

# Polymer nanocomposites: a new strategy for synthesizing solid electrolytes for rechargeable lithium batteries

W. Krawiec<sup>a</sup>, L.G. Scanlon, Jr.<sup>a</sup>, J.P. Fellner<sup>a</sup>, R.A. Vaia<sup>b</sup>, S. Vasudevan<sup>b</sup>,  
E.P. Giannelis<sup>b</sup>

<sup>a</sup> Wright Laboratory, 1950 Fifth Street, Wright-Patterson Air Force Base, OH 45433-7251, USA

<sup>b</sup> Cornell University, Department of Material Science and Engineering, Ithaca, NY 14853, USA

---

## Abstract

The ionic conductivity and lithium electrode–electrolyte interfacial stability have been measured for composite polymer electrolytes using micrometer- and nanometer-size alumina ( $\text{Al}_2\text{O}_3$ ) with polyethylene oxide (PEO) and lithium tetrafluoroborate ( $\text{LiBF}_4$ ). The influence of the nanometer-size alumina particles increases ionic conductivity by an order of magnitude compared with micrometer-size particles. The interfacial stability is increased a factor of two. Characterization of layered nanocomposite polymer electrolytes based upon melt intercalation of PEO in layered silicates (montmorillonite) show that the intercalated PEO is amorphous.

**Keywords:** Rechargeable lithium batteries

---

## 1. Introduction

One of the most promising ways to improve the morphological and electrochemical properties of polymer electrolytes is by the addition of ceramic fillers. Up-to-date, highly conducting ceramic fillers [1], zeolite [2], ionites [3], as well as electrically neutral ceramic inert fillers [3,4] have been investigated. It was shown that the addition of ceramics improves the conductivity of polyethylene oxide (PEO)-based electrolytes as well as their interfacial behavior in contact with the lithium electrode [2,4]. These effects may be explained by an enhanced degree of amorphicity of the PEO chains, hindered recrystallization, hard type modified solid–solid interphase leading to increased stability, and facilitation of the electron-transfer step at the lithium electrode by zeolite [2]. In all cases, particle size and content of ceramic appears as critical factors. It has been shown that mechanical and electrochemical properties of electrolytes increase with decreasing size of ceramic particles used and the increase of conductivity is connected with the processes occurring on the grain boundaries [3,4]. Despite greatly enhanced ionic conductivity and mechanical stability of composite polymer electrolytes (CPE) developed up-to-date, their application in rechargeable lithium batteries is still limited

by low lithium-transport number and conductivity at ambient temperature as well as by poor processing properties. In our laboratory, we have started investigations on the enhancement of the above-mentioned properties of CPE by control of the arrangement of matter on a very small scale. This work is a part of wide-scale investigations on nanocomposite polymer electrolytes (NCPE) and nanocomposite electrodes (NCE) prepared by conventionally introducing into the polymer matrix nanograins of different structures and electrical properties, as well as by intercalation of PEO in layered ceramic hosts. Taking into account unusual properties of nanocomposites [5,6] and assuming that in polymeric nanomaterials the grains added are so small that a relatively large volume of the solid mixture consists of grain boundaries (polymer nanocomposites containing only a few percent of ceramics behave like conventional microcomposited that are 60–70% ceramics) one can expect that reduction of the ceramic particle size from microns to nanometer should lead to further increase in ionic conductivity and allow one to synthesize lightweight composites which can be processed much like conventional plastic. Furthermore, the group of materials composed of alternating ultrathin rows of ceramics and polymer recently developed by Giannelis and co-workers [6,7], created a new type of

layered nanocomposite polymer electrolytes (LNCPEs) of single ionic conductivity. In these systems based on mica-type ceramic, the isomorphous substitution of silicon by aluminum forms immobilized and highly delocalized negative charge balanced by lithium cations residing in the nanosized galleries infused with PEO.

In this work, we present the results of a comparative study on the influence of micrometer- and nanometer-size alumina on ionic conductivity and lithium electrode polymer electrolyte interfacial stability. In addition, we will report on the ionic conductivity of an LNCPE that is a single-lithium-ion conductor.

## 2. Experimental

High molecular weight (mol. wt. = 400 000) PEO,  $\text{Al}_2\text{O}_3$  of particle size less than 10  $\mu\text{m}$ , and anhydrous acetonitrile (ACN) of less than 50 ppm of water were received from Aldrich Chemical Co., LTD. High surface area  $\text{Al}_2\text{O}_3$  of particle size 13 nm were obtained from Degussa Corporation. Ultradry  $\text{LiBF}_4$  containing less than 1 ppm of water was obtained from Alfa-Ceaser and used as-received. The glass ampoules of anhydrous salt were opened in a drybox under a helium atmosphere just before using. The lithium metal (Alfa) was in the form of a ribbon of 0.3 mm thickness. It was rinsed with a mixture of freshly purified hexane and heptane to remove the oil present on its surface (the oil coating applied by the manufacturer inhibited any possible surface reaction of the lithium during storage) and dried prior to use. Since experiments dealing with lithium passivation need a properly prepared electrode, the lithium bulk material was scraped to a metallic luster in a drybox just before using.

$\text{Al}_2\text{O}_3$ , molecular sieves (4A) and PEO were dried over phosphorous pentoxide ( $\text{P}_2\text{O}_5$ ) under vacuum for 48 h at 150, 200 and 50 °C, respectively. Anhydrous ACN was additionally dried and stored over dry molecular sieves which decreased the water content of the solvent to about 10 ppm.

LNCPEs were synthesized and characterized by Gianelis and co-workers, according to previously described procedures [6,7].

All CPEs have been prepared and stored in a drybox (Vacuum Atmospheres Corporation) equipped with a vacuum oven (Vacuum Atmospheres Corporation He-533) and devices for removal and analysis of oxygen ( $\text{O}_2$ ) and water. The  $\text{O}_2$  and water content of the helium (He) in the drybox was measured continuously with a calibrated  $\text{O}_2$  sensor (Vacuum Atmospheres Corporation A/O 316-H) and a solid-state moisture sensor (Vacuum Atmospheres Corporation AM-2), both of them sensitive to <0.1 ppm.

The  $\text{O}_2$  and water in the drybox were kept below 100 and 1 ppm, respectively. Transfer of the materials

between drybox was performed by using hermetically sealed He-filled glass vessels and desiccators, both equipped with O-rings.

Thin films (40–80  $\mu\text{m}$ ) of CPE were prepared as follows. The mixture containing 20–22 ml of acetonitrile, 1–1.5 g PEO and appropriate weighted quantities of  $\text{LiBF}_4$  and, whenever required,  $\text{Al}_2\text{O}_3$  was introduced into a 50 ml sealed mixing chamber of an OMNI Mixer-Homogenizer and stirred, with periodic interruptions, for 4 h at 10 000–16 000 rpm. The ratio between the monomeric units  $\text{CH}_2\text{CH}_2\text{O}$  and the number of lithium in the salt (O/Li) was in all cases fixed at 8/1. The homogeneous solution was then transferred into a 30 ml sealed chamber of the OMNI Ultrasonic Processor where the solution underwent ultrasonic agitation for 1–2 min at 20 000 KHz, in order to avoid secondary agglomeration of ceramic particles and remove gas bubbles present in the solution which could significantly affect the casting process. The degassed and warm homogeneous solutions were immediately cast on to fine polished Teflon molds and introduced into a vacuum desiccator. Then the acetonitrile was slowly (24 h) evaporated under vacuum and quantitatively collected in liquid nitrogen traps. All the electrolytes obtained in this manner were conditioned for 48 h over  $\text{P}_2\text{O}_5$  under vacuum at 50 °C and stored in a drybox, in a vacuum desiccator over dry calcium sulfate ( $\text{CaSO}_4$ ). Homogeneity as well as size of ceramic particles and their distribution in the electrolytes were continuously monitored by scanning electron microscopy (SEM). By this very fast fully controlled and environmentally friendly procedure homogeneous polymer electrolyte thin films, with no evidence of powder agglomeration, were routinely obtained.

All electrochemical experiments were carried out utilizing an EG&G PAR Model 5210 lock-in amplifier and Model 273A potentiostat/galvanostat controlled by EG&G PAR Model 270 Research Electrochemistry Software (d.c. polarization) or Model 398 electrochemical impedance software (conductivity and stability measurements) operated by a 486 GATEWAY 2000 computer. A.c. impedance was measured with 5 mV a.c. signal over a frequency range of 100 kHz to 0.1 Hz, and in some cases down to 0.01 Hz, at 6 points per frequency decade. In order to obtain the impedance parameters, all the experimental spectra were analyzed by means of Boukamp's Equivalent Circuit Software, Version 4.5. The fitting procedure was terminated only when the relative errors of impedance parameters remained generally confined below 5% ( $\chi^2$  fitting parameter  $<5 \times 10^{-5}$ ).

Disc samples of electrolytes were sandwiched between two equivalent metallic lithium (Li) or stainless-steel (SS) electrodes (electrode surface area 3.14  $\text{cm}^2$  or 1  $\text{cm}^2$ ). The LNCPE, CPE or Li/CPE/Li systems were introduced between two metallographic grade polished,

parallel SS current collectors. The collectors were kept under a constant mechanical pressure of approximately 10–12 lb/in<sup>2</sup> by using calibrated spring loaded terminals. The universal 'three-electrode' design of the cells allows for the introduction of a reference electrode by inserting, during cell assembly, a 10 μm Ni or Al wire between the two layers of the electrolyte and plating the wire with lithium from the negative electrode. All samples for the electrochemical measurements were prepared and loaded into sealed electrochemical vessels (each equipped with internal and external wire connections and thermocouple placed near the cell) in the drybox. The electrochemical vessels were then removed from the drybox, immersed in a thermostat-controlled bath and the wire leads were connected to the measuring equipment. The temperature of samples inside the electrochemical vessel were constantly monitored with an accuracy of 0.5 °C.

Ionic conductivity was determined from the a.c. impedance measurements with SS/CPE/SS cell configuration, over the temperature range –20 to 100 °C. The measurements were made every few degrees during heating. After reaching the desired temperature, the cell was kept at that temperature for 30–45 min to assure the temperature equilibrium of the sample before the measurement was made. Measurements were done at the open-circuit potential (OCP). The a.c. ionic conductivity was calculated from the complex impedance plot with nonlinear computer curve fitting.

The interphase resistance was studied by means of a.c. impedance spectroscopy applied to Li/CPE/Li cells at a temperature of 70 °C. The change of the impedance was continuously monitored for the first 100 h after cell assembly when most of the investigated phenomena occurred.

Determination of the water content of the composite polymer electrolyte materials by Karl Fisher technique was carried out on an automatic Mitsubishi moisture meter Model CA-06 equipped with Mitsubishi water vaporizer Model VA-06. The moisture content in these electrolytes was kept below 200 ppm.

Differential scanning calorimetry (DSC) experiments were conducted to estimate the degree of crystallinity in the CPEs. The experiments were carried out in the temperature range from –103 to 157 °C using a TA Instruments DSC (Model 2910) at a heating rate of 10 °C/min. The procedure for estimating the degree of crystallinity in PEO is described in Ref. [8].

### 3. Results and discussion

Fig. 1 illustrates the temperature dependence of the ionic conductivity for (PEO)<sub>8</sub>LiBF<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> nanocomposite electrolytes of various compositions. For comparison, the temperature dependence of conductivity

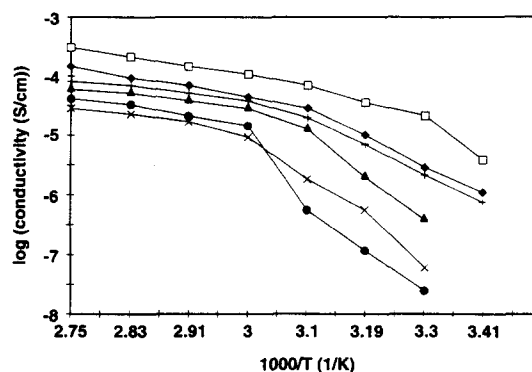


Fig. 1. Ionic conductivity vs. inverse temperature of composite (PEO)<sub>8</sub>LiBF<sub>4</sub>-Al<sub>2</sub>O<sub>3</sub> polymer electrolytes at various compositions. (●) 0 wt.% Al<sub>2</sub>O<sub>3</sub>; (▲) 5 wt.% nanosize Al<sub>2</sub>O<sub>3</sub>; (□) 10 wt.% nanosize Al<sub>2</sub>O<sub>3</sub>; (◆) 20 wt.% nanosize Al<sub>2</sub>O<sub>3</sub>; (×) 30 wt.% nanosize Al<sub>2</sub>O<sub>3</sub>, and (+) 10 wt.% microsize Al<sub>2</sub>O<sub>3</sub>.

measured for (PEO)<sub>8</sub>LiBF<sub>4</sub> and (PEO)<sub>8</sub>LiBF<sub>4</sub>-10 wt.% micro-sized Al<sub>2</sub>O<sub>3</sub> electrolytes are also included. One can observe that ionic conductivity of NCPEs varies as a function of nanoceramic content. At first, the conductivity increases with the addition of Al<sub>2</sub>O<sub>3</sub> reaching a maximum value for electrolytes containing 10 wt.% nanosized Al<sub>2</sub>O<sub>3</sub>. After that, the conductivity decreases gradually for samples containing over 30 wt.% of alumina.

The ionic conductivity is less than for the undoped (PEO)<sub>8</sub>LiBF<sub>4</sub> system. The ambient temperature ionic conductivity values obtained for NCPEs of 10 wt.% of alumina are one order of magnitude higher than values measured for analogous systems containing micro-sized alumina. Moreover, the ionic conductivity of optimized CPEs exceeds the values recorded for undoped (PEO)<sub>8</sub>LiBF<sub>4</sub> systems over the whole temperature range. The present observation is similar to that found by Scrosati and co-workers [4] for (PEO)<sub>8</sub>LiClO<sub>4</sub>-γ-LiAlO<sub>2</sub> system. Recent studies on comparison of nuclear magnetic resonance (NMR) and conductivity in (PEO)<sub>8</sub>LiClO<sub>4</sub>-γ-LiAlO<sub>2</sub> indicated that the local dynamics of the lithium ions, in particular the lithium mobility, is not changed by adding the γ-LiAlO<sub>2</sub> filler which supports the idea that the enhancement of conductivity by adding a filler is caused by stabilizing and increasing the fraction of the amorphous phase [9]. Table 1 shows that CPEs with the same amount of nanosize or microsize alumina have similar glass-transition temperatures and degrees of crystallinity. To account for the differences in ion conductivity over the whole temperature range for the microsize and nanosize alumina, grain boundary effects might be important. Slade and co-workers [10] have investigated the lithium transport in lithium bromide (LiBr)-Al<sub>2</sub>O<sub>3</sub> composites by <sup>7</sup>Li NMR and compared it with the behavior in pure lithium bromide. Their data suggested that there are two Li<sup>+</sup> environments, one more mobile than the

Table 1  
Differential scanning calorimetry data for nanocomposite polymer electrolytes (NCEs) containing  $\text{Al}_2\text{O}_3$  grains of 13 nm

$\text{Al}_2\text{O}_3$ (wt.%)	$T_g$ ( $^{\circ}\text{C}$ ) <sup>b</sup>	$T_m$ ( $^{\circ}\text{C}$ ) <sup>c</sup>	PEO crystallinity (%)
pristine PEO		64	97
0	-38	58	
1	-37	55	53
3	-38	53	51
5	-37	54	51
5 <sup>a</sup>	-37	53	51
10	-37	48	28
10 <sup>a</sup>	-33	44	21
20	-38	52	30
20 <sup>a</sup>	-35	56	41
30	-38	52	30
50		57	59

<sup>a</sup> Systems containing conventional microsize  $\text{Al}_2\text{O}_3$ .

<sup>b</sup>  $T_g$  = glass-transition temperature.

<sup>c</sup>  $T_m$  = crystalline melting point.

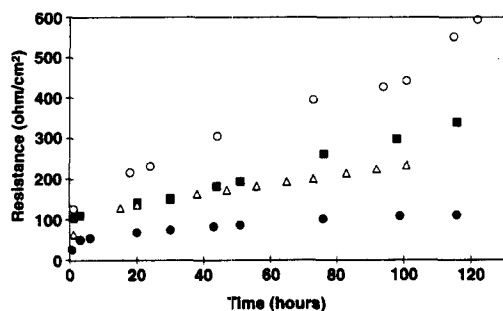


Fig. 2. Variation of interfacial resistance of (O)  $\text{Li}/(\text{PEO})_8\text{LiBF}_4/\text{Li}$ , (■)  $\text{Li}/(\text{PEO})_8\text{LiBF}_4$ , 10 wt.% of nanosize  $\text{Al}_2\text{O}_3/\text{Li}$ , (●)  $\text{Li}/(\text{PEO})_8\text{LiBF}_4$ , 20 wt.% of nanosize  $\text{Al}_2\text{O}_3/\text{Li}$ , and (Δ)  $\text{Li}/(\text{PEO})_8\text{LiBF}_4$ , 20 wt.% of microsize  $\text{Al}_2\text{O}_3$  at 70 °C under open-circuit conditions.

other, and the more mobile ions are not confined to the interface regions but exist on a high density of dislocations or grain boundaries. It was also found that the composite with a greater proportion of  $\text{Al}_2\text{O}_3$  had a much larger mobile ion concentration. Perhaps this same rationale can be proposed to describe the difference in behavior of nanosize CPE versus microsize CPE.

Fig. 2 presents the changes in interfacial resistance versus time recorded at 70 °C for  $(\text{PEO})_8\text{LiBF}_4\text{-Al}_2\text{O}_3$  electrolytes of different compositions sandwiched between two lithium electrodes. Previous works suggested then the evolution of interfacial resistance with time can be associated with continuous growth of a layer on the lithium electrode surface where the passivation layer is a product of the corrosion reaction of lithium with electrolyte components [11]. It can be seen from Fig. 2 that both the NCPes and conventional micro-sized CPEs are much more electrochemically stable in contact with the lithium electrode than undoped  $(\text{PEO})_8\text{LiBF}_4$  electrolyte. Stability of NCPes in contact

with lithium varies with the electrolyte composition reaching the optimum for a system containing 20 wt.% nanosized alumina.

One can also observe that the interfacial resistance of the electrolyte containing nanosized  $\text{Al}_2\text{O}_3$  is much lower than the interfacial resistance of the analogous micro-sized electrolyte indicating the importance of greatly increased ceramic surface area for stabilizing the interphase. Fig. 3 shows the evolution of  $\text{Li}(\text{PEO})_8\text{LiBF}_4\text{-10 wt.% nanosized Al}_2\text{O}_3$  interphase resistance as a function of time at 70 °C for electrolytes containing 200 ppm and 1.5% of moisture, respectively. The influence of the moisture content on the stability of electrolytes is clearly visible. The interfacial resistance of the sample stored in the drybox, in a vacuum desiccator over dry  $\text{CaSO}_4$  (moisture content below 220 ppm) is much lower than for the sample exposed for a long time to drybox atmosphere (moisture content 1.5%). Other experiments have shown that the moisture content in the electrolytes exposed for a short time to the air can rapidly increase reaching the equilibrium value (3–8%) which depends on electrolyte composition. Thus, to allow comparison of the stability of different electrolyte versus lithium electrode the experimental methods, material characteristics and especially moisture content should be described in detail.

Layered nanocomposite polymer electrolytes have been prepared by melt intercalation of PEO into various pristine silicate hosts with different cations,  $\text{Li}^+$  montmorillonite and  $\text{Na}^+$  montmorillonite. Isomorphous substitution of silicon by aluminum in the silicate layers forms immobilized and highly delocalized negative charge balanced by the lithium or sodium cations residing in the nanosized galleries infused with PEO. Thus, this process results in the formation of an LNCPE that is a single ionic conductor.

Fig. 4 shows the X-ray diffraction (XRD) patterns of  $\text{PEO-Na}^+$  montmorillonite hybrid heated to 80 °C at various stages of heating. Before heating, the XRD patterns contain peaks characteristic of both the unintercalated layered silicate ( $d = 1.06$  nm) and crystalline

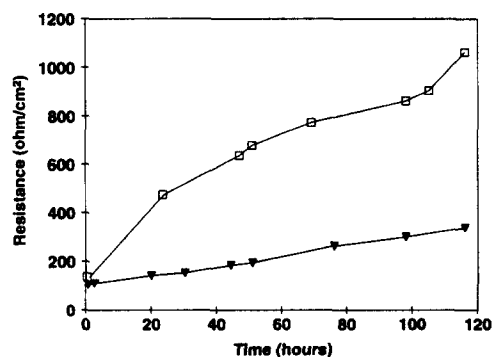


Fig. 3. Variation of interfacial resistance of  $\text{Li}/(\text{PEO})_8\text{LiBF}_4$ , 10 wt.% nanosize  $\text{Al}_2\text{O}_3/\text{Li}$  as a function of storage time for samples containing (▼) less than 200 ppm and (□) 1.5 wt.% water at 70 °C under open-circuit conditions.

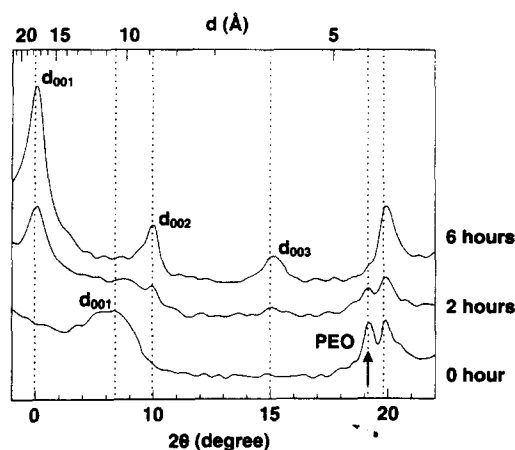


Fig. 4. X-ray diffraction patterns of PEO-Na<sup>+</sup> montmorillonite hybrid heated to 80 °C in air at various stage of heating.

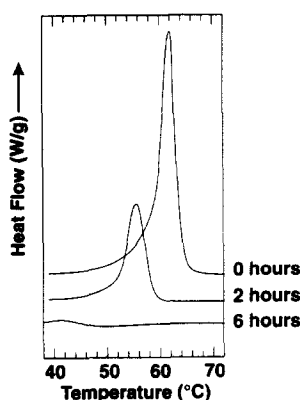


Fig. 5. Differential scanning calorimetry traces of PEO-Na<sup>+</sup> montmorillonite hybrid before and after heating to 80 °C in air. Heating rate was 20 °C/min.

PEO ( $d = 0.46$  nm). After heating to 80 °C, the intensity of the unintercalated silicate and crystalline PEO reflections is progressively reduced while a new set of peaks appear corresponding to the PEO-intercalated silicate. The primary repeat unit ( $d$ -spacing) of the resulting hybrid (1.77 nm) is identical to that obtained by intercalation from solution. The same results were obtained with the PEO-Li<sup>+</sup> montmorillonite hybrid. The magnitude of the change in  $d$ -spacing suggests that there are one or two layers of PEO intercalated between the silicate layers.

Fig. 5 shows the DSC traces of PEO-Na<sup>+</sup> montmorillonite hybrid before and after heating to 80 °C. Heating rate was 20 °C/min. The DSC data suggests that the intercalated PEO is amorphous. As the intercalation reaction progress, the area and position of the endotherm corresponding to melting of crystalline PEO is progressively reduced and subsequently vanishes for samples that only display the hybrids primary repeat unit in XRD. Over the temperature range scanned (30 to 100 °C), no new events are observed for the hybrids.

Table 2

Ionic conductivity of layered nanocomposite polymer electrolytes PEO-Li<sup>+</sup> montmorillonite vs. temperature

Temperature (°C)	30	40	60	70
Conductivity (S/cm)	$1.6 \times 10^{-6}$	$1.9 \times 10^{-6}$	$3.9 \times 10^{-6}$	$4.9 \times 10^{-6}$

Consequently, the intercalated polymer shows no melting transition as observed by DSC.

Table 2 presents the ionic conductivity values of the LNCPEs for the PEO-Li<sup>+</sup> montmorillonite hybrid containing 40 wt.% of PEO. The ionic conductivity changes only slightly (less than one order of magnitude) in the temperature range from 30 to 70 °C showing very unusual behavior in comparison with conventional polymer electrolytes reported up-to-date. These results are consistent with a completely amorphous PEO as suggested by the DSC data.

#### 4. Conclusions

Ionic conductivity as a function of particle size may suggest the importance of increased ionic mobility and ion concentration at the grain boundaries. Interfacial stability of composite polymer electrolytes depends on ceramic content and particle size. Layered nanocomposite polymer electrolytes may provide improved electrochemical performance characteristics because of the apparent synergism between the silicate host and polymer.

#### Acknowledgements

The authors express their gratitude to Allen Turner, Jeff Schaffer, Cameron Rippenhoff, Jim Malone, John Leonard and Marlene Houtz for assistance in developing new experimental techniques in preparing electrolytes and carrying out measurements; a special thanks to JoElla Pinckney for the data processing of this paper.

#### References

- [1] S. Skaarup, K. West and B. Zachau-Christiansen, *Solid State Ionics*, 28-30 (1980) 375.
- [2] M. Nookala, L.G. Scanlon, R.A. Marsh, B. Kumar and A.K. Sircar, *J. Appl. Electrochem.*, accepted for publication.
- [3] W. Wieczorek, *Mater. Sci. Eng.*, B15 (1992) 108.
- [4] F. Capuano, F. Core and B. Scrosati, *J. Electrochem. Soc.*, 138 (1991) 1918.

- [5] R. Dagani, *Chem. Eng. News*, (Nov. 23) (1992) 18.
- [6] E.P. Giannelis, *J. Met.*, (March) (1992) 28.
- [7] R.A. Vaia, H. Ishii and E.P. Giannelis, *Chem. Mater.*, 5 (1993) 1964.
- [8] Z. Florianczyk, K. Such, W. Wieczorek and M. Wasiucionek, *Polymer*, 32 (1991) 3422.
- [9] W. Gang, J. Roos, D. Brinkman, F. Capuano, F. Croce and B. Scrosati, *Solid State Ionics*, 53–56 (1992) 1102.
- [10] J.H. Strange, S.M. Rageb and R.C.T. Slade, *Philos. Mag. A*, 64 (1991) 1159.
- [11] F. Croce and B. Scrosati, *J. Power Sources*, 43/44 (1993) 9.