Final Report

NOVEL, SOLVENT-FREE, SINGLE ION CONDUCTING POLYMER ELECTROLYTES

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14. ABSTRACT

The work carried out within this project has lead to the development of new types of dual composite PEO-based electrolytes having outstanding properties. This also, and particularly, applies to the new member of the family discussed in this report, i.e. the electrolyte formed by the combination of a calyx(6)pyrrole, CP anion-trapping compound with a large anion lithium salt, such as lithium bis(oxalate) borate, LiBOB. The results here described show that this combination gives rise to PEO-based polymer electrolytes having excellent transport properties. Polymer electrolyte membranes of the PEO20LiBOB(CP)0.125 composition have in the 80°C temperature range a lithium transference number of about 0.5 (versus the 0.3 value of conventional PEO systems) and an ionic conductivity of the order of 0.001 Scm-1.

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AWARD-GRANT# FA8655-05-1-3011

INTERIM REPORT#1

February 1st-August 30, 2006

Summary

In this second year, the research work has been addressed to the investigation of the electrochemical properties of composite polymer electrolytes formed by adding calixpyrrole (CP) to ceramic powder- added PEO-LiX-based polymer electrolytes. Following the results obtained last year, we have selected as model system the $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolyte membrane. i.e. the electrolyte which has shown the highest value of lithium transference number, see 2005 progress report. Past results demonstrated the unique role of the CP component in enhancing the lithium ion transference number of the polymer electrolyte. In this year the work has been extended by further optimizing the electrolyte configuration. In particular, a highly surface functionalized ceramic, i.e. super-acid zirconia, has been dispersed in the electrolyte mass, in order to form ceramic-added composite $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolytes. The basic idea is to enhance the lithium ion transport by the promoting action of the ceramic additive, with the final goal of obtaining a new family of PEO-based, solvent-free polymer electrolytes having high values of lithium ion transference number combined with high conductivity. The preliminary results obtained in these first six months of research confirm the validity of this approach.

1.Introduction

In the 2005 reports we have shown that the addition of 1,1,3,3,5,5,-mezo-heksaphenil-2,2,4,4,6,6,-mezoheksamethytl calyx[6]pyrrole, hereby simply indicated as calixpyrrole (CP), to PEO-LiX based electrolytes greatly enhances the lithium ion transference number. This is associated to the X^- -anion-blocking-action of this macromolecule. In this year the work has been extended by further optimizing the electrolyte configuration. In particular, a highly surface functionalized ceramic, i.e. super-acid zirconia, hereby simply indicated as $S\text{-}ZrO_2$, has been dispersed in the electrolyte mass, in order to form ceramic-added composite $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolytes. The basic idea is to enhance the lithium ion transport by the promoting action of the ceramic additive, with the final goal of obtaining a new family of composite PEO-based, solvent-free polymer electrolytes having high values of lithium ion transference number combined with high conductivity. To test the validity of this concept, we have selected as model system the $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolyte membrane, to which different amounts of S-ZrO_2 have been added. In this first report we illustrate the conductivity behavior of these ceramic-added composite electrolyte samples.

2.Experimental.

Calixpyrrole (CP), provided by the University of Warsaw, $LiCF_3SO_3$ (Aldrich), PEO (600,000 MW, Aldrich reagent grade) were dried under vacuum at 45 °C, 60 °C, 100°C, and 80 °C, respectively. Zirconia, obtained by Mell Chemical in the form of S-$Zr(OH)_4$ was heat treated at 500 °C to turn it into the desired superacid version, S-ZrO_2.

Three samples, varying by the amount of dispersed S-ZrO_2 , were considered; their composition and acronym are reported in Table 1.

Electrolyte sample composition	Percentage of dispersed zirconia	Acronynm
$P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$	0	PEO-CP-SZ-0
$P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ + S-ZrO_2	5	PEO-CP-SZ-5
$P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ + S-ZrO_2	10	PEO-CP-SZ-10

Table 1. Composition of the polymer electrolyte samples investigated in this work

All the samples were prepared by a hot-pressing, solvent-free, synthesis originally developed and optimized in our laboratory. This unique synthesis procedure, which leads to totally solvent-free electrolyte samples, was described and reported in the 2005 progress reports. Figure 1 illustrates in scheme its basic steps.

The conductivity of the various electrolyte samples was measured by an impedance spectroscopy analysis of cells formed by sandwiching the given electrolyte sample between two stainless-steel blocking electrodes. The cells were housed in a Buchi owen to control the temperature. A Solartron impedance response analyzer was used for the measurement which were extended over a 10Hz-100kHz frequency range.

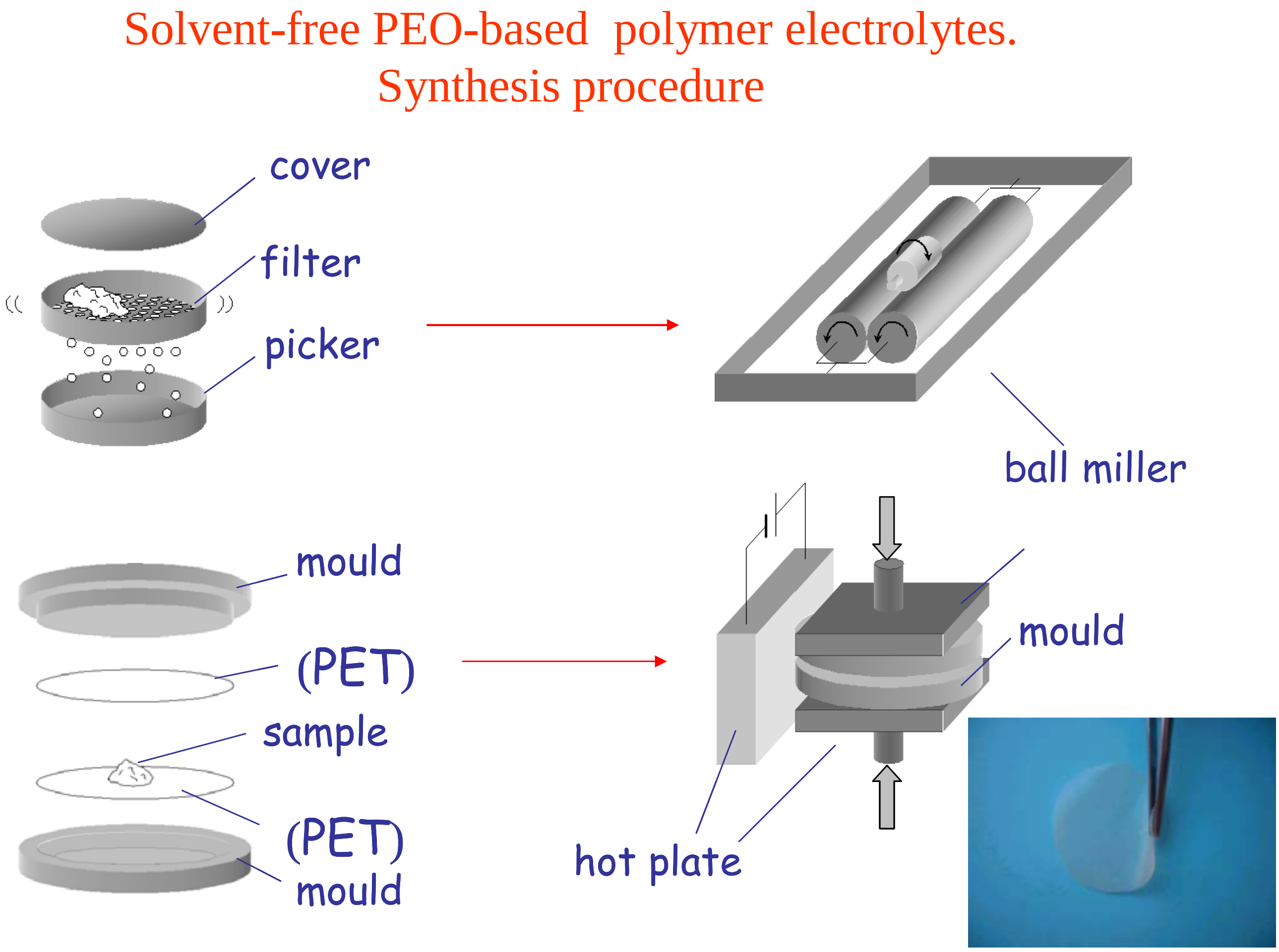

Figure 1. Scheme of the synthesis procedure of the solvent-free polymer electrolyte samples listed in Table 1.

3.Results.

Figure 1A shows in comparison the Arrhenius plot of a ceramic-free PEO-CP-SZ-0 polymer electrolyte with that of a S-ZrO_2-added, composite PEO-CP-SZ-5 polymer electrolyte. The addition of the ceramic filler has indeed a beneficial effect since clearly enhances the conductivity of the composite electrolyte, which is higher than that of the plain in all the entire high temperature range. The improvement in conductivity may be explained on the basis of interactions between the ceramic surface states and both the PEO chains and the lithium salts.

These interactions weaken the attraction force between the lithium ions and the oxygen atoms, this favoring lithium ion motion and thus, ultimately the ionic conductivity of the electrolyte. This increase in conductivity is a stable effect, as demonstrated by Figure 1B which shows the Arrhenius plot of the composite PEO-CP-SZ-5 sample determined with heating an cooling scans. The two scans overlap, this confirming that the transport properties are not affected by thermal excursions.

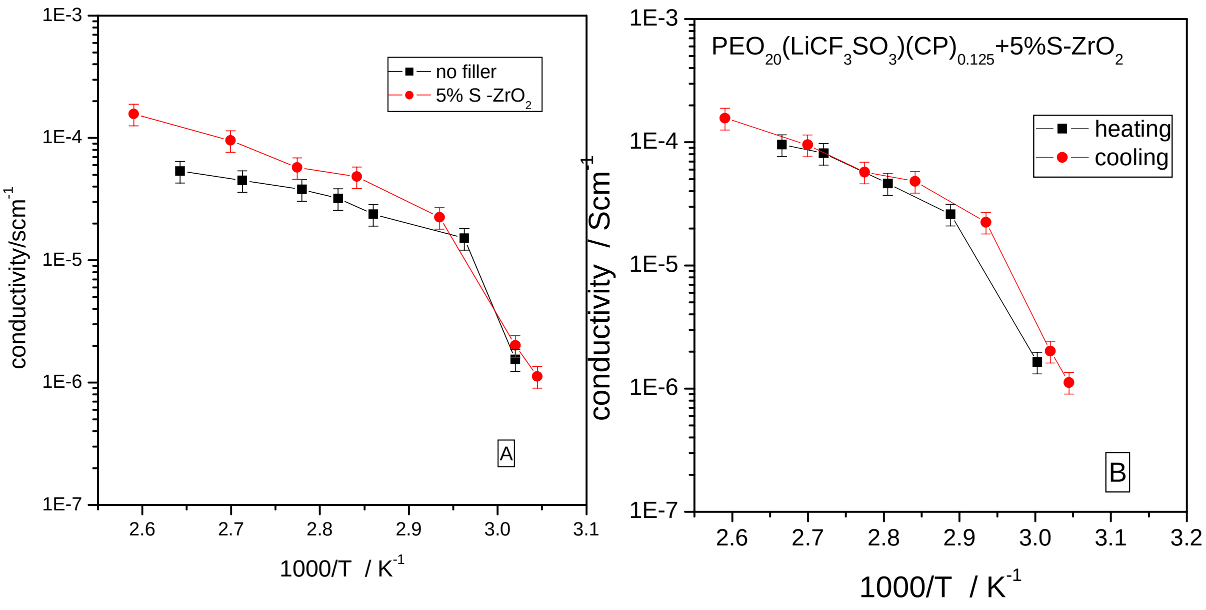

Figure 1*- Conductivity Arrhenius plots of a ceramic free P(EO)$_{20}$LiCF$_3$SO$_3$ (CP)$_{0.125}$ polymer electrolyte and of a composite P(EO)$_{20}$LiCF$_3$SO$_3$ (CP)$_{0.125}$ +5%S-ZrO$_2$ polymer electrolyte (A); conductivity Arrhenius plots of the composite P(EO)$_{20}$LiCF$_3$SO$_3$ (CP)$_{0.125}$ +5%S-ZrO$_2$ polymer electrolyte determined in heating and cooling scans (B) . Data obtained by impedance spectroscopy.*

Enhancement in conductivity have also been obtained with the sample PEO-CP-SZ-10 at higher content of the S-ZrO$_2$ ceramic additive, see Figures 2A and 2B.

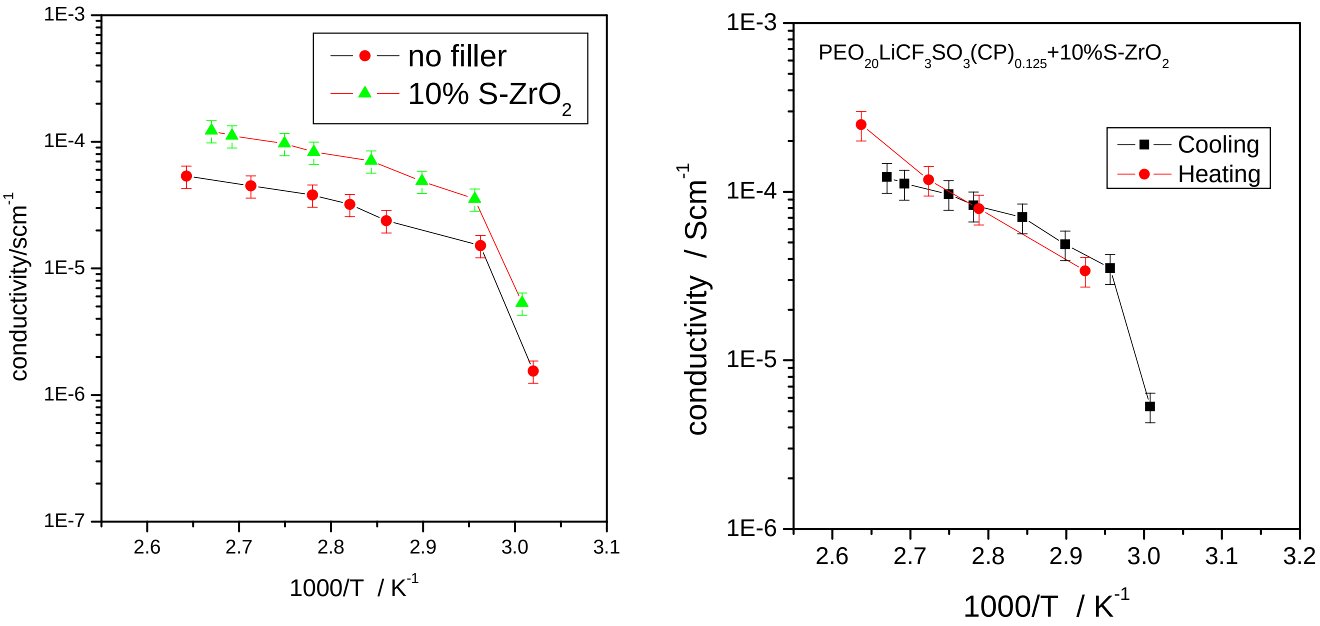

Figure 2- *Conductivity Arrhenius plots of a ceramic free* $P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125}$ *polymer electrolyte and of a composite* $P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125}$ *+10%S-*ZrO_2 *polymer electrolyte and conductivity Arrhenius plots of the composite* $P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125}$ *+10%S-*ZrO_2 *polymer electrolyte determined in heating and cooling scan .*
Data obtained by impedance spectroscopy.

Figure 3 reports in comparison the Arrhenius plots of the three samples studied in this work. The conductivity promotion effect exerted by the ceramic filler is clearly evidenced, with an extent which increases with increasing the ceramic content. This suggests to extend the investigation to samples containing higher weight percent of ceramic filler, to define the composition most effective in terms of conductivity enhancement. This work is in progress in our laboratory and will be discussed in the next progress report.

Conclusion and future work.

The results of this first part of the project demonstrate that the addition of a surface functionalized ceramic such as acid zirconia, S-ZrO_2 to $P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125}$ electrolytes, results in consistent enhancement of the ionic conductivity. This is an interesting result which shows the route for developing a new class of PEO-based, composite, solvent-free polymer electrolytes which combine high lithium ion transference number (as induced by the CP component) with high ionic conductivity (as promoted by the S-ZrO_2 ceramic component).

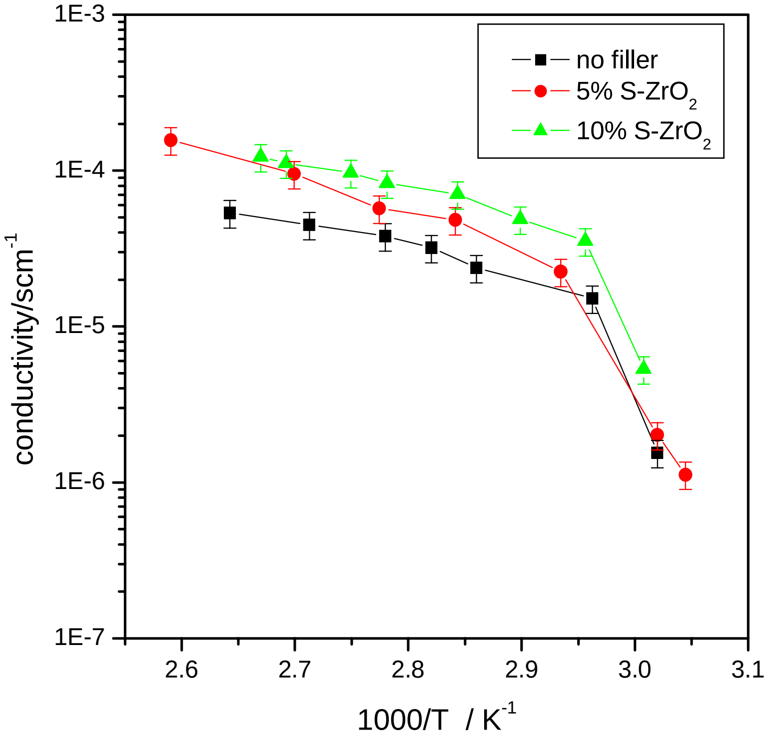

Figure 3- *Conductivity Arrhenius plots of the three polymer electrolyte samples developed in this work, namely the ceramic free* $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ *and the two composite* $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ +5%S-ZrO_2 *and* $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ +10%S-ZrO_2 . *Data obtained by impedance spectroscopy.*

For instance the conductivity at 90 °C passes from 4.2 x 10^{-5} Scm^{-1} to 6.8 x 10^{-5} Scm^{-1} and 9.7 x 10^{-5} Scm^{-1} moving from sample PEO-CP-SZ-0 to PEO-CP-SZ-5 and to PEO-CP-SZ-10. These results appear of practical relevance since polymer electrolytes having the above properties, to our knowledge, were never reported before. Accordingly, the future work will be addressed to the completion of the characterization of these new materials, by further establishing the role of the two additives, i.e. CP and S-ZrO_2, in promoting transport properties, both in terms of lithium ion transference number and of ionic conductivity.

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AWARD-GRANT# FA8655-05-1-3011

INTERIM REPORT#2

September1st- December 31, 2006

Summary

In this second report we describe the progresses obtained in the investigation of the electrochemical properties of composite polymer electrolytes formed by adding calixpyrrole (CP) to ceramic powder- added PEO-LiX-based polymer electrolytes. Following the results reported in the 2006 1st progress report, we have selected as model system the $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolyte membrane, to which different amounts of . highly surface functionalized ceramic, i.e. super-acid zirconia, $S\text{-}ZrO_2$, have been dispersed , in order to form ceramic-added $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ + $S\text{-}ZrO_2$ electrolytes. The basic idea is to obtain novel types of PEO-based, solvent-free, dual-composite polymer electrolytes, where the ceramic additive enhances the lithium ion transport and the CP additive increases the lithium ion transference number. The results obtained in this second semester, mainly directed to the evaluation of the best reciprocal composition of the electrolyte additives and to the determination of its lithium ion transference number, definitely confirm the validity of this approach, already outlined in a preliminary form by the results reported in the 1st progress report.

1.Introduction

Lithium polymer electrolytes have attracted great interest due to their potential application in batteries designed for powering hybrid vehicles. Among others, the systems based on the combination between poly(ethylene oxide), PEO and a lithium salt. LiX, are the most popular examples of polymer electrolytes of practical relevance. Major research efforts have been devoted worldwide to optimize these electrolytes, especially in view of increasing the lithium ion transference number, since a low value of this parameter reflects in concentration polarizations which in turn depress the limiting current and thus, the power density of the lithium battery.

Various attempts to reach this goal have been reported in the literature. A promising one is the addition of anionic receptors, such as boron, to the polymer matrix; however, this generally resulted in serious depression of the electrolyte ionic conductivity. In the 2005 reports we have shown that the addition of 1,1,3,3,5,5,-mezo-heksaphenil-2,2,4,4,6,6,-mezoheksamethytl calyx[6]pyrrole, hereby simply indicated as calixpyrrole (CP), to PEO-LiX based electrolytes greatly enhances the lithium ion transference number. This is associated to the X^- -anion-blocking-action of this macromolecule. The work in 2006 has been directed to a further optimization of the electrolyte configuration, carried out by by dispersing a highly surface functionalized ceramic, i.e. super-acid zirconia, hereby simply indicated as S-ZrO_2. The basic idea is to form dual-composite $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$+ S-ZrO_2 electrolytes, where the CP additive increases the lithium ion transference number and the ceramic additive enhances the lithium ion conductivity. To test this concept, we have selected as model system the $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolyte membrane, to which different amounts of S-ZrO_2 have been added. In the first progress report we have shown that the conductivity of these dual-composite electrolytes is indeed quite high. In this second progress report we confirm the validity of the concept by optimizing the reciprocal composition of the electrolyte components and demonstrating the high value of the lithium transference number of selected samples.

2.Experimental.

Calixpyrrole (CP, provided by the University of Warsaw), $LiCF_3SO_3$ (Aldrich), PEO (600,000 MW, Aldrich reagent grade) were dried under vacuum at 45 °C, 60 °C, 100°C, and 80 °C, respectively. Zirconia, obtained by Mell Chemical in the form of S-$Zr(OH)_4$ was heat treated at 500 °C to turn it into the desired superacid version, S-ZrO_2.

Five samples, having constant $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ composition but varying by the amount of dispersed S-ZrO_2 , were considered. Their total compositions and the corresponding acronyms are reported in Table 1. All the samples were prepared by a hot-pressing, solvent free synthesis originally developed in our laboratory and described in details in the 1st progress report. Figure 1 illustrates the typical appearance of one of these membrane

Electrolyte sample composition	Percentage of dispersed zirconia	Acronynm
$P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125}$	0	PEO-CP-SZ-0
$P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125} + S\text{-}ZrO_2$	5	PEO-CP-SZ-5
$P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125} + S\text{-}ZrO_2$	10	PEO-CP-SZ-10
$P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125} + S\text{-}ZrO_2$	15	PEO-CP-SZ-10
$P(EO)_{20}LiCF_3SO_3\ (CP)_{0.125} + S\text{-}ZrO_2$	20	

Table 1. Composition of the polymer electrolyte samples investigated in this work

Figure 1. Typical appearance of a CP- and $SZrO_2$-added $PEO_{20}LICF_3SO_3$ composite membrane.

The conductivity of the various electrolyte samples was measured by an impedance spectroscopy analysis of cells formed by sandwiching the given electrolyte sample between two stainless-steel blocking electrodes. The cells were housed in a Buchi owen to control the temperature. A Solartron impedance response analyzer was used for the measurement which were extended over a 10Hz-100kHz frequency range.

The lithium ion transference number was determined by the technique introduced by Bruce and co-workers: a constant dc voltage was applied across a symmetrical Li/sample/Li cell and the current was monitored through the cell until it reached a steady state, constant value.. An impedance analysis was carried out immediately before and after the application of the dc voltage to estimate the effect of changes of the passive layer resistance at the Li electrode interface. The cell was left to thermally equilibrate for at least one day before each measurement.

The transference number T_{Li+} was calculated by the following equation:

$$T_{Li+} = \frac{I_{ss}(\Delta V - R_o I_o)}{I_o(\Delta V - R_{ss} I_{ss})} \qquad [1]$$

where I_o is the initial current , I_{ss} is the steady state current, ΔV is the applied voltage, R_o and R_{ss} are the initial and final resistances, respectively, of the passive layer onto lithium metal electrodes.

3.Results.

Figure 2 shows in comparison the Arrhenius plots of the conductivity of a ceramic-free PEO-CP-SZ-0 polymer electrolyte with that of the various S-ZrO_2 -added, dual composite polymer electrolytes. The measurement was extended in a temperature range varying from 40 to 100 °C. As already shown in the 1st Progress Report, the addition of S-ZrO_2 into polymer electrolyte significantly enhances the conductivity of the dual-composite electrolytes, which is higher than that of the S-ZrO_2-free electrolyte in the entire high temperature range: in particular, the conductivity of the PEO-CP-SZ-15 sample shows an almost six fold increase over the measured temperature region. This improvement in conductivity may be explained on the basis of interactions between the ceramic surface states and both the PEO chains and the lithium salts. These interactions weaken the attraction force between the lithium ions and the oxygen atoms, this favoring lithium ion motion and thus, ultimately the ionic conductivity of the electrolyte.

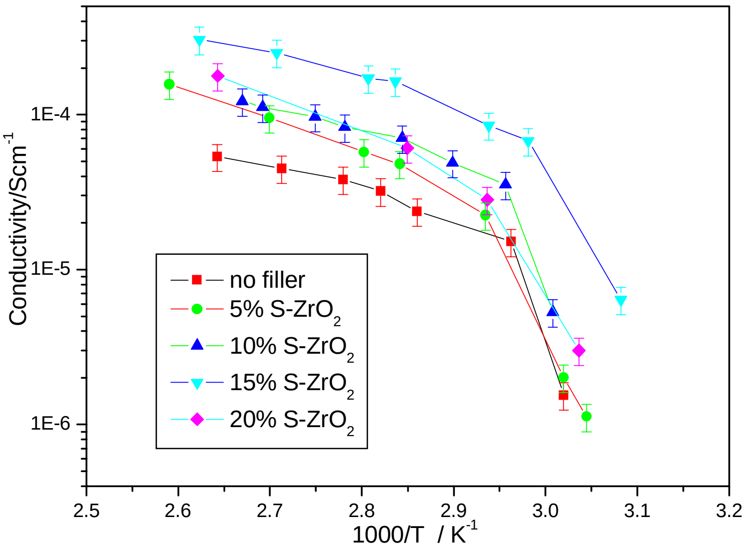

Figure 2- Arrhenius plots ionic conductivity for $PEO_{20}LiCF_3SO_3(CP)_{0.125}$ *electrolytes with and without* $S\text{-}ZrO_2$ *ceramic filler. Data obtained by impedance spectroscopy.*

Figure 3 shows the conductivity at 70 °C versus the $S\text{-}ZrO_2$ content of the various samples examined in this work. The conductivity increases with increasing ceramic content; however, the trend inverts at15% $S\text{-}ZrO_2$, probably due to a percolating ion blockage. Thus, the PEO-CP-SZ-15 appears to be the sample of choice on which to concentrate further characterization.

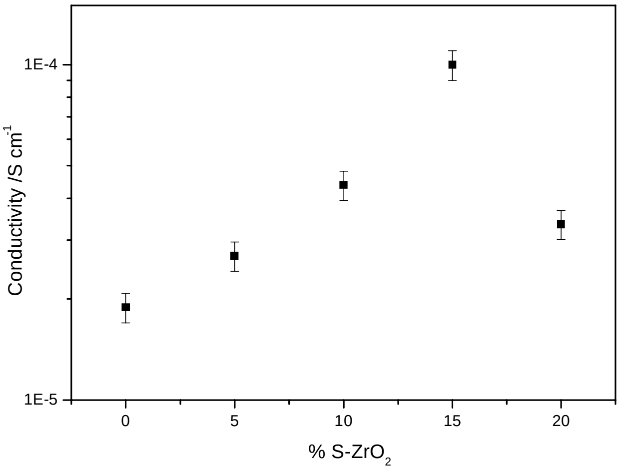

Figure 3- Conductivity versus $S\text{-}ZrO_2$ *content for the polymer electrolyte samples investigated in this work .70 °C . Data obtained by impedance spectroscopy.*

According to the procedure suggested by Bruce and co-workers, the lithium ion transference number, T_{Li}^{+}, of this electrolyte was measured by a combination of dc and ac polarizations. Figure 4(A) illustrates the chronoamperometic curve obtained at 70 °C by applying a 30 mV dc pulse across a Li / PEO-CP-SZ-15/ Li cell. This curve shows the value of the initial current I_o, and that of the steady state I_{ss} current that flow through the cell. It can be seen that the I_{ss}/I_o ratio is about 0.6 , this being a preliminary but firm suggestion that the value of T_{Li}^{+} is indeed high in this PEO-CP-SZ-15 electrolyte.

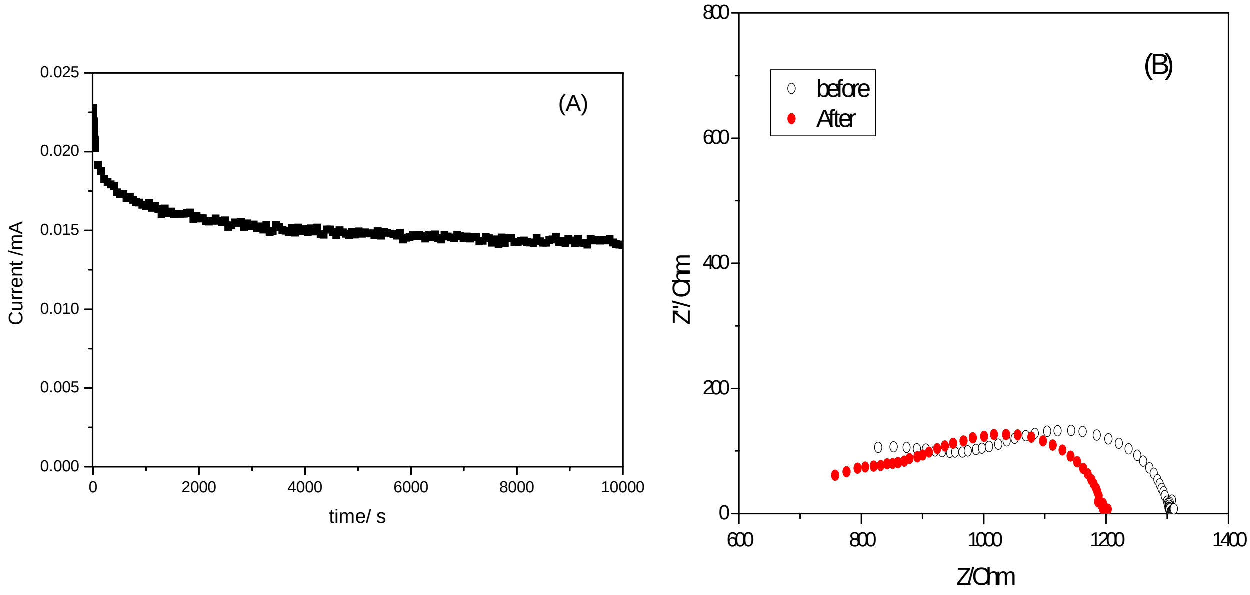

Figure 4 (A) Current time curve at 70 °C of a cell Li/ PEO-CP-SZ-15/Li cell (B) Impedance response of the same cell before and after dc polarization test.

Figure 4(B) shows the impedance plots of the cell before and after the dc polarization test. The spectra evolve along two convoluted semicircles, associated to the passive layer resistance and to the interface charge transfer, respectively. The de-convolution of the spectra was made using the nonlinear squares fit software which allowed to extract the initial R_o and the final R_{ss} passive layer resistance values. The T_{Li+} of the PEO-CP-SZ-15 electrolyte sample was then determined by using equation [1] to be 0.54 at 70 °C. This value is indeed much greater than that of standard PEO-based electrolytes which generally does not exceeds 0.3 .

Conclusion and future work.

The results reported in the 2006 two progress reports demonstrate that the addition of a surface functionalized ceramic such as acid zirconia, S-ZrO_2, to $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolytes, results in a consistent enhancement of the ionic conductivity. To our opinion this is an interesting result which opens the path for developing new class of PEO-based, dual-composite, solvent-free polymer electrolytes which combine high lithium ion transference number (as induced by the CP component) with high ionic conductivity (as promoted by the S-ZrO_2 ceramic component). For instance, a selected example of this class, i.e. the $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$+ 15% S-ZrO_2 has at 70 °C a conductivity of 1×10^{-4} Scm^{-1} and a lithium ion transference number of 0.54. These results appear of practical relevance since solvent-free, polymer electrolytes having the above properties, to our knowledge, were never reported before. The future work within this Project will be addressed to test these new electrolytes as separators in advanced, rechargeable lithium polymer batteries.

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AWARD-GRANT# FA8655-05-1-3011

INTERIM REPORT#3

January 1st- May 31, 2007

Summary

In the previous report we described the preparation and the properties of polymer electrolytes formed by the dispersion in a PEO-LiX based matrix of two additives, i.e.: i) 1,1,3,3,5,5,-mezo-heksaphenil-2,2,4,4,6,6,-mezoheksamethytl calyx[6]pyrrole, hereby simply indicated as calixpyrrole (CP), which acts as anion trapper and ii) highly surface functionalized, super-acid zirconia, S-ZrO_2, ceramic which acts as transport promoter. The basic idea was to obtain novel types of PEO-based, solvent-free, dual-composite polymer electrolytes, where the CP additive increases the lithium ion transference number and the ceramic additive enhances the lithium ion transport. The results obtained on model electrolytes of the $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ composition with different additions of the S-ZrO_2 ceramic, confirmed the validity of the approach since the effects of the S-ZrO_2 ceramic in rising the conductivity to a level of 1 x 10^{-4} Scm^{-1} at 70°C and of the CP in enhancing the lithium ion transference number to a value of 0.54, were clearly demonstrated . These results appear of practical relevance since to our knowledge solvent-free, polymer electrolytes having the above properties, were never reported before. Accordingly, the work of this semester has been addressed to the verification of this prevision. For this purpose, the new electrolytes were tested as separators in advanced, rechargeable lithium polymer batteries. The results confirm that the electrolytes are effectively very promising for the progress of the lithium battery science and technology.

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1.Experimental.

Calixpyrrole (CP, provided by the University of Warsaw), $LiCF_3SO_3$ (Aldrich), PEO (600,000 MW, Aldrich reagent grade) were dried under vacuum at 45 °C, 60 °C, 100°C, and

80 °C, respectively. Zirconia, obtained by Mell Chemical in the form of S-Zr(OH)$_4$ was heat treated at 500 °C to turn it into the desired superacid version, S-ZrO$_2$.

A hot pressed, solvent free PEO$_{20}$ LiCF$_3$SO$_3$(CP)$_{0.125}$ + 15% S-ZrO$_2$ composite membrane, previously discussed and characterized in our laboratory (see 2nd Progress Report) was chosen as selected electrolyte. This electrolyte was tested as separator in a battery assembled by sandwiching a lithium metal foil anode, the selected polymer electrolyte membrane and a LiFePO$_4$-based composite cathode film. The latter was prepared by blending the LiFePO$_4$ active material (80%) with Super-P carbon as the electronic conducting additive (10 mass %) and PVdF 6020 Solvay Solef(10 mass %) as the binder. The battery was fabricated using an amount of cathode active mass in order that a cycling current of 0.22 $Ag^{-1}cm^{-2}$ should correspond to a rate of 1C. The components of the cell were placed in a Teflon container with two stain-less steel electrodes used as the current collectors. Care was taken to avoid direct contact between metallic Li anode and a Teflon container. All assembling and testing procedures were done in a controlled, argon atmosphere, dry-box, having both humidity and oxygen content below 10 ppm.

The battery was characterised by galvanostatic cycling at temperatures varying from 80°C to 100 °C and in a 3.0-3.8 V voltage range.. The performance of the battery was evaluated in terms of specific capacity, charge/discharge efficiency and cycle life. Before the measurements, the battery was kept at the highest testing temperature, i.e at about 110 °C for at least 36 h to reach the thermal equilibrium, as well as to allow lithium diffusion inside the cathode film. The operating temperatures of the battery were controlled by a Buchi oven and data acquisition was done by using the Maccor 1400 battery tester.

Results

A dual composite polymer electrolyte, i.e. PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2, was chosen as the electrolyte for the fabrication of a new type of lithium rechargeable battery using lithium iron phosphate as the preferred cathode.

The choice of the electrolyte was motivated by the favorable results of our previous study which outlined the practical relevance of the PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2 dual composite membrane in terms of lithium ion transference number, reported as high as 0.5, and of ionic conductivity, reported of the order of 10^{-4} Scm^{1} (see 2nd Progress Report). The choice of the cathode was motivated by its operating voltage which falls within the electrolyte stability limit.

The charge-discharge process of the battery is the following:

$$Li^{+} + FePO_4 + e \underset{\text{discharge}}{\overset{\text{charge}}{\leftrightarrows}} LiFePO_4 \qquad [1]$$

to which is associate a maximum , theoretical capacity of 170 $mAhg^{-1}$ and a voltage plateau evolving around 3.4 V Li/Li^{+}.

Figure 1 shows some typical voltage profiles of the lithium polymer battery cycled at 100 °C and at a C/0.8 rate. The voltage evolves along the 3.5V plateau expected on the basis of process [1]. The capacity, referred to the cathode, is of the order of 140 $mAhg^{-1}$, i.e. approaching 80% of the theoretical value.

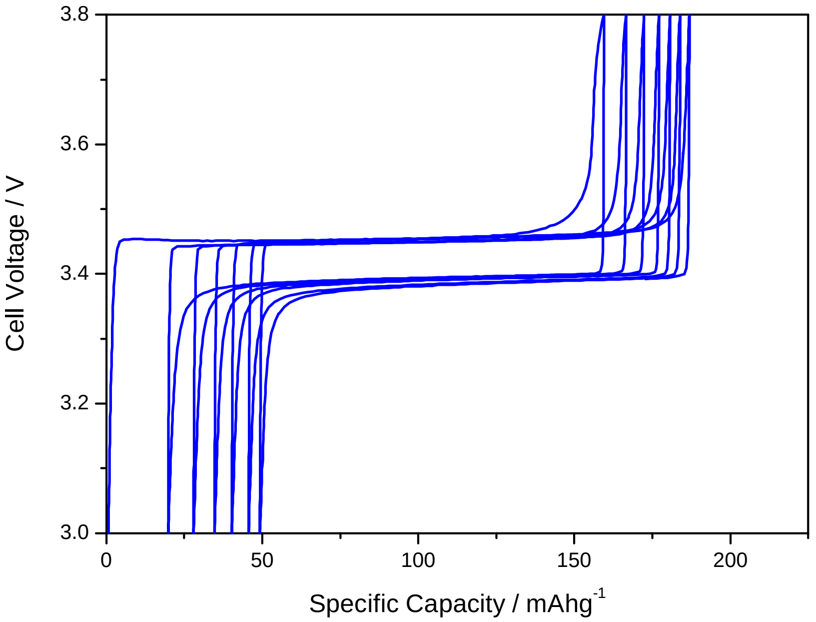

Figure 1. Typical voltage vs. specific capacity profiles of some consecutive cycles at 100°C of the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2/Li_4FePO_4 polymer battery at C/8 rate, corresponding to a current density of 0.075 $mAcm^{-2}$.

Figure 2 shows the evolution of the specific capacity versus cycle number at different rates. Some interesting conclusions can be driven from this result. First, one notices a low initial charge-discharge efficiency. This can be due to various phenomena, such as i) decomposition of the electrolyte with the formation of a passivating layer on the anode surface, and ii) to the formation of barrier potential due to anion accumulation at the vicinity of the anode-electrolyte interface may hinder the lithium ion motion during the subsequent discharge. The latter phenomena may take place whenever the C-rate changes: the largest the C-rate, the largest the barrier potential and *vice versa*. The full identification of the causes of the initial capacity decay, however, remains to be established.

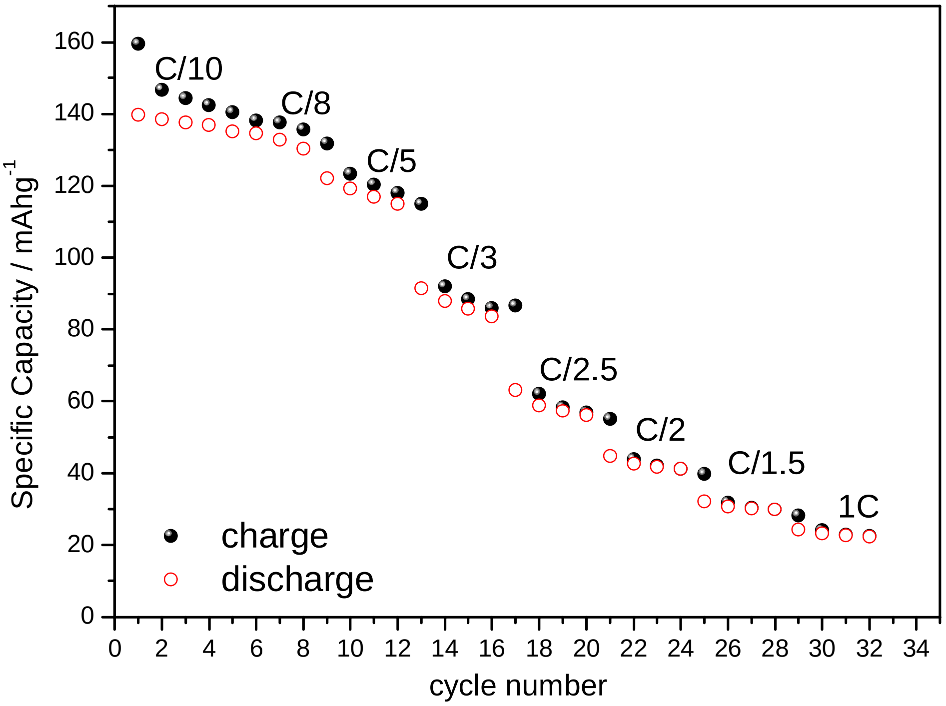

Figure 2. Capacity versus cycle number of the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15%ZrO_2/Li_4FePO_4 polymer battery at 100 °C and at various rates

Figure 2 also evidences the good rate capability of the battery which can operate at high charge-discharge efficiency over all the tested rates. This is further confirmed by Figure 3 which shows the trend of the specific capacity versus the current density and versus the reciprocal of the cycling rate. The capacity declines linearly up to a current density of 0.15 $mAcm^{-2}$ to then abruptly decay. Thus, 0.15 $mAcm^{-2}$ may be assumed as the limited current density. It is important to point out that this value is higher than that routinely obtained for conventional Li polymers batteries, reported to be of the order of 0.1 $mAcm^{-2}$. The high value of the limiting diffusion current density found for the battery examined in this work is associated with the high lithium ion transference number of the selected polymer electrolyte.

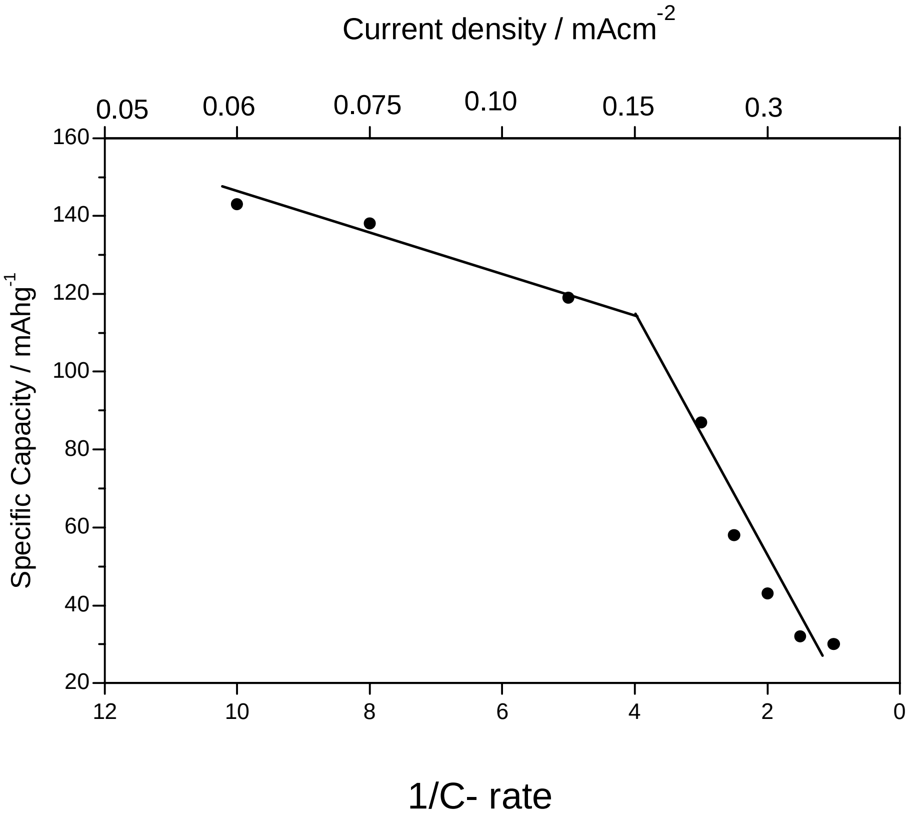

Figure 3 . Specific capacity vs current density and the reciprocal 1/C rate for the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S- ZrO_2/Li_4FePO_4 polymer battery at 108 °C

The response of the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2/Li_4FePO_4 battery was also studied at various temperatures. Accordingly, the battery was cycled at 108 °C at C/8 rate, then the temperature was lowered and maintained at the new value for several hours to reach the thermal equilibrium before the test restart. Figure 4, which summarizes the charge/discharge results, shows that the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2/Li_4FePO_4 battery can be cycled with a satisfactory value of capacity only when the temperature is higher than 93 °C. The capacity decay at lower temperature may be attributed to various factors, the main being the decay of the ionic conductivity of the polymer electrolyte. There are promising evidences, however, of further improvements of the battery performance for low power applications.

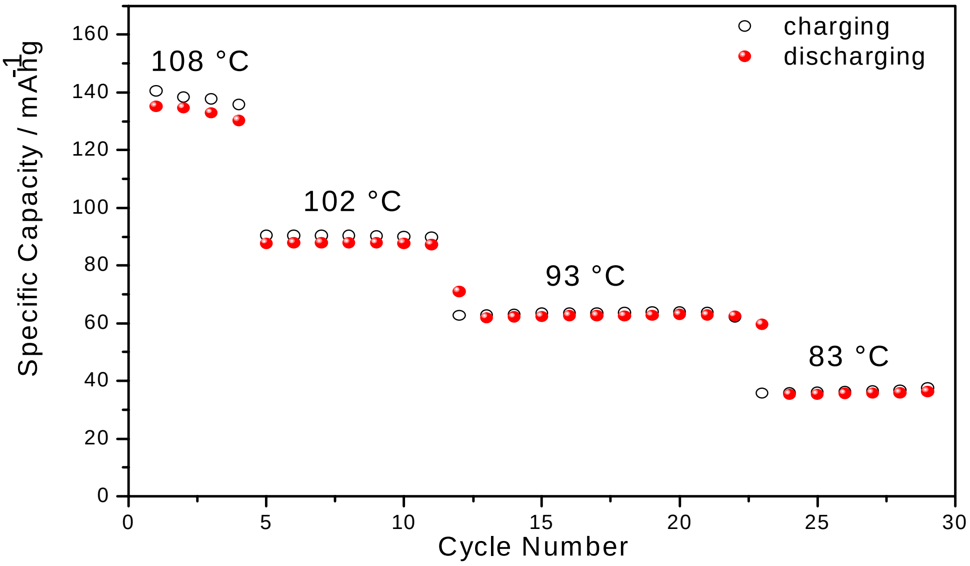

Figure 4. Specific capacity vs cycle number for the the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S- ZrO_2/Li_4FePO_4 polymer battery at various temperatures and at a C/8 rate.

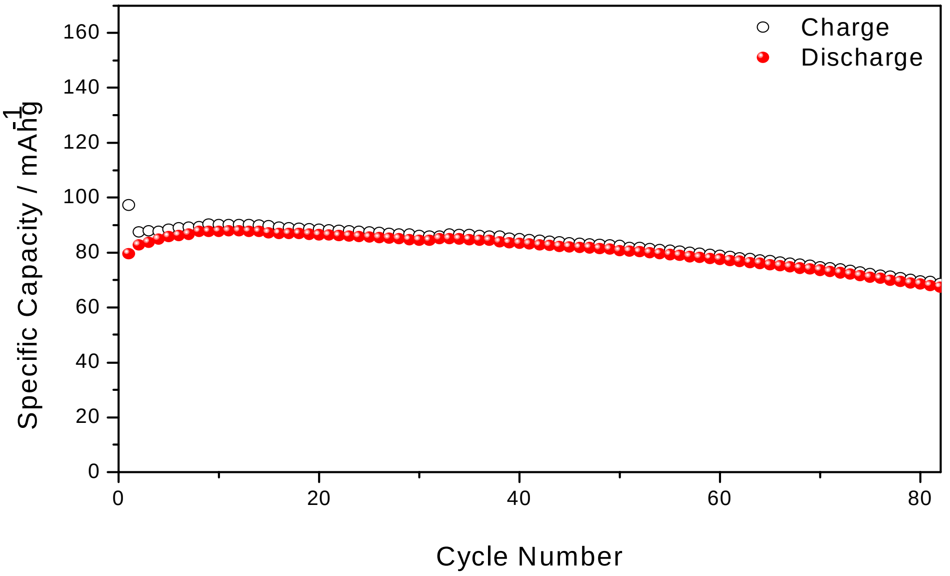

Figure 5. Cycling performance of the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2/Li_4FePO_4 polymer battery at 102 °C and at C/8 rate (Current density: 0.075 $mAcm^{-2}$).

Figure 5 shows the cycling performance of the Li/ PEO_{20} $LiCF_3SO_3(CP)_{0.125}$ + 15% S-ZrO_2/Li_4FePO_4 battery under the best operating conditions, i.e., at ~100 °C and at C/8 rate. A charge/discharge efficiency approaching 100 % and a capacity of the order of 90 $mAhg^{-1}$ were obtained. These values are of interest and confirm the practical importance of the dual-composite polymer electrolyte for battery application.

Conclusion and future work.

The work described in this report demonstrate the applicability of the selected $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolyte as a separator in a rechargeable lithium battery using lithium iron phosphate as cathode. This considering, further work will be directed in the next semester to confirm this important result by exploring whether dual electrolytes using other lithium salts than $LiCF_3SO_3$ have similar performance. Work will be also addressed to the optimization of the cell with the aim of further improving the battery performance.

NOVEL, SOLVENT-FREE, SINGLE ION CONDUCTING POLYMER ELECTROLYTES

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Summary

In the previous reports we have demonstrated the applicability in lithium batteries of the new, solvent-free, dual-composite polymer electrolytes developed in the course of this project and formed by dispersing in a PEO- LiX based matrix two additives, one being 1,1,3,3,5,5,-mezo-heksaphenil-2,2,4,4,6,6,-mezoheksamethytl calyx[6]pyrrole, hereby simply indicated as calixpyrrole (CP), which acts as anion trapper (thus enhancing the lithium ion transport) and the other an highly surface functionalized, super-acid zirconia, S-ZrO_2, ceramic which acts as transport promoter (thus enhancing the ionic conductivity).

In particularly, we have selected a $P(EO)_{20}LiCF_3SO_3$ $(CP)_{0.125}$ electrolyte and used it as separator in a rechargeable lithium battery based lithium iron phosphate as cathode. We showed in the 3rd progress report that this battery is capable to deliver a high specific capacity at reasonably high rates, as well as a good cycling life. In this last part of the project we have extended the investigation by exploring whether dual electrolytes using other lithium salts than $LiCF_3SO_3$ have similar performance in the new types of rechargeable lithium batteries. In this report we describe the results obtained with a dual electrolyte based on a poly(ethylene oxide)-lithium bis(oxalate) borate, PEO-LiBOB, combination and used as separator in a Li/$LiFePO_4$ battery.

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1.Experimental.

Calixpyrrole (CP, provided by the University of Warsaw), LiBOB (Libby) and PEO (600,000 MW, Aldrich reagent grade) were dried under vacuum at 45 °C, 40 °C and 150°C, respectively. Zirconia, obtained by Mel Chemical in the form of super acid $Zr(OH)_2$ was heat treated at 500 °C for two hours to turn it into the desired super acid version, S-ZrO_2 (SZ) and then vacuum dried at for 6 hours prior to use. The electrolyte components were carefully sieved and then introduced in their correct proportion inside sealed polyethylene bottles and thoroughly mixed by soft ball-milling for at least 24 hours to obtain homogeneous mixture of powders.

.Three polymer electrolyte samples where prepared and tested, all with the same PEO to LiBOB and PEO-LiBOB to CP ratios and varying by the amount of the ceramic additive, i.e. SZ.

The composition of these samples and their acronyms are shown in Table 1

Membrane sample (acronym)	Composition
PEO	$(PEO)_{20}LiBOB(CP)_{0.125}$
PEO-5%	$(PEO)_{20}LiBOB(CP)_{0.125}$+5%SZ
PEO-10%	$(PEO)_{20}LiBOB(CP)_{0.125}$+10%SZ

Table 1 : Composition and acronym of the polymer electrolyte samples prepared in this project.

The samples were prepared by varying the amount of dispersed SZ. The preparation was carried out following a procedure established in our laboratory. To avoid any contamination with the external ambient, all the samples were prepared in a controlled argon atmosphere having a humidity content below 10 ppm and were removed from the dry box for any further test only after housing them in sealed coffee bag envelopes.

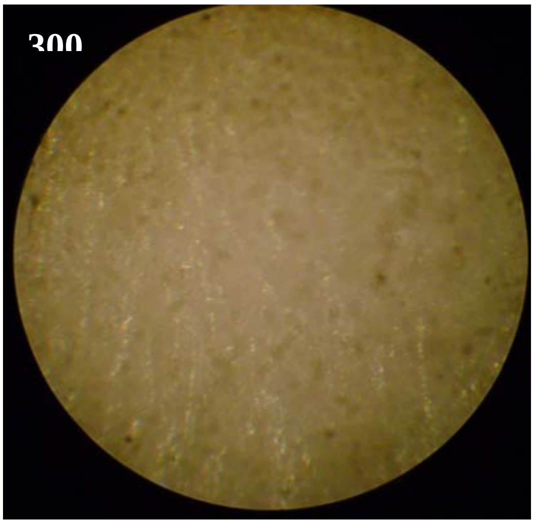

Figure 1-
Typical surface appearance of a $P(EO)_{20}LiBOB$ $(CP)_{0.125}$ dual composite polymer electrolyte membranes prepared in this project.

Homogeneous rigid membrane samples, having thickness ranging from 50 to 300 micrometers were obtained after hot pressing. They were stored in an argon filled dry box for subsequent measurements. Figure 1 shows the surface appearance of one of them chosen as a typical example, i.e. the $(PEO)_{20}LiBOB(CP)_{0.125}$ membrane. The optical picture clearly shows the homogeneity of the membrane, which is maintained in all the samples prepared in this work.

The Differential Scanning Calorimetric (DSC) study was performed using a Mettler DSC calorimeter. The samples were prepared in an argon filled dry box by sealing polymer electrolyte pieces (about 2 mg) in aluminum pans. They were heat treated at 100 °C for 1 hour and stored for 7 days at room temperature before scanning. Care was taken to use the same thermal history for all samples. The scanning tests were done under a nitrogen flow at 5 °C/ min heating rate in the 25 °C-120 °C temperature range.

The ionic conductivity measurements were performed by ac impedance spectroscopy. The conductivity cells were prepared by housing electrolyte membrane samples having an 8 mm diameter in a Teflon O-ring and sandwiching them between two blocking stainless steel electrodes. The O-ring circles the membrane sample such as to maintain fix sample thickness throughout the measurement. The cells were heated to about 100 °C and kept at this temperature for 24 hours to reach the thermal equilibrium. The measurements were made in the 100-40 °C temperature range on both cooling and heating scans. The cells were maintained at a given temperature for 24 hours to thermally equilibrate them before each measurement.

The Li/electrolyte/$LiFePO_4$ cells were assembled by sandwiching a lithium metal foil, the polymer electrolyte membrane and the $LiFePO_4$ composite cathode film. The latter was prepared by blending the $LiFePO_4$ active material (80%) with Super-P carbon as the electronic conductor (10 mass %) and PVdF 6020 Solay Solef(10 mass %) as a binder. The components of the cell were placed in a Teflon container having two stain-less steel plates as the current collectors. Care was taken to avoid direct contact between the Li anode and the Teflon container. All the assembling and the testing procedures were done in a controlled, argon atmosphere dry-box having both humidity and oxygen content below 10 ppm.

The cells were characterized by galvanostatic cycling in the 3.0-3.8 V range at different current densities and at different temperatures (80-1000 °C). The performance of the cells were evaluated in terms of specific capacity, charge/discharge efficiency and cycle life. Prior to the tests, the cells were kept at the highest testing temperature, i.e about 100 °C, for at least 36 h to reach the thermal equilibrium as well as to allow the diffusion lithium salt inside the cathode film. The operating temperature of the cell was controlled by a Buchi oven and the data acquisition was done by using the Maccor 1400 battery tester.

Results.

Figure 2 shows the DSC response of the three polymer electrolyte samples prepared in this project, see Table 1. The figure provides an useful comparison between the response of the SZ filler-free membrane and those containing different amounts of filler. A double peak feature is noticed for the curves associated with the ceramic-added samples. This may be associated to the influence of the ceramic filler on the melting process. However, overall the difference between the various samples is minor and this suggests that the dispersion of the SZ filler does not significantly influence the level of the amorphous content of the $(PEO)_{20}LiBOB(CP)_{0.125}$ polymer electrolyte. This is not surprising since the amorphicity is already promoted by the large lithium salt BOB anion and thus, a low effect by the filler is expected.

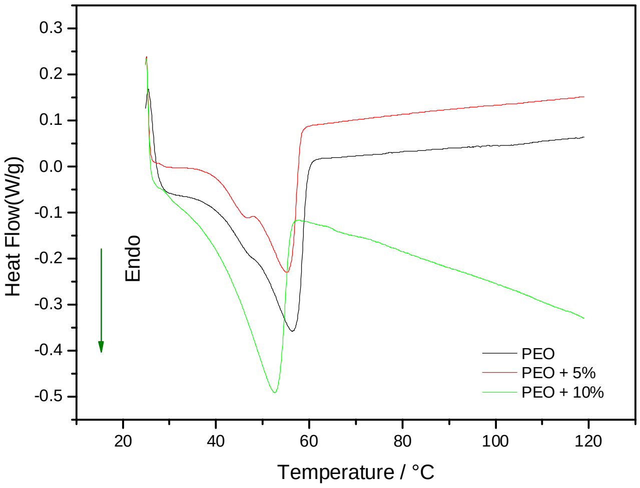

Figure 2 .
DSC response of the three polymer electrolyte samples prepared in this project, see Table 1 for sample identification

Table 2 summarizes the thermal data derived from the DSC analysis. For comparison purpose, also the data related to a CP-free, PEO-LiBOB membrane, that underwent comparable thermal history, are reported. The data of Table 2 confirm the above discussed scarce influence of the ceramic filler on the thermal properties of the electrolytes. Indeed, their melting temperature, Tm, does not significantly change passing from SZ-free to SZ-added membranes. However, the presence of calixpyrrole significantly modifies both Tm and ΔH_m and thus, it is reasonable to assume that, in addition to the large BOB anion, also the CP macromolecule contributes to enhance the amorphous content of the polymer. This further explains why the effect of SZ cannot be relevant in this respect.

Sample	Tm (°C)	$\Delta H_m (Jg^{-1})$
$P(EO)_{20}LiBOB(CP)_{0.125}$	56	61
$P(EO)_{20}LiBOB(CP)_{0.125}$ +5% SZ	55	54
$P(EO)_{20}LiBOB(CP)_{0.125}$ +10% SZ	53	58
$P(EO)_{20}LiBOB$	45.5	95

Table 2. Thermal data of $P(EO)_{20}LiBOB\ (CP)_{0.125}$ polymer electrolytes with and without addition of the SZ filler.

The lithium transference number, T_{Li}^{+}, of the CP-added polymer electrolyte sample, i.e. the $PEO_{20}LiBOB(CP)_{0.125}$ membrane, was determined by DC polarization test combined by impedance spectroscopy, see previous reports. A value of T_{Li}^{+} in the range of 0.50-0.60 was found. The value of T_{Li}^{+} for the pristine $PEO_{20}LiBOB$ electrolyte is of the order of 0.25-0.30. Thus, it is clear that the addition of CP has significantly increased the lithium transport.

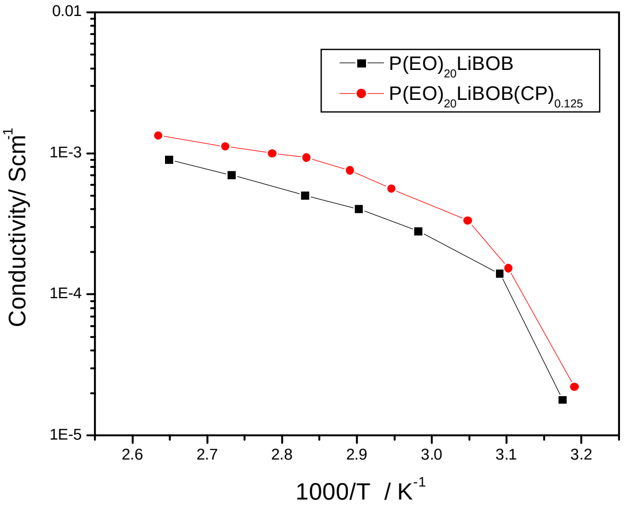

Figure 3.
Arrhenius plots of the ionic conductivity of the $P(EO)_{20}LiBOB$ and of $P(EO)_{20}LiBOB\ (CP)_{0.125}$ polymer electrolyte membranes.

Figure 3 shows the Arrhenius plots of the ionic conductivity of the membranes with and without addition of CP. The comparison between the two plots shows that the addition of

CP has not depressed the conductivity of the electrolyte but even partly raised it. This is probably associated to the already discussed effect of CP in promoting the amorphous content of the polymer. The results of Figure 3 is important since it shows that the unique combination of an anion trapping agent, CP, with a large anion lithium salt, LiBOB, leads to composite polymer electrolytes having a high lithium transference number without depression in ionic conductivity. This is a rare event, which makes the $PEO_{20}LiBOB(CP)_{0.125}$ membrane of considerable interest for practical applications.

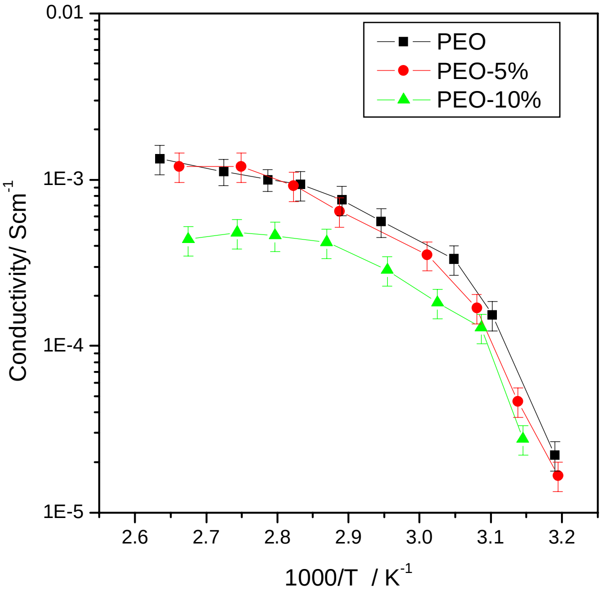

Figure 4-
Arrhenius plots of the ionic conductivity of the $P(EO)_{20}LiBOB$ and of $P(EO)_{20}LiBOB\ (CP)_{0.125}$ polymer electrolytes with and without addition of the SZ filler.

Figure 4 compares the conductivity Arrhenius plots of the CP-added polymer electrolytes with and without addition of the SZ ceramic filler. We notice that the filler has no positive effects on the conductivity but rather depresses it when added at high concentration. This is not surprising in view of the already discussed competition with the lithium salt: the large BOB anion promotes by itself the amorphous character of the polymer, this vanishing any possible contribution by the filler which then is present as inert component and, under this condition, may even depress the conductivity by blocking the percolation channels.

In a previous report we have shown that the dual composite electrolytes may efficiently act as separators in new types of rechargeable lithium batteries. It is than appeared to us of importance to extend the investigation on the LiBOB-based electrolyte family, especially considering the favourable transport properties outlined above. We have selected the $PEO_{20}LiBOB(CP)_{0.125}$ membrane as the representative of the family and tested this electrolyte in a prototype lithium cell using lithium iron phosphate as cathode:

$Li / PEO_{20}LiBOB(CP)_{0.125}/LiFePO_4$ [1]

The electrochemical process of this cell is expected to be the cycling lithium de-insertion-insertion in lithium iron phosphate:

$xLi + LiFePO_4 \leftrightarrows (1-x) Li + Li_{(1-x)} FePO_4$ [2]

to which is associated a theoretical specific capacity of 170 $mAhg^{-1}$. This is also the maximum capacity of the battery which, using an excess of lithium anode, is cathode limited.

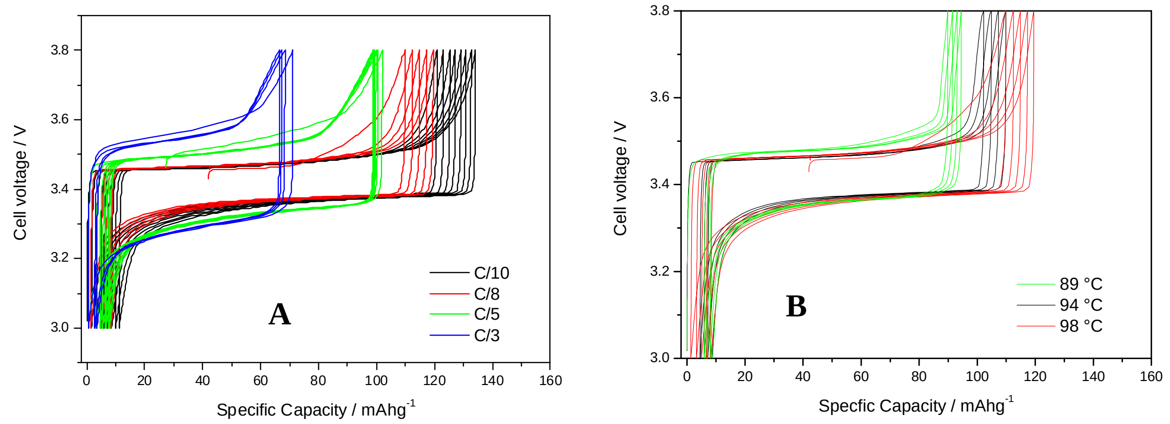

Figure 5- Voltage versus specific capacity profiles of consecutive cycles of the Li/ $P(EO)_{20}LiBOB (CP)_{0.125}/LiFePO_4$ battery at different rates (**A**) and at different temperatures (**B**).

Figure 5 shows some typical voltage profiles obtained at various C rates (Figure 5A) and at various temperatures (Figure 5B) . The two-phase, flat voltage plateaus evolving around 3.4V which are typical of the lithium iron phosphate process, are easily distinguishable. At C/10 rate, a specific capacity of the order of 120 $mAhg^{-1}$, i.e. 70% of the theoretical, is obtained. As expected, the capacity decays at higher rates, however still remaining at appreciable values.

Figure 6 shows the effect of the temperature on the capacity of the battery. At temperatures above 83 °C, the battery is capable of delivering a high capacity level, i.e. > 80 $mAhg^{-1}$ at current densities lower than 0.25 $mAcm^{-2}$, corresponding to C/5, C/8 and C/10 rates. The decay in capacity with increasing rate and decreasing temperature is, as expected, associated to the increase in ohmic drop. However, it is important to remark that the current density that the battery is able to sustain is quite higher than the limiting value of conventional PEO-based lithium batteries, usually reported as 0.1 mAcm^{-2} . In the battery here discussed, this value rises to 0.25 mAcm^{-2}, and this important increase is associated with the enhancement in the lithium transference number promoted by the addition of CP. This is another evidence of the practical relevance of the electrolyte developed in this work and, indirectly, of the validity of the concept adopted in our laboratory for preparing them.

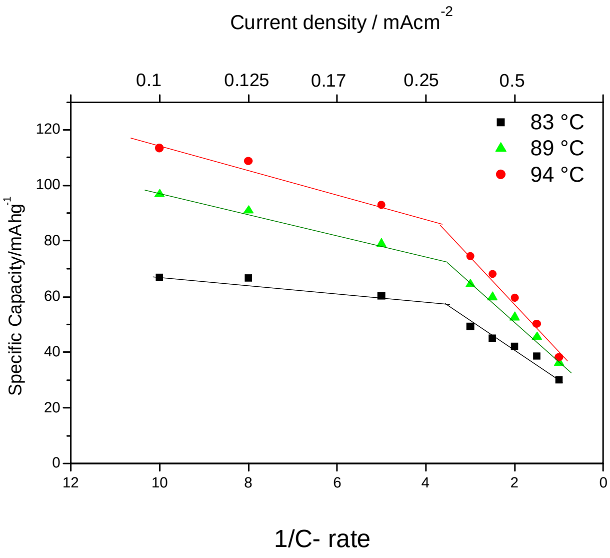

Figure 6.
Capacity versus 1/C rate at different temperatures of the Li/ P(EO)$_{20}$LiBOB (CP)$_{0.125}$/LiFePO$_4$ battery. Legends show the corresponding temperatures

Figure 7, which shows the capacity versus cycle number, evidences the cycling performance of the Li / PEO$_{20}$LiBOB(CP)$_{0.125}$/LiFePO$_4$ battery. With the exception of the first cycle, the charge-discharge efficiency is over 98%, this indicating the high reversibility of the electrochemical process [2]. The low value in the first cycle is typical of lithium intercalation processes, being associated to a rearrangement of the hosting structure upon initial uptake or release of the lithium ions.

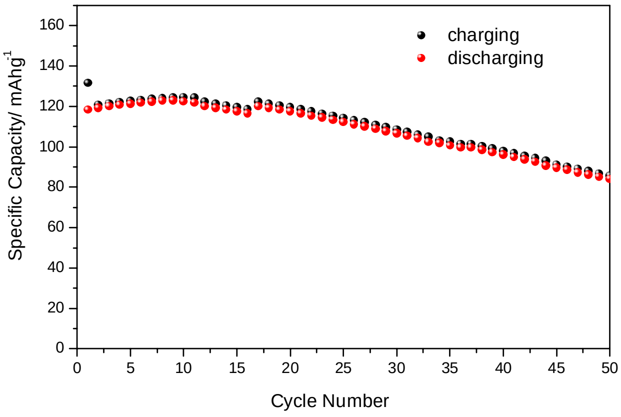

Figure 7. Capacity versus number of cycles of the Li/ P(EO)$_{20}$LiBOB (CP)$_{0.125}$/LiFePO$_4$ battery at 98°C. C-rate is C/10 corresponding to a current density of 0.1 mAcm^{-2}.

Conclusion and future work

The work carried out within this project has lead to the development of new types of dual composite PEO-based electrolytes having outstanding properties. This also, and particularly, applies to the new member of the family discussed in this report, i.e. the electrolyte formed by the combination of a calyx(6)pyrrole, CP anion-trapping compound with a large anion lithium salt, such as lithium bis(oxalate) borate, LiBOB. The results here described show that this combination gives rise to PEO-based polymer electrolytes having excellent transport properties. Polymer electrolyte membranes of the $PEO_{20}LiBOB(CP)_{0.125}$ composition have in the 80°C temperature range a lithium transference number of about 0.5 (versus the 0.3 value of conventional PEO systems) and an ionic conductivity of the order of 0.001 Scm^{-1}.

In previous reports we have demonstrated that the new class of electrolytes developed in this project act as effective separators in rechargeable lithium batteries. We have confirmed this practical importance also for the $PEO_{20}LiBOB(CP)_{0.125}$ electrolyte described in this report.

The entire project to which this report refers, has been carried out with the collaboration of three academic groups, namely the Technical University of Warsaw, leaded by Professor Wladek Wieczorek, the .Department of Chemistry of Tel Aviv University, leaded by Professor Emanuel Peled, and the Department of Chemistry, of the University “La Sapienza” of Rome, leaded by Professor Bruno Scrosati. All the groups acknowledged to financial support of the European Office of Aerospace Research and Development, Air Force Office of Scientific Research, United States Air Force Research Laboratory, EOARD, which has allowed to carry out the research work and, particularly, Dr. Laurence Scanlon for his continuous help and encouragement for our research plans. We plan to submit shortly a concise, joint final report, in which we will summarize the most relevant aspect of this successful project.