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# Scalable plasticized polymer electrolytes reinforced with surface-modified sepiolite fillers – A feasibility study in lithium metal polymer batteries

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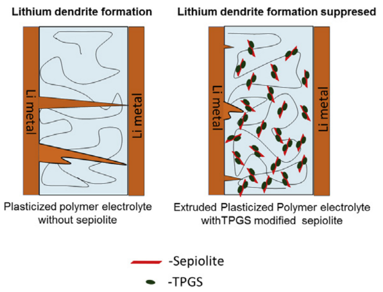
## HIGHLIGHTS

- Polymers having high RT conductivity of the order of $10^{-4}$ S/cm.
- Electrochemical stability of 4.5 V at 70 °C with good mechanical stability.
- Remarkable lithium plating/stripping characteristics with dendrite suppression.
- Good cycling capabilities for $LiFePO_4$ based Li metal polymer batteries.
- Easily upscalable Polymer electrolytes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Electrochemical properties of (polyethylene oxide) (PEO)/lithium trifluoromethanesulfonate (LiTf)/ethylene carbonate (EC)/sepiolite extruded composite electrolytes were studied. Appreciable electrochemical stability of 4.5 V at 70 °C was observed for polymer composite membranes with D-α-tocopherol-polyethylene glycol 1000 succinate-coated sepiolite fillers. Lithium plating/stripping analysis indicated no evidence of dendrite formation with good interfacial properties which were further confirmed by postmortem analysis of the cells. Solid state NMR studies show the presence of two $Li^+$ population in the membranes. The feasibility of these electrolytes has been shown with $LiFePO_4$ cathode materials. Initial discharge capacity of 142 mAh/g was observed remaining at 110 mAh/g after 25 cycles with a coulombic efficiency of 96%. The upscaling of these polymers can be easily achieved by extrusion technique and the capacity can be improved by varying the cathode architecture.

## 1. Introduction

Polymer electrolytes attract increasing interest because of their potential application as electrolytes in Li ion batteries. The main advantages of soft polymeric electrolytes are their toughness and flexibility, ease of fabrication into thin film of desirable sizes and the ability to form good electrode/electrolyte contact. Using Li

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metal as anode is to provide higher energy density, but its reactivity with liquid electrolytes to form passivation layers gives poor material utilization [1,2], while the formation of dendrites [3–6] on charge and other uncontrolled phenomena lead to serious safety problems. Therefore, research progresses have been focused on the development of solid state electrolytes with both high ionic conductivity and limited reactivity with lithium metal anodes.

As a rule, polymer electrolytes on their own, though shapeable, versatile, flexible, tough, light weight and processable, have low room temperature (RT) ionic conductivity ($\sigma$) in the range of $10^{-6}$ to $10^{-8}$ S•cm$^{-1}$ due to low effective carrier mobility. In the particular case of polyethylene oxide (PEO) and in the temperature range 0 °C to 60 °C this low carrier mobility is caused by the large crystalline fraction ($\chi_c \approx 60$ wt%) below the polymer melting temperature ($T_m \approx 65$ °C) and by the slow $T_g$-controlled relaxation of the amorphous fraction, this last feature being common to all polymers even if molten because of their macromolecular nature. Several strategies aimed at improving RT conductivity while preserving the inherent advantages of polymers have been explored in the last two decades, the main focus being on plasticization or gelling [7–11]. Though gels may show liquid-like RT conductivity in the range $10^{-2}$ to $10^{-4}$ S/cm by blending low molecular weight compounds with a polymer matrix, leakage problems and pressure build up were reported over consecutive cycling [12,13]. A plasticized polymer electrolyte was shown to be promising by Sun et al. [14] due to its high ionic conductivity, but poor mechanical stability was a hindering factor.

It has been recently shown that it is possible to prepare highly plasticized polymer electrolytes with high RT conductivity by melt mixing of PEO, ethylene (EC)- or propylene carbonate (PC), and lithium triflate (LiTf) [15,16]. At wt % ratios of 46/40/14 these electrolytes were found to have $\sigma \approx 0.9\ 10^{-3}$ S/cm at 30 °C, however in the absence of a physical crosslinker they lacked a solid-like dimensional stability. The addition of 5 wt% of sepiolite fibers with appropriate surface modification (TPGS-S) [17] preserves the high RT conductivity, making the electrolyte solid-like even over 80 °C, i.e. well above the PEO $T_m$. Herein the electrochemical properties of these plasticized PEO composite electrolytes have been studied while addressing the feasibility of these electrolytes in Li metal polymer secondary batteries.

## 2. Materials

PEO ($M_w = 5 \times 10^6$ g mol$^{-1}$), lithium triflate salt (LiTf) obtained from Aldrich and sepiolite from TOLSA S.A., were dried under vacuum for 24 h. EC, polyethylene glycol (PEG, $M_w = 1000$ g mol$^{-1}$) and D-$\alpha$ tocopherol polyethylene glycol 1000 succinate (TPGS), both from Aldrich, were used as received.

The modifications on the sepiolite were carried out by mixing sepiolite with TPGS water solution, by means of a lab dissolver (Dispermat LC2) operating at 10,000 rpm for 20 min. The resulting suspension was dried in an oven at 100 °C overnight. The final product called TPGS-S was further washed and dried at 100 °C [16,17].

The polymer composites were prepared by extrusion. After premixing the components, they were melt-compounded in a Haake minilab extruder. Processing was carried out at a shear rate of 80 rpm for 25 min at 120 °C. The extruded composites were hot pressed at 75 °C into films 100 μm thick and used for all the studies. $LiFePO_4$ (Aleees, Taiwan), Carbon black (Csp-Imerys®) and PVDF-HFP (Solvay) were dried and used to prepare self-standing cathode membranes.

## 3. Characterisation

### 3.1. Thermogravimetric analysis (TGA)

Dynamic TGA experiments under air atmosphere were carried out in a TA Q-500, from 25 °C to 800 °C at a heating rate of 10 °C/min. The samples were circular discs of 5 mm diameter which were cut from the original compression molded films.

### 3.2. Electrochemical characterisation

The ionic conductivity of the electrolytes was determined by electrochemical impedance in a NOVOCONTROL GmbH Concept 40 broadband dielectric spectrometer in the temperature range −80 °C to 80 °C and in the frequency range between 0.1 and 107 Hz, using gold electrodes. The electrochemical stability of the electrolytes was determined using linear sweep voltammetry (LSV) at 70 °C. Cells were scanned from 1 to 5 V with a sweep rate of 10 mV/s in coin cells (CR2032) using a stainless steel disc as the working electrode, a lithium disc as counter and reference electrode. Li plating/stripping studies were carried out using symmetric cells with polymer membranes sandwiched between two Li discs as non-blocking electrodes. Galvanostatic cycling studies were done using $LiFePO_4$ self-standing membranes as positive electrode. Pvdf-HFP was used as a binder and Carbon black (Csp®) as a conductive additive. The self-standing cathode membranes were hot pressed on to the polymer electrolyte and the final electrode + electrolyte thickness was around 115 μm. Li metal foil was used as the negative electrode. Cells were assembled in an Ar filled glove box. Once assembled, the cells were cycled between potential window of 2.8–3.9 V. All electrochemical measurements were carried out using a VMP3 (Biologic®, Claix, France) system.

### 3.3. Scanning electron microscopy analysis (SEM)

SEM (Hitachi SU-8000) has been used to characterise the nanofiller dispersion and also inspect the morphology of PEO crystallization in the composite electrolyte membranes. Post-mortem analysis was carried out using a FEI quanta$^{Tm}$ 250 to study the interface between Li metal and polymer electrolyte.

### 3.4. Solid state NMR experiments

All magic angle spinning nuclear magnetic resonance (MAS-NMR) spectra were recorded with a Bruker Avance III 500 spectrometer working at a frequency $\nu_o = 500.24$ MHz and $\nu_o = 152.56$ MHz for $^1H$ and $^7Li$. The non-selective $\pi/2$ pulse durations were 2.5, and 3 μs for $^7Li$ and $^{19}F$ spectra. Rotor-synchronized echo experiments were carried out for the $^{19}F$ spectra in order to avoid interferences with $^{19}F$ background signals. The spectra were referenced using solid LiF as with $^{19}F$ resonating at −204 ppm and $^7Li$ to −1 ppm.

## 4. Results and discussion

The systematic investigation of optimal formulation performed in previous work [15–17] allowed identifying a group of polymer electrolytes which possessed high RT conductivity, a solid like behaviour at T > 70 °C, and that could be easily prepared by extrusion. These electrolytes appear in Table 1.

Electrolytes without TPGS-S, namely samples S17 and S18, do not display a rheological pseudo solid behavior, and hence do not show dimensional stability in the temperature interval of interest (up to 70 °C). Electrolyte samples S20 and S23 do behave as pseudo solids, being S23, which contains a 10wt% of TPGS-S, more rigid