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PEO based polymer electrolyte lithium-ion battery

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Abstract

Nanocomposite ZrO_2-added PEO-based solid polymer electrolytes and nanocomposite Ag-added $LiFePO_4$ cathodes have been utilized to realize all solid state metallic lithium batteries. In this work the electrochemical properties of these materials will be illustrated and discussed.

Keywords: Batteries; Impedance; Nanocomposites; Sol-gel processes; ZrO_2

1. Introduction

We have previously[1–4] illustrated and discussed the transport properties of various types of nanocomposite polymer electrolytes formed by dispersing into a PEO-LiX matrix selected types of nanosized ceramic powders. The electrochemical investigation of these materials has clearly demonstrated that the ceramic fillers induce quite relevant effects, such as a consistent enhancement of the Lithium transference number and of the ionic conductivity, both below and above the PEO crystallization temperature, and an improvement of capability and cyclability of PEO based nanocomposite polymer electrolyte lithium batteries.[5] These effects have been interpreted assuming a specific role of the ceramic filler that is not limited to the sole action of preventing crystallization of the polymer chains, but also, and in particular, promotes specific interactions between the surface groups of both the PEO segments and the electrolyte ionic species.[6] It is possible to explain the effects caused by the presence of the ceramic filler assuming an enhancement of salt dissociation and a stabilisation of the amorphous phase in the polymer matrix. Both these phenomena have been attributed to some acid-base Lewis type ceramic-electrolyte interactions between the polar surface groups of the inorganic filler and the electrolyte ionic species.[7]

In order to confirm these hypotheses, we have now studied the system formed by dispersing nano-particle size of ZrO_2, a compound well known in the literature for having strong Lewis acid groups on its surface. We have assembled a prototype of lithium metal rechargeable battery with a new cathodic material $LiFePO_4 + 1\%$ Ag which features have been demonstrated to be very compatible with the working conditions of PEO based polymer electrolytes.

2. Experimental

The zirconia ceramic filler was prepared by hydrolysis of Zirconium isopropoxide at ambient temperature in aqueous alcoholic solution. The powder thus obtained was milled for 2 h and then calcinated at 500 °C. The choice of calcination temperature results by analysis of TG/DTA that was performed by a thermoanalyzer (STA 409, Netzsch) in air flow (80 ccm^{-1}) with a heating rate of 10 $°Cm^{-1}$ in the temperature range 25–900 °C. Morphology and mean particle diameters (about 20 nm) were determined by scanning electron microscopy (SEM).

The nanocomposite polymer electrolyte was obtained using a casting technique by mixing PEO 600.000 (Aldrich), with $LiCF_3SO_3$ (Fluka, purum) and ZrO_2 nanometric powder. The $LiCF_3SO_3$-PEO concentration ratio was fixed to 1/20 and the amount of ceramic added to 10% of the total $PEO_{20}LiCF_3SO_3$ weight. The impedance spectroscopy of the membrane was carried out by measuring in the 1 Hz–100 KHz frequency range, the

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response of cells formed by sandwiching the given electrolyte membrane sample between two polished stainless-steel electrodes. A Solartron, mod 1260 frequency response analyser was used to run all the impedance tests. The lithium ion transference number, T_+ was evaluated using the method proposed by Jacobsen and Soerensen.[8] Accordingly, the T_+ values were determinate by studying the impedance spectra in the 1mHz–100 KHz frequency range, of a Li/$P(EO)_{20}$ $LiCF_3SO_3 + \%\ ZrO_2$ /Li cell.

The Li-Polymer electrolyte compatibility was evaluated studying the time evolution of the impedance spectra in the 1 Hz- 100 KHz frequency range of a Li-electrolyte sample-Li cell.

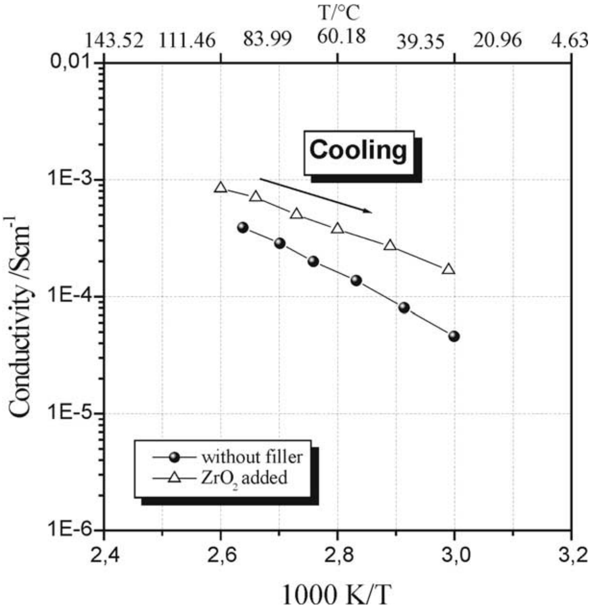

Fig. 1. Arrhenius plot of conductivity of $P(EO)_{20}LiCF_3SO_3$ +10 wt.% ZrO_2 composite polymer electrolyte. The conductivity of a $P(EO)_{20}LiCF_3SO_3$ ceramic-free sample is also reported for comparison purposes. Data obtained impedance measurements.

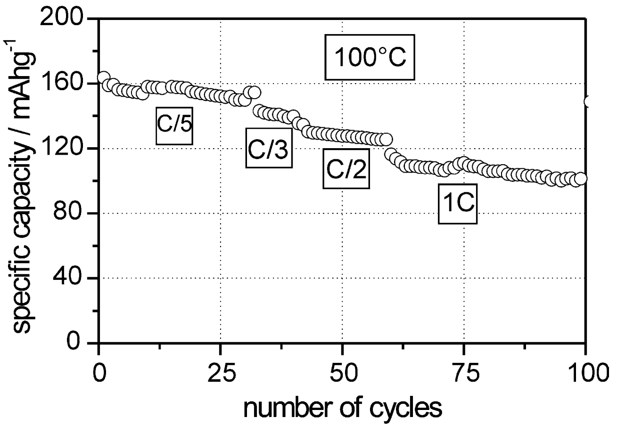

Fig. 2. Galvanostatic cycling test of: $LiFePO_4$ 1%Ag\$P(EO)_{20}LiCF_3SO_3$ + 10 wt.% ZrO_2\Li at different current densities.

The assembled cell is constituted by a lithium metal foil as anode, the nanocomposite polymeric membrane as electrolyte, and a film-type $LiFePO_4$ active material (83%) added with 1 weight percent of silver, mixed with a carbon (M.M.M. Carbon Belgium Super P, 12 wt%) conductive additive and a PVdF (Solvay Solef 6020, 5 wt%) binder, as cathode. The galvanostatic cycling test was carried out at different temperatures using a Maccor battery cycler setting charge cut-off voltage of 3.8 V.

3. Results and discussion

The Arrhenius plot of the PEO-based electrolyte added with ZrO_2 is shown in Fig. 1 together with that of a $P(EO)_{20}LiCF_3SO_3$ ceramic-free sample. It is evident that the addition of the filler causes an enhancement of about one order of magnitude in conductivity values above 60 °C (around the crystallization temperature of the sample).

The lithium ion mobility[8] was evaluated by the transference number using the well known Jacobsen Soerensen formula: $T_+ = R_{bulk}/(R_{bulk} + Z_{diff}) = 0.42$. The T_+ value at 85 °C of the ZrO_2 added sample shows a significant increase when compared with that measured for the ceramic-free sample ($T_+ = 0.27$). This behaviour confirms the model developed by Croce and co-workers. The increase in conductivity and lithium ion mobility reflects the stability of the Li metal-nanocomposite polymer electrolyte interface.

The decomposition voltage of the nanocomposite PEO based membrane was evaluated by running sweep voltammetry on a lithium-steel cell. Two main favourable features can be derived from the results obtained: the current onset is detected around 4.2 V versus Li, which is assumed as the membrane anodic breakdown voltage; this voltage is high enough to allow the safe use of the membrane in connection with the $LiFePO_4 + 1\%$ Ag electrode which typically cycle around 3.5 V. (ii) the residual current prior to the break-down is extremely small, giving clear evidence of the high purity of the membrane.

Fig. 2 shows the cycle performance of Li/$P(EO)_{20}LiCF_3SO_3 + 10w/o\ ZrO_2/LiFePO_4 + 1\%$ Ag cell operated at different currents. The capacity of the cell decreases with the improvement of current density, but for high current values (0.3 $mAcm^{-2}$) there is no lithium-ion diffusion process inside the PEO membrane at 100 °C.

4. Conclusions

It was demonstrated that the lithium metal rechargeable battery has features largely exceeding those so far reported for other more conventional types of lithium polymer batteries and for other nanocomposite polymer electrolytes, in terms of very high power capability at 1C. These properties make $P(EO)_{20}LiCF_3SO_3 + 10w/o$ ZrO_2 a very promising electrolyte material for the development of an efficient rechargeable lithium polymer battery working near the crystallization temperature of the composite polymer electrolyte.

References

1. Croce, F., Appetecchi, G. B., Persi, L. and Scrosati, B., *Nature*, 1998, **394**, 456.
2. Croce, F., Curini, R., Martinelli, A., Persi, L., Ronci, F., Scrosati, B. B., Croce, F. and Persi, L., *J. Electrochem. Soc.*, 2000, **5**, 1718.
3. Scrosati, B. and Caminiti, R., *J. Phys. Chem. B*, 1999, **103**, 10632.
4. Appetecchi, G. B., Croce, F., Persi, L., Ronci, F. and Scrosati, B., *Electrochim. Acta*, 2000, **45**, 1481.
5. Croce, F., Serraino, Fiory, F., Persi, L. and Scrosati, B., High-rate, long-life lithium-nanocomposite polymer electrolyte battery. *Electrochemical and Solid State Letters*, 2001, **4**(8), A121–A123.
6. Tesi Sperimentale (a.a1999–2000) Sintesi e caratteriazione elettrochimica di elettroliti polimerici ionoconduttori nanocompositi a base di Polietilenossido, Seraino Fiory, F., Croce, F. and Scrosati, B.
7. Croce, F., Persi, L., Scrosati, B., Serraino Fiory, F., Plichta, E. and Hendrickson, M. A., Role of the ceramic fillers in enhanching the transport properties of composite polymer electrolytes. *Electrochimica Acta*, 2001, **46**, 2461–2475.
8. Sorensen, P. R. and Jacobsen, T., Electrochim. Acta, 1982, 1671.