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Performance of acrylate-poly(ethylene oxide) polymer electrolytes in lithium batteries

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Results for the performance of lithium/MnO_2 batteries containing solid polymer electrolytes based on poly(ethylene oxide) blends with some acrylic derivatives are presented. The ionic conductivities of the electrolytes are promising for battery application. It was found, however, that interfacial phenomena impair the battery efficiency. Impedance spectroscopy shows resistive limitations at the anode interface of the batteries, caused either by formation of an electrically distinguishable resistive layer or by chemical interaction between the polymer and lithium, influencing, most probably, the kinetics of the lithium oxidation reaction.

1. Introduction

Lithium batteries with solid polymer electrolytes offer attractive advantages: elimination of electrolyte leakage, rechargeability, applicability of thin film technology in the production process [1]. However, no commercial products of this type are available to date due to severe problems with low conductivity and ambient temperature efficiency of cells. Batteries with poly(ethylene oxide) (PEO)-based electrolytes operating at elevated temperatures were examined [2] and efforts were made to construct polymer-based batteries efficient at moderate ambients [3]. A major problem lies with resistive layers formed between lithium and the conducting polymer [4]. Polymer electrolytes synthesized in the form of PEO blends with acrylic derivatives exhibit promising conductivities for applications in low-temperature lithium batteries. The lithium/manganese dioxide system was chosen to study the performance of the electrolytes, with special attention to the interfacial phenomena at the lithium anode.

2. Experimental details

2.1. *Polymer electrolytes*

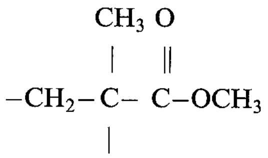
The electrolytes consisted of PEO blended with several acrylic derivatives (ratio 4 : 1), and $LiClO_4$ in a ratio 10 : 1 (EO unit moles to salt moles). The following polymers were synthesized:

(i) Thermally polymerized PEO-poly(methylmetacrylate) (PMMA)blend, termed P1. Methyl metacrylate was thermally polymerized in the presence of high-molecular weight PEO ($M_w = 5 \times 10^6\,\text{g mol}^{-1}$) for 48 h at 85–90 °C. The product was purified of residual monomer by vacuum distillation, dissolved in dichloromethane (DCM) and finally precipitated during evaporation of DCM. The structure of the blend was analysed by infrared spectroscopy, X-ray diffraction and differential scanning calorimetry [5]. Infrared spectra showed no traces of monomer and of water in the product. The M_w for the blend was $6 \times 10^5\,\text{g mol}^{-1}$. Chemical analysis of the blend, followed by i.r. and XRD measurements, proved the presence of poly(methyl metacrylate), poly(ethylene oxide) and a grafted phase with i.r. spectra characteristic for both PEO and PMMA and XRD pattern different from PEO. The M_w value of the grafted phase was $1.4 \times 10^5\,\text{g mol}^{-1}$. The grafted phase was separated from the polymer blend and added to PEO to form another electrolyte. In additional experiments it was found that the conductivity and electrochemical performance of the grafted phase electrolyte did not differ significantly from the thermal blend.

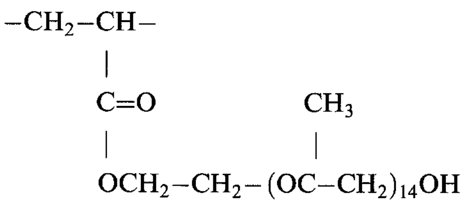
(ii) Poly(poly(propyleneglycol)acrylate) (PPGA) blend with PEO, termed P2, was obtained by free-radical polymerization of a macromer according to the procedure described in [6]. Samples contained 14 or 6 EO monomeric units in side chains. Product was purified of solvents and substrate residues similarly to the P1 blends and dried under vacuum. Polymer electrolyte was prepared by dissolving PEO, PPGA and $LiClO_4$ in DCM-acetonitrile 1 : 2 mixture, followed by evaporation of the solvents. The M_w of the product was $1.6 \times 10^5\,\text{g mol}^{-1}$. This electrolyte exhibited the highest conductivity values (see Table 1), however the presence of hydroxyl groups in the side chains is a potential drawback for lithium battery performance. In order to overcome probable negative effects the endcapped polymer was synthesized:

(iii) Poly(poly(methoxypropyleneglycol)acrylate) blend with PEO, termed P3. To prepare this electrolyte the same procedure as in (ii) was applied.

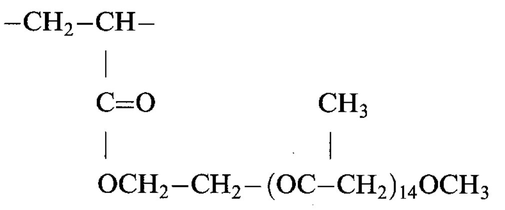
Structures characteristic of each polymer are presented below:

P1 

$$-CH_2-\underset{|}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OCH_3$$

P2 

$$-CH_2-\underset{\underset{\underset{OCH_2-CH_2-(O\overset{\overset{CH_3}{|}}{C}-CH_2)_{14}OH}{|}}{C=O}}{\underset{|}{CH}}-$$

P3 

$$-CH_2-\underset{\underset{\underset{OCH_2-CH_2-(O\overset{\overset{CH_3}{|}}{C}-CH_2)_{14}OCH_3}{|}}{C=O}}{\underset{|}{CH}}-$$

Conductivity values of the electrolytes are given in Table 1.

2.2. *Measurements*

Two types of electrochemical cells were used for measurements:

(i) Batteries assembled of thin discs of pure lithium (99.9%) foil, polymer electrolyte foil and cathode composite foil (MnO_2 and graphite powders suspended in polymer matrix, 55 and 25% by weight, respectively). The thickness of polymer foil was 450 μm.

(ii) symmetric Li/polymer electrolyte/Li and cathode foil/polymer electrolyte/cathode foil cells.

All samples were prepared and hermetized in a glove-box with argon atmosphere, purified of oxygen and water. All materials were dried and degassed under vacuum prior to placing in the glove-box.

Open-circuit voltages (o.c.v.) of the lithium batteries were measured at different temperatures. To evaluate the short-circuit current the batteries were short-circuited with a 1 ohm resistor and the momentary current was registered. After restoring the o.c.v. value the batteries were discharged at constant current density of 10^{-2} A m^{-2}.

The symmetric cells served for measurements of impedance spectra. The impedance data were analysed by means of a nonlinear least squares technique to calculate the parameters of the equivalent electrical circuits: resistance R, capacitance C or constant phase element Q. The time and temperature dependences of these parameters were also studied.

In a separate experiment a prolonged electrolysis of a Li/polymer/Li cell was carried out (current density 10^{-2} A m^{-2}) and impedance spectra were registered each 24 h.

The conductivities of the polymer electrolytes were determined by means of the impedance method using stainless steel blocking electrodes.

3. Results

The parameters of lithium batteries and electrolyte conductivities at two chosen temperatures are presented in Table 1. Figure 1 shows typical discharge curves registered with batteries containing P1, P2 and P3 electrolytes at 76 °C.

The impedance spectra are plotted in the Z_{re} against Z_{im} form. The frequency range was the same for all measurements – from 5 Hz to 500 kHz. Figures 2, 3, and 4 present the impedance spectra of P1, P2 and P3 electrolytes in lithium symmetrical cells. Two or three semicircles may be observed on these spectra and the corresponding equivalent circuits are calculated as a series of (RQ) parallel subcircuits. With regard to frequency range the semiarcs are termed HFA, MFA and LFA (high, middle and low frequency arc, respectively). In general, the HFA tends to disappear at higher temperatures and its R value decreases with temperature proportionally to the increase in electrolyte conductivity.

The LFA forms visibly at higher temperatures. The corresponding R value decreases quickly with increasing temperature. The time dependence is different for each electrolyte: for P2 the R_{LFA} grows in time (at constant temperature); for P1 and P3 this value does not change significantly.

In the spectrum of the P2 electrolyte a third arc is observed in middle frequency range at elevated temperatures. Its R value increases with time (at constant temperature).

The Li/P2 electrolyte/Li cell was electrolysed for seven days and impedance spectra analysed each 24 h. No significant differences between polarized and nonpolarized samples (thermostated at the same temperature) were observed.

The impedance spectrum for the cathode/polymer electrolyte/cathode cell only gives one semicircle (RC) in the high frequency range. (Fig. 5).

4. Discussion

The lithium batteries displayed o.c.v. values typical of the Li/MnO_2 system: the o.c.v. was 3.2 V at 30 °C and 3.5 V at 76 °C. However, the measured values of short circuit current were significantly lower than the values

Table 1. Electrolyte conductivities and performance of Li/polymer electrolyte/MnO_2 batteries

	Conductivity of electrolytes containing P1, P2 and P3 polymers/Scm^{-1}		*Battery short-circuit current*	
	30 °C	*76 °C*	*30 °C* *μA*	*76 °C* *mA*
P1	6×10^{-5}	1.3×10^{-3}	80	14
P2	1×10^{-4}	1×10^{-2}	150	20
P3	8×10^{-5}	5×10^{-4}	120	10

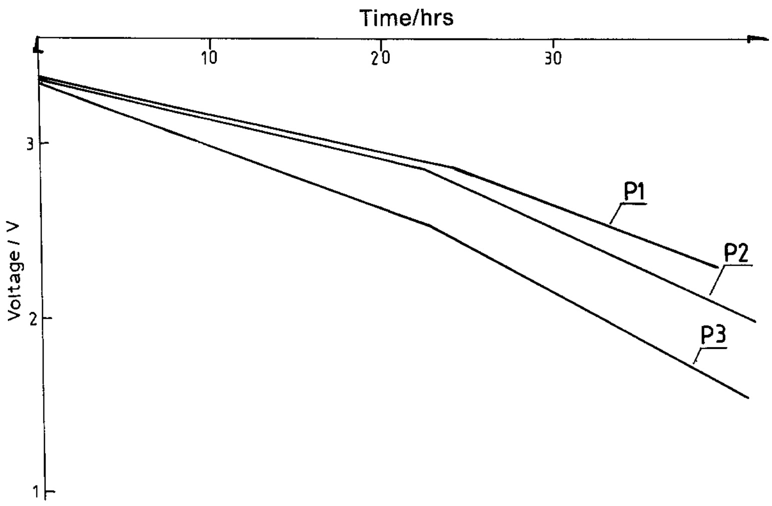


Fig. 1. Typical discharge curve of batteries with P1, P2 and P3 electrolytes. Theoretical capacity 5.5 A s. Discharge current 10 μA.

estimated on the basis of the resistances of the separate components (lithium and cathode discs, electrolyte film). This effect is due to the formation of additional resistances between the electrodes and the polymer electrolytes studied. The impedance studies undertaken to clarify the nature of these resistances revealed the following phenomena:

(i) The impedance of cathode/polymer electrolyte/cathode cells consists only of one (*RC*) element in the high frequency range. Temperature dependence of R_{HFA} and of resistance of a separate P2 electrolyte disc were compared (Fig. 6). As the values decrease with temperature at a similar rate, it might be assumed that the impedance spectrum reflects only the bulk properties of the electrolyte and the cathode/polymer interface does not contribute to the undesired resistive effects in the lithium batteries. Small differences between R_{cat} and R_{el} lines are most probably due to the technique of cell assembly. Constant pressure applied to contact the foils and electrodes gives different results for three flexible foils (cathode cell) and for one foil placed between rigid steel electrodes (conductivity measurements).

(ii) In the impedance spectra of Li/polymer electrolyte/Li cells two or three semiarcs are formed. The numerical analysis of data shows that

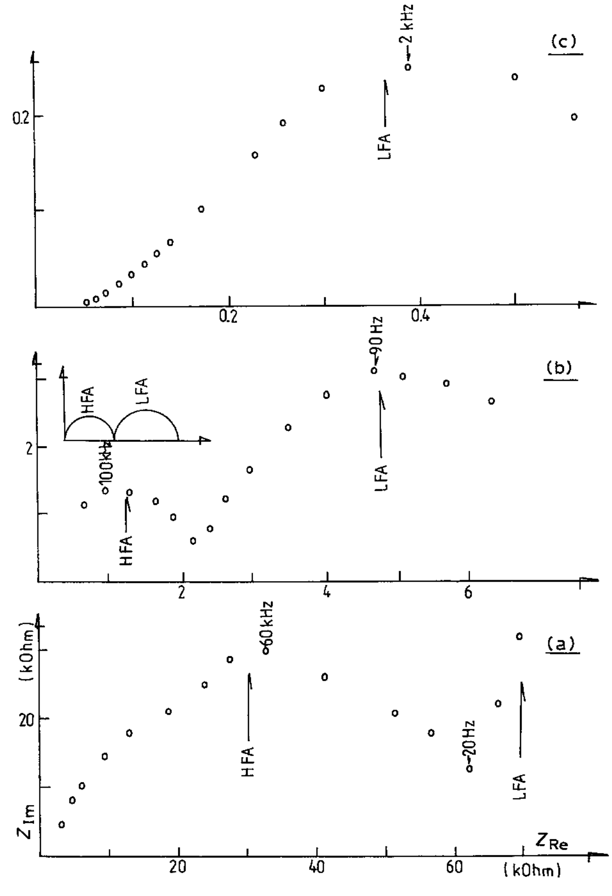


Fig. 2. Impedance spectra (Nyquist coordinates) of Li/P1 electrolyte/Li cells at: (a) 30 °C, (b) 40 °C and (c) 76 °C.

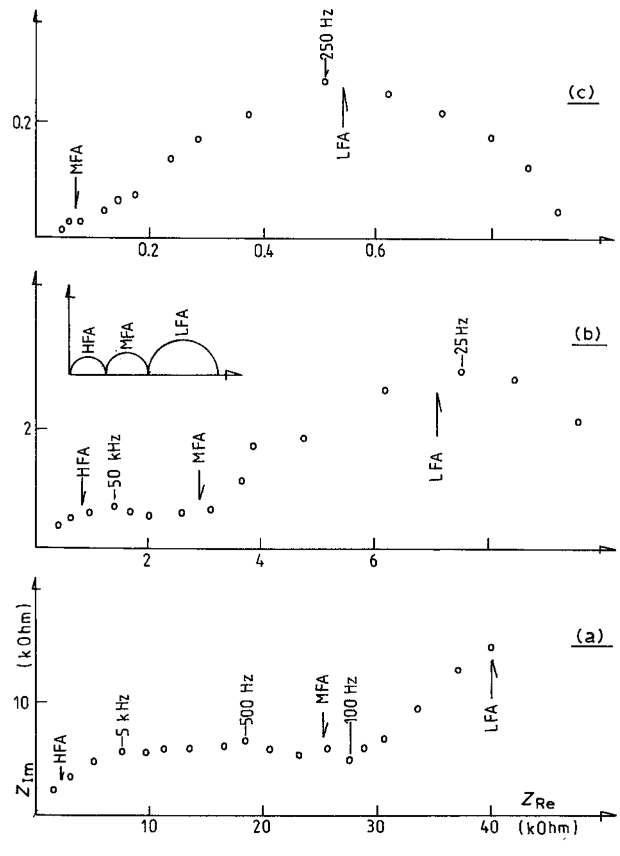


Fig. 3. Impedance spectra (Nyquist coordinates) of Li/P2 electrolyte/Li cells at: (a) 30 °C, (b) 40 °C and (c) 76 °C.

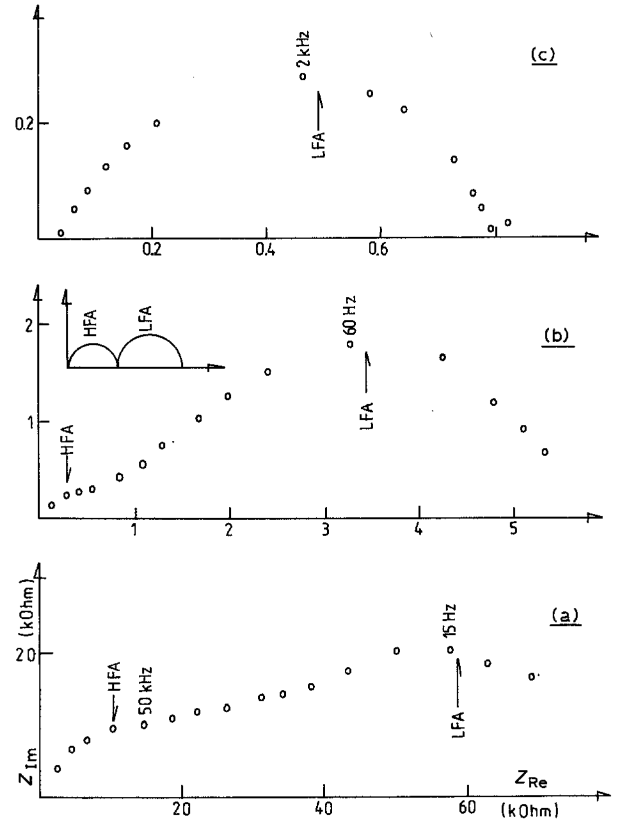


Fig. 4. Impedance spectra (Nyquist coordinates) of Li/P3 electrolyte/Li cells at: (a) 30 °C, (b) 40 °C and (c) 76 °C.

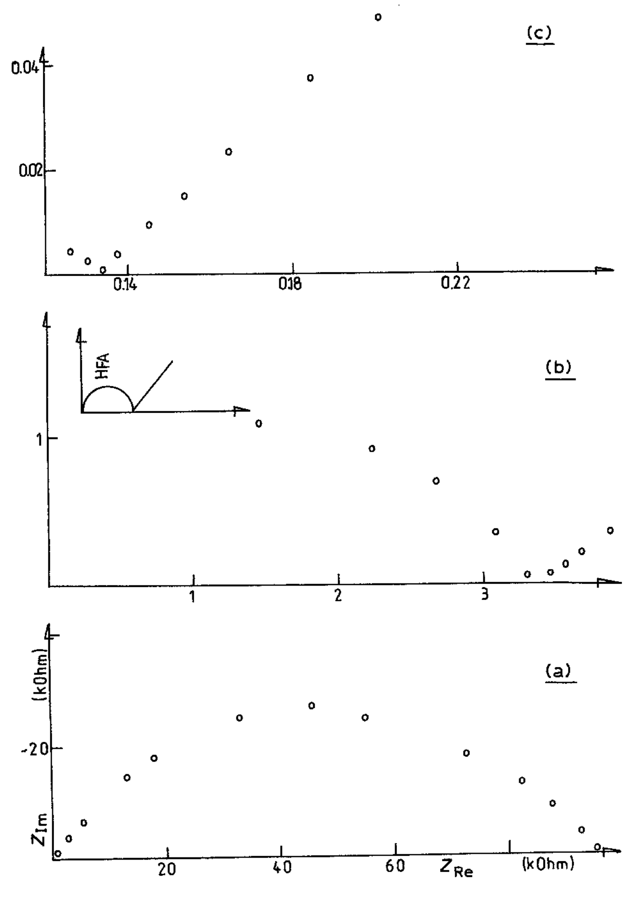


Fig. 5. Impedance spectra (Nyquist coordinates) of cathode/P2 electrolyte/cathode cells at: (a) 30 °C, (b) 40 °C and (c) 76 °C.

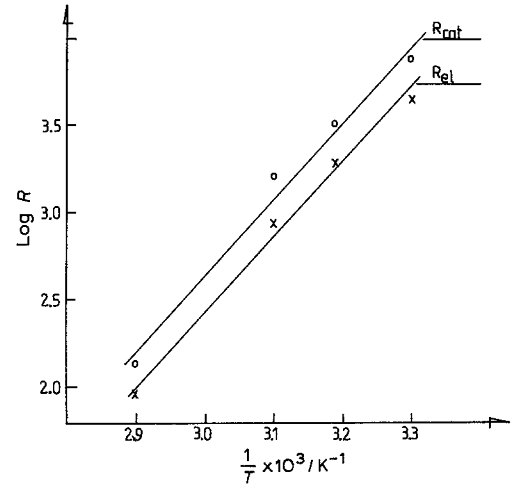


Fig. 6. Resistances of P2 electrolyte disc and R_{HFA} of P2 cathode cell against temperature dependence. (○) R_{cat}: HFA resistance, (×) R_{el}: P2 disc resistance.

the electrical equivalent circuit consist of a series of parallel (*RQ*) elements. The HFA represents the bulk properties of the electrolyte with values similar to those analysed in (i). (see Figs 3 and 5). The presence of further arcs is connected with interfacial phenomena at the Li/polymer phase boundary.

The oxidation–reduction reaction $Li \rightarrow Li^{1+}$ is represented by a well-formed arc at low frequencies. This arc is present in the spectra of all three electrolytes studied. As the arcs are very close to regular semicircles, the *Q* values calculated numerically can be approximated to capacitance values. The order of magnitude (about 10^{-6} F cm^{-2}) is similar to the values of double layer capacity at solid electrodes.

(iii) The MFA is present only in Li/P2 electrolyte spectra and may be attributed to a resistive layer formed at the phase boundary as a result of chemical or electrochemical reaction between lithium and the

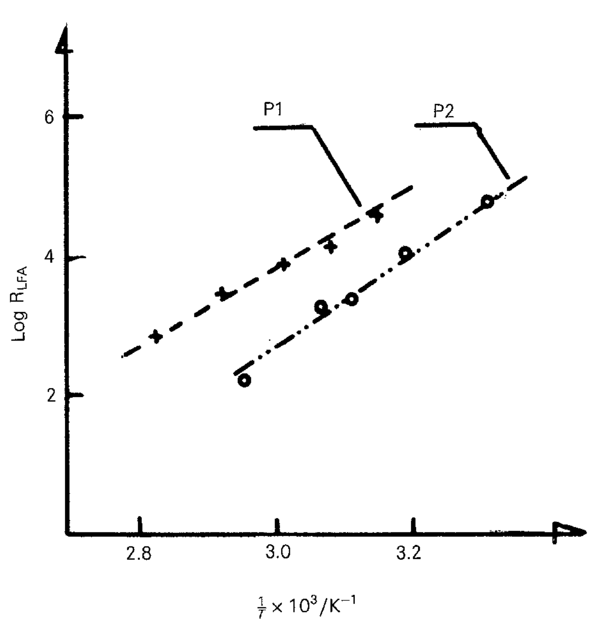


Fig. 7. Temperature dependence of LFA arc resistance for P1 and P2 electrolytes. An Arrhenius plot.

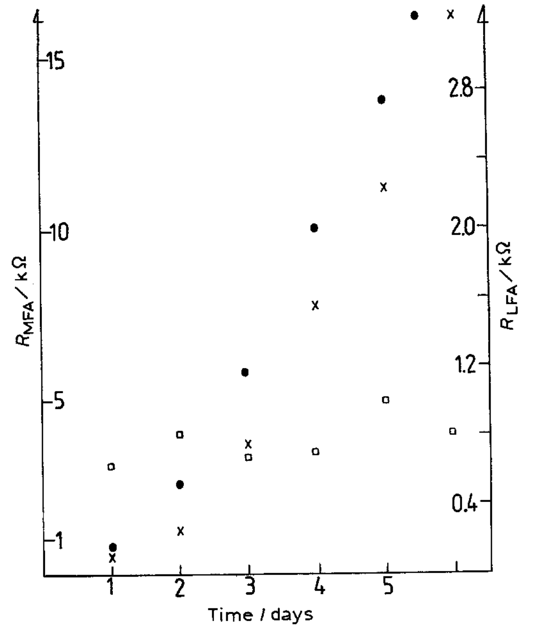


Fig. 8. Time dependence of R_{MFA} (●) and R_{LFA} (×) resistances for P2 electrolyte and R_{LFA} resistance (□) for P1 electrolyte.

polymer. As the P2 polymer contains hydroxyl groups in the side chains, they are most probably responsible for the formation of this layer.

The R values in the (RQ) subcircuit equivalent to MFA increases quickly with time at elevated temperature. The rate of growth is similar in experiments with polarised and nonpolarized cells. It may therefore be assumed, that the process of layer formation is chemical in nature and the additional current across the phase boundary does not contribute to it.

(iv) The temperature dependence of the LFA resistance was analysed on $\log(R^{-1}) = f(1/T)$ coordinates (Fig. 7). The resulting activation energy of the electrochemical process is $\sim 8.4 \times 10^4\,\mathrm{J\,mol^{-1}}$ for P1 and P2 electrolytes. This order of magnitude suggests that the limiting stage for electrode reaction is charge-transfer or chemical reaction.

(v) The LFA resistance for the P2 electrolyte increases quickly with time; the rate of growth is proportional to that of the MFA resistance (Fig. 8) – resistive film formation arc. No such phenomenon is observed in P1 and P3 electrolytes – the R_{LFA} values are fairly constant with time. Obviously, the formation of the resistive film influences the charge and mass transfer kinetics.

(vi) Although the impedance data do not reveal formation of the resistive layer in the case of P1 and P3 electrolytes, some interaction between lithium and these polymers occurs to cause the discrepancy between the measured and expected resistances of lithium batteries.

5. Conclusions

The lithium conducting polymer electrolytes based on PEO blends with acrylic derivatives can be applied to construct Li/MnO_2 batteries, but the performance of such cells is not satisfactory, especially regarding the applicable current density and yield. Although the characteristics of the battery is determined by several factors, it was found that the primary and decisive one is the formation of resistive layers at the phase boundary between the lithium and the polymer in the case of an electrolyte containing hydroxyl groups. Other examined polymer blends are free of hydroxyl groups but, nevertheless, their performance in Li cells is still not satisfactory. The impedance measurements could not trace a separate layer with distinguishable electrical parameters in this case, but some interaction must take place at the phase boundary, influencing the electrode kinetics of lithium oxidation.

Acknowledgements

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