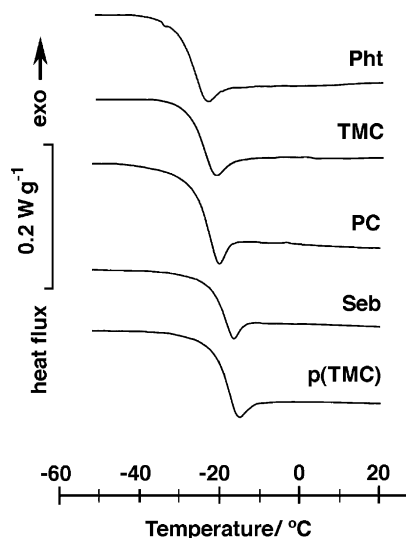


Fig. 1. Glass transitions of p(TMC) host and 15 wt.% plasticizer-p(TMC) compositions.

### 3. Results and discussion

#### 3.1. Thermal analysis

Figs. 1 and 2 are included to illustrate the results of characterization of plasticized polymers and electrolytes by DSC and TGA. This study confirms that all the low molecular weight additives used shifted the host polymer  $T_g$  to lower temperatures and that the electrolytes prepared were amorphous over the range of temperature studied. The  $T_g$ s of electrolyte compositions prepared without plasticizers were found to be higher than that of the pure host polymer. This observation is consistent with the traditional view that interactions between the polymer chains and guest ionic species result in an increased rigidity of the polymer matrix. The addition of any of the plasticizer molecules studied caused a shift of the onset of the  $T_g$  to lower temperatures.

The presence of additive has a variable effect on the thermal events observed at higher temperatures. The nature of this thermal feature has been confirmed by thermogravimetric analysis to be degradative decarboxylation, and the effect of the guest salt on the host polymer is a significant destabilization, in both triflate and perchlorate-based plasticizer-free electrolyte compositions. Rather surprisingly, the addition of plasticizers appears to cause a slight increase in the thermal stability of some electrolytes relative to additive-free materials. This observation has been previously reported [7] in plasticized PEO-based polymer electrolytes. Unfortunately, when the electrolyte composition contains lithium triflate and TMC, one of the most promising salt-plasticizer combinations, the onset of decomposition is reduced and occurs at approximately 208 °C.

At higher temperatures the polymer host matrix degrades through processes which are endothermic in the case of electrolytes based on triflate and endothermic, followed by exothermic events, where the sample contains the perchlorate salt. While these processes apparently place an upper temperature limit on the application of the electrolytes based on p(TMC) in devices, in real applications where the electrolyte is held at high operating temperatures, even at temperatures below the nominal degradation limit, progressive thermal degradation would be expected to occur. For devices operating at temperatures between ambient and about 80 °C the plasticized electrolytes described would however be sufficiently stable.

#### 3.2. Ionic conductivity

Previous studies carried out on p(TMC)-based electrolytes without additives [15] demonstrated that while these materials are good solid-state solvents for a variety of lithium salts, the highest conductivities observed for electrolytes containing lithium perchlorate or lithium triflate are slightly lower than those of comparable materials based on the (ethylene oxide) repeat unit [17]. The introduction of low molecular weight organic molecules into the polymer elec-

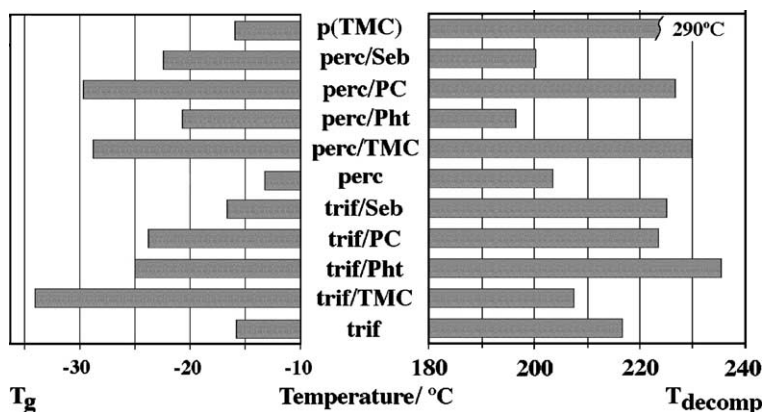


Fig. 2. Glass transition and decomposition temperatures of 15 wt.% salt-plasticizer compositions for  $p(\text{TMC})_n\text{LiClO}_4$  and  $p(\text{TMC})_n\text{LiCF}_3\text{SO}_3$  based electrolytes.

trolyte networks often results in a marked improvement in the observed ionic conductivity of poly(ethylene oxide)-analogue electrolytes [7,18–20]. Although the improvement in conductivity in certain electrolyte systems has been interpreted in terms of plasticization of the polymer structure [18] or an alteration in the ion transport mechanism [20], other effects related to the viscosity of the ionic environment may also contribute. The possibility of the enhancement being caused by an increase in the dielectric constant of the conducting medium, for example, has led to the suggestion [21] that a host polymer with a larger dielectric constant may result in greater ion pair dissociation and hence improved ionic conductivity.

The structure of the p(TMC) host matrix was expected to show a high degree of chemical compatibility with the selected plasticizing additives and indeed some electrolytes with compositions of up to 20 wt.% of these additives were found to be homogeneous with no marked alteration in their mechanical properties. The use of limited quantities of additives was however perceived as a means by which an improvement in ionic conductivity might be achieved without entering the composition range where chemical incompatibilities with

lithium or insertion electrodes or dimensional instability might occur.

The ionic conductivities of the various polymer electrolytes as a function of salt and additive composition are illustrated in Figs. 3 and 4. The results of this study show that the presence of any of the additives caused an increase in the electrolyte conductivity. As may be confirmed by reference to these results, in some systems the greatest enhancement in conductivity was observed in electrolytes with only 5 wt.% additive. In contrast, the increase in ionic conductivity observed with lithium triflate/propylene carbonate, or lithium triflate/bis(2 ethylhexyl)sebacate electrolytes, was directly proportional to the plasticizer content. In this latter electrolyte, at compositions with greater than 15 wt.% additive, the films were found to be mechanically less resistant and less easily manipulated. High plasticizer content films in the lithium triflate/sebacate-based system also showed slight opacity, suggesting that phase separation may eventually occur with this combination. In terms of total ionic conductivity of triflate-based systems the most encouraging results were obtained with the use of the monomer, trimethylene carbonate, as additive. In this electrolyte system a

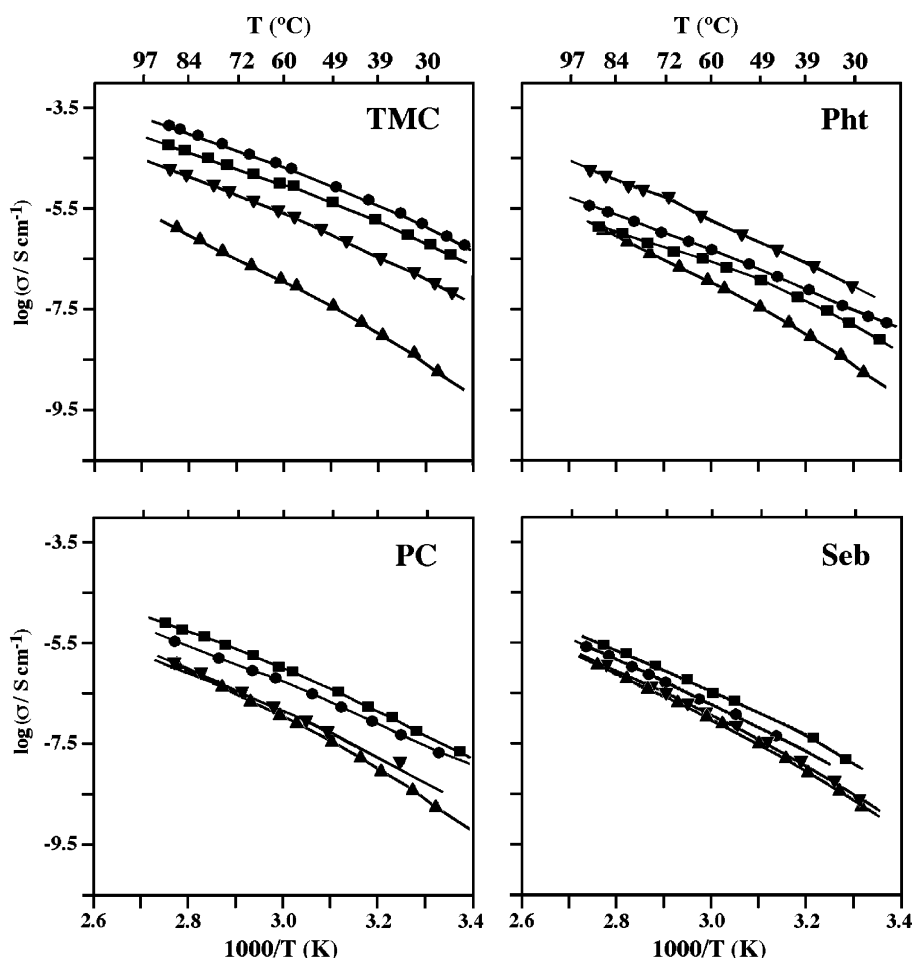


Fig. 3. Variation of  $(TMC)_n$  Li triflate conductivity with temperature, guest salt and additive ((▲) 0 wt.%; (▼) 5 wt.%; (●) 10 wt.% and (■) 15 wt.%).

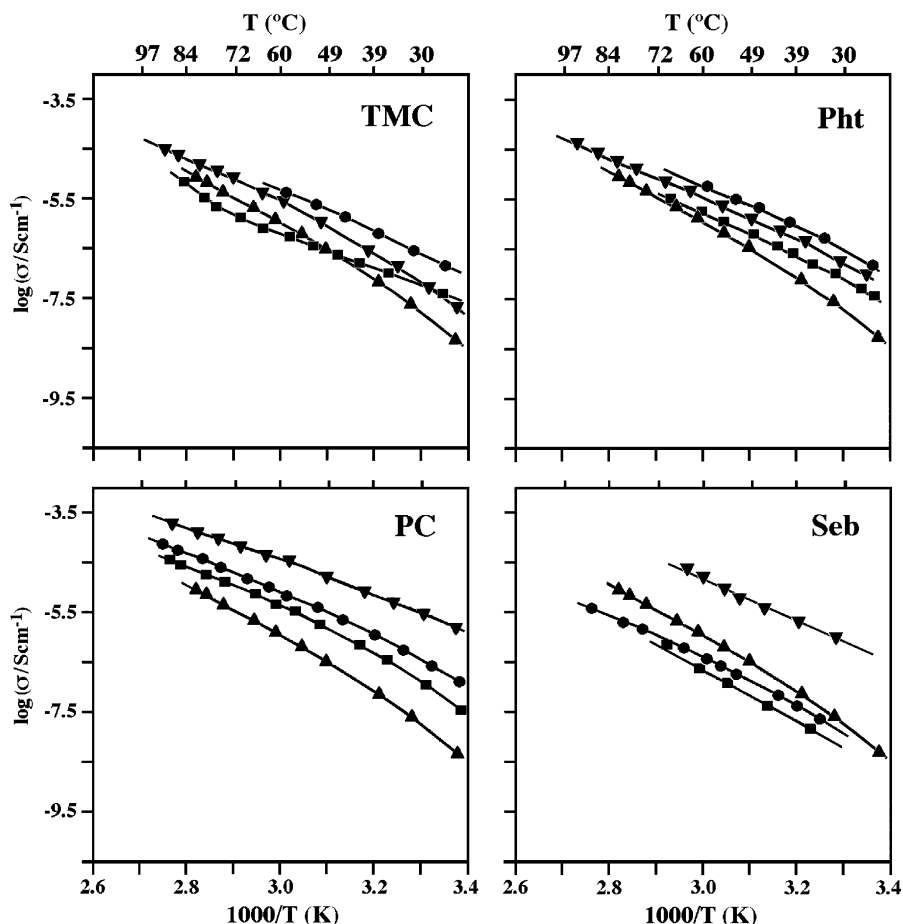


Fig. 4. Variation of  $(\text{TMC})_n$  Li perchlorate conductivity with temperature, guest salt and additive ((▲) 0 wt.%; (▼) 5 wt.%; (●) 10 wt.% and (■) 15 wt.%).

conductivity enhancement by a factor of greater than 100 was observed.

The results illustrated in Fig. 4 confirm that the electrolyte based on lithium perchlorate with propylene carbonate shows a higher conductivity than any other salt–plasticizer combination.

In previous studies [22] of the interrelationship of free volume and ion solvation of electrolytes based on other polymer–salt–plasticizer combinations, Labrèche and Prud'homme concluded that the optimum electrolyte composition was determined by the ability of the plasticizing molecule to compete with polymer structural units in ion complexation. The results observed in the current study of the p(TMC) host polymer are consistent with the model proposed by these latter authors in which the formation of a neutral or charged complex of low mobility was postulated. If small amounts of plasticizer are present in the electrolyte, complexation to both the guest salt species and the host polymer is possible. As the amount of plasticizer is increased an optimum composition is reached in which ion interactions between the solubilizing polymer and the plasticizer are such that ion mobility is maximized. A further increase in plasticizer content may eventually cause displacement of the host polymer by plasticizer molecules within

the salt complexes and a decrease in ionic mobility. The composition at which the optimal salt–plasticizer interaction takes place, for any given host polymer, is likely to depend on the nature of ion–polymer, ion–plasticizer interactions. In the lithium triflate–PC system, for example, the maximum conductivity is observed at a composition with unacceptable dimensional stability. When the same plasticizer was used with lithium perchlorate a high electrolyte conductivity was achieved with only 5 wt.% additive, suggesting that the choice of anion is critical for good conductivity. In certain ternary electrolyte systems it has been possible to interpret the polymer–salt–plasticizer interactions using IR [23] of NMR studies [24] and spectroscopic studies of the plasticized polycarbonate electrolytes are currently underway with the objective of improving our understanding of component interactions.

#### 4. Conclusion

A new host polymer matrix based on polycarbonate rather than polyether coordinating units, with lithium triflate and perchlorate guest species, has been used to prepare plasticized polymer electrolytes. While the conductivity performance of



the electrolytes characterized still falls short of values suitable for lithium battery applications, and that of the best of the amorphous poly(ethylene oxide)-based systems, the use of appropriate quantities of plasticizer has been shown to increase the conductivity of polycarbonate electrolytes to a level which encourages further research into optimization of electrolyte composition. It must however be recognized that the conductivities of the novel materials described only approach levels acceptable for technological applications at temperatures greater than 80 °C, an aspect which may limit the practical importance of these systems. A better understanding of the polymer–salt–plasticizer interactions and optimization of electrolyte composition may lead to the formulation of electrolytes with suitable properties for practical devices.

The results of thermal analysis have confirmed that the new series of polymer electrolytes are completely amorphous. The inclusion of additive in the electrolyte composition allows encouraging levels of conductivity to be achieved at lower salt compositions, relative to the additive-free films. With certain electrolyte compositions the presence of additives also has a useful stabilizing effect on the composite films. The onset of thermal degradation of electrolytes based on lithium perchlorate is however strongly influenced by the amount of salt present in the electrolyte composition. In practical terms this means that a suitable choice of electrolyte composition may provide a useful increase in thermal stability and a significant improvement in the ionic conductivity.

While the polycarbonate electrolytes present adequate mechanical properties, both with and without plasticizing additives, and are capable of dissolving large quantities of lithium salts without phase separation or the formation of polymer–salt complexes, materials which are to be considered as serious candidates for commercial application in primary or secondary cells must also satisfy various other performance parameters. Both chemical and electrochemical compatibility of the electrolytes, relative to the lithium metal electrode, are essential and are dependent on all the electrolyte components. In this respect polymer electrolytes based on lithium triflate [25], with a redox stability window of 4.1 V, are considered to be appropriate for use in primary cells. Lithium perchlorate is also well characterized as a suitable component of both liquid [26] and polymer electrolytes [27]. Although plasticizing additives are included in the electrolyte composition with the objective of enhancing the conductivity performance of the material, the presence of such molecules may be advantageous [19] or deleterious in relation to the electrode stability. The p(TMC) polymer host described in this paper has not yet been characterized, but acyclic alkyl carbonates have already been shown to perform adequately [28] as single solvents for Li-ion cell electrolytes. The materials introduced in this presentation are clearly still at a very preliminary stage in their development and further characterization, including detailed studies of electrochemical stability and the behavior of prototype cells based on optimized electrolyte compositions, is certainly

necessary to determine the extent to which their potential may be realized.

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