



Ion-conducting lithium bis(oxalato)borate-based polymer electrolytes

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ABSTRACT

Poly(2-ethoxyethyl methacrylate) polymer gel electrolytes containing immobilised lithium bis(oxalato)borate in aprotic carbonates: propylene carbonate (PC), propylene carbonate–ethylene carbonate (PC–EC 50:50 vol.%) and diethyl carbonate–ethylene carbonate (DEC–EC 50:50 vol.%) were prepared by a direct radical polymerisation. The electrolyte composition was optimised to achieve suitable ionic conductivity 0.5 and 2.4 mS cm^{−1} at 25 and 70 °C respectively along with good mechanical properties. The electrochemical stability up to 5.1 V vs. Li/Li⁺ was determined on gold electrode by voltammetrical measurements. The polymer electrolytes with high-boiling solvents (PC and PC/EC) showed higher thermal stability (up to 110–120 °C) compared to the liquid electrolytes. The proposed area of application is in the lithium-ion batteries with cathodes operating at elevated temperatures of 70 °C, where higher electrochemical stability of the polymer electrolytes is employed.

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1. Introduction

Modifications of recently used chemical power sources (lithium and lithium-ion batteries, supercapacitors) are following economical, environmental and safety regulations and demands. In the case of the device electrolyte, substitution of common liquid electrolytes with solid or polymer systems is highly appreciated. In last four decades, many attempts were done since Fenton et al.'s [1] and Armand's [2] independently introduced poly(ethylene oxide)–LiClO₄ binary electrolytes.

Beyond many others, acrylate and methacrylate-based polymers and copolymers play important role due their wide availability, low toxicity and good electrochemical stability. Monomer and polymer structure can be modified and functionalised following various demands on the polymer functionality [3–6], system polarity or polymerisation volume contraction. On contrary to many other polymers, methacrylate-based electrolytes can be directly prepared by the radical polymerisation, when the casting method is bypassed. Commonly developed and studied polymer electrolytes are ternary systems consisting of a polymer, an aprotic solvent and a lithium salt. Their high electrochemical stability allows their application as a part of the electrolyte in lithium-ion batteries [7–11].

Aliphatic carbonates dominate among the solvents used in the polymer electrolytes and propylene carbonate (PC) is attractive due to its high dielectric constant, wide temperature range of liquidity (down to −49 °C) and low vapour pressure. Unfortunately propylene carbonate is co-intercalated into the graphite anode during the charge process, when PC molecules are strongly solvating the Li⁺ cation. This co-intercalation causes the exfoliation of the graphite structure and disintegration of electrode [12,13]. The solution of this problem can be in employing additives that form stable SEI layer preventing the graphite disintegration such as ethylene carbonate [14], vinylene carbonate [15] or 2-cyanofurane [16]. Another approach is included in our paper and is based on using lithium bis(oxalato)borate as a salt and a partially cross-linked polymer stabilising the structure of the electrolyte.

Introducing weakly coordinating bis(oxalato)borate anion (BOB[−]) and its derivatives in 2001 and 2002 included important improvement in the area of the electrolytes for lithium-ion batteries [17,18] due to its stabilising effect of the graphite anode, low tendency to hydrolyse contrary to LiPF₆ and good electrochemical stability in contact with aluminium current collectors. The graphite anodes can be used with LiBOB even in the case of pure propylene carbonate [19]. Since 2001, also polymer electrolytes with LiBOB were prepared by Scrosati and coworkers [20] and West and coworkers [21].

In our recent paper we present results of investigation of new LiBOB-based polymer electrolytes in different solvents (PC, PC–EC and DEC–EC) entrapped in the structure of partially cross-linked

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2-ethoxyethyl methacrylate polymer network. The main advantages of the studied electrolytes are in the improvement of the SEI layer by present LiBOB and/or ethylene carbonate, higher thermal stability and lower reactivity especially towards oxidation. Also the influence of the present polymer on the electrolyte overall reactivity has to be included following the conclusions of Kim et al. [8], Wan and coworkers [22] and Tatsuma et al. [23].

The lower reactivity of the polymer electrolyte compared to the liquids was suggested by Song et al. [22], when the overall reactivity of the electrolyte can be lowered by present polymer that can be considered as electrochemically stable. Georén and Lindbergh proposed the effect of the polymer on the reaction rate with similar effect [24]. Good stability of polymer electrolytes towards oxidation would allow the application of polymer electrolytes in combination with cathodes operating at higher temperatures (around 70 °C) such as Li_2MSiO_4 ($M = \text{Fe}$ and/or Mn) [25,26]. Our work is based on our previous investigation of polymer gel electrolytes containing embedded PC– LiClO_4 electrolytes combined with various methacrylates, where we achieved the ionic conductivity values 0.7 mS cm^{-1} at 20 °C together with wide electrochemical window (over 5.0 V vs. Li/Li^+) (ref. [27,28]).

2. Experimental

Monomer, 2-ethoxyethyl methacrylate was obtained from Sigma–Aldrich and distilled under reduced pressure. The cross-linking agent, 1,6-hexandiol dimethacrylate (HexadiMA, Sigma–Aldrich) was used as received. The polymerisation initiator, 2,2'-azobis(isobutyronitrile) (AIBN; Sigma–Aldrich) was recrystallised from chloroform and dried at 20 °C in a vacuum. All monomers and the initiator were stored at 4 °C before use.

Propylene carbonate, ethylene carbonate and diethyl carbonate (anhydrous; all from Sigma–Aldrich) were used as received. Battery grade lithium bis(oxalato)borate was obtained from Chemetall. All chemicals were stored in an argon-filled glove box (MBraun, Germany).

2.1. Polymer electrolyte preparation

Polymer electrolytes were prepared using direct, radical thermally initiated polymerisation following our previous experiments [27,28]. The initial mixture was prepared in a glove box and contains monomer (EOEMA), cross-linking agent (HexadiMA; 0.3 mol.% of monomer), polymerisation initiator AIBN (1 mol.% of monomers) and 0.7 m (molality) solution of LiBOB in PC, PC–EC (50:50 vol.%) or DEC–EC (50:50 vol.%). After homogenisation, the cell for sample preparation was filled with the initial mixture and placed into an oven for a period of 2 h at 80 °C. The design of the cell disallows the contamination of the electrolyte by water or oxygen.

The polymer membranes were prepared either in PTFE cell or *in situ* on aluminium or copper foil electrodes what ensures a perfect contact between the electrolyte and the electrode.

The electrolyte composition of the electrolyte (polymer–solvent(s)–salt) is expressed in molar percentage, when the amount of cross-linking agent is involved in polymer content.

2.2. Electrolyte characterisation

Scanning electron microscopy (SEM) studies were performed using a Philips XL30 CP microscope equipped with EDX (energy dispersive X-ray), Robinson, SE (secondary electron) and BSE (back-scattered electron) detectors. The sample was placed on an adhesive C slice and coated with Au–Pd alloy layer of 10 nm thick.

X-ray patterns were obtained with a PANalytical Xpert'PRO diffractometer, using Bragg–Brentano geometry, in θ/θ reflection

mode. The instrument was equipped with a cobalt X-ray tube (Co $K\alpha$ radiation; 40 kV, 30 mA, line focus), a β -filter and X'Celerator multichannel detector. The X-ray patterns were collected in the angular range of 4–50° 2 Θ with a step size of 0.0167° and counting time of 100 s per step.

The simultaneous TGA–DTA measurement was taken in air and argon at the heating rate of 5 °C min^{-1} . Another TGA measurement was done isothermally at 70 °C for the period of 100 min. Experiments were performed with a Simultaneous Thermal Analysis Netzsch STA 409 (Germany). The DSC analysis was performed in the temperature range from –160 to 100 °C at the heating rate of 10 °C min^{-1} .

The potentiogalvanostat PGSTAT 30 (Eco Chemie, The Netherlands) and VMP3 potentiostat/galvanostat (Bio-Logic, France) were used for electrochemical measurements including the modules for impedance measurements. Conductivity measurements were performed by using the impedance spectroscopy, when the influence of temperature was studied in the range from 20 to 70 °C. Here, a slice of gel (2 cm \times 2 cm) was sandwiched between two parallel stainless steel blocking electrodes and a single potential impedance spectrum was measured in the frequency range from 200 kHz to 1 Hz. The obtained spectrum was analysed by the Eco-Chemie Autolab software producing the values of the equivalent circuit elements.

The initial electrochemical investigation of prepared polymer gel electrolytes was performed with a gold (BASi, 1.6 mm in diameter) working electrode and a glassy carbon counter electrode. The solid-state PMMA–Cd– Cd^{2+} system was used as a reference electrode, which was developed in our laboratory for electrochemical investigation of liquid and polymer aprotic systems $E(\text{PMMA–Cd–Cd}^{2+}) = 2.66 \text{ V vs. Li/Li}^+$ in propylene carbonate [29].

The electrochemical characteristics on aluminium and copper were measured in a vacuum-sealed triplex foil (coffee bag foil) cells in a two-electrode system. The working electrodes were 16 mm discs of copper or aluminium foil, which were covered with the *in situ* prepared polymer electrolyte or with a glass wool separator soaked with the reference liquid electrolyte (DEC/EC–LiBOB). As a counter and reference electrode thin lithium foil was used. Cyclic voltammetric measurements were performed at 80 °C with a scan rate of 2 mV s^{-1} in the potential range from +3 to 0 V vs. Li/Li^+ , when Cu substrate was used and in the potential range from +5 to +1 V, when Al substrate was used.

3. Results and discussion

3.1. Physical properties, XRD and SEM analysis

The prepared electrolytes are elastic and homogeneous membranes of a thickness from 0.5 to 1.0 mm. All used chemicals are colourless, therefore the prepared membranes are highly transparent. No phase-to-phase separation (neither solvent exudation nor salt crystallisation) was observed during storage in an inert atmosphere. The samples stored at air became slightly opaque due to the absorption of water.

Fig. 1 illustrates the morphology of the surface of PEOEMA–PC–LiBOB electrolyte investigated by scanning electron microscope. Amorphous structure was found in all electrolytes. The inhomogeneities on Fig. 1 are caused by partial evaporation of the solvent in vacuum of the microscope chamber. The homogenous structure of the polymer electrolytes was confirmed also by the optical microscope observation.

Fig. 2 shows the diffraction patterns of LiBOB, PEOEMA and PEOEMA–PC–LiBOB electrolyte. The measurements showed no remaining peaks attributed to LiBOB in the pattern of PEOEMA–PC–LiBOB electrolyte and the PEOEMA polymer itself is

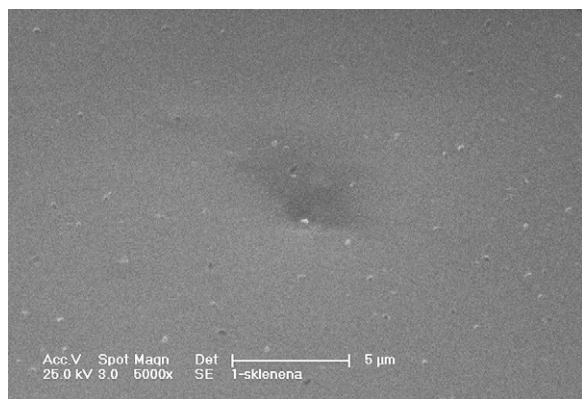


Fig. 1. Typical surface morphology of PEOEMA-PC-LiBOB electrolyte (38:58:4 mol.%) on the SEM image (5000 \times magnification).

amorphous with only weak diffraction peaks at $2\theta = 8.9^\circ$ and 21° . This indicates that the lithium salt is fully dissolved in the structure of the polymer electrolyte. The peaks of PEOEMA are only slightly shifted in the presence of PC-LiBOB.

Prepared membranes are well sticky, but do not leave any traces on glass or electrode after removal. The 180° peel tests (following ISO 8510-2:2006) showed very good adhesion of the PEOEMA electrolytes to various substrates (e.g. FTO- WO_3 and FTO- V_2O_5 coated glasses [28]). Moreover, the *in situ* polymerisation with aluminium or copper foil is enhancing the contact between the electrodes and the electrolyte. A similar method of the *in situ* preparation was successfully used in the case of the electrochromic device based on the intercalation principle and employing PEOEMA-PC-LiClO₄ polymer electrolyte [28]. The polymer network was partially cross-linked by dimethacrylate units, what improved the mechanical properties and also has a positive effect on the ion mobility at this level of cross-linkage (0.3 mol.% of monomer) [27].

The polymer electrolytes with immobilised DEC/EC solvents have a typical odour of partially evaporating DEC solvent if the electrolyte is stored in open space. Contrary to that, the electrolytes with PC and PC/EC solvents are long-term stable and the solvent does not evaporate.

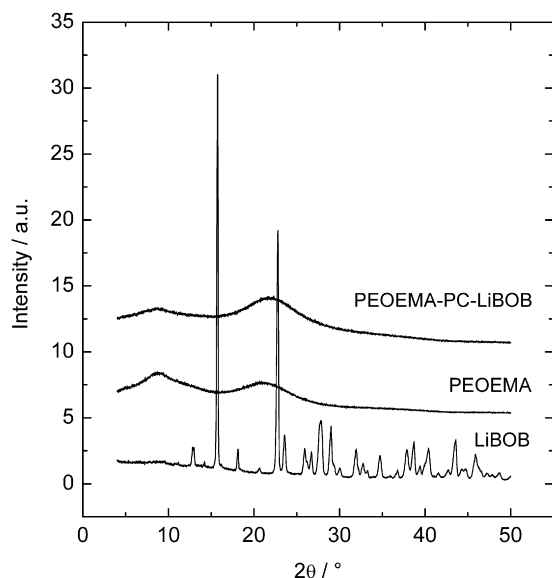


Fig. 2. X-ray diffraction patterns of pure LiBOB and PEOEMA and PEOEMA-PC-LiBOB electrolyte (45:51:4 mol.%).

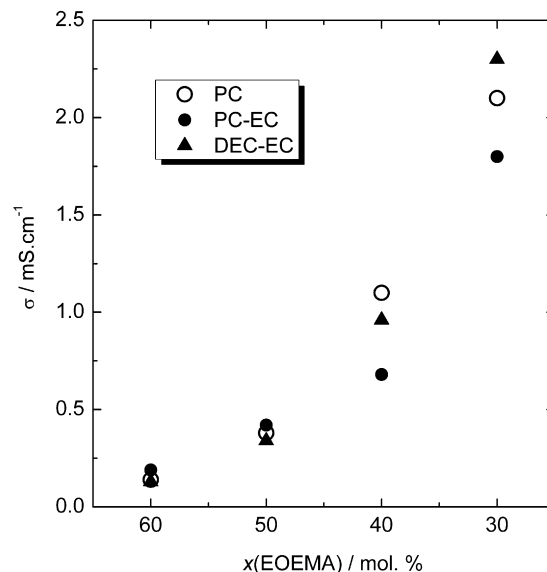


Fig. 3. Isothermal dependence of the polymer electrolyte conductivity on the content of polymer and type of the immobilised solvent PC, PC-EC or DEC-EC (measured at 70°C).

3.2. Impedance and conductivity measurements

The recently used liquid electrolytes with LiBOB achieve the highest conductivity about 3 mS cm^{-1} at room temperature at the concentration $0.6\text{--}0.7\text{ mol kg}^{-1}$ (ref. [30,31]). On the other hand, the binary system PEOEMA-PC is practically non-conductive (below 10^{-7} S cm^{-1} at 20°C ; ref. [28]). Our task was to optimise the electrolyte composition, thus the ratio PEOEMA-solvent-LiBOB. Following the investigation of Jow et al., the concentration of LiBOB in particular solvents was chosen to be 0.7 mol kg^{-1} and three series of polymer electrolytes were prepared: PEOEMA-PC-LiBOB, PEOEMA-PC/EC-LiBOB and PEOEMA-DEC/EC-LiBOB with decreasing content of the polymer. It is important to stress the fact, the not only the absolute concentration of the lithium salt is important, but the ratio salt-solvent plays important role because of a strong tendency of lithium salts to form ion-ion pairs at higher salt concentrations both in polymer and liquid aprotic electrolytes [27,31].

Decreasing content of the polymer affects the mechanical properties of the electrolyte (increasing fluidity and elasticity) along with an improvement of the conductivity. Fig. 3 presents the dependency of the ionic conductivity at 70°C on the polymer content. The positive effect on the conductivity is clearly visible while the conductivity of PEOEMA-PC-LiBOB electrolyte increases from 1.4×10^{-4} to $2.1 \times 10^{-3}\text{ S cm}^{-1}$ due to reduction of the polymer amount used for the electrolyte preparation from 60 to 30 mol.%. A similar improvement was observed also in the case of polymer electrolytes with PC/EC and DEC/EC (see Fig. 3). Despite lower content of polymer, the mechanical properties of the gels with a lower content of PEOEMA remain good and allow the manipulation and investigation. Following the results of the electrolyte composition optimisation, for further electrochemical experiments we focused on the samples with c. 30 mol.% content of PEOEMA.

As we are aiming our further work on the tests with cathodes operating at temperatures of $60\text{--}80^\circ\text{C}$, we studied the influence of temperature on the ionic conductivity. Fig. 4 presents the relationship between the ionic conductivity of prepared polymer electrolytes and temperature, the data are plotted in Arrhenius coordinates (specific conductivity is plotted as a decadic logarithm). All three samples exhibit similar conductivity and reach reason-

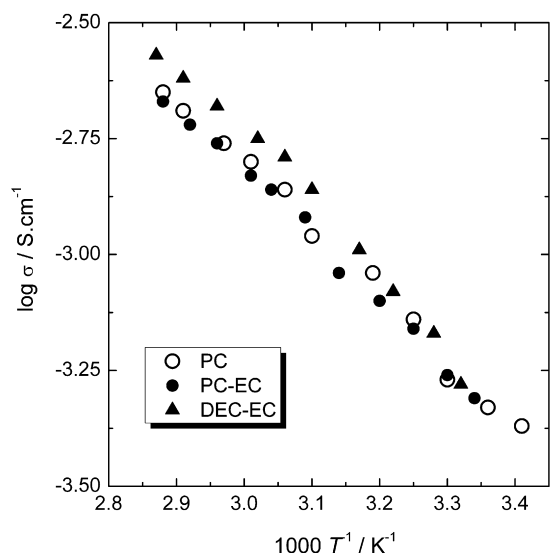


Fig. 4. Arrhenius plot for PEOEMA electrolytes with PC-LiBOB, PC/EC-LiBOB and DEC/EC-LiBOB (temperature range 25–70 °C; for the electrolyte composition see Table 1).

able values of $1.9\text{--}2.4 \times 10^{-3} \text{ S cm}^{-1}$ at 70 °C, but also remain above $10^{-4} \text{ S cm}^{-1}$ at room temperature. Compared to our previously studied PEOEMA-PC-LiClO₄ [28] we have achieved higher conductivities both in the within the temperature region (see Table 1).

The obtained data can be fitted with the Vogel–Tamman–Fulcher (VTF) equation in the logarithmic form:

$$\sigma T^{1/2} = A \exp \left[\frac{-E_A}{R(T - T_0)} \right] \quad (1)$$

In this particular relationship A is the parameter related to the number of charge carriers, E_A is the activation energy for conduction, R is the universal gas constant and T_0 the ideal glass transition temperature indicating the temperature at which the free volume extrapolates to zero. The analysis of the experimental conductivity data in terms of the VTF relationship leads to the determination of three empirical parameters: A , E_A and T_0 , when T_0 is determined by fitting the experimental data with relationship (1). The conductivity activation energy corresponds to a slope in the Arrhenius coordinates (see Fig. 4) and explains how conductivity is influenced by temperature.

Calculated E_A values for chosen polymer electrolytes are summarised in Table 1. We can see similar values for all three electrolytes, that are lower than the E_A for previously studied PEOEMA-PC-LiClO₄ electrolyte [27,28]. Our previous investigations and also the results published by Bohnke [32] and Harris [34] showed, that the conduction activation energy is strongly dependent on the electrolyte composition, mainly on the ratio salt-solvent and the lowest values are usually found at the salt concentrations, where the conductivity is highest, thus the salt is most dissociated.

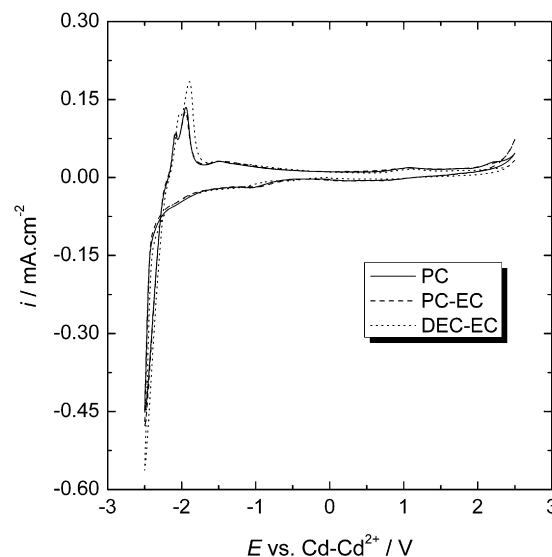


Fig. 5. Cyclic voltammograms of the PEOEMA electrolytes with PC-LiBOB, PC/EC-LiBOB and DEC/EC-LiBOB on gold electrode at 5 mV s^{-1} measured at 25 °C (counter electrode glassy carbon, reference electrode PMMA-Cd-Cd²⁺; for the electrolyte composition see Table 1).

3.3. Voltammetrical measurements

Lithium bis(oxalato)borate exhibits excellent cyclability and electrochemical stability, especially in the contact with the graphite anodes, where the reduction of the anion supports formation of a stable solid electrolyte interface (SEI), even in pure propylene carbonate solutions [19]. This effect principally allows the application of PC-based electrolytes without any further additives for the SEI layer formation, because of the propylene carbonate molecules tendency to co-intercalate into the graphite structure [12,13]. However, to support the SEI formation we prepared also the polymer electrolytes with PC/EC and DEC/EC solvents, as ethylene carbonate is used as a SEI-forming co-solvent in usual lithium-ion batteries [14,16,33].

The initial voltammetrical measurements of prepared electrolytes were done on gold electrode, where its higher catalytic activity should show the electrochemical behaviour close to the thermodynamic limit. Fig. 5 shows the cyclic voltammograms of prepared PEOEMA electrolytes. At the potential from -1 to -1.1 V vs. Cd/Cd²⁺ of the first scan we found an irreversible cathodic wave followed at -2.6 V vs. Cd/Cd²⁺ by deposition of lithium. In consequent scans the character of the voltammogram remains unchanged. The cathodic wave at -1 V can be attributed to formation of a protective layer on the surface of the gold electrode similarly to the regular SEI layer formed on materials used in lithium-ion batteries.

The split of the anodic peak of lithium oxidation into two peaks at -2.1 and -1.9 V is difficult to be explained, however it was already observed by some authors on stainless steel or gold electrodes. Aurbach et al. distinguishes between the lithium bulk dissolution and later decomposition of the Li-Au alloy and even

Table 1
Specific conductivities (at 25 and 70 °C) apparent activation energy values (E_A) and the glass transition temperatures determined by DSC (T_g) of studied polymer electrolytes containing LiBOB. For comparison, data for PEOEMA-PC-LiClO₄ electrolyte are given from [29].

Polymer electrolyte	Composition (mol.%)	σ (25 °C) (S cm^{-1})	σ (70 °C) (S cm^{-1})	E_A (kJ mol^{-1})	T_g (°C)
PEOEMA-PC-LiBOB	34:62:4	4.6×10^{-4}	2.1×10^{-3}	27.2	-96.2
PEOEMA-PC/EC-LiBOB	32:28/36:4	5.0×10^{-4}	1.9×10^{-3}	25.4	-96.4
PEOEMA-DEC/EC-LiBOB	34:22/40:4	5.0×10^{-4}	2.4×10^{-3}	25.1	-80.8
PEOEMA-PC-LiClO ₄	48:46:6	1.8×10^{-4}	7.0×10^{-4}	32.3	-78.0

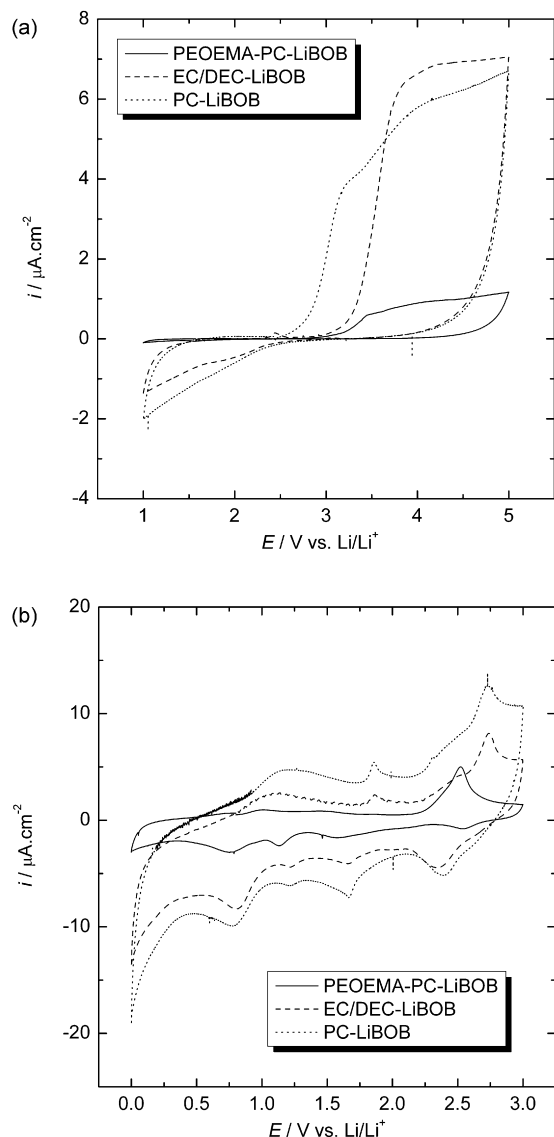


Fig. 6. Cyclic voltammograms of the PEOEMA-PC-LiBOB (52:45:3 mol.%) polymer electrolyte and PC-LiBOB and DEC/EC-LiBOB liquid electrolytes (both 0.7 m) on aluminium (A) and copper (B) 2 mV s^{-1} measured at 80°C .

stripping of lithium UPD [35,36]; Croce et al. suggests, that the second peak is corresponding to the stripping of an intermetallic compound between the deposited lithium and the substrate [37]; Chaix et al. presents similar results [38].

The impedance measurements before and after cycling did not show any increase of the interfacial resistivity, concluding, that no non-conductive layer is formed. The investigation of the anodic stability limit showed, that the electrolytes are stable up to $5.1 \text{ V vs. Li/Li}^+$.

However the voltammetrical measurements on the inert electrodes help to understand the processes connected with the function of the electrolyte, the electrochemical behaviour of the electrolyte with commonly used current collectors in the lithium-ion batteries (copper for the anode and aluminium for the cathode) is necessary. Fig. 6A and B show similar behaviour of PEOEMA-PC-LiBOB and common DEC/EC-LiBOB electrolyte both on copper and aluminium foil measured at 80°C . The lower current observed on the voltammogram of polymer electrolyte can be explained either by lower conductivity of the electrolyte or by overall lower reactivity.

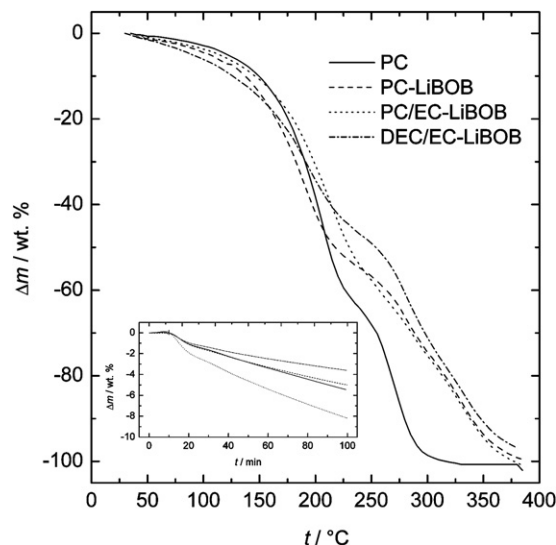


Fig. 7. TGA curves for PEOEMA polymer electrolytes with PC-LiBOB, PC/EC-LiBOB, DEC/EC-LiBOB gel electrolytes and of PEOEMA-PC binary system (5°C min^{-1} heating rate, temperature range $30\text{--}380^\circ\text{C}$; argon atmosphere); inserted: TGA curves measured 100 min at constant temperature of 70°C .

3.4. Thermal stability

Concerning applications, thermal stability is another principal parameter to be considered along with electrochemical and long-term stability and reasonable conductivity. Fig. 7 shows TGA of the samples with different carbonates. The weight loss was found less than 5 wt.% up to 110°C for the electrolytes with PC and PC/EC. This change can be explained as a partial evaporation of the immobilised solvent. In the case of PEOEMA-DEC/EC-LiBOB was the weight loss higher, 7.5 wt.% due to higher volatility of DEC. On the other hand, the isothermal TGA done at 70°C showed, that the electrolyte with DEC/EC electrolyte is losing less solvent than the other samples. In comparison with common liquid electrolytes, the weight loss is suppressed by present polymer.

It is well known that methacrylates decompose in two exothermic reaction processes: degradation of the polymer end groups ($240\text{--}280^\circ\text{C}$) and total decomposition of the monomer units (above 310°C). As LiBOB is decomposing irreversibly at $290\text{--}300^\circ\text{C}$ (ref. [39]), the degradation of the electrolytes is practically (97 wt.%) finished at $340\text{--}350^\circ\text{C}$, similarly to results published by Grillone [40]. However, the present salt is partially retarding the decomposition of the electrolyte at temperatures above 200°C (see Fig. 7). Considering the safety reasons and proposed electrolyte application at temperatures about $70\text{--}80^\circ\text{C}$, the electrolyte thermal stability is sufficiently high.

4. Conclusions

Polymer gel electrolytes consisting of poly(2-ethoxyethyl methacrylate), lithium bis(oxalato)borate and different aprotic solvents (propylene carbonate, ethylene carbonate and dimethyl carbonate) have been prepared as desirable electrolytes for lithium-ion batteries operating at elevated temperatures (70°C). The electrolytes have been characterised by X-ray diffraction, scanning electron microscopy, impedance spectroscopy, voltammetry, thermogravimetric analysis and differential scanning calorimetry.

The composition of the electrolyte was optimised to achieve both good mechanical and electrochemical properties. The maximum value of the ionic conductivity is $2.4 \cdot 10^{-3} \text{ S cm}^{-1}$ at 70°C for PEOEMA-DEC/EC-LiBOB (34: 22/40: 4 mol.%) sample. The elec-

trochemical stability toward oxidation of all prepared electrolytes was found up to 5.1 V vs. Li/Li⁺. Studied polymer electrolytes exhibit higher electrochemical and thermal stability compared to the conventional liquid electrolytes such as DEC/EC–LiBOB.

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