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Investigation on lithium–polymer electrolyte batteries

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Abstract

Lithium–polymer batteries using vanadium oxide-based composite electrodes and operating at moderate temperatures ($\sim 90^\circ\text{C}$) have been investigated. The work was developed within the advanced lithium–polymer batteries for electric vehicles (ALPE) project, an Italian integrated project, devoted to the realization of lithium–polymer batteries for electric vehicle applications. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The stringent demand for environmentally compatible vehicles has motivated various researches and projects on the development of electrochemical power sources characterized by high energy and/or high power density, good cyclability, reliability and safety [1–4]. Rechargeable lithium batteries are one of the most promising answers to this demand especially because of their performances in terms of gravimetric energy and density [3,4]. In its most conventional form, a rechargeable lithium battery comprises a lithium metal anode, a lithium ion conductor as electrolytic separator and a metal oxide cathode able to intercalate reversibly lithium ions. The reactivity of the lithium electrode towards most of the electrolytes, in particular liquid electrolytes, leads to uncontrolled phenomena with formation of surface layers [5] that cause uneven lithium deposition in the charge process eventually resulting in dendritic growth and cell short-circuiting.

The approach developed in the advanced lithium–polymer batteries for electric vehicles (ALPE) project to optimize the stability of the lithium electrode/electrolyte interface was to develop solid state lithium–polymer electrolytes [6,7] with a solvent-free procedure [8]. Following the same procedure composite cathode materials were also prepared. The results of the investigations on single

components and entire cells obtained within the ALPE project, the Italian National project devoted to the development of batteries for electric vehicles, are reported in the following.

2. Experimental

The polymer electrolyte and composite cathode films were prepared by following a solvent-free procedure previously described [9]. Briefly, the high-purity components polyethylene oxide (PEO, Union Carbide, WSR301, MW from 100,000 to 4,000,000), $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$ and LiCF_3SO_3 (3 M), $\gamma\text{-LiAlO}_2$ (Cyprus, HSA 10, particle size < 100 nm), carbon (Super P MMM Carbon), crystalline V_2O_5 (Pechiney), and silver- and copper-doped V_2O_5 xerogel ($\text{Ag}_{0.5}\text{V}_2\text{O}_5$ and $\text{Cu}_{0.1}\text{V}_2\text{O}_5$, University of Minnesota) were dried in an oven under vacuum at 120°C for 48 h with the exception of PEO that was dried at 50°C . After drying, all the materials were carefully sieved through 400 mesh and finally, gently mixed in the desired proportions (see Table 1) by ball milling for at least 4 h. After mixing, all mixtures were hot-pressed by a ATS FAAR hydraulic press ($90\text{--}110^\circ\text{C}$, 200 kg cm^{-2}) for 10 min or extruded with a Friul-Filieri single screw extruder ($90\text{--}130^\circ\text{C}$). Both procedures allowed to obtain homogeneous films from 0.1 to 0.5 mm which thickness was further reduced by calendaring.

Throughout the whole procedure, particular care was taken to avoid exposure of the materials to humid air. The preparation steps as well as samples handling were

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Table 1
Composition of composite materials investigated

Variable	Composition	Range	Fraction (w)
Composite electrolytes			
LiX content	PEO _n (MW = 4 × 10 ⁶) LiN(SO ₂ CF ₂ CF ₃) ₂	4 < n < 50	
LiX content	PEO _n (MW = 3 × 10 ⁵) LiCF ₃ SO ₃ :16.7 (w/w) γ-LiAlO ₂	4 < n < 50	
Molecular weight	PEO ₂₀ LiCF ₃ SO ₃ :16.7 (w/w) γ-LiAlO ₂	10 ⁵ < MW < 10 ⁶	
Filler nature	PEO ₂₀ LiCF ₃ SO ₃ (no filler)	2% < x < 10%	
	PEO ₂₀ LiCF ₃ SO ₃ :2% (w/w) Super P		
	PEO ₂₀ LiCF ₃ SO ₃ :16.7% (w/w) γ-LiAlO ₂		
Composite cathodes			
Act. material	Cu _{0.1} V ₂ O ₅ XRG:PEO ₂₀ LiCF ₃ SO ₃ :Super P		55:35:10
Act. material	Ag _{0.5} V ₂ O ₅ XRG:PEO ₂₀ LiCF ₃ SO ₃ :Super P		55:35:10
Act. material	V ₂ O ₅ :PEO ₂₀ LiCF ₃ SO ₃ :Super P		55:35:10

executed in a controlled environment dry-room (Corridi s.r.l.; RH < 0.1%) and the produced composite materials were stored inside coffee-bag packages sealed under vacuum. Water analysis (Karl Fisher method) of the final films indicated a water content below 0.001% (w/w). Chemical analysis showed that the actual composition of the final products (films) did not differ more than 0.1% from the nominal (selected) value.

The electrochemical tests were performed on two-electrode cells, realized by sandwiching a polymer electrolyte film between two selected electrodes (copper, stainless steel, lithium and composite cathode). The so-formed cells were sealed under vacuum inside a coffee-bag like envelopes. Finally, the sealed cells were laminated at 100°C by roll pressing to ensure a good electrode/polymer electrolyte contact.

Both the ionic conductivity of the electrolyte films and the lithium anode–polymer electrolyte interface were evaluated by impedance spectroscopy on symmetric cells equipped with copper (stainless steel) and lithium electrodes, respectively. The impedance of the samples was measured by means of a frequency response analyzer (FRA, Solartron mod. 1260) in the 1 Hz–100 kHz frequency range. Lithium–polymer electrolyte batteries were realized using lithium and a composite cathode film. The batteries were tested by using a Maccor S4000 battery cycler.

Cells assembly and tests were performed in the dry-room. The cells were thermally stabilized at temperatures ranging from 20 to 100°C in forced circulation ovens.

3. Results and discussion

3.1. Polymer electrolyte conductivity and interfacial properties with the lithium anode

A few classes of polymer electrolytes (see Table 1) were prepared to investigate the effect of the salt nature and concentration, the polymer molecular weight, and the nature of the filler on the ionic conductivity of the polymer

electrolyte and on the characteristic of the lithium anode–polymer electrolyte interface.

Fig. 1 illustrates the evolution of the ionic conductivity of the polymer electrolytes as a function of the temperature. The results are reported in four panels corresponding to the four classes of polymer electrolytes prepared (Table 1). A comparison of the conductivity curves allows to identify several effects and “non-effects” associated with the different nature of the polymer electrolytes. The most evident effect is associated with the nature of the lithium salt (compare panels A and B). The PEO_nLiN(SO₂CF₂CF₃)₂ complexes always show a higher ionic conductivity than the corresponding PEO_nLiSO₃CF₃ complexes. Such an effect, about one order of magnitude, is certainly associated with the amorphizing properties of the large N(SO₂CF₂CF₃)₂[−] anion that strongly reduces the crystallinity of the complexes even at ambient temperature [10]. The lithium salt concentration plays a role although its effect varies with the nature of the salt (see panels A and B). PEO_nLiSO₃CF₃ complexes always show a negative trend of the conductivity with the salt concentration as a result of the strong tendency of the salt to form ionic aggregates (couples and triplets) [11]. On the other hand, PEO_nLiN(SO₂CF₂CF₃)₂ complexes show a maximum in conductivity that shifts from n = 8 to 20 from ambient temperature to about 100°C. Such a behavior is due to the combination of two effects associated with the N(SO₂CF₂CF₃)₂[−] anion: the amorphization of the polymer structure even at temperatures below the PEO melting point (~60°C) [10]; and a relatively moderate tendency (ability) to form ionic aggregates. At lower temperatures the first effect is predominant and a larger concentration of the salt results in a larger fraction of amorphous phase in the polymer electrolyte and then in a larger conductivity of the latter. As the temperature approaches the melting point, the amorphous fraction of the polymer electrolyte increases and the effect of the ionic aggregates begin to play a role. As a matter of the fact the maximum conductivity shifts toward lower salt concentration. Above the polymer electrolyte melting point, the first effect (amorphization) does not play any role and the maximum ionic conductivity is always obtained with

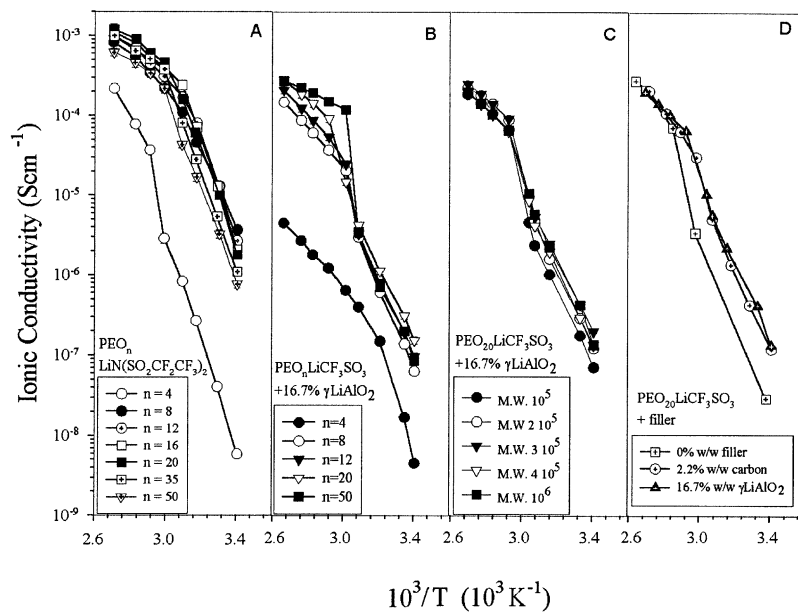


Fig. 1. Arrhenius plot of the polymer electrolytes investigated. The four panels refer to the four classes of polymer electrolytes described in Table 1.

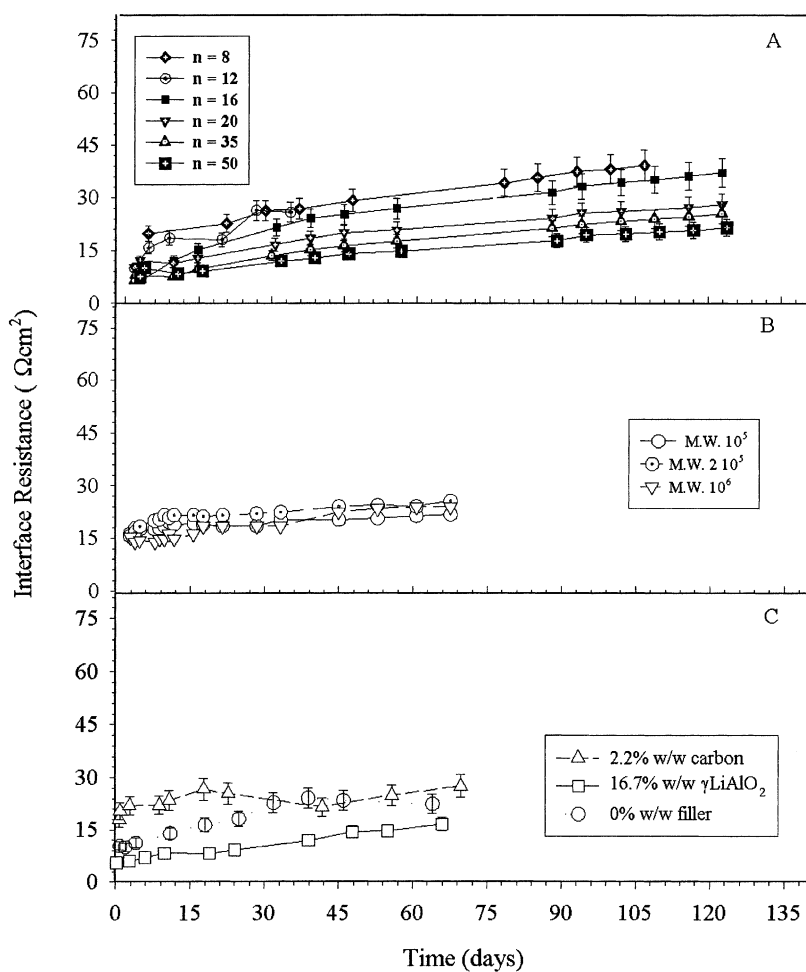


Fig. 2. Behavior of the lithium anode–polymer electrolyte interfacial resistance vs. storage time at 90°C. The three panels refer to the first, third and fourth classes of polymer electrolytes described in Table 1, respectively.

the $n = 20$ composition where is the maximum concentration of free ions [10].

The results reported in Fig. 1 (panels C and D) clearly show a few “non-effects” of the polymer electrolyte formulation on its ionic conductivity. The most important is certainly the presence of a filler [12]. The addition of 2% (w/w) carbon powder or as much as 16.7% (w/w) of ceramic powder (γ -LiAlO₂) does not increase the ionic conductivity of the PEO₂₀LiCF₃SO₃ polymer electrolyte. Also non-affecting the ionic conductivity of the electrolyte is the molecular weight of the polymer (PEO), at least in the range investigated (from 10⁵ to 10⁶).

The evolution of the interfacial impedance at the polymer electrolyte–lithium anode interface in rest condition at 90°C is illustrated in Fig. 2. Panels A–C refer, respectively, to the first, third and fourth class of polymer electrolytes reported in Table 1. At short storage times there are some differences associated with the nature of the salt and of the filler. However, upon long-time storage, the salt concentration is the only parameter truly affecting the impedance of the lithium–polymer electrolyte interface. Similar results have

been obtained in dynamic conditions when a current is passed through the cell [9,12].

3.2. Lithium–polymer electrolyte batteries

In Fig. 3 is reported the cycle performance of a few lithium–polymer electrolyte batteries containing the composite cathodes indicated in Table 1. From panel A is seen that the cathodes were able to deliver capacities going from about 240 mAh g⁻¹ (Ag_{0.5}V₂O₅) to 280 mAh g⁻¹ (V₂O₅). The shape of the discharge curves changed substantially going from the crystalline V₂O₅ to the amorphous-doped V₂O₅ xerogels [13]. However, the sharp steps of crystalline disappeared during the following charge as a result of the well known amorphization of the crystalline V₂O₅ structure upon deep lithium intercalation [14]. Substantially different was the cycling behavior of the batteries (see panel B). Among the three different composite cathodes only Cu_{0.1}V₂O₅ xerogel showed a low capacity fading. After 100 cycles such a composite electrode was still able to deliver about 90% of the second cycle capacity. Such a

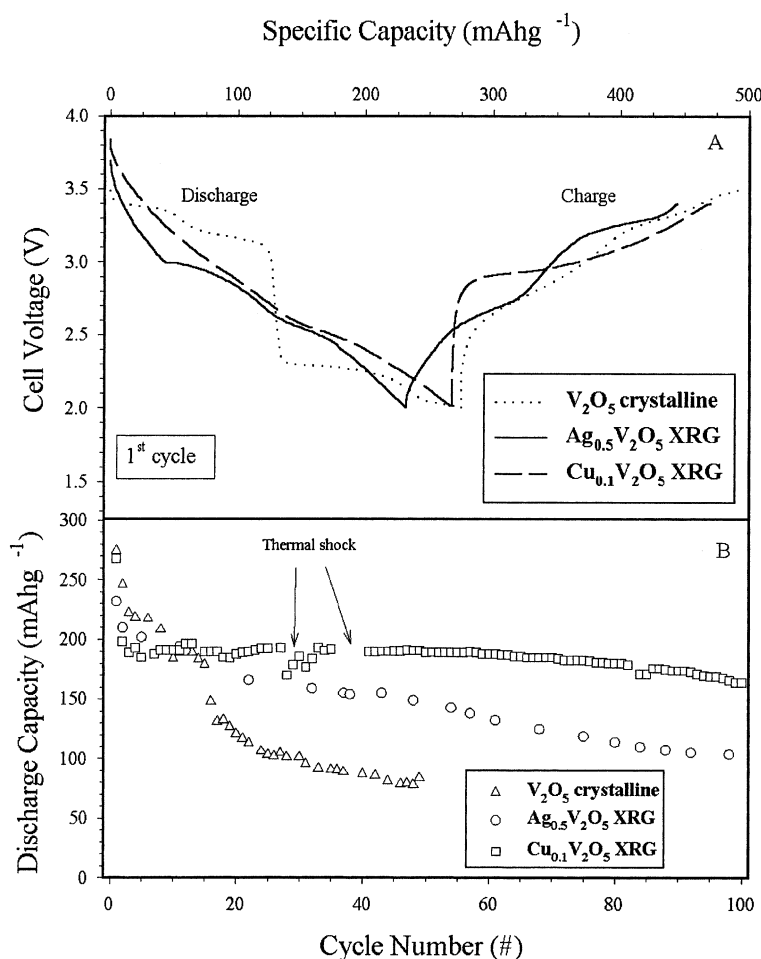


Fig. 3. First discharge–charge cycle and cycling behavior of lithium–polymer electrolyte batteries containing vanadium oxide-based cathodes at 90°C. The cells were cycled within 3.4 and 2.0 V with a current density of about 0.1 mA cm⁻².

result is in very good agreement with previously published results that have shown the superior cycle life performance of $\text{Cu}_{0.1}\text{V}_2\text{O}_5$ xerogel [13] with respect to other vanadium pentoxide-based cathodes.

4. Conclusions

In this work were reviewed the investigations on lithium-polymer electrolyte-based batteries which operate at about 90°C performed within the ALPE project. The battery components were prepared through a solvent-free procedure which allows to obtain homogeneous composites having good mechanical properties.

The ionic conductivity of the PEO-LiX complexes were found to be strongly affected by the nature of the salt, slightly affected by its concentration and not influenced by the nature and the amount of filler or the PEO molecular weight. The last evidence is particularly important in view of technological applications. Composites containing low molecular weight PEO can be easily processed in a variety of ways (extrusion, blowing, hot-calendering) not requiring the use of any solvent. The absence of solvent in the preparation not only reduces the production costs but also improve the performance of the polymer electrolyte-lithium anode interface [12].

The lithium-polymer electrolyte interface was found to be affected only by the salt concentration. The addition of the filler, 16.7% in weight of $\gamma\text{-LiAlO}_2$ which particle size is lower than 100 nm, to the polymer electrolyte did not improve the performance of such an interface. However, it should be considered that the material preparation and the cell assembly were performed in an extremely dry and clean environment that is not easily reproducible in a factory. In less controlled environments, the addition of a filler dispersed in the polymer electrolyte might trap impurities and water thus, exerting a beneficial effect on the stability of the lithium-polymer electrolyte interface [1,5].

Among the various vanadium oxide-based composite cathodes tested in full battery configurations the best performance in terms of capacity and cycle life have been obtained with copper-doped V_2O_5 XRG.

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References

- [1] B. Scrosati, *Nature* 373 (1995) 557.
- [2] S.P. Beaton, G.A. Bishop, Y. Ziang, L.L. Ashbaugh, D.R. Lawson, D.H. Stedman, *Science* 268 (1995) 991.
- [3] J. Aragane, K. Matsui, H. Andoh, S. Sukuki, H. Fukuda, H. Ikeaya, K. Kitaba, R. Ishikawa, *J. Power Sources* 68 (1997) 13.
- [4] F.R. Kalhammer, A. Kozawa, C.B. Moyer, B.B. Owens, *Electrochem. Soc. Interface* 5 (1996) 32.
- [5] F. Croce, B. Scrosati, *J. Power Sources* 43 (1993) 9.
- [6] M. Armand, M. Duclot, French Patent No. 78 32976 (1978).
- [7] F. Capuano, F. Croce, B. Scrosati, *J. Electrochem. Soc.* 138 (1991) 1918.
- [8] G.B. Appetecchi, F. Croce, G. Dautzenberg, M. Mastragostino, F. Ronci, B. Scrosati, F. Soavi, A. Zanelli, F. Alessandrini, P.P. Prosini, *J. Electrochem. Soc.* 145 (1998) 4126.
- [9] P.P. Prosini, S. Passerini, R. Vellone, W.H. Smyrl, *J. Power Sources* 75 (1998) 73.
- [10] G.B. Appetecchi, W.H. Henderson, P. Villano, S. Passerini, in preparation.
- [11] C.D. Robitaille, D. Fauteux, *J. Electrochem. Soc.* 133 (1986) 315.
- [12] G.B. Appetecchi, S. Passerini, *Electrochem. Acta* 45 (2000) 2139.
- [13] F. Coustier, J. Hill, S. Passerini, W.H. Smyrl, *J. Electrochem. Soc.* 146 (1998) 1355.
- [14] J. Scarmenio, S. Passerini, F. Decker, A. Talledo, A.A. Andersson, *Electrochem. Acta* 38 (1993) 1637.