Advanced, high-performance composite polymer electrolytes for lithium batteries

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Abstract

Progress in lithium battery technology may be achieved by passing from a conventional liquid electrolyte structure to a solid-state, polymer configuration. In this prospect, great R&D effort has been devoted to the development of suitable lithium conducting polymer electrolytes. The most promising results have been obtained with systems based on blends between poly(ethylene oxide) and lithium salts. In this work we show that the transport and interfacial properties of these electrolytes may be greatly enhanced by the dispersion of a ceramic filler having an unique surface state condition. The results, in addition to their practical reflection in the lithium polymer electrolyte battery technology, also provide a valid support to the model which ascribes the enhancement of the transport properties of ceramic-added composites to the specific Lewis acid–base interactions between the ceramic surface states and both the lithium salt anion and the PEO-chains.
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1. Introduction

Lithium batteries are acquiring a leading role in various important markets with particular impact on consumer electronics and, perhaps in the future, on electric or hybrid cars. However, considering the evolution of these markets and their associated energy and power demands, new and improved battery configurations are required. Among the various approaches presently being followed to achieve this goal, that based on the passage from a conventional liquid electrolyte structure to an advanced polymer electrolyte configuration, is expected to be among the most relevant to the progress of lithium battery technology [1].

The key component in this progress is a polymer electrolyte which must have properties in terms of lithium conductivity and electrode compatibility, which matches those offered by liquid electrolytes. Among the many types of lithium conducting membranes developed and characterized to meet this requirement, the most interesting are those based on poly(ethylene oxide), PEO [2]. These membranes, which are formed by the combination of PEO and a lithium salt, LiX, are often referred as true solid polymer electrolytes, SPEs, as they do not contain plasticizing solvents and their polymer chains act simultaneously as both structural and solvating agents [3]. Indeed, PEO-based SPEs have a series of specific features, such as high conductivity, low cost, and good chemical stability, which account for the great amount of work which has been devoted to their preparation and characterization.

Obviously, the real breakthrough in this field would be the development of solvent-free, polymer electrolytes having conductivity levels similar to those of liquid solutions over a wide temperature range. Unfortunately, this has not been yet achieved and the most promising electrolytes, i.e., the PEO-based SPEs, do not yet fulfil this requirement. The main issue is the ionic conductivity which remains at high levels only when in the amorphous state, i.e., at temperature exceeding 70 °C. Obviously, this narrows the range of practical application. Another drawback is associated to the low value of the transference number of the lithium cations, which is generally of the order of 0.2–0.4 [3] and this also may affect the use of these PEO-based electrolytes in practical batteries. In fact, a low cation transference number implies that the current is mainly carried by anions and in turn, may result in concentration polarization which reflects

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negatively on the rate of a battery based on lithium-operating electrodes.

Although this may in part be counterbalanced by proper design of the electrode structure, certainly an enhancement of the lithium ion transference number remains an important requirement. Recently, we have reported that this may be obtained by dispersing nano-particulate ceramic fillers, such as TiO_2, Al_2O_3 and SiO_2, into the PEO-based polymer matrix [4]. This leads to a new class of SPEs which have been referred as Nano Composite Polymer Electrolytes (NCPEs). We have demonstrated that one of the key roles of the filler is that of acting as a solid plasticizer for PEO by kinetically inhibiting the chain crystallization on annealing from the amorphous state at 70 °C [4,5]. This in turn lowers the temperature of stabilization of the amorphous phase and thus, increases of the electrolyte's useful range of conductivity. In addition, the ceramic filler promotes preferential lithium pathways and we have associated this effect with the Lewis acid–base interactions occurring between the ceramic surface states and both the lithium salt X^- anions and the PEO segments [6–8].

In recent work we have confirmed this model by selecting a highly functionalized ceramic filler, i.e. a sulphate-promoted superacid zirconia, S-ZrO_2, and dispersing it into a PEO–LiBF$_4$ matrix [9]. We have shown that the presence of this unique ceramic filler, due to its specific surface state condition, results in an exceptional increase in the value of the lithium transference number of the associated NCPE [9]. In this paper we extend the study of the influence of this particular filler on the properties of PEO-based polymer electrolytes using a detailed thermal, transport and interfacial investigation.

2. Experimental

The preparation of superacid, sulphated zirconia, S-ZrO_2, as well as that of S-ZrO_2-added PEO–LiX composite polymer electrolytes, have been described in a previous work [9] to which the reader is referred for details. In this work we have prepared and characterized PEO-based membrane samples using $LiClO_4$ as the lithium salt and having different S-ZrO_2 contents. We have prepared and tested various samples to investigate the effect of the amount of the dispersed S-ZrO_2 filler. For comparison purposes, also ceramic-free, PEO$_{20}$($LiClO_4$) samples have been prepared. Table 1 summarizes the composition of the various samples considered in this work.

The thermal properties of the various electrolyte samples have been evaluated by DSC studies. The samples were held for 90 min at 100 °C to assure homogeneization and then were stored for six days prior to the DSC test. This was run with two

Table 1
List of samples tested in this work

Sample acronym	Composition
SZ-free PEO	PEO$_{20}$($LiClO_4$)
SZ-PEO-5	PEO$_{20}$($LiClO_4$) + 5% S-ZrO_2
SZ-PEO-10	PEO$_{20}$($LiClO_4$) + 10% S-ZrO_2

PEO, poly(ethylene oxide); SZ, superacid ZrO_2.

consecutive heating and cooling scans in the 25–100 °C temperature range.

The conductivity was measured by impedance spectroscopy analysis of cells formed by sandwiching the given electrolyte sample between two stainless-steel blocking electrodes. The cells were housed in a Buchi oven to control the temperature. A Solartron impedance response analyzer was used for measurements over a 100 Hz–100 kHz frequency range. The resistance of the electrolyte was given by the high frequency intercept determined by analyzing the impedance response using an appropriate fitting program [10].

The electrochemical stability window was evaluated by measuring the current–voltage response of a MCMB carbon electrode in a cell using the given sample as the electrolyte and a lithium foil as the counter electrode. The current onset of the cell was associated with the decomposition voltage of the electrolyte. The value of this voltage is kinetically controlled by the nature of the selected working electrode. In this work we have chosen MCMB in order to approach the condition occurring in practical lithium batteries where carbon is in fact always present in the cathode blends.

The compatibility with the lithium metal electrode was determined by monitoring the time evolution of the impedance response of a symmetrical Li/given electrolyte sample/Li cell. The value of the Li interfacial impedance and its changes with time of contact with the electrolyte, were obtained with the analysis of the response using an appropriate fitting program [10].

3. Results and discussion

As already pointed out in our previous work [4–8] and also confirmed by results obtained in various laboratories throughout the world [11–13], it is now well established that the properties of PEO-based polymer electrolytes are enhanced by the dispersion of selected, low particle size ceramics. We have proposed that this action is associated to specific Lewis acid–base interactions between the ceramic surface states and both the lithium salt X^- anion and the PEO segments [5,8]. On the basis of this model, it is expected that the action of the ceramic fillers is greatly correlated to the degree of acidity of the surface states. To confirm this, we have selected an unique ceramic filler, i.e. sulphate-promoted superacid zirconia, S-ZrO_2, which has a high degree of surface acidity, i.e. an acid strength stronger than 100% H_2SO_4 [14]. This exceptional acidity is associated with the coordinated unsaturated Zr^{4+} cations which have a high electron accepting ability, the latter being enhanced by the nearness of the charge withdrawing SO_4 groups [15]. This finally results in the presence at the surface of the oxide of a high density of acidic sites both of Lewis and Bronsted forms [9].

In a previous work, we have shown that indeed the dispersion of this surface-modified, S-ZrO_2 in PEO-based systems induces exceptional improvements in the value of the lithium transference number of the resulting NCPEs [9]. In this paper we have extended the investigation of these new types of S-ZrO_2-added NCPEs by comparing their thermal, interfacial and conductivity response with those of the corresponding ceramic-free PEO membranes.
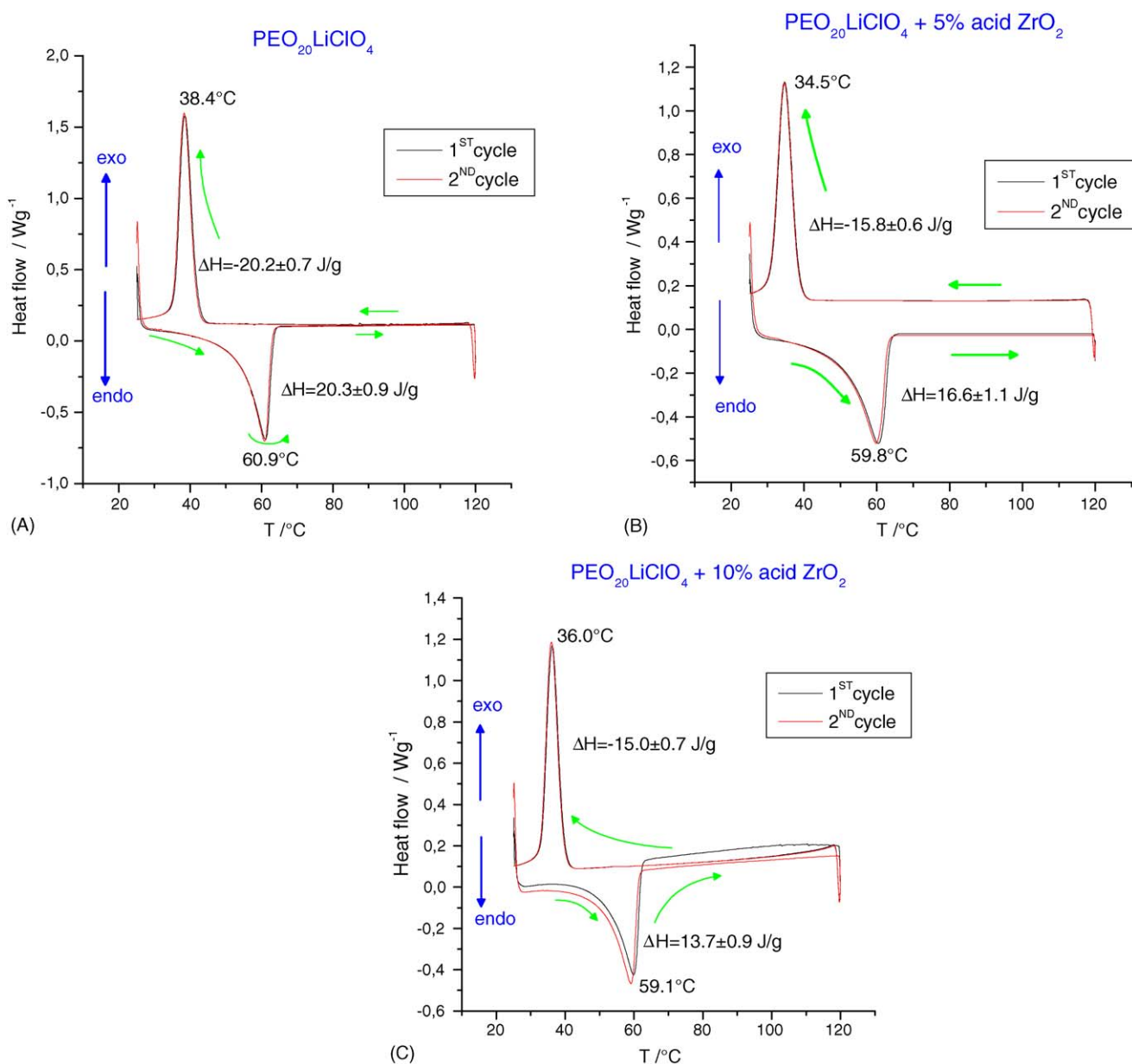
Fig. 1. Differential scanning calorimetry, DSC traces of electrolyte samples SZ-free PEO (PEO$_{20}$(LiClO$_4$)) (A), SZ-PEO-5 (PEO$_{20}$(LiClO$_4$) + 5% acid ZrO$_2$) (B) and SZ-PEO-10 (PEO$_{20}$(LiClO$_4$) + 10% acid ZrO$_2$) (C). Scanning rate: 5 °C min^{-1}.

Fig. 1 shows the DSC traces of electrolyte samples SZ-PEO-5 (Fig. 1B) and of SZ-PEO-10 (Fig. 1C) in comparison with that of a plain, SZ-free PEO sample (Fig. 1A). All the traces clearly show the melting-crystallization peaks of the electrolytes. However, the analysis of the figure also shows that by passing from the zirconia-free samples to the acid–zirconia added composite samples, there is a decrease in the values of the melting temperature, T_f, as well as an enthalpy change, ΔH_f, associated to the transition.

These differences are further evident in Fig. 2, which shows in comparison the heat flow associated to the melting of the three samples, and by Table 2 which reports the related T_f and ΔH_f values. The data clearly show that the dispersion of the S-ZrO$_2$ promotes amorphicity which in turn is expected to favour

ion transport and thus, to enhance the ionic conductivity of the electrolyte.

This is indeed confirmed by conductivity tests. Fig. 3 shows, in comparison, the Arrhenius plots of the two zirconia-added

Table 2
Values of the melting temperature T_f and of the enthalpy changes ΔH_f, associated to the melting process of the PEO, SZ-PEO-5 and SZ-PEO-10 samples

Sample	T_f (°C)	ΔH_f (J g^{-1})
PEO	60.9	20.3 ± 2.0
SZ-PEO-5	59.8	16.6 ± 1.1
SZ-PEO-10	59.1	13.7 ± 0.9

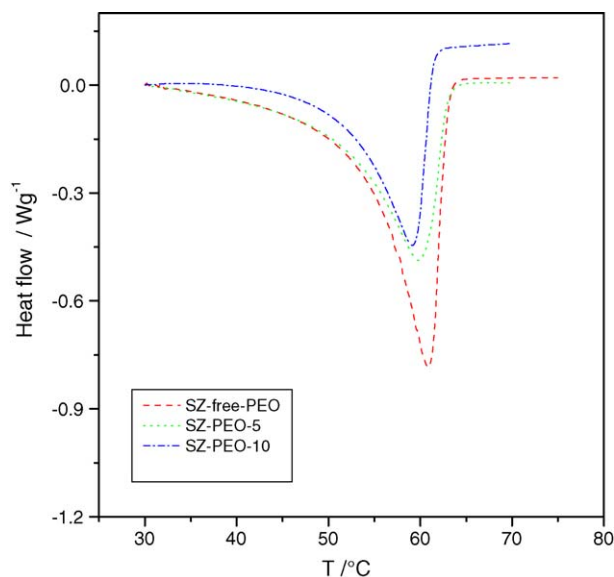Data derived from the DSC results of Fig. 1.

Fig. 2. Heat flow associated to the melting of the SZ-free PEO, SZ-PEO-5 and SZ-PEO-10 samples. Data derived from the DSC results of Fig. 1.

electrolyte composite samples with that of a plain, zirconia-free electrolyte. All the samples show the well known break in conductivity due to the crystallization of the PEO chains. However, the conductivity of the S-ZrO$_2$ composite samples is almost one order of magnitude higher than that of the ceramic-free electrolyte. In addition, in agreement with the DSC data, the conductivity break occurs at lower temperatures.

Fig. 3 shows that the conductivity of the composite samples averages 0.001 S cm^{-1} in a temperature range extending from 100 °C to about 60 °C. This exceptional behavior is a firm

demonstration of the unique role of the fillers in kinetically inhibiting the crystallization of the PEO chains, as well as in promoting lithium conducting pathways as a result of the Lewis acid–base interactions occurring between the ceramic surface states and both the lithium salt ClO$_4^-$ anion and the PEO segments [4,5].

We have shown in a previous work that this combined effect results in a dramatic increase of the lithium transference number of the S-ZrO$_2$-added composite electrolytes [9]. The results above described demonstrate that this promoting action extends also to the conductivity which reaches levels rarely observed for PEO-based polymer electrolytes at temperature limits as low as 60 °C.

These properties make the S-ZrO$_2$-added composite electrolytes of interest for applications in polymer electrolyte, lithium rechargeable batteries. In this respect, it is important to test the compatibility of the electrolyte with the lithium electrode. This has been performed by monitoring the time evolution of the impedance response of symmetrical Li/electrolyte/Li cells kept at open circuit. Under these conditions, it is possible to evaluate the value of the resistance of the lithium/electrolyte interface which in turn, can be associated with the growth of a passivating layer on the lithium surface.

Fig. 4 shows the results for cells using the SZ-PEO-5 and SZ-PEO-10 samples, respectively, as the electrolyte. Although slightly increasing with time, the value of the interfacial resistance is very low, i.e. maintained within 10 Ω cm^2. This in turn demonstrates that in these ZrO$_2$-based NCPEs, the lithium passivation layer is extremely thin and most importantly, that the growth of this layer is very modest.

This unique interface stability is certainly promoted by the dispersed filler. As already pointed out in previous work [5,6],
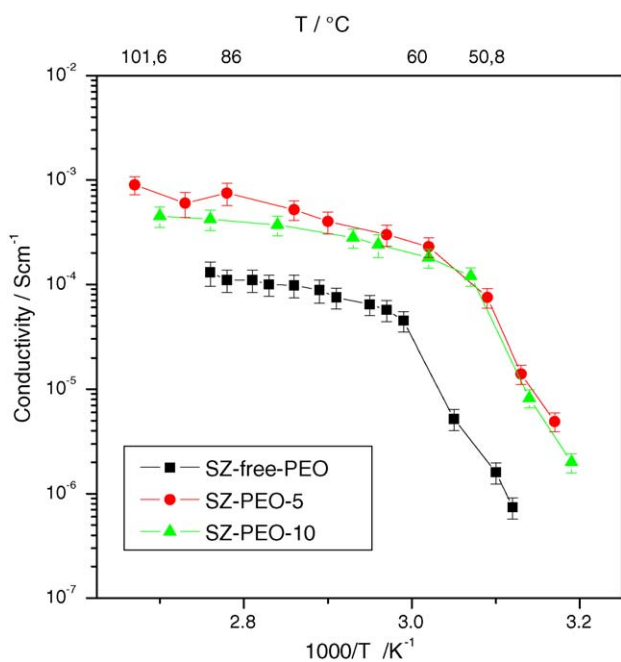

Fig. 3. Arrhenius plots of the two zirconia-added SZ-free PEO, composite electrolyte samples SZ-PEO-5 and SZ-PEO-10 in comparison with that of the plain SR-free PEO sample. Data determined by impedance spectroscopy.
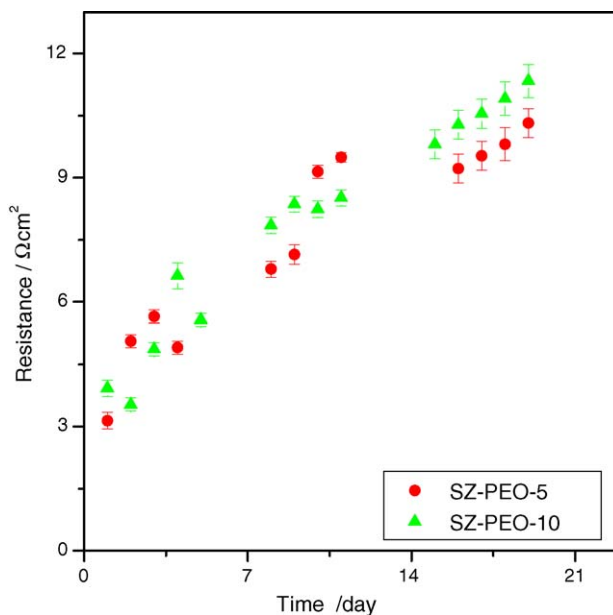

Fig. 4. Time evolution of the impedance response of symmetrical Li/electrolyte/Li cells kept under open circuit voltage. Electrolyte: SZ-PEO-5 and SZ-PEO-10. Temperature 100 °C. Data obtained by impedance spectroscopy.
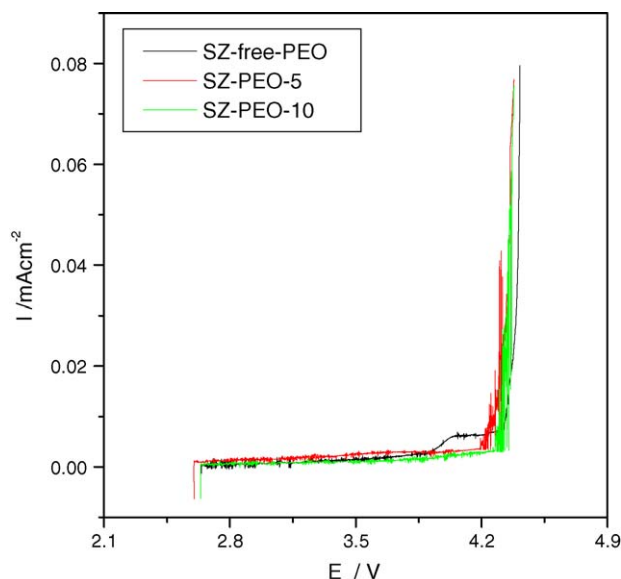
Fig. 5. Current–voltage response of a MCMB carbon electrode in a cell using the SZ-free PEO, SZ-PEO-5 and SZ-PEO-10, respectively, as the electrolyte. Lithium foil counter electrode. Scan rate: $0.1\,mV\,s^{-1}$. Temperature $100\,^\circ C$.

the dispersion of ceramic fillers in PEO-based electrolytes, in addition to enhancing conductivity, also improve the stability of the interface with the lithium metal electrode. The latter promotion action has been assumed to be associated with both a scavenging effect, since the fillers, due to their affinity with the liquid, trap liquid impurities removing them from the interface, as well as to a shielding effect, since the fillers, being of low particle size and finely dispersed in the polymer bulk, inhibit dendrite growth [6]. This model, already applied to other types of composite polymer electrolytes, is finally confirmed in this work by the data in Fig. 4.

Lithium rechargeable batteries are usually based on lithium insertion cathodes which operate around 4 V. It is then important to determine whether the selected electrolyte can withstand this voltage level. Fig. 5 compares the current–voltage response of a MCMB carbon electrode in cells using the SZ-free PEO, the SZ-PEO-5 and the SZ-PEO-10, respectively, as the electrolyte and a lithium foil as the counter electrode. Under these conditions, the current onset of the cells may be assumed to be the decomposition voltage of the given electrolyte. One can see that while the cell based on plain, ceramic-free electrolytes shows some current flow around 4.0 V, those based on the two S-ZrO$_2$-added composite electrolytes are inert up to 4.2 V with a very low residual current prior to this voltage. This demonstrates the high stability and purity of these electrolytes.

4. Conclusion

The data reported in this work confirm the unique role of the S-ZrO$_2$ fillers in enhancing the properties of PEO-based polymer electrolytes. By reporting and discussing the thermal, transport and interfacial behavior of S-ZrO$_2$ added electrolytes, we show that these new types of NCPEs have conductivity values which largely exceed that of the corresponding S-ZrO$_2$-free polymer electrolytes. In addition, these NCPEs have an exceptionally stable interface with the lithium metal electrode and an electrochemical stability window which extends to 4.2 V versus Li. These features make the S-ZrO$_2$-based NCPEs very promising electrolytes for the development of advanced, high-performance lithium polymer rechargeable batteries operating in a medium temperature range. Preliminary results obtained in previous work confirm this expectation [9]. This investigation is in progress in our laboratories. The detailed evaluation of the charge–discharge characteristics of these batteries under different temperature and rate conditions, as well as of their thermal stability, will be reported in a following paper.

Acknowledgements

References

[1] B. Scrosati, Chem. Rec. 5 (5) (2005) 286.
[2] C.A. Vincent, B. Scrosati, Bull. Mater. Res. Soc. 25 (2000) 28.
[3] F. Gray, M. Armand, in: J.O. Besenhard (Ed.), Handbook of Battery Materials, Wiley/VCH, Wenheim, 1999, p. 499.
[4] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, Nature 394 (1998) 456.
[5] F. Croce, R. Curini, A. Martinelli, L. Persi, F. Ronci, B. Scrosati, J. Phys. Chem. B 103 (1999) 10632.
[6] F. Croce, B. Scrosati, Ann. N. Y. Acad. Sci. 984 (2003) 194.
[7] G.B. Appetecchi, F. Croce, L. Persi, L. Ronci, B. Scrosati, Electrochim. Acta 45 (2000) 1481.
[8] A.S. Aricò, P. Bruce, B. Scrosati, J.-M. Tarascon, W. van Schalkwijk, Nat. Mater. 4 (2005) 366.
[9] F. Croce, L. Settimi, B. Scrosati, Electrochem. Commun. 8 (2006) 364.
[10] V. Boukamp, Solid State Ionics 20 (1986) 31.
[11] D.R. Mac Farlane, P.J. Newman, K.M. Nairn, M. Forsyth, Electrochim. Acta 43 (1998) 1333.
[12] B. Kumar, S. Rodrigues, L. Scanlon, J. Electrochem. Soc. 148 (2001) A1191.
[13] J. Maier, Prog. Solid State Chem. 23 (1995) 171.
[14] R.J. Gillespie, Acc. Chim. Res. 1 (1968) 202.
[15] V. Bolis, G. Magnaccia, G. Cerrato, C. Morterra, Langmuir 13 (1997) 888.