

Deakin Research Online

Deakin University's institutional research repository

This is the published version (version of record) of:

Ferry, Anders, Edman, Ludvig, Forsyth, Maria, MacFarlane, Douglas R. and Sun, Jianzeng
1999-08-15, Connectivity, ionic interactions, and migration in a fast-ion-conducting polymer-
in-salt electrolyte based on Poly(acrylonitrile) and LiCF₃SO₃, *Journal of applied physics*,
vol. 86, no. 4, pp. 2346-2348.

Available from Deakin Research Online:

<http://hdl.handle.net/10536/DRO/DU:30030114>

Reproduced with the kind permission of the copyright owner

Copyright : 1999, American Institute of Physics

COMMUNICATIONS

Connectivity, ionic interactions, and migration in a fast-ion-conducting polymer-in-salt electrolyte based on poly(acrylonitrile) and LiCF_3SO_3 Anders Ferry^{a)}*Department of Materials Engineering, Monash University, Clayton, 3168 VIC, Australia*

Ludvig Edman

Department of Physics, Umeå University, S-901 87 Umeå, Sweden

Maria Forsyth

Department of Materials Engineering, Monash University, Clayton, 3168 VIC, Australia

Douglas R. MacFarlane and Jianzeng Sun

Department of Chemistry, Monash University, Clayton, 3168 VIC, Australia

(Received 15 December 1998; accepted for publication 5 May 1999)

The ionic conductivity of a polymeric fast-ion-conductor based on LiCF_3SO_3 salt and poly(acrylonitrile), $[\text{CH}_2\text{CH}(\text{CN})]_n$, is enhanced by ~ 5 orders of magnitude when the composition approaches the "polymer-in-salt" regime; i.e., when the salt content increases from N:Li=12:1 to 1.2:1 (or ~ 70 wt % of salt). This is in contrast to common salt-in-polymer electrolytes where a conductivity maximum typically is encountered at intermediate compositions. We suggest that connectivity effects in a microscopically phase segregated material may influence the long-range migration of charge carriers. Conductivity data are augmented with Raman spectroscopic investigations, thus probing microscopic details regarding the state of the dissolved salt. © 1999 American Institute of Physics. [S0021-8979(99)00116-4]

Investigations of ionically conducting polymer-salt complexes are currently at focus due to intriguing ionic transport properties and, foremost, by a great potential for a range of electrochemical applications including solid thin-film batteries. For a recent review, see, e.g., Ref. 1. These materials are typically based on various polyethers, such as poly(ethylene oxide) (PEO), into which several inorganic salts are readily dissolved.² Common features of these so-called *polymer electrolytes* are that the cation-coordinating macromolecule is the majority component, and that ionic transport occurs in amorphous regions of the material, assisted by segmental motions of the polymer host matrix. Consequently, such salt-in-polymer materials exhibit high conductivities only for temperatures well above the glass transition temperature of the system.² Polymer-in-salt electrolytes constitute a related concept, where high ionic conductivities are achieved by producing a rubbery version of a glassy electrolyte.³ These materials thus ideally combine desirable features of polymer electrolytes (e.g., excellent mechanical properties) and fast-ion-conducting glasses (e.g., only cationic motion). In this communication we report conductivity data, augmented with Raman spectroscopic studies, for mixtures based on poly(acrylonitrile) (PAN) and

LiCF_3SO_3 salt over an extended range of composition, including the traditional salt-in-polymer as well as the polymer-in-salt composition regimes.

Transparent, thin-film PAN/ LiCF_3SO_3 electrolytes were prepared by a "solvent-free" hot pressing procedure.⁴ Ionic conductivities were measured as a function of temperature and salt content using the ac impedance method. Fourier transform (FT) Raman spectra were recorded as a function of temperature using a Bruker IFS 66 spectrometer with a Raman module FRA 106 and a near infrared YAG laser with a wavelength of 1064 nm.

Figure 1 shows ionic conductivity as a function of temperature for PAN/ LiCF_3SO_3 electrolytes of compositions: N:Li=12:1, 2.0:1, and 1.2:1, respectively. The lowest temperature (i.e., 95 °C) reported for the 12:1 complex is above the onset temperature for polymer segmental motions on the order of kHz associated with T_g type motions for all compositions, according to preliminary proton NMR data.⁵ (Broad glass transitions have previously been reported for these materials in the range 50–65 °C).⁴ Thus, the dramatic enhancement of ionic conductivity (i.e., ~ 5 orders of magnitude going from N:Li=12:1 to 1.2:1 at 95–105 °C) cannot simply be attributed to vast differences in glass transition temperature between the samples, although we note that the glass transition temperature in PAN-based electrolytes typi-

^{a)}Electronic mail: anders.ferry@physics.umu.se

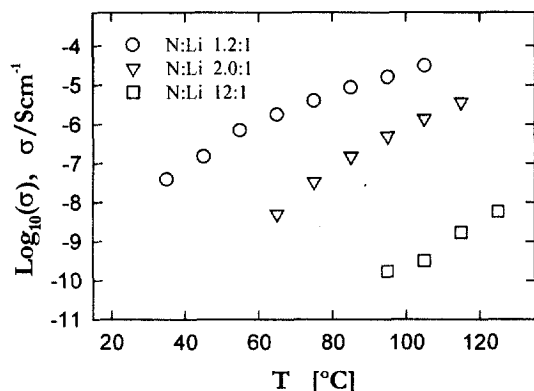


FIG. 1. Ionic conductivity as a function of temperature for PAN/LiCF₃SO₃ electrolytes of composition: Ni:Li=12:1, 2.0:1, and 1.2:1, respectively.

cally decreases upon complexation with salts.⁴⁻⁶ Large concentration-dependent increases in the ionic conductivity of low-permittivity electrolytes are generally interpreted in terms of changes in the ionic speciation (e.g., triple-ion formation⁷ or redissociation⁸) or, for heterogeneous systems, in terms of dynamic percolation effects.⁹ Clearly, when entering the polymer-in-salt composition regime, the mobility of at least some subset of available charge carriers is greatly enhanced in the present materials.

Raman spectroscopy is a powerful tool for probing microscopic details in electrolytic systems; in particular, the characteristic $\delta_s(\text{CF}_3)$ and $\nu_s(\text{SO}_3)$ internal modes of the CF₃SO₃⁻ anion are sensitive to change in the local anionic environment.¹⁰⁻¹² For instance, spectroscopically "free" CF₃SO₃⁻ anions give rise to a band at $\sim 753 \text{ cm}^{-1}$ in the $\delta_s(\text{CF}_3)$ region, with larger aggregations of ions gradually shifting up in frequency (e.g., Li⁺·CF₃SO₃⁻ contact ion pairs are found at $\sim 758 \text{ cm}^{-1}$, and Li₂CF₃SO₃⁺ triple ions at $\sim 763 \text{ cm}^{-1}$).^{10,11,13}

Figure 2 shows the $\delta_s(\text{CF}_3)$ mode for complexes of composition N:Li=1.2:1 (or $\sim 70 \text{ wt } \%$ of salt) and 10:1, respectively, after correction for a weak polymer back-

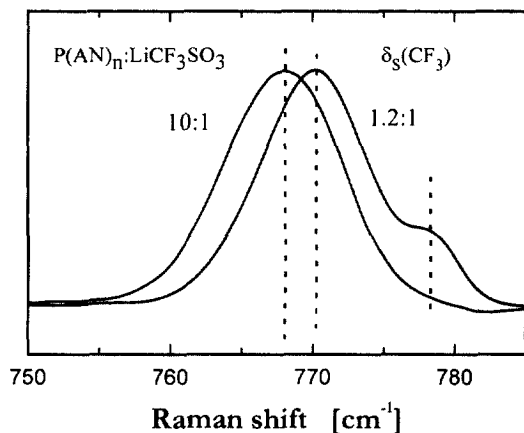


FIG. 2. Normalized Raman spectra corresponding to the $\delta_s(\text{CF}_3)$ mode of the CF₃SO₃⁻ anion for similar sample compositions (i.e., N:Li=1.2:1 and 10:1, respectively) as in Fig. 1. Dotted lines serve as guides to the eye. Spectra were recorded at 20 °C and a weak polymer background has been subtracted.

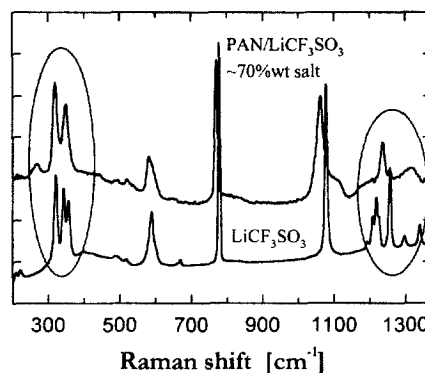


FIG. 3. Raman spectra of pure dry LiCF₃SO₃ salt and the salt-rich PAN/LiCF₃SO₃ complex, respectively. Notably, distinct spectral features characteristic of the crystalline LiCF₃SO₃ salt in the regions 320–360 and 1200–1260 cm^{-1} are absent in the salt-rich electrolyte. These regions are encircled.

ground. For N:Li=1.2:1, the main spectral component centered at $\sim 770 \text{ cm}^{-1}$ is attributable to CF₃SO₃⁻ anions interacting extensively with lithium ions.¹⁰ (This approximate assignment can also be inferred by analogy to the related PEO/NaCF₃SO₃ system.¹⁴) The relatively broad component at $\sim 779 \text{ cm}^{-1}$ is due to even larger ionic aggregations, possible precursors to salt recrystallization, by analogy to findings for concentrated PEO/NaCF₃SO₃ systems and also for LiCF₃SO₃ in acetone.^{14,15} For the pure crystalline LiCF₃SO₃ salt we only observe a narrow band centered at $\sim 779 \text{ cm}^{-1}$ in this region. Distinct spectral features characteristic of the crystalline salt in the regions 320–360 and 1200–1260 cm^{-1} are, however, considerably different in the electrolyte demonstrating that there is no significant amount of recrystallized salt present in this material, despite the high salt content (see Fig. 3). Similarly, the characteristic $\nu_s(\text{SO}_3)$ mode appears as a moderately structured feature centered at $\sim 1062 \text{ cm}^{-1}$, rather than as a sharp band at $\sim 1078 \text{ cm}^{-1}$ as we observe for the pure polycrystalline salt (Fig. 3). Interestingly, for the dilute salt-in-polymer complex, the entire $\delta_s(\text{CF}_3)$ band envelope is downshifted in frequency, as compared to the more conductive 1.2:1 complex. Thus, a more efficient ionic transport mechanism appears to be associated with a higher degree of ionic aggregation. In fact, we have previously suggested that this might be the case for cationic transport in less concentrated salt-in-polyether systems,^{11,16} where, for PEO, solvated cations are located inside the PEO helix, intramolecularly coordinated to ether oxygens in a crown-ether-like fashion.¹⁷ The fact that we do not observe any free anions (i.e., spectral bands at ~ 753 or $\sim 1032 \text{ cm}^{-1}$)¹⁰ or Li⁺·CF₃SO₃⁻ contact ion pairs in our spectra at moderate to low salt contents (i.e., N:Li=10-60:1, not shown) suggests a formation of well-defined salt-rich P(AN)_n:LiCF₃SO₃ domains upon salt solvation. In view of the above, and previous work on the influence of spatial disorder on ionic transport properties in other polymer/salt systems,⁹ we suggest that the dramatic enhancement of the ionic conductivity reflects dynamic connectivity effects in a phase-separated electrolyte passing through a "smeared" percolation threshold. This conjecture is also in accord with the apparent decoupling of

ion migration from polymer structural relaxations.⁴ Since these samples are optically transparent, any salt-rich heterogeneities must be of smaller dimensions than the wavelength of visible light. Notably, in a dynamically disordered system, subject to microscopic heterogeneities, a smeared rather than a sharp percolation threshold is indeed expected,⁹ in accordance with our observations. We have recently suggested that local effects of phase segregation/self-organization, induced by ordering dipolar interactions,¹⁸ would be a general feature of salt-in-polymer electrolytes, at least on some small length scale.^{12,19,20} Our observations show that the role of the PAN matrix in the polymer-in-salt composition region of these electrolytes involves solubilization of the salt, and hence suppression of salt crystallinity. Interestingly, the ionic substructures present in the PAN/LiCF₃SO₃ system seem to be relatively stable since spectral features reflecting the local anionic environment do not change with temperature in the interval of 20–100 °C for all compositions investigated. This observation is also consistent with our conjecture that dynamic connectivity effects, rather than changes in the ionic speciation, are related to the observed conductivity enhancement. Still, at the extremely salt-rich compositions where significant ionic conductivity is observed, charge transport may not be well described in terms of discrete ionic entities. In view of low, and *sometimes even negative*, cationic transference numbers for typical salt-in-polymer complexes,^{16,21} it has been anticipated that primarily anions are mobile in concentrated solvent-free complexes of PAN/LiClO₄.²² Considering the glassy nature of these materials, however, one would expect Li⁺ to be the main charge-carrying member.^{3,23} The ion dynamics of these materials in the polymer-in-salt regime will be further investigated by solid-state NMR techniques in our laboratory, in an attempt to elucidate the interplay between microscopic details and observable macroscopic ionic transport properties.

This work was supported by the Wenner-Gren Foundation (A.F. is currently a Wenner-Gren research fellow). Partial support from stiftelsen Carl Trygger is also gratefully

acknowledged (A.F.), as is support from Vattenfall Utveckling AB and the Kempe Foundation (L.E.). The authors also acknowledge Professor Per Jacobsson at Chalmers University of Technology for use of his excellent FT-Raman facilities.

- ¹ A. Ferry, in *Recent Research Developments in Macromolecules Research*, edited by S. G. Pandalai (Research Signpost, Trivandrum, India, 1999), Vol. 4, p. 79.
- ² See e.g., P. G. Bruce and C. A. Vincent, *J. Chem. Soc., Faraday Trans.* **89**, 3187 (1993).
- ³ C. A. Angell, C. Liu, and E. Sanchez, *Nature (London)* **362**, 137 (1993); M. Ingram, *ibid.* **362**, 112 (1993).
- ⁴ M. Forsyth, J. Sun, and D. R. MacFarlane, *Solid State Ionics* **112**, 161 (1998).
- ⁵ A. Ferry, L. Edman, M. Forsyth, D. R. MacFarlane, and J. Sun, presented at the 6th International Symposium on Polymer Electrolytes, Hagama, Japan, Nov. 1–6 (1998).
- ⁶ M. Watanabe, M. Kanba, K. Nagaoka, and I. Shinohara, *J. Polym. Sci., Polym. Phys. Ed.* **21**, 939 (1983).
- ⁷ R. M. Fuoss and C. A. Kraus, *J. Am. Chem. Soc.* **55**, 2387 (1933).
- ⁸ A. M. Sukhotin, *Russ. J. Phys. Chem.* **33**, 450 (1959).
- ⁹ A. Ferry, *J. Chem. Phys.* **107**, 9168 (1997), and references therein.
- ¹⁰ W. Huang, R. Frech, and R. A. Wheeler, *J. Phys. Chem.* **98**, 100 (1994).
- ¹¹ A. Ferry, *J. Phys. Chem. B* **101**, 150 (1997).
- ¹² A. Ferry, G. Orädd, and P. Jacobsson, *J. Chem. Phys.* **108**, 7426 (1998).
- ¹³ R. Frech, S. Chintapalli, P. G. Bruce, and C. A. Vincent, *Chem. Commun. (Cambridge)*, 157 (1997).
- ¹⁴ M. M. Doeff, A. Ferry, Y. Ma, L. Ding, and L. C. DeJonghe, *J. Electrochem. Soc.* **144**, L-20 (1997).
- ¹⁵ J. R. Stevens and P. Jacobsson, *Can. J. Chem.* **69**, 1980 (1991).
- ¹⁶ A. Ferry, M. M. Doeff, and L. C. DeJonghe, *J. Electrochem. Soc.* **145**, 1586 (1998).
- ¹⁷ See, e.g., P. G. Bruce, *Philos. Trans. R. Soc. London, Ser. A* **354**, 415 (1996).
- ¹⁸ A. R. Khokhlov and E. E. Dormidontova, *Phys. Usp.* **40**, 109 (1997).
- ¹⁹ A. Ferry and M. M. Doeff, in *Current Trends in Polymer Science*, edited by R. Richard (Research Trends, Trivandrum, India, in press).
- ²⁰ A. Ferry (unpublished).
- ²¹ A. Ferry, M. M. Doeff, and L. C. DeJonghe, *Electrochim. Acta* **10–11**, 1387 (1998).
- ²² Z. Wang, B. Huang, R. Xue, X. Huang, and L. Chen, presented at the 11th International Conference on Solid State Ionics, Honolulu, Hawaii, Nov. 16–21, 1997.
- ²³ C. A. Angell, *Solid State Ionics* **9–10**, 3 (1983); *Annu. Rev. Phys. Chem.* **43**, 693 (1992).