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14. ABSTRACT

This report results from a contract tasking Universita di Roma La Sapienza as follows: The main task of this project is to design and characterize novel types of lithium conducting polymer electrolytes. This task will be pursued by the combined efforts of three academic groups having world-wide recognized experience in polymer electrolyte science, namely, the Group of Professors Wladyslaw Wieczorek and Florjanczyks of the Warsaw University of Technology in Poland, the Group of Professor Emanuel Peled at the University of Tel Aviv, Israel and the Group of Professor Bruno Scrosati at the University 'La Sapienza' of Rome, Italy. Broadly, the Polish Group will be involved in the synthesis of the new polymer electrolytes; the Italian Group will act as the coordinator of the Project, in their basic electrochemical characterization; and the Group in Israel in the fabrication and test of laboratory cell prototypes.

The work plan to be carried out at the Chemistry Department of the University La Sapienza of Rome will involve the following items: 1) Determination of the conductivity of the samples of polymer in salt electrolytes provided by the Warsaw Group; and 2) Determination of the electrochemical properties of the optimized polymer in salt electrolytes synthesized by the Warsaw Group. The electrochemical characterization will involve the determination of the ionic conductivity of the lithium-ion transference number and of the characteristics of the lithium metal interface.

15. SUBJECT TERMS
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NOVEL, SOLVENT-FREE, SINGLE ION CONDUCTING POLYMER ELECTROLYTES
3rd year

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FINAL REPORT

Summary

The research carried out within the third year of this project was directed to the characterization of $P(EO)_{20}(LiX)_1(calixpyrrole)_x$ electrolyte membranes. Several samples, varying from i) the PEO molecular weight ($1x10^5$ and $4x10^6$), ii)the nature of the lithium salt (LiI, $LiBF_4$) and iii) the calixpyrrole content ($0 \leq x \geq 0.5$), were prepared and tested in terms of lithium ion transference number, T_{Li}^+ , thermal properties and ionic conductivity.

The results confirm that calixpyrrole has an anion-trapping action similar if not higher, than that previously observed by calixerene (see second year reports). The results here presented further confirm the specific role of the additive in enhancing the lithium ion transport in $P(EO)_{20}(LiX)_1(calixpyrrole)_x$ electrolyte membranes. Furthermore, it was established that $LiBF_4$-containing samples showed a larger transference number than the corresponding membranes based on LiI. This has been associated with a difference in the stability of the calixpyrrole-anion complexes, which, for the case of the BF_4^- anion is indeed expected to be higher than that for the case of the I^- anion. Indeed. single lithium ion transport, i.e., $T_{Li+} = 1$, was observed for the $LiBF_4$-based electrolyte membranes even at small calixpyrrole concentration and at low lithium salt concentration, e.g., EO/Li = 100.

The unique action of the calixarene additive in trapping the anions was further confirmed by the NMR results obtained in Professor Greenbaum laboratory at the Hunter College of the City University of New York.

The thermal studies have demonstrated that neither the BF4 anion nor the calixpyrrole additive have a plasticizing effect on the PEO chains; this is not surprising since both the anion and the additive do not have an electron delocalized structure.

Conductivity studies, carried out on a selected sample of the calixarene-added membranes showed that, although the conductivity of the calixpyrrole-added membranes is lower than that of the PEO-LiX pristine samples, the difference is much more contained that that observed for the calixarene-added membranes (see second year reports) especially in the medium-high temperature range. For instance, at 75°C the conductivity passes from $7.6*10^{-5}$ Scm^{-1} for the plain membrane to $5*10^{-5}$ Scm^{-1} for the calixpyrrole-added membrane, this finally demonstrating that the use of calixpyrrole indeed made the difference..

This is a very important result since it demonstrates that a PEO-based electrolyte having a lithium transference number approaching unity with a minor decay in conductivity is indeed a reality. To our knowledge a similar achievement was so far never reported in the literature.

1.Experimental.

Calixpyrrole, 1,1,3,3,5,5-mezo-hexaphenyl-2,2,4,4,6,6-mezo-hexamethyl-6-pyrrole, was provided by the university of Warsaw. Calixpyrrole, LiI (Aldrich reagent grade, 99.99%), PEO (Aldrich reagent grade, $1x10^5$ and $4x10^6$ molecular weight) were dried under vacuum at 60°C, 60°C and 100 °C, respectively, for 48 hours prior to use. Acetonitrile, CH_3CN (Aldrich battery grade, 99.93% water below 50 ppm), dichloromethane, CH_2Cl_2 (Aldrich biotech grade, 99.9% water below 20 ppm) and $LiBF_4$ (Merck battery grade, water below 30 ppm), were used as received.

The $P(EO)_{20}(LiX)_1(calixpyrrole)_x$ electrolyte membranes were prepared by following the procedure proved to be suitable for the calixarene-based membranes, see second year reports. Accordingly, an acetonitrile-dichloromethane mixture was employed instead than pure solvents to account for the different solubility of involved material components. As shown schematically in Figure 1, the lithium salt was first dissolved in CH_3CN at room temperature and then PEO was added in the same solution that was stirred to achieve full dissolution. Calixpyrrole was dissolved in CH_2Cl_2 in a different flask. Then the two separate solutions were mixed and magnetically stirred to obtain an homogeneous slurry. The latter was cast on Teflon™ sheets and the solvents were slowly removed (1 day) at room temperature. Finally, after drying under vacuum at 50°C for at least 48 hours, membranes having average thickness of 100 μm and a good mechanical strength, were obtained. The preparation of the membranes and the related electrochemical tests were carried out in an argon-controlled atmosphere dry-box having an humidity content below 10 ppm.

Several membrane samples were prepared. Table 1 shows the composition of the various samples examined in this project. The EO/Li molar ratio was fixed to 20. LiI and $LiBF_4$ were used as alternative LiX lithium salts. The PEO molecular weight was set on 100,000 and 4,000,000, respectively. The calixpyrrole/LiX molar ratio varied from 0 to 0.5.

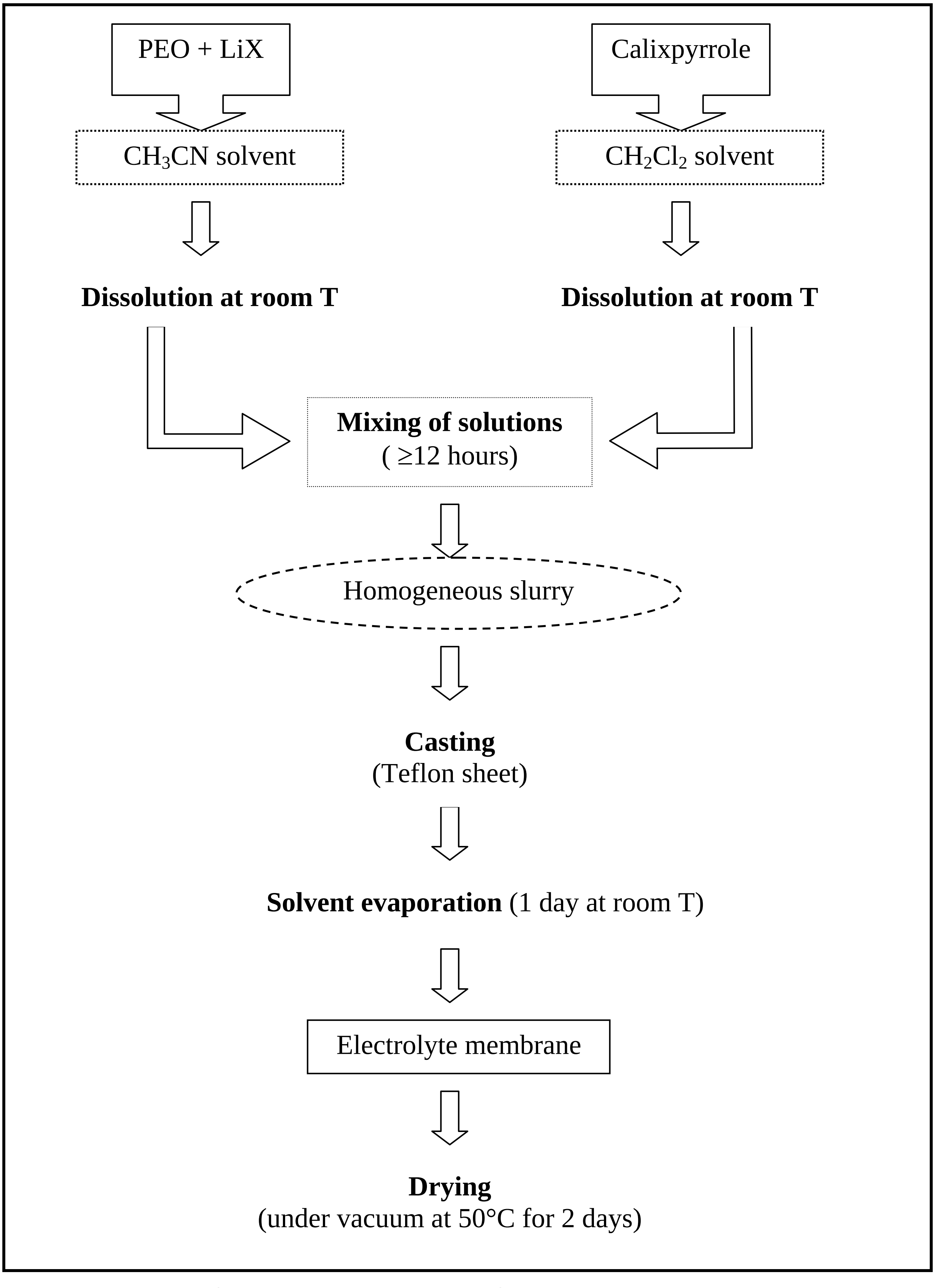

Figure 1 *- Outline of the preparation procedure of PEO:LiX:Calixpyrrole electrolyte membranes.*

***Table 1** - Composition of the $P(EO)_n(LiX)_1(Calixpyrrole)_x$ membrane samples.*

EO/Li molar ratio (#)	**Lithium salt**	**PEO molecular weight (#)**	**Calixpyrrole/LiX ratio (#)**
50 **100**	**LiI**	**100,000**	**0**
			0.25
			0.5
			1.0
		4,000,000	**0**
			0.25
			0.5
			1.0
	$LiBF_4$	**100,000**	**0**
			0.25
			0.5
			1.0
		4,000,000	**0**
			0.25
			0.5
			1.0

The lithium transference number, $T_{Li}{}^{+}$, was determined through a procedure reported in details in previous reports. Basically, voltage pulses varying from 10 mV to 30 mV were applied to a Li / $P(EO)_{20}(LiX)_1(calixpyrrole)_x$ electrolyte/ Li cell and the initial current, Io and the steady-state current, Iss were measured. A concurrent impedance analysis was carried out before and after the application of the voltage pulses to estimate the effect of changes of the passive layer resistance at the Li electrode interface. All the transference number measurements were performed at 70 °C. The cells were left to thermally equilibrate for at least one day before each measurements.

According to this method, T_{Li+} was calculated by the following equation:

$$T_{Li+} = \frac{I_{SS}}{I_0} = \frac{I_{SS}}{\Delta V/(R_e + R_p)} \tag{1}$$

where:
I_0 = initial current (t = 0);
I_{ss} = steady state current;
ΔV = applied voltage pulse;
R_e = electrolyte resistance ;
R_p = passive layer resistance onto the lithium metal electrodes.

The thermal behaviour was studied by Differential Scanning Calorimetry, DSC, using a Mettler DSC mod.821 calorimeter. The conductivity of the membranes were determined by Impedance Spectroscopy, IS, using a Frequency Response Analyzer (F.R.A.), Schlumberger Solartron mod.1260. Both DSC and IS instruments are part of our laboratory's instrumental park.

Pulse Field Gradient NMR studies were run in Professor Greenbaum's Laboratory in New York.

2.Results.

Figure 2 shows in scheme the structure of calixpyrrole. As for the case of calixarene , also calixpyrrole acts as an anion-trapping agent, thus enhancing the value of the lithium ion transference number. However the interaction between calixpyrrole and the BF_4^- anions are expected to be stronger than those between calixarene and the I^- anions. Thus, the use of the former is expected to produce comparable effect of the latter, however at lower concentration. This is in turn expected to reflect favorably in overall transport properties since the lower is the concentration of the additive, the lower is the induced decay in conductivity of the electrolyte. This expectation was confirmed by the experimental results obtained in this project.

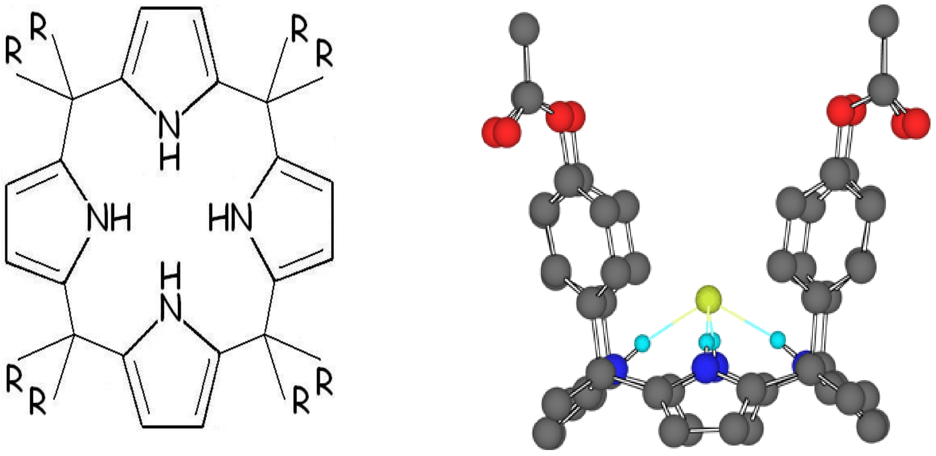

Figure 2- *Scheme of the calixpyrrole structure*

2.1. Lithium ion transference number.

The lithium ion transference number of the membranes was determined following the dc-ac method described in the experimental section. Figure 3 shows a typical result obtained for a selected membrane sample. Figure 3A illustrates the chronoamperometric curve obtained following a 10 mV dc pulse, ΔV applied to a cell formed by sandwiching a $P(EO)_{100}LiBF_4(CP)_{0.25}$ membrane between two lithium metal electrodes. This curve, filtered by the noise, identifies the value of the steady state current, Iss flowing through the cell. Figure 3B shows an impedance plot of the cell prior and after the dc pulse. This curves identifies the initial , R_b and the final, R_p values of the membrane resistance. The value of the initial current, i.e. the current flowing through the cell at the application of the pulse, Io is given by the ratio between $\Delta V/(R_b+R_p)$. Finally, the T_{Li+} value is provided by the ratio between steady state and initial current, Iss/Io, which in the case under test results to be $T_{Li+} > 0.95$. This result demonstrates that calixpyrrole indeed promotes enhancement of the lithium transference number at the same level of calixarene but at a much lower concentration (compare second year results).

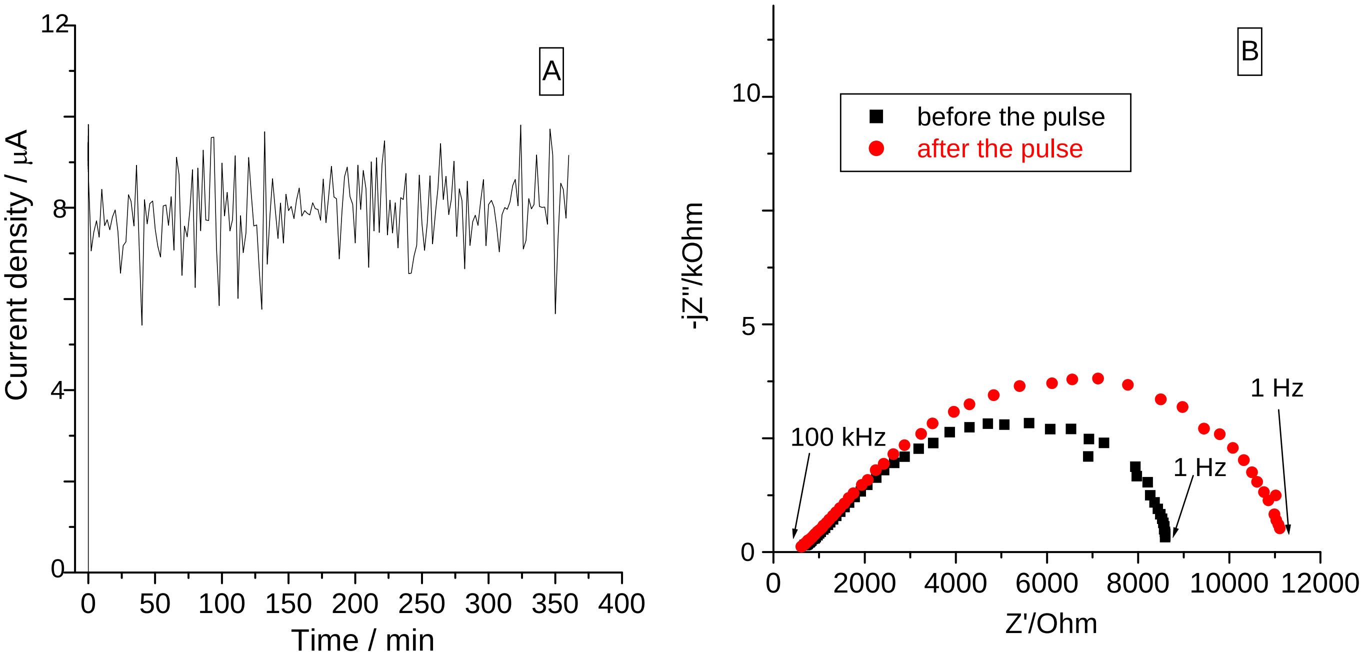

Figure 3- *(A) Current-time curve of a Li / $P(EO)_{100}LiBF_4(CP)_{0.25}$/Li cell following a 10 mV dc pulse at 70 °C. B) Impedance response of the same cell before and after the dc pulse.*

Table 2 summarizes the results obtained for the various membranes examined in this project. It may be clearly seen that for all the samples tested there is an enhancement of the lithium ion transport number, with T_{Li}^{+} values varying from 0.56 to 1.0.

Figure 4 illustrates the dependence of the lithium ion transference number on the calixpyrrole/LiX molar ratio for electrolyte membranes based on LiI and $LiBF_4$, respectively (see legend) and using a 4,000,000 molecular weight PEO. The figure shows that the T_{Li}^{+} value remarkably increases even at moderate calixpyrrole content, this clearly confirming the strong anion-trapping action of the additive. Indeed, the transference number increases from 0.2-0.3 to 0.75-0.8 passing from to calixpyrrole-free $P(EO)_{20}(LiX)_1$ to $P(EO)_{20}(LiX)_1(calixpyrrole)_{0.2}$ electrolyte membranes. In this trend the $LiBF_4$-containing samples (blue squares) exhibited a larger T_{Li}^{+} increase than the corresponding membranes based on LiI (red squares), especially at low calixpyrrole content ($0 \leq x \geq 0.125$). This may be related to the strength of the calixpyrrole:anion complexes which is expected to increase when passing from the I anion to the BF_4 anion.

Table 2 *- Lithium ion transference number of different $P(EO)_n(LiX)_1(Calixpyrrole)_x$ electrolyte membrane samples at 70°C.*

Salt	EO/Li molar ratio (#)	PEO molecular weight (#)	Calixpyrrole/LiX molar ratio (#)				
			0	0.125	0.25	0.5	1.0
LiI	20	100,000	0.20 ± 0.05	n. a.	0.75 ± 0.05	n. a.	(*)
		4,000,000	0.25 ± 0.05	0.56 ± 0.05	0.75 ± 0.05	0.78 ± 0.05	(*)
	50	100,000	n. a.	(*)	n. a.	n. a.	n. a.
		4,000,000	n. a.	(*)	0.75 ± 0.05	n. a.	n. a.
	100	100,000	n. a.	(*)	n. a.	n. a.	n. a.
		4,000,000	n. a.	(*)	n. a.	n. a.	n. a.
$LiBF_4$	20	4,000,000	0.32 ± 0.05	0.78 ± 0.05	0.81 ± 0.05	0.85 ± 0.05	(*)
	50	100,000	n. a.	(*)	0.79 ± 0.05	n. a.	n. a.
		4,000,000	n. a.	(*)	n. a.	n. a.	n. a.
	100	100,000	n. a.	(*)	n. a.	n. a.	n. a.
		4,000,000	n. a.	(*)	0.95 ÷ 1.0	n. a.	0.92 ± 0.05

n. a. = data not available
(*) = sample not prepared

Figure 5 reports the T_{Li+} dependence behavior of $LiBF_4$-based samples as a function of the calixpyrrole content for different EO/Li molar ratios (see legend). The trends show an increase of T_{Li+} with the decrease of the salt concentration. The $EO/LiBF_4$ ratio = 100 samples (red squares) exhibit a practically single ion conductivity, i.e., T_{Li+} close to 1, for a calixpyrrole/$LiBF_4$ ratio higher than 0.25. The corresponding $EO/LiBF_4$ = 20 membranes (blue squares) show a transference number close to 0.8. The higher value shown by the $EO/LiBF_4$ = 100 samples may be attributed to poor formation of multiple ions and/or of ionic agglomerates at low salt concentration, since both these effects are expected to promote trapping of BF_4 anions by the calixpyrrole additive.

Figure 6 shows the transference number of $P(EO)_n(LiX)_1(calixpyrrole)_{0.25}$ membrane samples as a function of the EO/Li molar ratio for the two types of lithium salt (see legend). The $LiBF_4$-containing samples (blue squares) exhibit an increase of T_{Li+} from 0.8 to 1 in passing from EO/Li = 20 to EO/Li = 100. On the contrary, no variation of transference number, i.e., stable on the 0.75 value, is observed for LiI-based samples. Once more, this may be due to the stability of the calixpyrrole:BF_4 complex which is expected to be higher than that of the corresponding calixpyrrole:I complex.

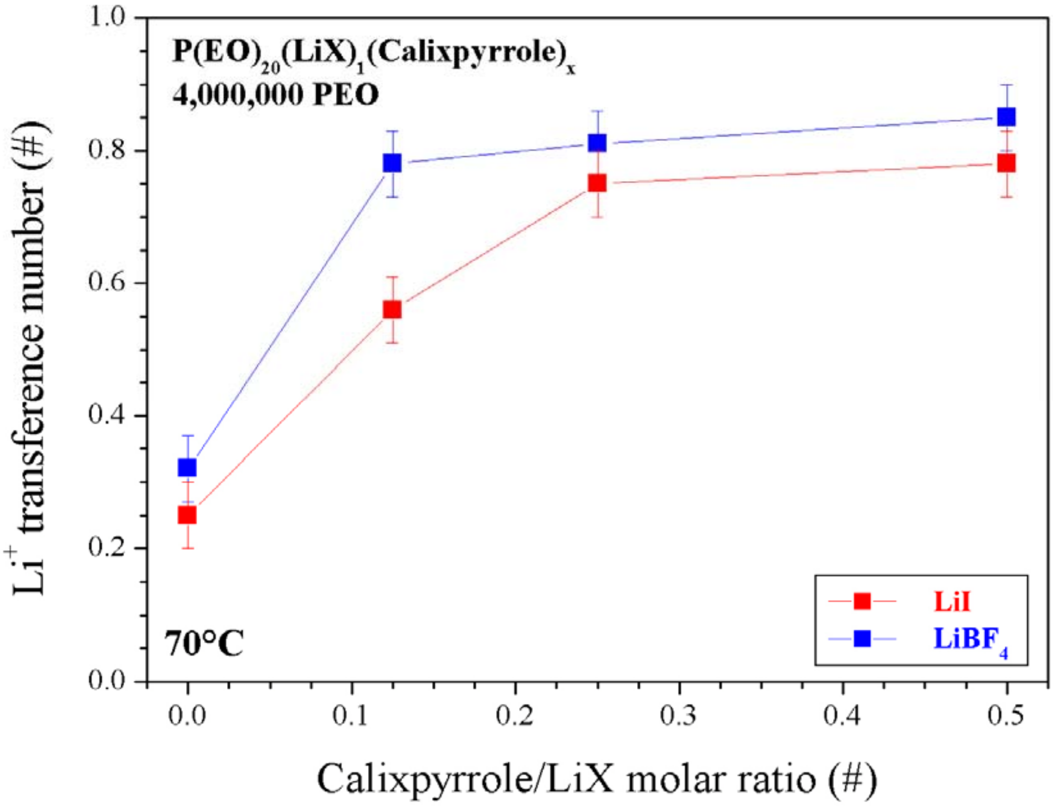

Figure 4. *Lithium ion transference number vs. Calixpyrrole/LiX molar ratio dependence of* $P(EO)_{20}(LiX)_1(Calixpyrrole)_x$ *electrolyte membranes for different lithium salts (see legend). T = 70°C. PEO molecular weight: 4,000,000.*

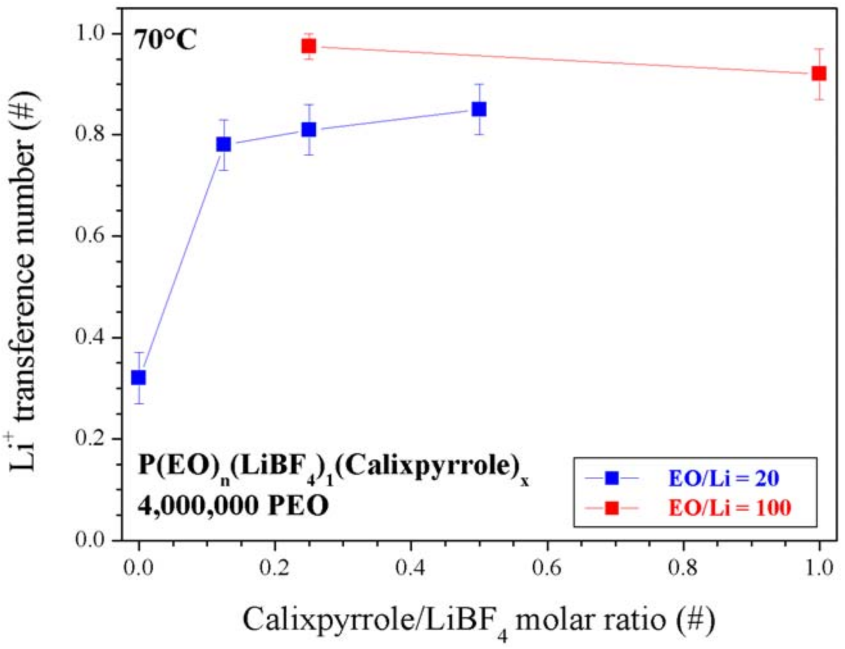

Figure 5. *Lithium ion transference number vs. Calixpyrrole/LiBF*$_4$ *molar ratio dependence of* $P(EO)_n(LiBF_4)_1(Calixpyrrole)_x$ *electrolyte membranes for different EO/Li molar ratios (see legend). T = 70°C. PEO molecular weight: 4,000,000.*

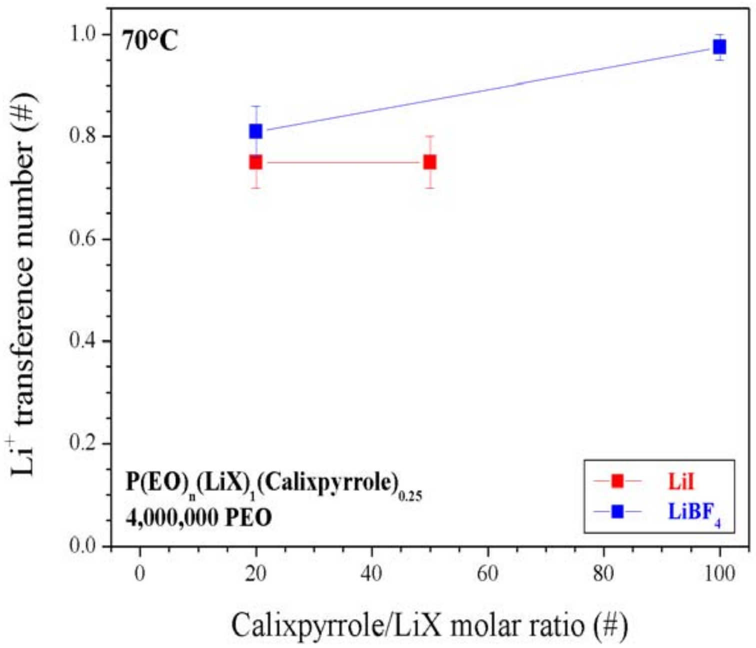

Figure 6. *Lithium ion transference number vs. EO/Li molar ratio dependence of* $P(EO)_n(LiX)_1(Calixpyrrole)_{0.25}$ *electrolyte membranes for different lithium salts (see legend). T = 70°C. PEO molecular weight: 4,000,000*

2.2 Thermal properties.

According to the results obtained in the initial screening tests (see above) and to the work sharing agreement with the other partners of this project, the final chemical physical and electrochemical characterization was concentrated on diluted samples using $LiBF_4$ as the preferred lithium salt. The selected EO/Li concentration was 100 molar ratio and that of calixpyrrole was 0.25 molar ratio, in order to obtain membranes of the following composition: $P(EO)_{100}LiBF_4(CP)_{0.25}$, where CP stays for calixpyrrole.

Figure 7 shows in comparison the DSC traces of three membranes, i.e., i)a pure PEO membrane, ii)a $P(EO)_{100}LiBF_4$ membrane and iii) a $P(EO)_{100}LiBF_4(CP)_{0.25}$ membrane.

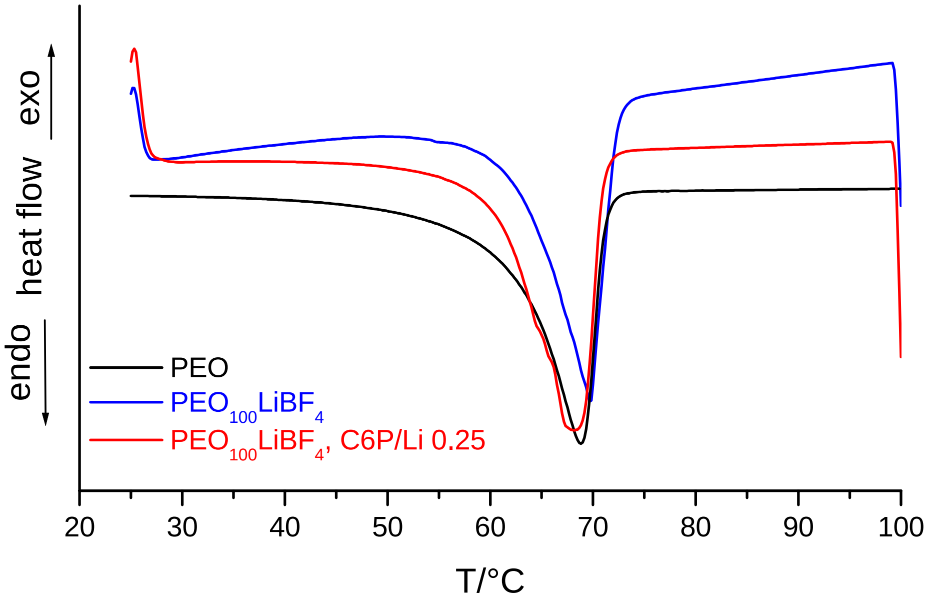

Figure 7*. DSC traces of the following three membrane samples: i) pure PEO, ii) $P(EO)_{100}LiBF_4$ and iii) $P(EO)_{100}LiBF_4(CP)_{0.25}$. Heating rate: 10 C/min.*

No substantial differences are noticed in terms of PEO melting temperature, this demonstrating that neither the BF_4 anion nor the calixpyrrole additive have a plasticizing effect on the PEO chains. This is not surprising since both the anion and the additive do not have an electron delocalized structure as is instead the case for active plasticizing agents such as the LiBOB or the LiDTCA salts.

2.3 Conductivity

Figure 8 shows in comparison the Arrhenius plots of a plain $P(EO)_{100}LiBF_4$ electrolyte membrane and of a calixpyrrole-added $P(EO)_{100}LiBF_4(CP)_{0.25}$. membrane. Both curves break around 70 °C this confirming the indication provided by the DSC data (see Figure 7).

A relevant information is given by the comparison between the trend of the two conductivity curves. Although the conductivity of the calixpyrrole-added membrane is lower than that of the plain sample, the difference is much more contained that that observed for the calixarene-added membranes (see previous reports) especially in the medium-high temperature range, this demonstrating that the replacement indeed made the difference. Figure 8 shows that at 75°C the conductivity passes from $7.6*10^{-5}$ Scm^{-1} for the plain membrane to $5*10^{-5}$ Scm^{-1} for the CP-added membrane. This is a very important result since it demonstrates that a PEO-based electrolyte having a lithium transference number approaching unity with a minor decay in conductivity is indeed a reality. To our knowledge a similar achievement was so far never reported in the literature. Thus, the result was protected by a patent and described in a scientific papers (see below).

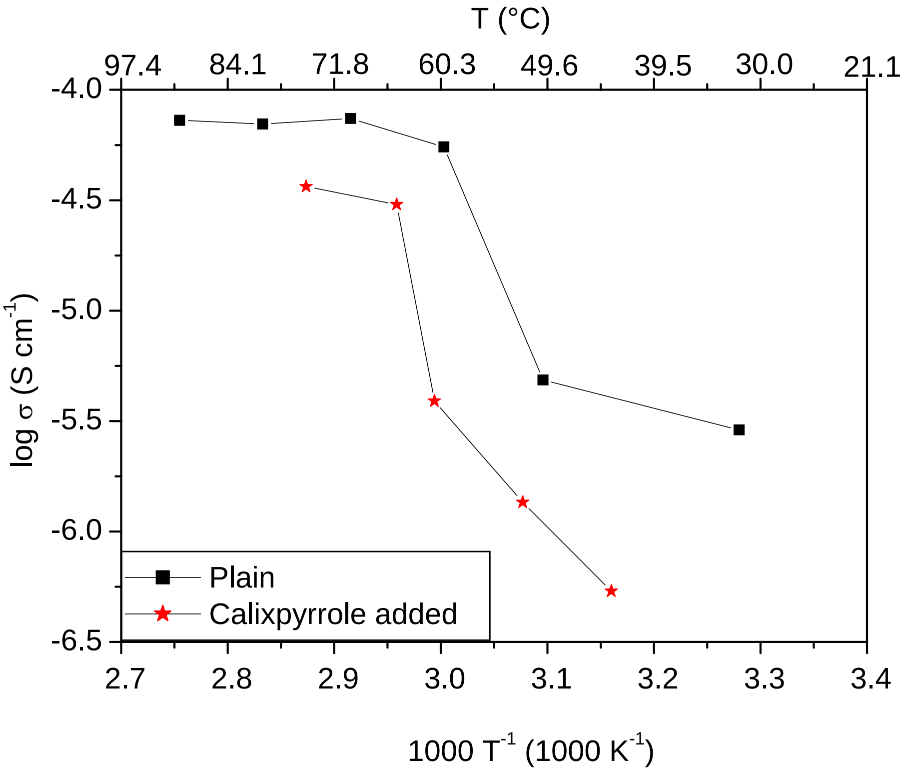

Figure 8*- Arrhenius plots of a plain $P(EO)_{100}LiBF_4$ membrane and of a composite $P(EO)_{100}LiBF_4(CP)_{0.25}$. membrane.*

2.4. NMR.

The anion trapping action of calixpyrrole was finally confirmed by the NMR results obtained in Professor Greenbaum Laboratory, see Table 3. The proton diffusion are 3.4×10^{-8} and 6.5×10^{-8} cm^2/s for samples without and with calixpyrrole, respectively. This is consistent with the measured value of pure high MW PEO, about 6×10^{-8} cm^2/s. Note that the effect of the calixpyrrole seems to be a mild plasticizing one (increasing chain mobility). The lithium diffusion is 2.0×10^{-7} and 2.5×10^{-7} cm^2/s for samples without and with calixpyrrole, respectively. The lithium diffusion is 25% higher for the calixpyrrole containing samples, but this could possibly be explained by the plasticizing effect mentioned previously. The most relevant result is the fluorine (anion) diffusion which passes from 2.75×10^{-7} to 3.6×10^{-7} cm^2/s by the addition of calixpyrrole , i.e with about a 30% decrease. The NMR data clearly show that the Li^+ diffusion of the polymer and Li^+ diffusion is enhanced by the addition of calixpyrrole, this accounting for the observed increase of the Li^+ transference number.

Table 3 *-Multinuclear NMR diffusion results for* $PEO_{100}LiBF_4$*. membrane without and with CP at 90°C (all in* cm^2/s*)*

Nucleous	No CP	With CP
^1H	6.5×10^{-8}	3.4×10^{-8}
^7Li	2.5×10^{-7}	2.0×10^{-7}
^{19}F	2.75×10^{-7}	3.6×10^{-7}

Conclusion and future work.

The overall data here discussed demonstrate that the main goal of the project, i.e. the development of single lithium ion conducting polymer electrolytes, has been achieved. We realize that this important result has been made possible only thank to the collaborative involvement of the three laboratories participating in this project. The University of Warsaw gave a tremendous support by identifying, synthesizing and providing the anion-trapping additives. The laboratories of the universities of Tel Aviv and Rome contributed to the success of the project by characterizing the samples received from Warsaw and by suggesting the routes for reaching the final goal. To obtain this result various meetings were held during the three year course of the project to jointly discuss the progressive development of the research and identify the best way to proceed. In the last year, following a granted permission by the U.S. Air Force Lab, the project benefited by a contribution of Professor Steve Greenbaum of the Hunter College of New York.

On behalf of the all groups involved, we would like to thank Dr. L. Scanlon of the Air Force Laboratory and the U.S. Air Force Office in London for providing the financial support and thus, the practical possibility of forming our research team. We like to think that the result obtained, i.e. the disclosure of a new polymer electrolyte with unique transport properties, is scientifically and technologically relevant. As future work, we plan to test this electrolyte in laboratory prototype cells in order to confirm its relevance for the progress of the lithium polymer battery technology.

List of publications and patents produced within the project.

Publications:

-A. Blazejczyk, W. Wieczorek, R. Kovarsky, D. Golodnitsky, E. Peled, L.G. Scanlon, G.B. Appetecchi and B. Scrosati, "- Novel Solid Polymer Electrolytes with Single-Lithium-Ion Transport" *J. Electrochem. Soc.*, in press
-A-Blazejczyk, W. Wieczorek, B. Scrosati, G.B. Appetecchi, D. Golodnitsky, R. Kovarsky, E. Peled " Programming polymer electrolyte properties using calixarene agents as anion-trapping receptors" Chemistry of Materials, submitted

Invention disclosure:

Title:Novel Solid Polymer Electrolytes with Single-Lithium-Ion Transport
Authors: A. Blazejczyk, W. Wieczorek, R. Kovarsky, D. Golodnitsky, E. Peled, Lawrence G. Scanlon Jr., G. Appetecchi, B. Scrosati.