

Short Communication

A new solid-state electrolyte: rubbery 'polymer-in-salt' containing $\text{LiN}(\text{CF}_3\text{SO}_2)_2$

Li Feng *, Hailin Cui

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130 022 People's Republic of China

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Abstract

A new class of rubbery 'polymer-in-salt' electrolytes for application in solid-state lithium batteries has been explored by differential scanning calorimetry and a.c. impedance analysis. Simple phase diagrams of $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{LiClO}_4$ and $\text{LiC}(\text{CF}_3\text{SO}_2)_3 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$ have been drawn, which are very important to determine polymer-in-salt electrolyte materials. The conductivities obtained by a.c. impedance measurement are smaller for the electrolyte that contains acetate LiOAc salt than for the electrolyte without this salt.

Keywords: Electrolytes; Polymers; Phase diagram

1. Introduction

It is well known that solid-state polymer lithium rechargeable batteries have attracted considerable attention in recent decades [1]. A very important objective in developing such batteries is to find an electrolyte with the desired electrical conductivity, mechanical properties and stability against powerfully oxidizing and reducing electrodes at room temperature [2,3]. In 1993, Angell et al. [4] reported a new class of ionic conductors — 'polymer-in-salt' materials in which lithium salts were mixed with small quantities of polymer, such as polypropylene oxide or polyethylene oxide. The polymer is endowed with rubbery properties by virtue of the entanglement mechanism. The mechanism of ion movement in the electrolyte is quite different from that in a common polymer electrolyte.

The lithium imide salt $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in recent years has also sparked an interest for lithium batteries because its safety, thermal stability and conductivity are superior to those of some inorganic salts (e.g. LiClO_4 , LiAsF_6) that are widely used in lithium batteries [5–7]. In this paper, we report an investigation of several kinds of electrolyte that contain $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as a component in order to determine the optimal composition.

2. Experimental

The chemical compounds LiOAc , LiClO_4 , LiNO_3 , LiAlCl_4 and polyethylene oxide (PEO, mol. wt. 3×10^5) were

* Corresponding author.

reagent grade and supplied by Aldrich. The compound $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ was obtained from 3 M, and $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ from CoValent Associates. Before use, all compounds were dried at different temperatures under vacuum. The samples were prepared and ground in a Millar–Howe, high integrity, glove box filled with argon so that the O_2 and H_2O concentration were maintained at less than 5 ppm. The samples were then dissolved in acetonitrile and dried by increasing the temperature slowly over one day. Differential scanning calorimetry (DSC) experiments were carried out on a PerkinElmer DSC-7 instrument combined with a TAC 7/3 instrument controller. The scanning range of temperature was from -10 to 350°C . The electrolyte samples, with a diameter of 13 mm, were prepared by solvent casting and hot pressing. The conductivities were determined using an a.c. impedance method over a frequency range from 100 kHz to 0.2 Hz, with a Solartron 1255 frequency analyzer coupled to a 1286 electrochemical interface.

3. Results and discussion

A simple binary eutectic phase diagram for the system $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{LiClO}_4$, according to the DSC results, is given in Fig. 1. The salts start to melt as the sample is heated to about 197°C . The initial melting point is 40°C lower than that of the component $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. The binary eutectic composition in Fig. 1 consists mainly of salt $\text{LiN}(\text{CF}_3\text{SO}_2)_2$. It is about $70\% \text{LiN}(\text{CF}_3\text{SO}_2)_2 + 30\% \text{LiClO}_4$, at which the

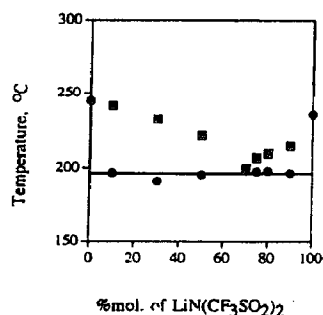


Fig. 1. Phase diagram of the $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{LiClO}_4$ system: (■) melting point, and (●) initial melting point.

salts can be melted completely at a constant temperature. Usually, this is an optimal salt composition for forming rubbery polymer-in-salt electrolyte. Fig. 2 is a binary phase diagram of the salts $\text{LiC}(\text{CF}_3\text{SO}_2)_3 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$. It is obvious that the phase diagram has a much lower initial melting temperature of about 173 °C. The organic salt $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ has been identified as a promising electrolyte for lithium batteries in recent years; it is comparable with Li-imide $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in terms of conductivity [8,9] and has good safety, as well as thermal and electrochemical stability. Both of the electrolytes have a large flexible anionic structure that can act as a plasticizer in complexes with PEO [9,10]. The eutectic composition is about 45% $\text{LiC}(\text{CF}_3\text{SO}_2)_3 + 55\% \text{LiN}(\text{CF}_3\text{SO}_2)_2$, see Fig. 2.

The DSC results for some binary and more than two-component salts are listed in Table 1. It is concluded that multi-

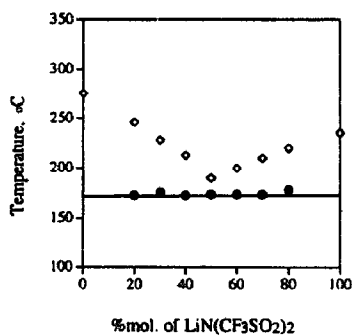


Fig. 2. Phase diagram of the binary eutectic $\text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{LiC}(\text{CF}_3\text{SO}_2)_3$: (◇) melting point, and (●) initial melting point.

Table 1
DSC results for multi-component salt electrolytes

Salts systems	Initial melting temperature (°C)
$\text{LiNO}_3 + \text{LiOAc} + \text{LiN}(\text{CF}_3\text{SO}_2)_2$	153
$\text{LiOAc} + \text{LiClO}_4 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$	148
$\text{LiI} + \text{LiOAc} + \text{LiClO}_4 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$	134
$\text{LiAlCl}_4 + \text{LiC}(\text{CF}_3\text{SO}_2)_3 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$	83
$\text{LiC}(\text{CF}_3\text{SO}_2)_3 + \text{LiCF}_3\text{SO}_3$	213
$\text{LiClO}_4 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$	197
$\text{LiOAc} + \text{LiAsF}_6$	188
$\text{LiC}(\text{CF}_3\text{SO}_2)_3 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$	173

component salts systems would have lower initial melting temperatures than two-component salt electrolytes. For example, the initial melting point is 148 °C for the system $\text{LiOAc} + \text{LiClO}_4 + \text{LiN}(\text{CF}_3\text{SO}_2)_2$, but only 83 °C for the system $\text{LiAlCl}_4 + \text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{LiC}(\text{CF}_3\text{SO}_2)_3$. The compound LiAlCl_4 shows the highest conductivity. Adding a small amount of this compound can improve the conductivity of a multi-component salt electrolyte. The lower the initial melting temperature of the mixed salt electrolyte, the easier the movement of ions in the solid-state electrolyte at room temperature. Fig. 3 shows the DSC traces for a rubbery polymer-in-salt electrolyte formed by mixing 20% PEO into multi-component salts. It is seen that the initial melting temperature decreased after forming the rubbery polymer-in-salt electrolyte. The first peak at the initial melting point is small; only a small amount of the electrolyte is melted at the temperature. Almost all of the mixtures begin to melt when the second peak appears on the DSC curve. If the electrolyte $\text{PEO} + [\text{LiAlCl}_4 + \text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{LiC}(\text{CF}_3\text{SO}_2)_3]$ was used in solid-state lithium batteries, the cell could operate at a temperature as high as 80 °C, that is, at below the melting temperature of the polymer-in-salt electrolyte.

The a.c. impedance experiments were performed on several kinds of polymer-in-salt electrolyte using stainless-steel (SS) blocking electrodes. Impedance plots of the cell $\text{SS}/\text{PEO} + [\text{LiAlCl}_4 + \text{LiN}(\text{CF}_3\text{SO}_2)_2 + \text{LiC}(\text{CF}_3\text{SO}_2)_3]/\text{SS}$ at different experimental temperatures are shown in Fig. 4. The impedance spectra consist of two segments. One is a semi-circle at high frequencies which cannot be observed on some spectra at higher temperature conditions because of the limit of the high-frequency scale of the instrumentation. This is related to the bulk resistance of the electrolyte. The other appears in the form of a 'spike' at low frequency. This may be associated with the charge build-up between the electrolyte and the blocking metal electrode. The equivalent circuit is presented in Fig. 4 to explain the impedance spectra. With decreasing temperature, the bulk impedance, or the intercept of the 'spike' on the real axis, increases gradually. The reason is that the movement of ions in the melt electrolyte becomes weaker.

The variation of conductivity with temperature for several kinds of polymer-in-salt electrolytes with $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ as a component is shown in Fig. 5. Clearly, the conductivity is small for the electrolyte containing the component salt LiOAc and is about $10^{-7} \text{ S cm}^{-1}$ at ambient temperature. This is probably because the common solvent salt LiOAc is a very poor electrolyte in terms of conductivity and causes a decrease in the conductivity of the whole electrolyte material. Moreover, an electrolyte material with a higher content of PEO does not display any improvement in conductivity. The electrolyte containing acetate-free (LiOAc) salt has a conductivity as high as 10^{-5} to $10^{-6} \text{ S cm}^{-1}$ at ambient temperature. Dominey et al. [11] reported that the conductivity of Li-imide in PEO was about $10^{-9} \text{ S cm}^{-1}$ at 25 °C. Values as high as $10^{-5} \text{ S cm}^{-1}$ at room temperature have been disclosed [8,12] for the conductivity of a polymer electrolyte

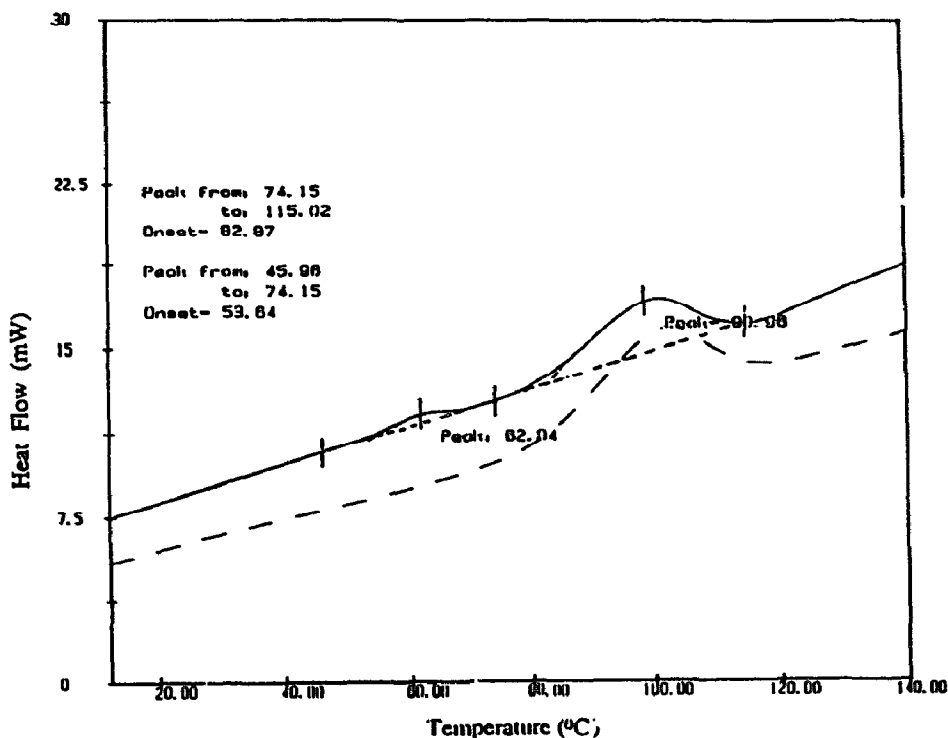


Fig. 3. DSC traces for electrolytes: (—) 20%PEO + 80%[LiAlCl₄ + LiC(CF₃SO₂)₃ + LiN(CF₃SO₂)₂]; (---) 35%AlCl₄ + 65%[LiC(CF₃SO₂)₃ + LiN(CF₃SO₂)₂]; scanning rate = 20.0 °C/min.

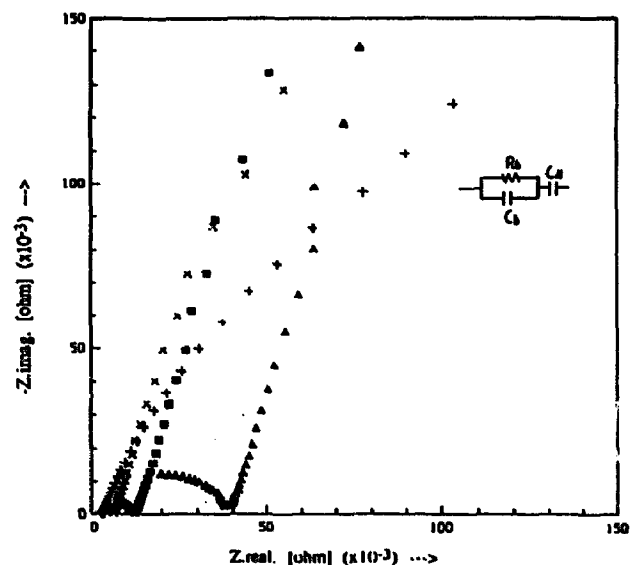


Fig. 4. Complex impedance plots for an SS/PEO + [LiAlCl₄ + LiC(CF₃SO₂)₃ + LiN(CF₃SO₂)₂]/SS cell: (○) 71 °C; (×) 65 °C; (■) 56 °C, and (▲) 45 °C. In equivalent circuit, R_b, C_b and C_{dl} represent bulk resistance, and bulk and double-layer capacities, respectively.

with salt LiN(CF₃SO₂)₂. Therefore, it is seen that rubbery 'polymer-in-salt' electrolyte could be comparable in conductance to common polymer electrolyte. Further studies are being conducted on multi-salt components of polymer-in-salt electrolyte in order to obtain lower a melting point or glass transition for the whole system.

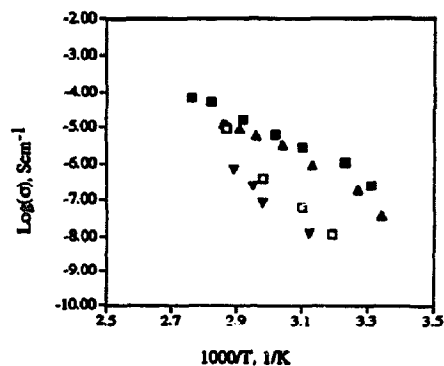


Fig. 5. Dependence of conductivity on temperature for the electrolytes: (■) 20%PEO + 80%[LiClO₄ + LiN(CF₃SO₂)₂]; (▲) 20%PEO + 80%[LiAlCl₄ + LiC(CF₃SO₂)₃ + LiN(CF₃SO₂)₂]; (□) 30%PEO + 70%[LiClO₄ + LiOAc + LiN(CF₃SO₂)₂], and (▼) 40%PEO + 60%[LiOAc + LiN(CF₃SO₂)₂].

4. Conclusions

Rubbery polymer-in-salt electrolytes provide a new research field in the development of solid-state electrolyte materials. Several kinds of multi-salt electrolyte with a component of LiN(CF₃SO₂)₂ have been studied. The binary eutectic phase diagrams for LiN(CF₃SO₂)₂ + LiC(CF₃SO₂)₃ and LiClO₄ + LiN(CF₃SO₂)₂ have been drawn in simple terms. Adding some salt components, such as LiAlCl₄, to the binary system can lower the initial melting temperature of the electrolyte.

Impedance spectra have been studied with SS blocking electrodes (SS/polymer-in-salt electrolyte/SS) and explained through an equivalent circuit. It is found that the electrolytes with an acetate-free (LiOAc) salt have better conductivity than those containing component LiOAc. Therefore, it is suggested that each salt component in a polymer-in-salt electrolyte should be advantageous in both decreasing the initial melt temperature of the system, and improving the conductivity.

References

- [1] R. Koksang, I.I. Olsen, P.E. Tonder, N. Knudsen, J.-S. Lundsgaard and S. Yde-Andersen, *J. Power Sources*, 32 (1990) 175–185.
- [2] S. Skaarup, K. West, S. Yoe-Andresen and R. Koksang, in B.V. Chowdar, Q.-G. Liu and L.Q. Chen (eds.), *Recent Advances in Fast Ion Conduction Materials and Devices*, World Scientific, Singapore, 1990, pp. 83–95.
- [3] R. Huq, R. Koksang, P.E. Tonder and G.C. Farrington, *J. Power Sources*, 32 (1990) 186.
- [4] C.A. Angell, C. Liu and E. Sanchez, *Nature*, 362 (11) (1993) 137.
- [5] J.T. Dudley, D.P. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvalt, M.W. Juzkow, B. Denis, P. Duric, P. Aghakian and J.-R. Dahn, *J. Power Sources*, 35 (1991) 59.
- [6] A. Webber, *J. Electrochem. Soc.*, 138 (1991) 2586.
- [7] S.D. Brown, S.G. Greenbaum, M.G. McLin, M.C. Wintersgill and J.J. Fontanella, *Solid State Ionics*, 67 (1994) 257.
- [8] A. Vallee, S. Resner and J. Prud'homme, *Electrochim. Acta*, 37 (1992) 1579.
- [9] P.R. Sorensen and T. Jacobsen, *Electrochim. Acta*, 27 (1982) 1671.
- [10] J.T.S. Irvin, D.C. Sinclair and A.R. West, *Adv. Mater.*, 2 (1990) 132.
- [11] L.A. Dominey, V.R. Koch and T.J. Blakley, *Electrochim. Acta*, 9 (1992) 1551.
- [12] M. Armand, W. Gorecki and R. Andreani, in B. Scrosati (ed.), *2nd Int. Symp. Polymer Electrolytes*, Elsevier Applied Science, New York, 1990, p. 91.