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14. ABSTRACT This report results from a contract tasking Tel Aviv University as follows: The main task of this project is to design and characterize novel types of lithium conducting polymer electrolytes. Year 1: Casting of uniform polymer electrolyte films. Measurements of conductivity, cation transference number and Li/PE interfacial resistance. Characterization of the materials. Year 2: Enhance ionic conductivity by creating ordered structures under external magnetic fields (MF). Year 3: The selected polymer electrolyte will be tested in a lithium battery prototype with a thin-film electrodeposited cathode.					
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**NOVEL, SOLVENT FREE, SINGLE ION CONDUCTING POLYMER
ELECTROLYTES**

AWARD GRANT No FA86655-05-1-3013

Report #8

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Abstract

This work represents the electrochemical and structural study of the dual modified composite LiBOB-based polymer electrolyte. This chelated borate anion has a unique tetrahedron structure wherein no hydrogen is present. The main advantage of the use of LiBOB salt is the high ionic conductivity at low-ambient temperatures and low solid-electrolyte interphase resistance. The conductivity of LiBOB:PEO₂₀:CP_{0.125} with SiO₂ is slightly lower than $10^{-5} \Omega^{-1}\text{cm}^{-1}$ at 30°C, a value higher by about two orders of magnitude than that of the semi-crystalline LiCF₃SO₃ (LiTf) system. The transference number of dual modified LiBOB polymer electrolyte approaches 0.8 at 75°C. Our electrochemical study showed a wide stability window of the dual modified polymer electrolyte.

1. Introduction

In our previous report we investigated the effect of calixpyrrole (1,1,3,3,5,5-meso-hexaphenyl-2,2,4,4,6,6-mezo-hexamethyl-6-pyrrole, (CP)) and SiO₂ additives on the conductivity and transference number of the LiTf:PEO₂₀ semi-crystalline PEs. Additionally, the enhanced performance of this dual composite polymer electrolyte as a membrane in MoO_xS_y/Li rechargeable battery was observed. We showed that these composite polymer electrolytes characterized by high lithium transference number (due to calix[6]pyrrole) combined with high ionic conductivity and low R_{SEI} are promising candidates for high-power solid lithium and Li-ion batteries.

In this current research, we were interested in further investigating the effect of CP as an anion trap in amorphous LiBOB-based polymer electrolytes (*lithium bis(oxalate)borate*, LiBC₄O₈). The large BOB anion is expected to interfere with the crystallization process of the PEO chains, possibly resulting in an increase of PEO amorphicity and improving lithium-ion transport. In addition to its plasticizing effect, the LiBOB salt offers other important advantages such as: no risk of production of harmful gases and/or other undesired compounds upon contact with occasional water impurities, thermal stability up to 200°C, low cost and environmental compatibility.

The PEs that were investigated were based on composition of LiBOB:PEO₂₀:CP_{0.125}. This composition was chosen, in order to compare to the LiTf:PEO₂₀-semicrystalline PEs that exhibited the most satisfying conductive properties. In addition, the effect of SiO₂ 130 and 380m²/g on LiBOB polymer electrolytes was studied.

The performance of these polymer electrolytes as membranes in MoO_xS_y/Li rechargeable batteries was investigated as well.

2. Experimental

Calix[6]pyrrole, LiBC_4O_8 (LiBOB) and PEO (5×10^6 MW, Aldrich reagent grade) were dried under vacuum at 100°C, 150°C and 50°C, respectively, for 48 hours prior to use. Acetonitrile (Aldrich battery grade, 99.93%, water content below 50 ppm) -ACN and dichloromethane (Aldrich biotech grade, 99.9%, water content below 20 ppm) were used as solvents.

LiBOB was dissolved in ACN at room temperature inside a sealed flask, and then PEO was added. The solution was carefully stirred in order to dissolve completely the PEO. The nanoporous SiO_2 powder (Degussa) was also vacuum dried at 200°C for 48 hours and added to the above solution which was magnetically stirred at room temperature for 24 hours. CP was dissolved in dichloromethane at room temperature in a different flask. Then, the two separate solutions were mixed for at least 24 hours by magnetic stirring to obtain a homogeneous slurry. Successively, the slurry was cast on Teflon sheets and the solvents were slowly removed (24 hours) by room temperature evaporation. Free-standing, homogeneous membrane samples were obtained having a thickness of 90-150 μm and good mechanical strength. Finally, the membranes were dried under vacuum at 50°C for at least 48 hours.

2.1. Experimental techniques

2.1.1. Structural characterization

A JSM-6300 scanning microscope (Jeol Co.) equipped with a Link elemental analyzer and a silicon detector was used for the study of surface morphology. X-ray-diffraction data were obtained with CuK_α radiation on Scintag Θ - Θ powder diffractometer equipped with a liquid-nitrogen-cooled germanium solid-state detector. The DSC tests of the vacuum-dried samples were carried out at a scan rate of 10 deg/min in hermetically sealed alodined aluminum pans with a TA Instruments module 2010 and System Controller 2100.

2.1.2. Conductivity measurements

Ionic conductivity at 0–90°C of the solid polymer electrolytes was determined by means of impedance spectroscopy. Solid electrolytes in the form of discs were pressed between two lithium metal electrodes and hermetically sealed in a coin cell construction. The cell assembling was executed in an argon controlled atmosphere dry-box having humidity content

below 10 ppm. The measurements were carried out on a Solartron 1255 Impedance Analyzer over the frequency range of 1mHz –1MHz.

2.1.3. Lithium ion transference number measurements

The lithium ion transference number (t_+) of the membrane samples were measured between 55°C and 90°C based on the steady state technique. According to this method, the transference number of lithium ions, as the carriers of charge flowing through the Li//solid-electrolyte//Li cell, could be calculated with the following equation:

$$t_{Li^+} = \frac{I_{ss} \cdot (\Delta V - I_0 R_0)}{I_0 \cdot (\Delta V - I_{ss} R_{ss})}$$

I_0 =initial current ($t=0$); I_{ss} =steady state current; ΔV =applied voltage pulse; R_0 =electrolyte resistance; R_{ss} =passive layer resistance onto the lithium metal electrodes.

2.1.4. Cyclic voltammetry measurements

The electrochemical stability window measurements were made with the use of a 263A Potentiostat interfaced with power-suite software and a PC. Cyclic-voltammetry measurements were performed at various temperatures with the use of a Li/PE/SS coin type cell over a wide range of potentials at sweep rates of 20mV/s. The coin cells were thermally equilibrated for at least two hours at each operating temperature before the beginning of measurements.

2.1.5. Cycle life measurements and polarization curve tests

The composite polymer electrolyte was tested as a membrane in a battery comprised of a MoO_xS_y cathode that was prepared in our laboratory, and a Li metal anode. Cycle life tests and peak-power tests (polarization curves) were conducted using a Maccor battery cycler at various temperatures. The cells were thermally equilibrated for at least two hours at each operating temperature before the onset of measurements.

The polarization curve tests of the LiBOB:PEO₂₀-based membranes with and without additives were conducted at various temperatures in a Li/PE/ MoO_xS_y battery configuration. These measurements were executed by applying an ascending step current for a defined amount of time in the range of 10 μ A to 3mA. The batteries were allowed to rest between every step for one minute. As a result of the applied current, the voltage and the capacity of the batteries were measured.

3. Results

3.1. Structural characterization

The SEM micrographs of the LiBOB:PEO₂₀ polymer electrolytes with and without CP_{0.125} and silica additives are shown in Fig 1. The LiBOB:PEO₂₀ membranes that do not contain additives (Fig. 1a) have clear, crystalline grain structure with about ~50 μm grain size. The LiBOB:PEO₂₀ films containing only the silica additive (Fig. 1b), exhibit the same grain size as the pure membrane. From Fig.1c, it can be seen, that the membranes containing LiBOB:CP ratio of 1:0.125, have larger grains than those of the additive-free PE. Incorporation of silica into the LiBOB:PEO₂₀:CP_{0.125}-based membranes smoothes the surface inter-grain boundaries substantially (Figs. 1d, 1e, 1f).

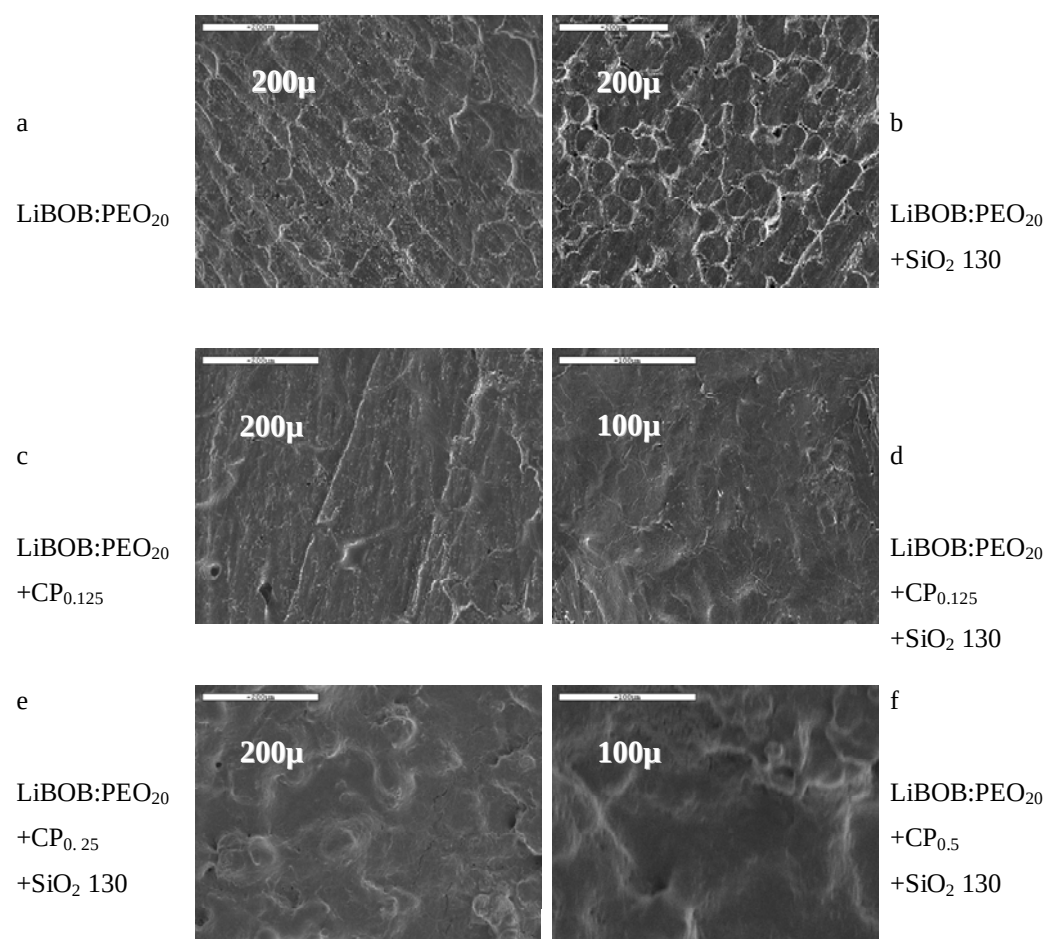


Figure 1. SEM images of LiBOB:PEO₂₀ PEs with and without CP and SiO₂ 130 additives.

3.2.1. XRD tests

Figs. 2a and 2b are shown to compare the diffraction patterns of the LiBOB-PEO with the LiTf and LiBF₄-based polymer electrolyte. As can be seen from the Figures, the XRD lines characteristic to the polymer host predominate. Strong Bragg reflection (120) at about 19.2° and combined (112) + (032) reflection at 23.5°, prevail in the XRD patterns of all the samples (Fig. 2a). In the concentrated LiCF₃SO₃:P(EO)₉ film the suppression of the combined reflection at 23.5° and appearance of the XRD peak at 12.1° is attributed to structural rearrangement of the PEO chains in the polymer electrolyte and formation of 1:3 salt:PEO complex (Fig. 2b).

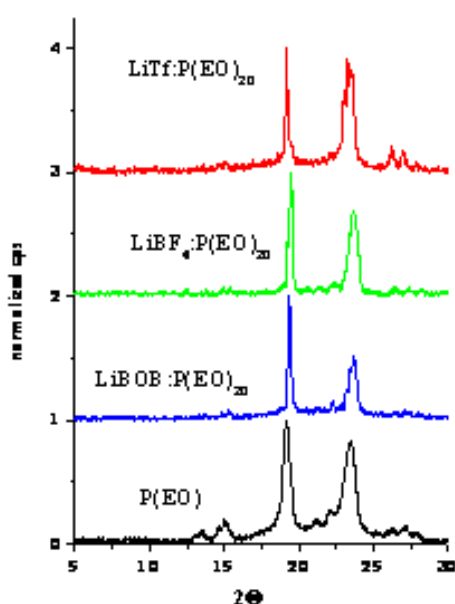


Fig. 2a. XRD patterns of PEO and dilute polymer electrolytes

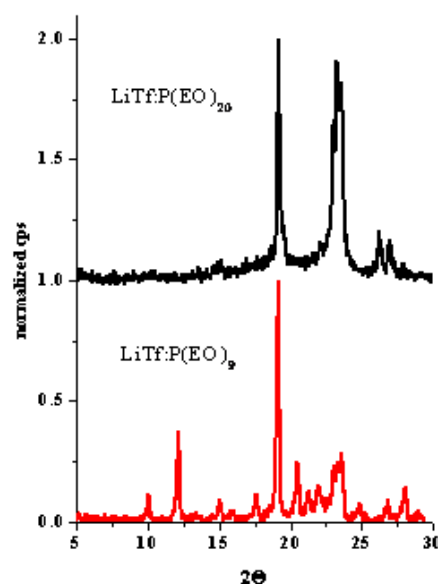


Fig. 2b. XRD patterns of dilute and concentrated LiTf:P(EO) PEs

The diffraction patterns of pure 1:20 lithium bisoxalatoborate PE, and those doped by CP and silica are similar to the pattern of neat PEO. In light of this fact the absence of LiBOB:P(EO)₃ Bragg lines can be explained by a small concentration of 1:3 complex in 1:20 polymer electrolyte. With calix[6]pyrrole addition to the neat LiBOB:P(EO)₂₀ polymer electrolyte (Fig. 2c, red curve), the ratio of integrated intensities of these lines changes, and widths decrease. With incorporation of silica (green curve) the relative contribution of combined (112) + (032) reflection increases and its integrated intensity becomes comparable

to the (120) reflection. Increase of CP concentration up to 1:0.5 salt-to-additive ratio in the SiO₂-containing PE is followed by a progressive broadening of the XRD peaks. Contrary to LiTf:P(EO)₂₀CP_{0.5}-SiO₂ PE no additional Bragg lines, which may be associated with calixpyrrole-BOB complex were distinguished in the diffraction patterns (Fig. 2d). This however, does not exclude interaction between anion, CP and silica in the PEO matrix.

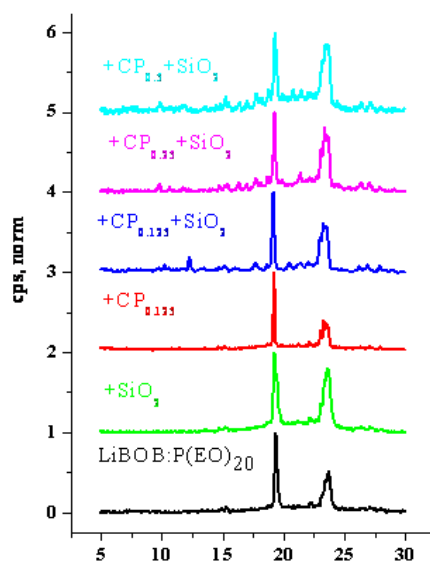


Figure 2c. XRD patterns of LiBOB:P(EO)₂₀ PEs with and without CP and SiO₂ 130 additives.

3.2.2. DSC-TGA analysis

DSC data of the polymer electrolytes studied are summarized in the Figures 3a and 3b and Table 1. Table 1 contains, in addition, melting points temperatures and enthalpy values of lithium triflate polymer electrolytes. The DSC traces of pure LiBOB:P(EO)₂₀ electrolyte are characterized by three endothermic peaks (Fig.3a-green curve). The first two phase transitions occur without weight loss (Fig.3a-blue TGA curve). The 1st peak represents two overlapped melting transitions of the eutectic and uncomplexed PEO. The endotherm at 96.2°C is associated with liquidus point, which is related to the dissolution of 1:3 complex in the melt mixture. The shoulder at the left branch of the 2nd endotherm may point to the formation of at least two LiBOB:PEO complexes of different EO:Li ratio. Decomposition of LiBOB-based PE starts at 289.6°C and vigorously continues at 378.3°C. Noteworthy that host polymer, PEO is thermally stable until 406°C.

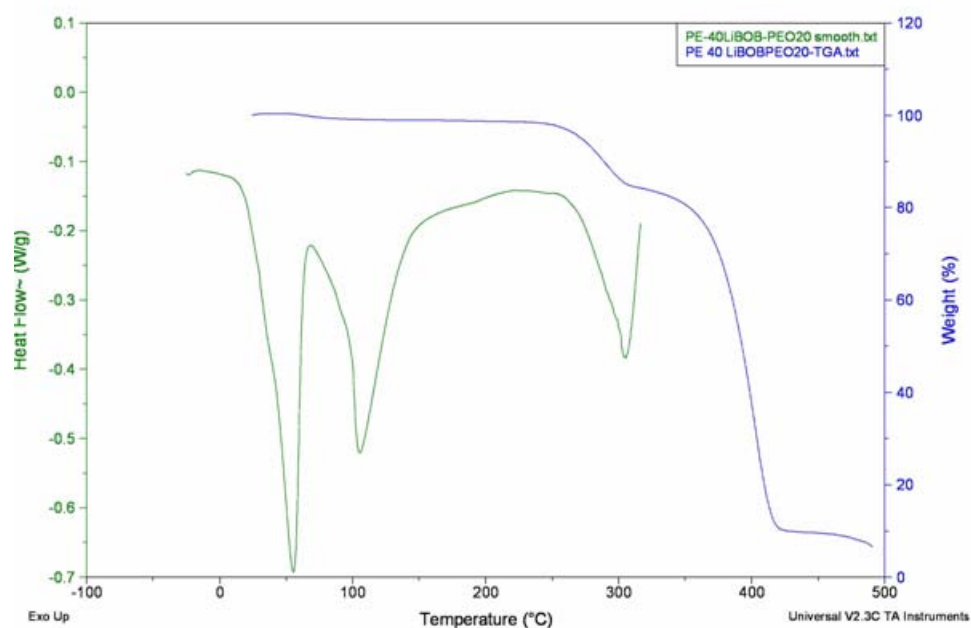


Fig.3a. DSC (green curve) and TGA (blue curve) thermograms of pure LiBOB:P(EO)₂₀ membrane

Incorporation of silica induces separation of eutectic and PEO melting transitions and shifts liquidus point towards low temperature, while overall enthalpy value of these peaks remains almost the same (Fig. 3b).

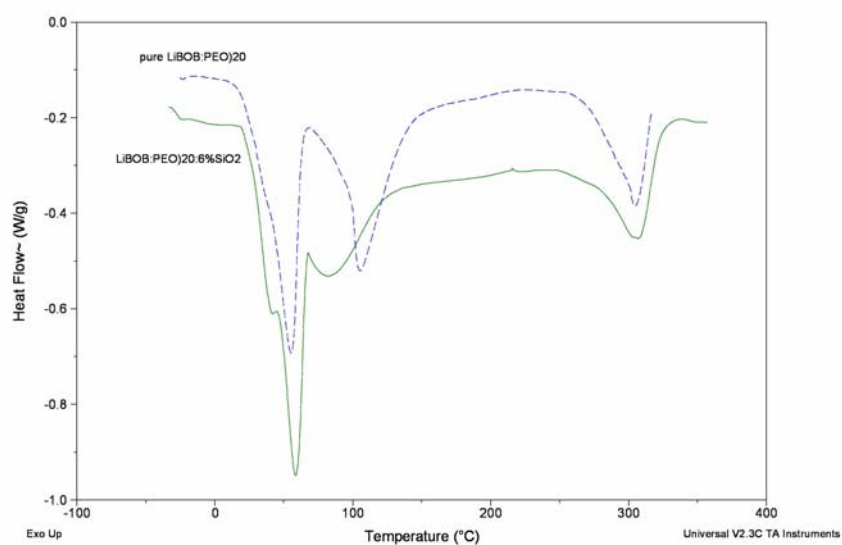


Fig.3b. DSC thermograms of pure LiBOB:P(EO)₂₀ and membrane containing silica

Calixpyrrole itself is thermally stable compound, which melts at 250°C and decomposes at 330°C. Addition of calix[6]pyrrole to LiBOB-polymer electrolyte is followed by broadening of the liquidus peak and appearance of the endotherm at about 208°C possibly associated with decomposition of the CP-anion complex (brown curve, Fig.3c).

DSC trace of dual composite PE, containing both CP and SiO₂, reflects all the above mentioned phase transitions (green curve-Fig.3c).

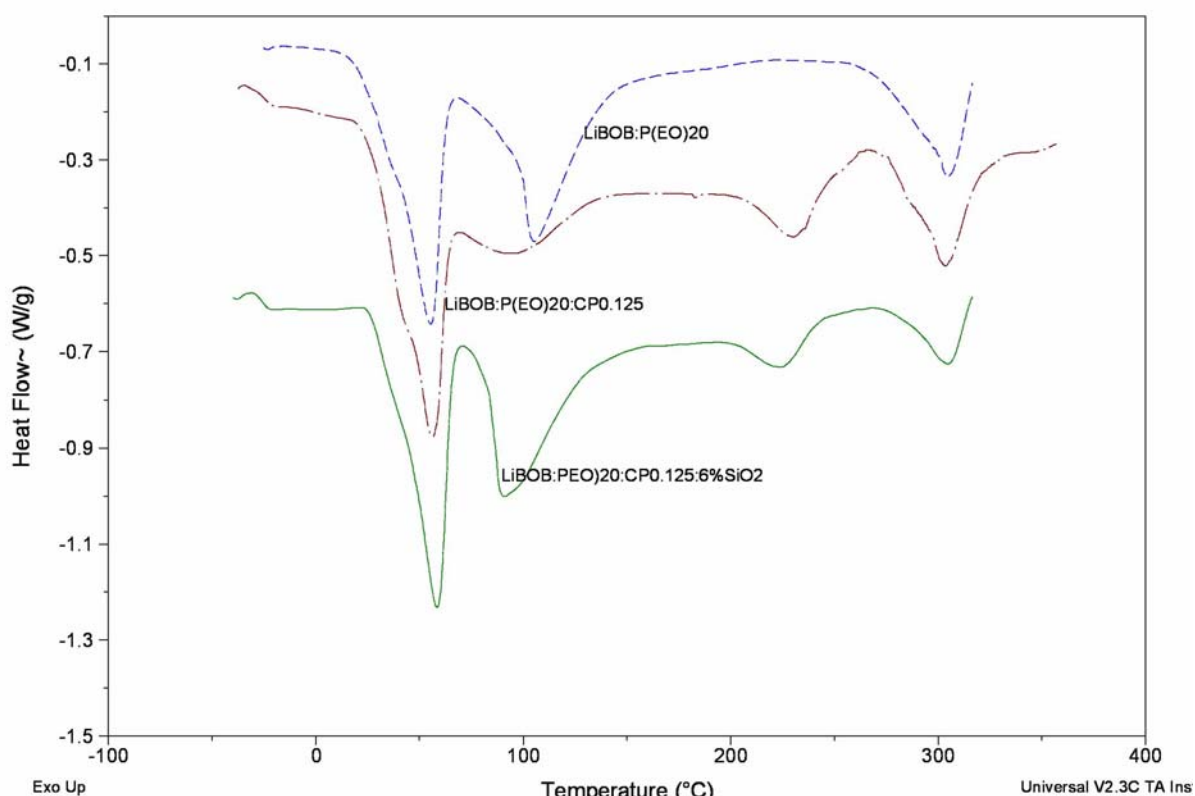


Fig.3c. DSC thermograms of LiBOB:P(EO)₂₀ with silica and calixpyrrole additives

Increase of the CP concentration is followed by the change of the shape of the thermograms (Fig.3d). The shoulder of the 2nd endotherm develops to additional broad peak, the enthalpy of which increases at the expense of the 1st low-temperature transition. With increase of the CP content from 0.125 to 0.25 and 0.5 CP-to-salt ratio the temperature of the decomposition of CP-BOB complex shifts from 208 to 215 and 218°C, respectively and the enthalpy of this peak increases by a factor of 5 (from 10.7 to 31.0 and 50.7 J/g). At the same time the weight loss, associated with complex decomposition changes from 2.5 to 5.1 and 6.9 % (Fig.3e, marked by star). Melting of the excess of CP (not bound to any PE

component) and of the trap released after the decomposition of complex may influence the broad shape of the peak.

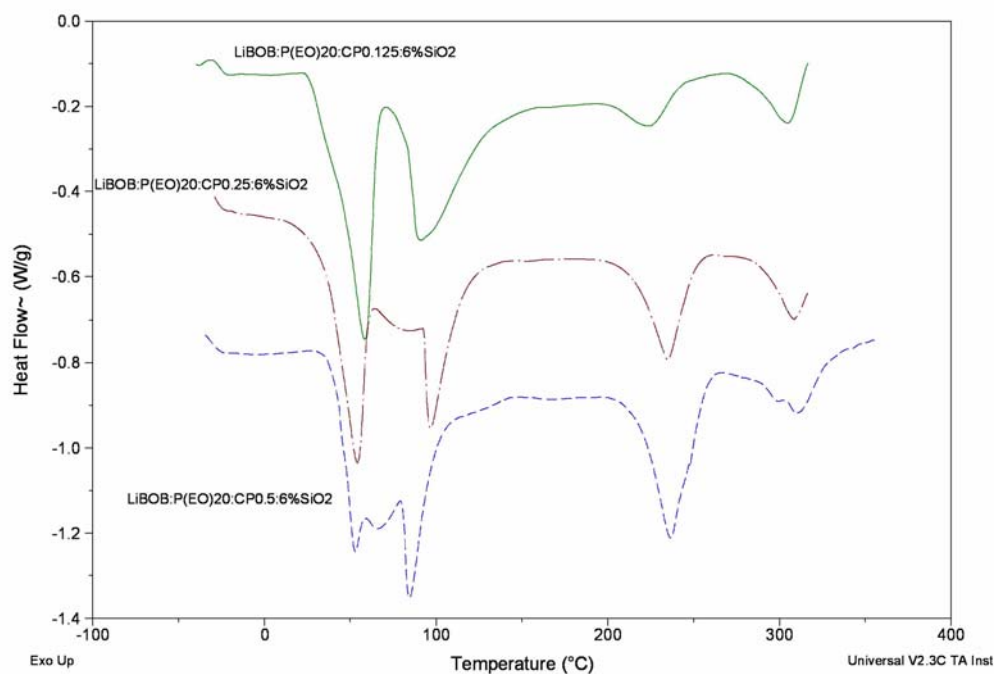


Fig. 3d. DSC thermograms of LiBOB:P(EO)₂₀ with silica and calixpyrrole additives

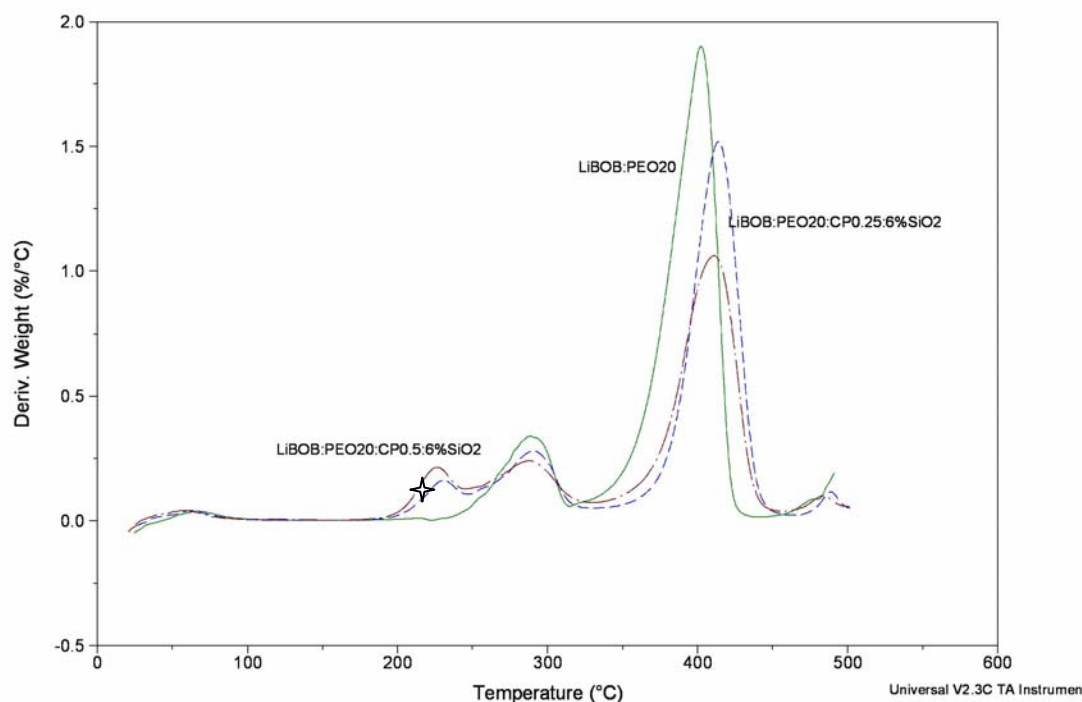


Fig. 3e. DTG thermograms of LiBOB:P(EO)₂₀ with silica and calixpyrrole additives
Noteworthy that silica does not influence significantly the temperature and weight loss of the transition associated with anion trap-BOB complex (Fig.3f, marked by star), however the dual modified LiBOB:P(EO)₂₀ membrane is the most thermally stable at high temperatures (Table 1). This may indicate the complex character of PEO-CP and PEO-SiO₂ interactions, the mechanism of which is still unclear.

Table 1. Weight loss (WL) of LiBOB:P(EO)₂₀ polymer electrolytes at 450°C.

Composition	WL,%
LiBOB:P(EO) ₂₀	97.7
LiBOB:P(EO) ₂₀ :6%SiO ₂	93.5
LiBOB:P(EO) ₂₀ :CP _{0.125}	93.9
LiBOB:P(EO) ₂₀ :CP _{0.125} :6%SiO ₂	78.6
LiBOB:P(EO) ₂₀ :CP _{0.25}	83.7
LiBOB:P(EO) ₂₀ :CP _{0.25} :6%SiO ₂	78.7
LiBOB:P(EO) ₂₀ :CP _{0.5} :6%SiO ₂	72.0

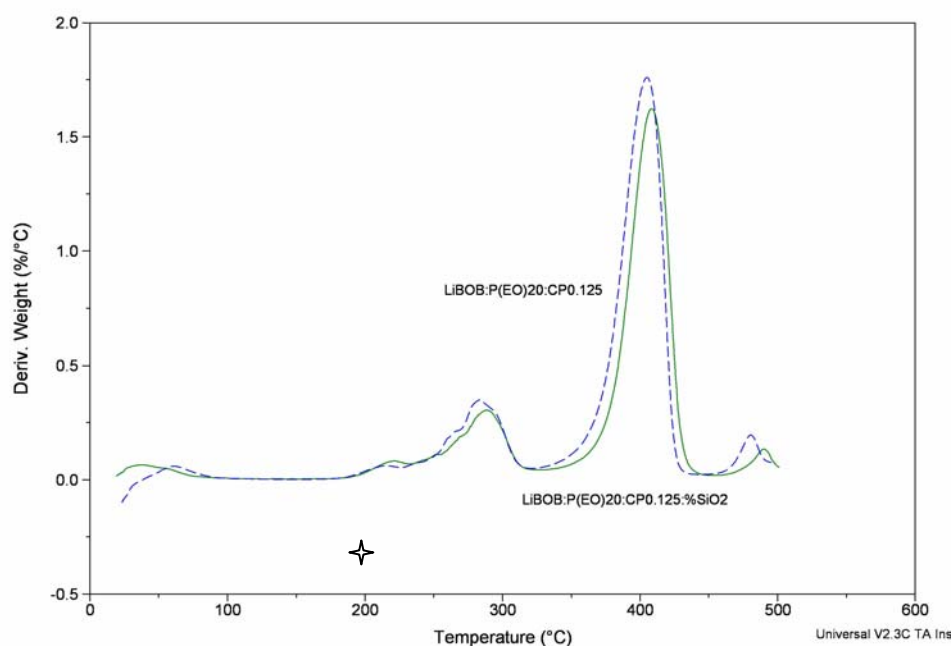


Fig. 3f. DTG thermograms of LiBOB:P(EO)₂₀:CP_{0.125} with and without silica

From the Table 2 one can see that typically the enthalpy and melting temperature values of the 1st endotherm of LiBOB-PEs are lower than those of LiTf-based membranes, indicating that former electrolytes are less crystalline than later.

Table 2. DSC data of the LiCF₃SO₃:P(EO)_n polymer electrolytes containing CP and silica

PE composition	Onset point of the main endotherm (T _{on})°, C	Enthalpy of the main endotherm (ΔH), J/g	Total enthalpy of the peaks (up to 150°C) (ΔH) J/g	Height of the main endotherm, W/g	Width of the main endotherm, °C
PEO (cast in AN+DCM)	59.2	160		1.8	10.0
LiTf:P(EO) ₂₀	59.6	120		1.7	10.0
LiBOB:P(EO) ₂₀	32	65.6	128.2	0.49	17.7

			2 peaks		
LiTf:P(EO) ₂₀ :SiO ₂	48.1	124		1.2	
LiBOB:P(EO) ₂₀ :SiO ₂	38.1	3	146.4	0.67	25
		overlapping peaks (2 nd >1 st >3 rd)			
LiTf:P(EO) ₂₀ :CP _{0.125}	53.0	116		1.5	10.3
LiBOB:P(EO) ₂₀ :CP _{0.125}	38.3	96.3	124.7	0.76	21.7
LiTf:P(EO) ₂₀ :CP _{0.125} 6%SiO ₂	61.6	124	148.6	1.5	11.8
LiBOB:P(EO) ₂₀ :CP _{0.125} 6%SiO ₂	38.8	64.2	136.9	0.56	16.6
LiTf:P(EO) ₂₀ :CP _{0.25}	57.0	86		1.4	7.9
LiBOB:P(EO) ₂₀ :CP _{0.25}	38.8	3 peaks	143.8	0.68	15.6
LiTf:P(EO) ₂₀ :CP _{0.25} 6%SiO ₂	55.0	89	156.6	1.1	10.3
LiBOB:P(EO) ₂₀ :CP _{0.25} 6%SiO ₂	37.6	3 peaks	134.2	0.56	15.1
LiTf:P(EO) ₂₀ :CP _{0.5}	60.2	103	130.7	2.2	6.4
LiTf:P(EO) ₂₀ :CP _{0.5} :SiO ₂	53	87	156.1	1.1	10.5
LiBOB:P(EO) ₂₀ :CP _{0.5} :SiO ₂	36.5	3 peaks	127.3	0.29	16.0

3.2. Conductivity results

3.2.1. Bulk and Grain Boundary (GB) Conductivity

Fig. 4 displays the Arrhenius plots of the bulk conductivities of LiBOB:PEO₂₀ free-of-additives and CP and SiO₂ containing polymer electrolytes. Increase of temperature up to 50°C is followed by a considerable enhancement of the bulk conductivities of all electrolytes. In the case of GB conductivity (Fig. 5) this enhancement is smaller, with a less steep slope than in the case of bulk conductivity. When comparing the bulk and GB conductivities of LiBOB:PEO₂₀ to that of LiTf:PEO₂₀, it should be mentioned that the slope of the Arrhenius plots at T<T_m for the LiTf:PEO₂₀-semi crystalline system is much more steep. This is probably due to the relatively high conductivities that the less crystalline LiBOB:PEO₂₀

exhibits at temperatures below its melting point, in comparison to the low conductivities of LiTf:PEO₂₀ film. The conductivity data are in a good agreement with SEM and DSC tests. Incorporation of CP at 1/8 of the salt content causes deterioration by about 2.5 times of the bulk and GB conductivities in comparison to the pure-LiBOB-based film at all temperatures. Further incorporation of SiO₂ 130 and 380 m²/g results in an enhancement of the bulk and GB conductivities in comparison to the solely-CP-incorporated PE. Contrary to the LiTf-based PEs σ_{gb} is close to σ_{bulk} over all temperature range studied and the highest bulk and GB conductivity values at near ambient temperatures were achieved for dual modified composite PEs with SiO₂ 130.

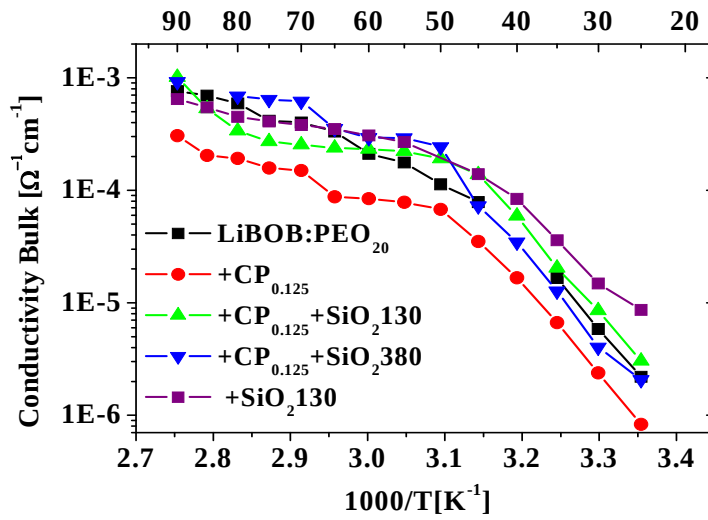


Figure 4. Arrhenius plots of bulk conductivity of LiBOB:PEO₂₀-based polymer electrolytes with CP (1:0.125) and SiO₂ additives.

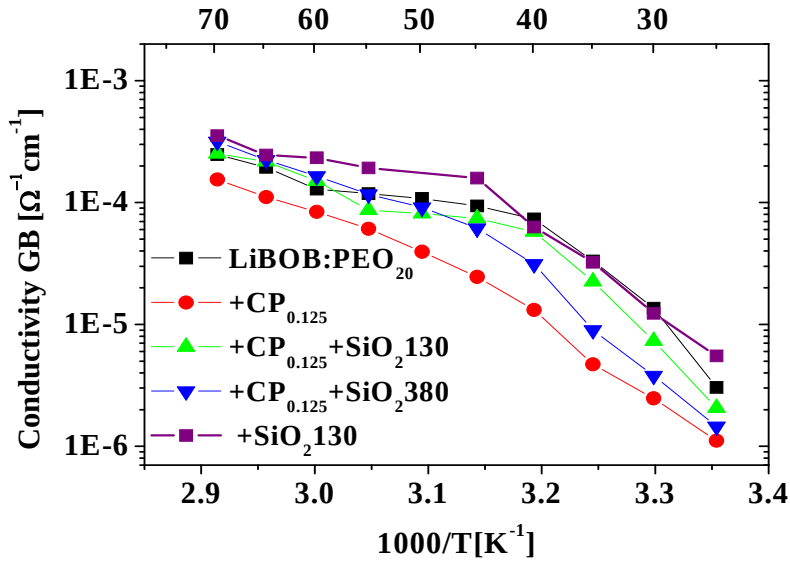


Figure 5. Arrhenius plots of GB conductivity of LiBOB:PEO₂₀-based polymer electrolytes with CP (1:0.125) and SiO₂ additives.

3.2.2. SEI Resistance

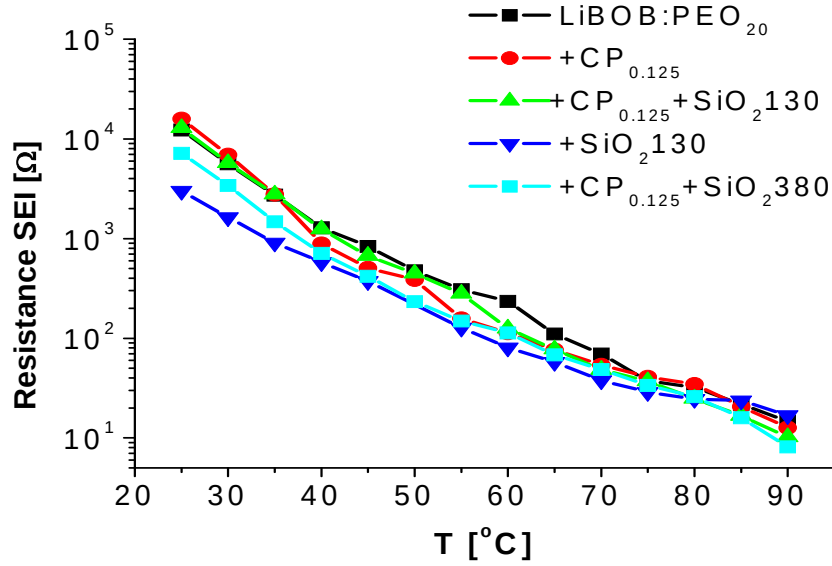


Figure 6. SEI resistance for Li/LiBOB:PEO₂₀/Li cell with and without CP and SiO₂ additives in the PEs.

When studying the effect of incorporation of CP and SiO₂ 130 m²/g (1:0.125 salt-to-additive ratio) on the interfacial resistance of the Li/LiBOB:P(EO)₂₀/Li cell (Fig. 4), it was found that

there is almost no change of the SEI resistance in comparison to the pure PE film. For this type of PE, the addition of silica to the neat electrolyte caused not much more than a slight improvement in the Li/PE interfacial resistance at low-medium temperatures. This is probably due to the amorphous nature of the LiBOB:PEO₂₀ polymer electrolyte.

3.3. Lithium ion transference number results

As can be seen from table 3, LiBOB-based polymer electrolytes containing 0.125 mole of calix[6]pyrrole, display a significant enhancement in the transference number at all temperatures. For an example, pure LiBOB:PEO₂₀ exhibited t_{Li+} value of 0.43 at 75°C, while addition of CP_{0.125} to the matrix increased the t_{Li+} to 0.76 at this temperature. Further addition of SiO₂ 130 and 380 to the matrix did not deteriorate the transference number much (0.72 and 0.70 for SiO₂ 130 and SiO₂ 380, respectively).

Incorporation of only the SiO₂ 130 additive to the matrix caused a minor enhancement of the transference number in comparison to the neat LiBOB:P(EO)₂₀.

Table 3. Transference number experimental data for LiBOB:PEO₂₀ electrolytes with and without CP and SiO₂ additives.

Polymer electrolyte composition	Temperature [°C]	t ₊
LiBOB:P(EO) ₂₀	75	0.43
LiBOB:P(EO) ₂₀	90	0.41
LiBOB:P(EO) ₂₀ :(CP) _{0.125}	60	0.64
LiBOB:P(EO) ₂₀ :(CP) _{0.125}	75	0.76
LiBOB:P(EO) ₂₀ :(CP) _{0.125}	90	0.68
LiBOB:P(EO) ₂₀ :(CP) _{0.125} + 6% SiO ₂ 130 m ² /g	60	0.63
LiBOB:P(EO) ₂₀ :(CP) _{0.125} + 6% SiO ₂ 130 m ² /g	75	0.72
LiBOB:P(EO) ₂₀ :(CP) _{0.125} + 6% SiO ₂ 130 m ² /g	90	0.61
LiBOB:P(EO) ₂₀ :(CP) _{0.125} + 6% SiO ₂ 380 m ² /g	55	0.62
LiBOB:P(EO) ₂₀ :(CP) _{0.125} + 6% SiO ₂ 380 m ² /g	60	0.63
LiBOB:P(EO) ₂₀ :(CP) _{0.125} + 6% SiO ₂ 380 m ² /g	75	0.70
LiBOB:P(EO) ₂₀ :(CP) _{0.125} + 6% SiO ₂ 380 m ² /g	90	0.60
LiBOB:P(EO) ₂₀ + 6% SiO ₂ 130 m ² /g	60	0.49
LiBOB:P(EO) ₂₀ + 6% SiO ₂ 130 m ² /g	75	0.47
LiBOB:P(EO) ₂₀ + 6% SiO ₂ 130 m ² /g	90	0.43

Increase of the CP content to 1:4 and 1:2 additive-to-salt ratio has a minor effect on the t_+ . This observation raises a question of the mechanism of BOB-anion immobilization by the CP trap. Additional tests, like FTIR, are essential to elucidate the structure of the complex and mechanism of bonding.

Table 4. Summary of conductivity, resistance and transference number values for LiBOB:PEO₂₀ polymer electrolytes with and without CP and SiO₂ additives at 90°C.

Polymer (90°C)	R_{bulk} [Ω]	σ_{bulk} [Ωcm]⁻¹	R_{sei} [Ω]	t₊	d[μm]
LiBOB:PEO ₂₀	8.723	7.64x10 ⁻⁴	14.715	0.41	80
+ SiO ₂ 130	12	6.48x10 ⁻⁴	16.9	0.43	100
LiBOB:PEO ₂₀ :CP _{0.125}	21.72	3.07x10 ⁻⁴	12.69	0.68	120
+CP _{0.125} + SiO ₂ 130	8.762	2.36x10 ⁻⁴	10.175	0.61	150
+CP _{0.125} + SiO ₂ 380	9.043	9.22x10 ⁻⁴	8.17	0.70	150

Table 5. Summary of conductivity, resistance and transference number values for LiBOB:PEO₂₀ polymer electrolytes with and without CP and SiO₂ additives at 75°C.

Polymer (75°C)	R_{bulk} [Ω]	σ_{bulk} [Ωcm]⁻¹	R_{sei} [Ω]	t₊	d[μm]
LiBOB:PEO ₂₀	15.98	4.17x10 ⁻⁴	69.495	0.43	80
+ SiO ₂ 130	19	4.09x10 ⁻⁴	28.9	0.47	100
LiBOB:PEO ₂₀ :CP _{0.125}	42.26	1.58x10 ⁻⁴	41.025	0.76	120
+CP _{0.125} + SiO ₂ 130	32.813	2.71x10 ⁻⁴	37.07	0.72	150
+CP _{0.125} + SiO ₂ 380	12.96	6.43x10 ⁻⁴	33.72	0.63	150

3.4. Cyclic voltammetry

Cyclic voltammetry measurements were performed at various temperatures using a Li/SPE/SS cell arrangement over a wide voltage range (0.5-5.0 V) and sweep rate of 20mV/s.

This test is crucial for further continuation of the research of LiBOB-based polymer electrolyte as a battery membrane for the following reasons. First, there is an interest in conducting these tests in order to determine the electrochemical stability of the polymer electrolytes, as well as the influence of the CP and ceramic additives upon this stability. Secondly, the possibility of electro-polymerization of the CP additive was suspected, particularly at high temperatures. In addition, ether-based solvents are known to oxidatively degrade at relatively low voltage (e.g. 2.5-3.5 V vs. Li^+/Li). As a result, there is an interest in determining the electrochemical stability of the PEO-based polymer systems. Establishing the voltage window for these materials is especially important, given that the electrochemical stability will dictate which cathodes are appropriate in battery applications.

As shown in Fig.7, when cyclic-voltammetry tests were performed at different temperatures on a pure and silica-incorporated lithium BOB polymer electrolyte, electrochemical instability is observed even at 60°C over a voltage range of 0.5-5.0V vs. Li^+/Li in the anodic and cathodic regions, which is dramatizes at higher temperatures (75 and 90°C). In the cathodic region, reduction reactions of the salt, impurities and PEO form soluble products as well as SEI. The irreversible anodic peak at 2.0-2.5V may be associated with the oxidation of PEO, the BOB anion and possibly the SS electrode.

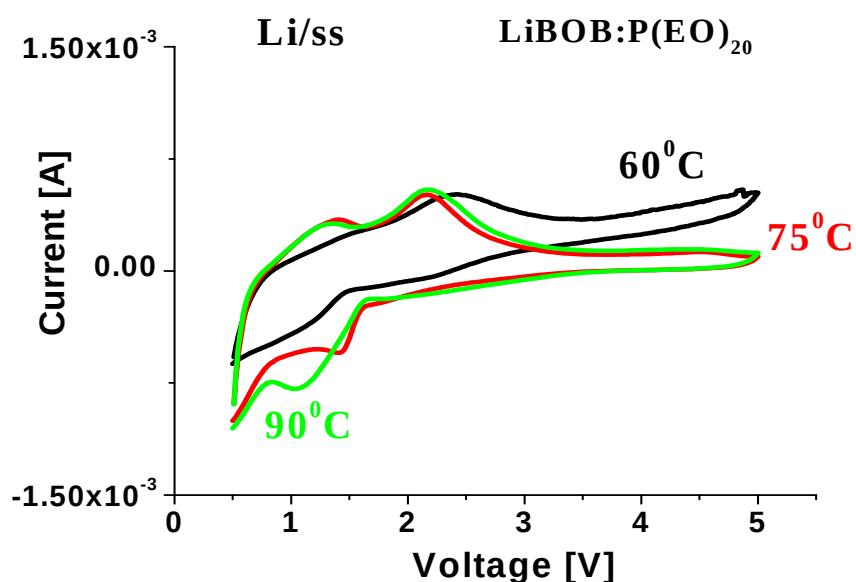


Figure 7. Cyclic voltammograms of Li/SPE /SS cells at 60, 75 and 90°C.

The introduction of the calixpyrrole additive to the LiBOB-based membrane at 75°C (Fig.8), causes a decrease in the oxidative and reductive instability in comparison to the pure PE. The combined positive impact of the anion trap and inorganic filler is even more pronounced. As displayed in this figure, the single-cation-conducting composite polymer electrolyte shows significantly enhanced electrochemical stability. This is probably due to the formation of a CP-BOB complex, followed by suppressed anion reduction. Silica, in addition, can eliminate undesired reactions, due to the fact that silica serves as a scavenger and adsorbs PE impurities.

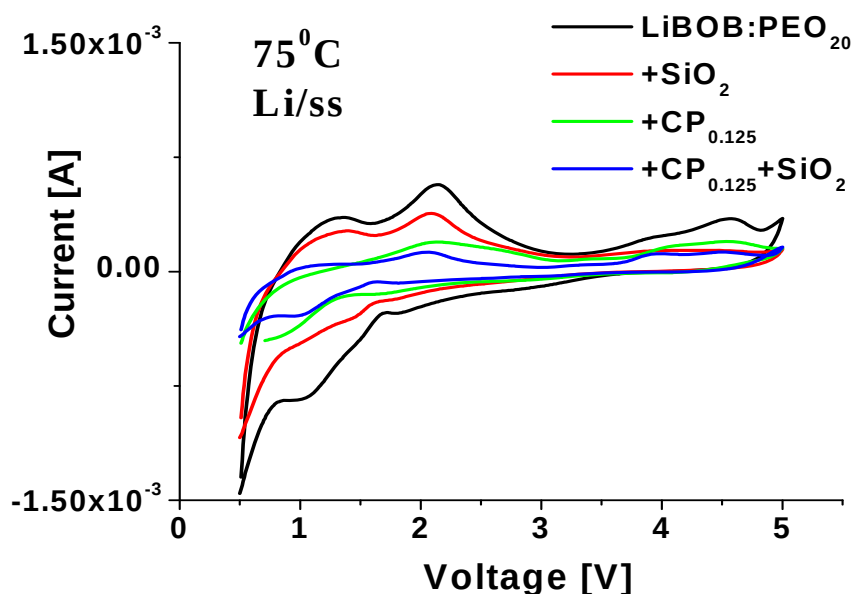
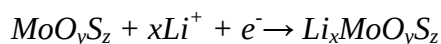


Figure 8. Cyclic voltammograms of Li/LiBOB:PEO₂₀/SS cells with and without CP and SiO₂ 130 additives at 75°C.

3.5. Cycle life and polarization curve results

3.5.1. Cycle life results

Li/MoO_xS_y thin-film batteries with pure and additives-incorporated polymer electrolytes were assembled and run over 100 reversible cycles in the temperature range of 75, 90 and 110°C at a low discharge rate of about 0.5C (Fig. 9). At 75°C, the capacity is very stable for



to which is associated a voltage maximum of 2.7 V Li/Li⁺.

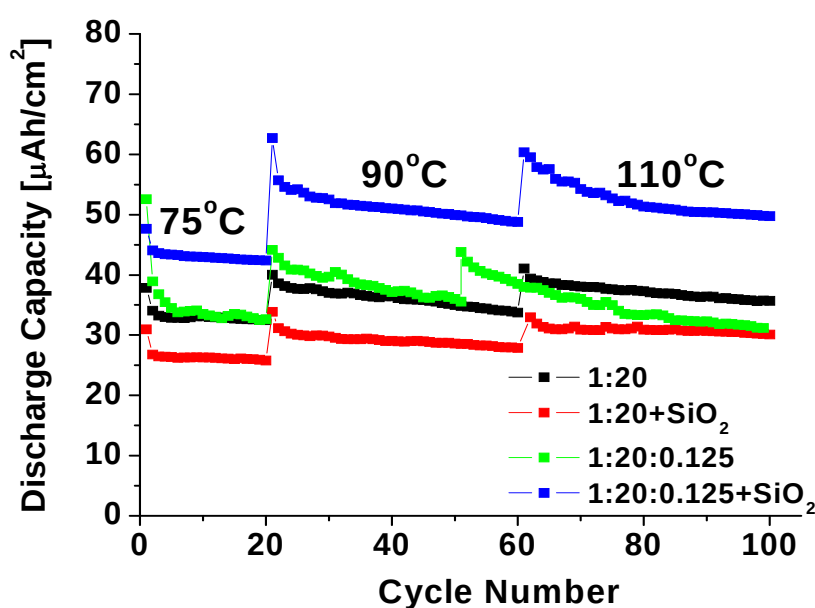


Figure 9. Cycle life curves of Li/LiBOB:PEO₂₀ /MoO_xS_y thin-film batteries with and without CP and SiO₂ 130 additives at various temperatures.

3.5.2. Polarization curves

The polarization curves of the pure polymer electrolyte and the additives-incorporated membranes at various temperatures are shown in Figure 10. From the graphs that show the power as a function of the applied current at 75°C (Figure 10a), it can be seen that the peak power of the Li/MoO_xS_y thin film cell with the pure LiBOB:PEO₂₀ membrane is about 2.2mW/cm² (at 66C). Incorporation of CP to the Li/MoO_xS_y cell, caused to a drastic

At 90°C the results are more satisfactory than those recorded at 75°C. As can be seen from the graph (Fig. 10b), the peak power of the cell with the pure LiBOB:PEO₂₀ film and that containing CP is about 2.1mW/cm² (at 80C) and 1.3mW/cm² (at 33C) respectively, however the thickness of the film in the CP containing cell is larger (150 vs 90 micron) than that of the CP free film, a fact that causes higher internal resistance. While adding both CP and silica, the high peak power value of about 2.1mW/cm² (55C) was achieved.

As can be seen from Fig. 10c, a higher and more stable power capability (2.5mW/cm²) was measured for all cells. It is worth mentioning that over the all temperature range studied the cell with dual modified PE does not reach its maximal peak power values. It expected that continuation of the tests at current densities higher than 3 mA/cm² may show much better results than pure polymer electrolyte with t₊ lower than 0.5.

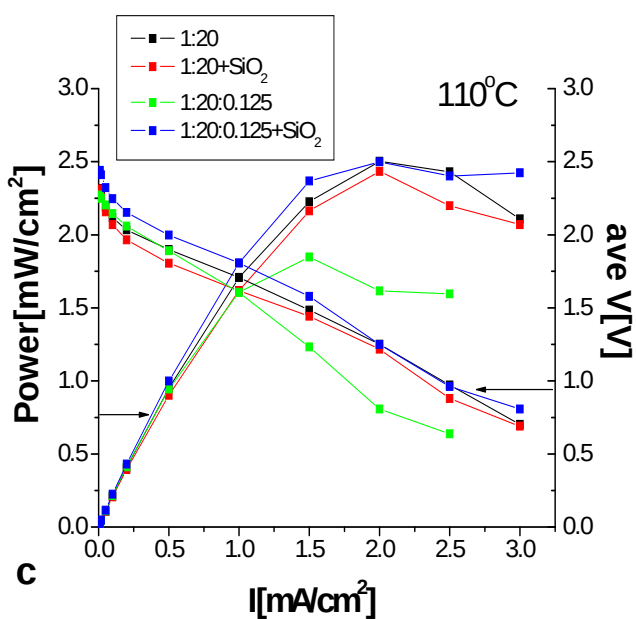
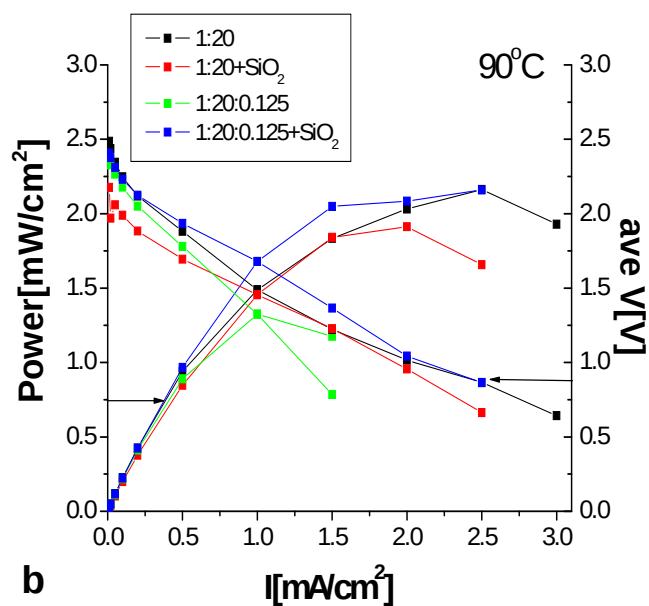
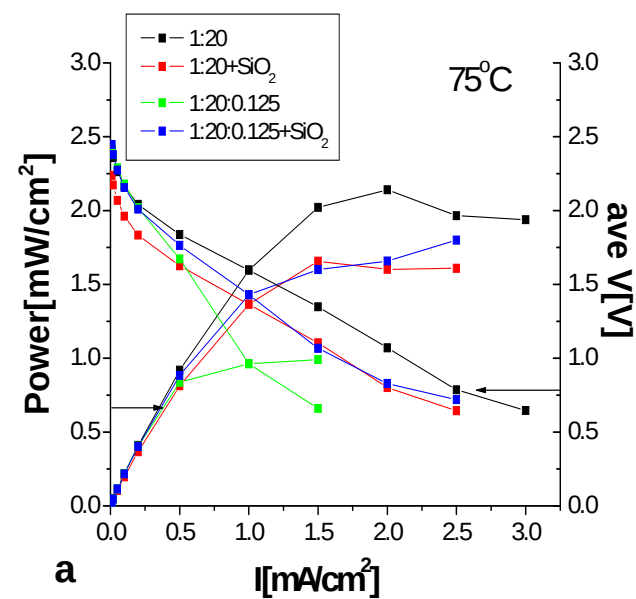


Figure 10. Polarization curves of thin-film Li/LiBOB:PEO₂₀:CP_{0.125}:SiO₂/MoO_xS_y cells at a) 75°C; b) 90°C and c) 110°C.

Conclusions

The work presented in this report demonstrate the applicability of the selected LiBOB:PEO₂₀:CP_{0.125} + SiO₂ 130 polymer electrolyte as a membrane in a rechargeable lithium battery using a MoO_xS_y as a cathode. The supplementation of calixpyrrole and silica additives to the LiBOB:PEO₂₀ matrix caused an impressive improvement on the lithium transference number, ionic conductivity and electrochemical stability. These results, together with our previous results using different lithium salt, LiCF₃SO₃, give rise to the conclusion that these additives-incorporated PEs display satisfactory performances as separators for high-power lithium batteries for multi applications.