



# Electrochemical performance of lithium-ion polymer cell using gel polymer electrolyte based on acrylonitrile-methyl methacrylate-styrene terpolymer

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## Abstract

Gel polymer electrolyte (GPE) was prepared by encapsulating organic electrolyte solution in acrylonitrile-methyl methacrylate-styrene (AMS) terpolymer and applied as a solid electrolyte material for lithium-ion polymer battery. The composite electrodes prepared with mesocarbon microbeads and  $\text{LiNi}_{0.83}\text{Co}_{0.17}\text{O}_2$  active materials were used as anode and cathode, respectively, and cycling characteristics of these half-cells (Li/GPE/carbon and Li/GPE/ $\text{LiNi}_{0.83}\text{Co}_{0.17}\text{O}_2$ ) has been investigated using the AMS-based gel polymer electrolytes. The lithium-ion polymer battery employing a carbon anode, an AMS-based polymer electrolyte and a lithium-nickel-cobalt oxide cathode was assembled, and its charge/discharge cycling characteristics were investigated. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Acrylonitrile-methyl methacrylate-styrene; Cycling characteristics; Gel polymer electrolyte; Lithium-ion polymer battery; Lithium-nickel-cobalt oxide; Mesocarbon microbeads

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## 1. Introduction

Polymer electrolytes have received considerable attention as solid electrolyte materials in advanced applications such as rechargeable lithium batteries, because the use of polymer electrolyte makes the fabrication of highly safe batteries possible and permits the development of thin batteries with design flexibility [1–4]. Conventional poly(ethylene oxide) (PEO)-based polymer electrolytes are the most com-

monly studied, and exhibited conductivities ranging from  $10^{-8}$  to  $10^{-5}$  S/cm at room temperature, which excludes practical application at ambient temperature [5]. In order to enhance the room temperature conductivity, several classes of gel polymer electrolytes have been developed and characterized. Gel polymer electrolytes also called ‘plasticized polymer electrolytes’ are prepared by incorporating liquid electrolytes into a matrix polymer such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVdF), poly(vinyl chloride) (PVC), poly(vinyl pyrrolidone) (PVP) and poly(vinyl sulfone) (PVS) [6–9]. The ionic conductivities of these systems exceed  $10^{-4}$  S/cm at room temperature, which is necessary

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for battery applications. In our group, electrical properties of the gel polymer electrolytes (GPE) based on acrylonitrile-methyl methacrylate-styrene (AMS) terpolymer and cycling performance of Li/GPE/LiMn<sub>2</sub>O<sub>4</sub> or Li/GPE/LiNi<sub>0.5</sub>Co<sub>0.5</sub>O<sub>2</sub> cells employing AMS-based gel polymer electrolyte have been reported [10,11]. However, the growth of dendrites on lithium metal often lead to disconnection and electrical isolation of active lithium, resulting in loss of capacity and internal shorting during charge/discharge cycles. These problems are expected to be effectively alleviated by replacing lithium metal with carbon anode material. Thus, we tried to use mesocarbon microbeads (MCMB) as an active anode material in place of lithium in this work. Commercially available lithium ion batteries use lithium cobalt oxide (LiCoO<sub>2</sub>) as a cathode material. However, its cost is high due to the high price of cobalt. Other materials such as LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> can be another cathode candidates. LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> has higher capacity and lower material cost than LiCoO<sub>2</sub>. It also exhibits better thermal stability and rechargeability than LiNiO<sub>2</sub>. Among all the nickel-cobalt compounds,  $x = 0.8$  in LiNi<sub>x</sub>Co<sub>1-x</sub>O<sub>2</sub> has been reported to show the best electrochemical charge-discharge behavior [12,13]. For these reasons, LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> was selected as an active cathode material in our work.

In this study, the gel polymer electrolytes composed of AMS terpolymer, liquid electrolyte, and silica powder have been prepared. The composite electrodes based on MCMB and LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> were also prepared, and their cycling characteristics have been investigated in the AMS-based gel polymer electrolytes. With these materials, we have assembled the lithium-ion polymer cells and investigated their electrochemical performance.

## 2. Experimental

### 2.1. Preparation of polymer electrolytes

Poly(acrylonitrile-co-methyl methacrylate-co-styrene) (hereinafter abbreviated to AMS) was prepared by emulsion polymerization with a small amount of potassium persulfate as an initiator, as

previously described [10]. From the <sup>1</sup>H NMR spectroscopy, the molar composition of AN, MMA and ST was determined to be 57:27:16. Gel polymer electrolyte (GPE) was made from AMS, plasticizing electrolyte solution and silanized fumed silica. AMS was first dissolved in anhydrous tetrahydrofuran (THF). After the polymer has been completely dissolved, a predetermined amount of liquid electrolyte and silanized fumed silica (Cabot Co.) were added and the solution was further stirred. The organic liquid electrolyte used was 1 M LiClO<sub>4</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume) solution (Mitsubishi Chemical, battery grade). The resulting viscous solution was cast with a doctor blade apparatus onto a release paper, then left to evaporate the solvent slowly at room temperature. After evaporation of THF, the film was separated from a release paper. The thickness of cast film was in the range of 60–100 μm. All procedures for preparing polymer electrolytes were carried out in a dry box filled with argon gas.

### 2.2. Fabrication of lithium-ion polymer cells

The composite carbon anode was prepared by coating the slurry of MCMB, polymer electrolyte and super-P carbon on a copper foil with a doctor blade. MCMB was purchased from Osaka Gas Company, which was treated at 2800°C and coded MCMB-2528. The composite cathode contained the same polymer electrolyte and electronic conductor along with LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> (Sumitomo Chemical) active material, which was cast on aluminum foil. The thickness of composite electrodes ranged from 60 to 100 μm, and their active mass loading corresponded to capacity of about 2.0 mA/cm<sup>2</sup>. A lithium metal of 50 μm thickness supplied from Cyprus Foote Mineral Co. was used as an anode for half cell (Li/GPE/carbon, Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub>) tests. A lithium ion polymer cell of cross-sectional area 20 cm<sup>2</sup> was assembled by sandwiching the gel polymer electrolyte between composite carbon anode and composite LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cathode. The cell was then enclosed in a metallized plastic bag and vacuum sealed in order to permit testing outside of a dry box. All assemblies of the cell were carried out in a dry box filled with argon gas.

### 2.3. Electrical measurements

Polymer electrolyte film was cut into  $2 \times 2 \text{ cm}^2$  squares and sandwiched between two stainless steel (SS) electrodes. In order to measure the interfacial resistance of Li/GPE, this sample was also sandwiched between the two lithium electrodes. A.C. impedance measurement was then performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range of 0.1 Hz–1 MHz with an amplitude of 10 mV. The charge and discharge cycling tests of Li/GPE/carbon, Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> and carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cells were conducted galvanostatically using a Toyo battery test equipment (TOSCAT-3000U).

### 3. Results and discussion

The capacity to retain electrolyte solution and mechanical state of the gel polymer electrolyte was found to be dependent on the AN/MMA/ST molar composition of the AMS terpolymer, as previously reported [10]. In the AMS terpolymer, MMA unit is able to trap large amount of liquid electrolyte due to the good compatibility with plasticizing solution, while AN and ST units provide enough mechanical strength for the processing of free-standing films, thereby eliminating the need for cross-linking. To prepare the gel polymer electrolytes with higher uptake of liquid electrolyte without solvent exudation and acceptable mechanical stability, the desirable AN/MMA/ST molar composition was 57:27:16. The gel polymer electrolyte was consisted of 18 wt% AMS terpolymer, 73 wt% 1 M LiClO<sub>4</sub>-EC/DMC and 9 wt% SiO<sub>2</sub>. The fine silica powder was added in order to reinforce the physical strength of the gel polymer electrolyte films. The gel polymer electrolytes obtained were 60 to 100 μm thick films which exhibit good mechanical strength. Fig. 1 shows the Arrhenius plot of ionic conductivities for the gel polymer electrolyte. Ionic conductivity reaches the order of  $5.3 \times 10^{-4} \text{ S/cm}$  at room temperature. It is found that the ionic conductivity decreases as temperature decrease; it falls to  $5.7 \times 10^{-5} \text{ S/cm}$  at  $-20^\circ\text{C}$ . However, an abrupt decrease in ionic conductivity due to the crystallization of

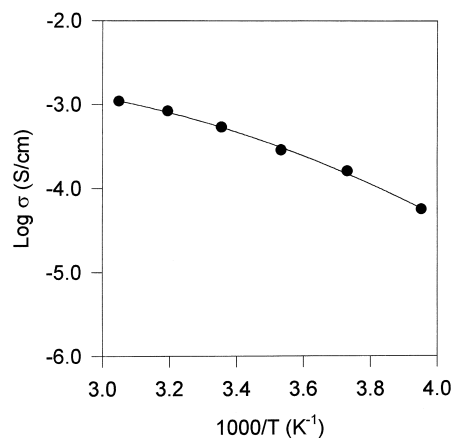


Fig. 1. Arrhenius plot of ionic conductivities for the gel polymer electrolyte containing 18 wt% AMS terpolymer, 73 wt% 1 M LiClO<sub>4</sub>-EC/DMC and 9 wt% SiO<sub>2</sub>.

plasticizing solvent was not observed. Since the MMA unit in the AMS terpolymer has a carbonyl group in the side chain, the strong specific interaction between MMA unit and aprotic solvent (EC or DMC) makes the plasticizer difficult to phase-separate from a matrix polymer. It could lead to a retardation of crystallization of aprotic solvent, which results in absence of an abrupt decrease of ionic conductivity at low temperatures. The interfacial behavior of a lithium electrode in contact with gel polymer electrolyte was examined by monitoring the impedance of a Li/GPE/Li cell at room temperature for 30 days. The impedance of the cell, measured in the frequency range of 0.1 Hz to 100 kHz, increased from 224 to 436 Ω cm<sup>2</sup> in 10 days and then showed little change in the next 20 days. This result suggests that the gel polymer electrolyte containing AMS, LiClO<sub>4</sub>-EC/DMC, SiO<sub>2</sub> has good interfacial characteristics and long term stability for lithium electrode.

To estimate the capacity and cyclability of the composite carbon anode with AMS-based gel polymer electrolyte, we fabricated the Li/GPE/carbon half cells. The open-circuit potential of the half cell was about 3.2 V. The cell was cycled between 0.01 to 1.5 V at a constant current density of 0.2 mA/cm<sup>2</sup> (C/10 rate). The charge/discharge curve of Li/GPE/carbon half cell at room temperature is shown in Fig. 2. This figure shows typical curves for lithium

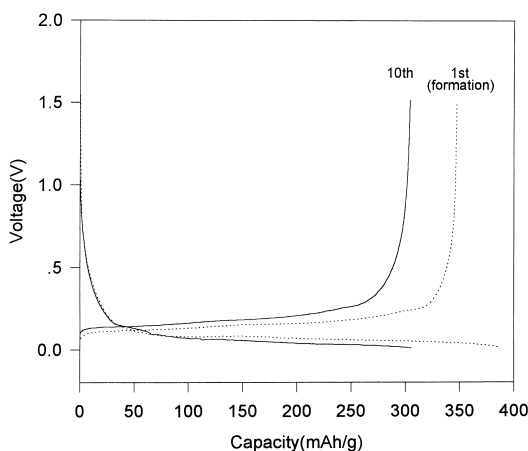


Fig. 2. Charge–discharge curves of Li/GPE/carbon half cell at a constant current density of  $0.2 \text{ mA/cm}^2$  (C/10 rate).

insertion/removal processes in graphitic carbons. The coulombic efficiency of the 1st and 10th cycles are calculated to be 89.6% and 99.6%, respectively. The large irreversible capacity observed in the first cycle is caused by the formation of passivating film on the surface of the carbon electrode due to the decomposition of electrolyte, as previously reported by other authors [14,15]. The process of carbon passivation during the initial cell cycling is referred to as the formation period. The formation of passivation layer consumes a part of the carbon capacity which corresponds to an irreversible capacity loss. This passivation film could prevent the electrolyte from further reduction by the active lithium, and thus limit the degradation of electrolytes. The Li/GPE/carbon half cell initially delivered a capacity of 347 mAh/g, and has a reversible capacity of 305 mAh/g at 10th cycle. Fig. 3 shows reversible capacities of Li/GPE/carbon half cell as a function of cycle number. It is found that the capacity after initial few cycles is constant, after which the charge–discharge cycles are nearly 100% efficient. From these results, MCMC is thought to be suitable as an anode material with the AMS-based gel polymer electrolyte for rocking-chair lithium polymer batteries. The decay in capacity observed during initial cycles is due primarily to the solid electrolyte interface layer formation on carbon electrode, as discussed earlier.

We also fabricated the Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> half cells using the same AMS-based gel polymer

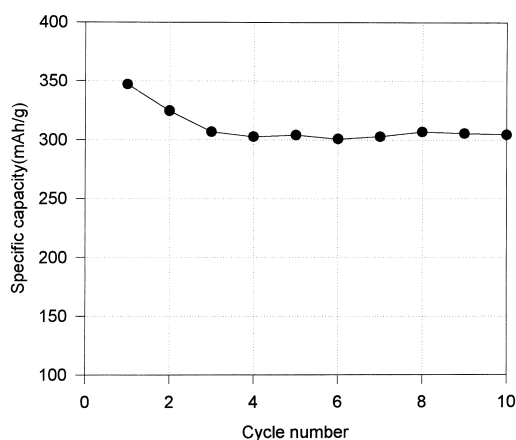


Fig. 3. Reversible capacity of Li/GPE/carbon half cell as a function of cycle number at  $0.2 \text{ mA/cm}^2$ .

electrolytes. The cell was cycled between 3.0 to 4.2 V at a constant current density of  $0.2 \text{ mA/cm}^2$  (C/10 rate). Fig. 4 shows charge–discharge curve of Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> half cell at the first and 10th cycle, respectively. This cell has a first charge capacity of 201 mAh/g followed by reversible discharge capacity of 183 mAh/g. The Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> half cell delivered a discharge capacity of 182 mAh/g, and its coulombic efficiency increased to 99.5% at the 10th cycle. An increase of coulombic efficiency is associated with an improved interfacial property during charge–discharge cycles of the cell. Fig. 5 shows the discharge capacities of

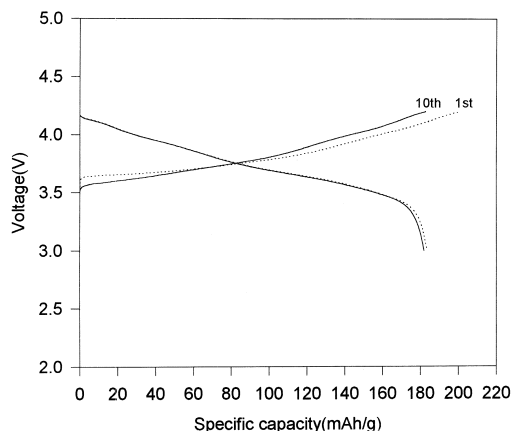


Fig. 4. Charge–discharge curves of Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> half cell at a constant current density of  $0.2 \text{ mA/cm}^2$  (C/10 rate).

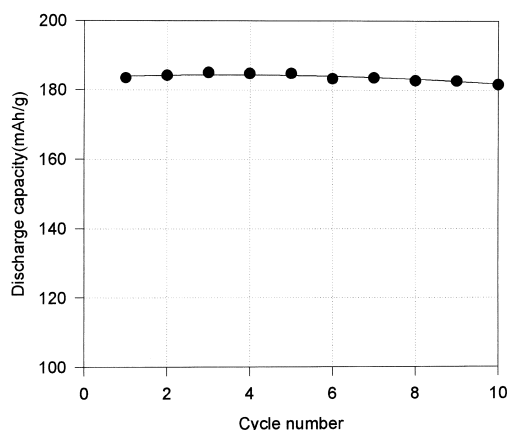


Fig. 5. Discharge capacity of Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> half cell as a function of cycle number at 0.2 mA/cm<sup>2</sup>.

the Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell as a function of cycle number. This figure shows excellent capacity retention of Li/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell. This is a convincing indication of a good interfacial contact in the composite cathode.

In order to evaluate the electrochemical performance of lithium-ion polymer cell using the AMS-based gel polymer electrolyte, we fabricated a carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell. The assembled cell was subjected to the cycle tests in the following order: preconditioning with cut-off voltages of 4.2 V for the upper limit and 2.7 V for the lower limit at C/20 rate (0.1 mA/cm<sup>2</sup>) for the first cycle, followed by two C/10 rate cycles, and subsequent C/2 rate cycles. Fig. 6 shows a preconditioning charge/discharge cycle of a carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell at C/20 rate, and subsequent two charge/discharge cycles at C/10 rate. This cell delivered a discharge capacity of 41.2 mAh (2.1 mAh/cm<sup>2</sup>) during the first preconditioning cycle. This value is equivalent to capacity of 165 mAh/g for an active LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> material in the composite cathode. The voltage drop in passing from charge to discharge was observed to be small. These results indicate that the lithium-ion polymer cell employing AMS-based gel polymer electrolyte is capable of delivering a high capacity. The cycling efficiency which the cell utilize the capacity added during charge is 80.1% at the first cycle. With further constant-current charge/discharge cycles at C/10 rate, the discharge capacity maintained a constant value, while an increase of

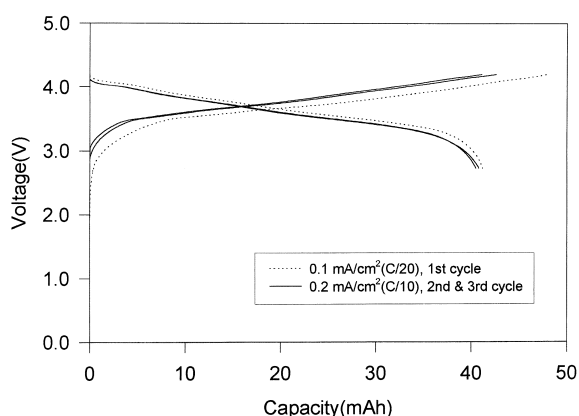


Fig. 6. Charge–discharge curves of carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell during initial three cycles at low current densities.

charging efficiency can be clearly seen in this figure. After early three cycles (one cycle at C/20 and two cycles at C/10), the cell was charged at a current density of 1.0 mA/cm<sup>2</sup> (C/2) up to a target voltage of 4.2 V. This was followed by a constant voltage charge with a decline of current until the final current was reached to 20% of charging current (i.e. 0.2 mA/cm<sup>2</sup>). And it was discharged down to a cut-off voltage of 2.7 V at the same current density. Fig. 7 shows the discharge capacities as a function of cycle number in the carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell. This cell initially delivered 38.0 mAh and the

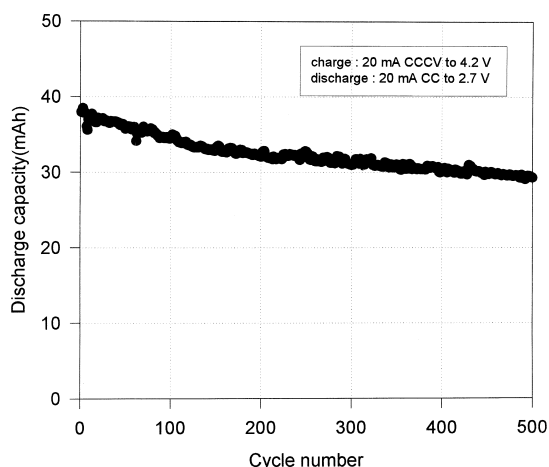


Fig. 7. Discharge capacities of carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell as a function of cycle number at 1.0 mA/cm<sup>2</sup> (0.5 C).

discharge capacity of the cell slowly decreased with cycling. Decline in the capacity is primarily due to the physical changes in the active materials and interfaces, which gradually increase cell internal resistance during the cycling. The discharge capacity was maintained to be 29.3 mAh/g at the 500th cycle, which was 77.1% of initial capacity. The charge/discharge efficiency was about 100% through cycling. This is a convincing indication of a good capacity retention of a lithium-ion polymer cell employing AMS-based gel polymer electrolyte.

We tried to obtain the rate capability of carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell. Fig. 8 represents the discharge capacities of carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell obtained at different current density from 0.2 to 4.0 mA/cm<sup>2</sup>. The cell delivered a discharge capacity of 40.9 mAh at C/10 rate. The discharge capacity was slowly decreased with current rate, which is due to the polarization. It showed an attractive capacity of 34.0 mAh at 1C rate, which was 83% of discharge capacity at C/10 rate. However discharge capacity is found to abruptly drop 21.0 mAh at 2C rate. The reduced capacity in the carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell at high rate may be mainly related to the lower diffusion rate of lithium ions in the gel polymer electrolyte as compared to that of liquid electrolyte. More efforts for improving the high-rate performance of lithium ion-polymer cell, for example, incorporation of highly conductive electrolyte into AMS terpolymer, minimi-

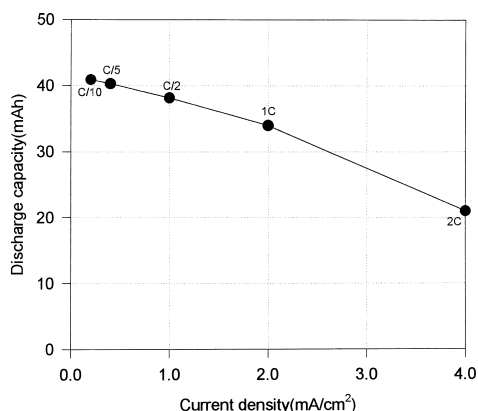


Fig. 8. Discharge capacities of carbon/GPE/LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cell as a function of current density at 25°C.

zation of GPE film thickness and preparation of composite electrodes with high surface, are in progress in our laboratory. Improvements in this area will be reported in the near future.

#### 4. Conclusions

Gel polymer electrolyte composed of AMS terpolymer, LiClO<sub>4</sub>-EC/DMC and silanized fumed silica showed high ionic conductivity and good mechanical properties to allow preparation of thin films (<100 μm). The composite electrodes prepared with MCMB and LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> showed a stable discharge capacity of 305 and 182 mAh/g in the AMS-based gel polymer, and their charge-discharge cycles after a few initial cycles were proven to be 100% efficient. Lithium-ion polymer cells consisted of MCMB anode, AMS-based gel polymer electrolyte and LiNi<sub>0.83</sub>Co<sub>0.17</sub>O<sub>2</sub> cathode showed excellent cycling characteristics. At a current density of 1.0 mA/cm<sup>2</sup> (0.5 C), the cell was shown to retain 77% of initial capacity after 500 cycles.

#### References

- [1] M.B. Armand, J.M. Chabagno, M. Duclot, in: Extended Abstract of Second International Meeting on Solid Electrolytes, St Andrews, Scotland, Sept. 1978.
- [2] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Review, Vol. vols. 1 and 2, Elsevier Applied Science, London, 1987 and 1989.
- [3] J.S. Tonge, D.F. Shriver, in: J.H. Lai (Ed.), Polymers for Electronic Applications, CRC Press, Boca Raton, FL, 1989, Chap. 5.
- [4] F.M. Gray, Polym. Electrolytes, Royal Society of Chemistry, Cambridge, 1997.
- [5] F.M. Gray, Solid Polym. Electrolytes, VCH, New York, 1991.
- [6] K.M. Abraham, M. Alamgir, J. Electrochem. Soc. 137 (1990) 1657.
- [7] K. Tsunemi, H. Ohno, E. Tsuchida, Electrochim. Acta 28 (1983) 591.
- [8] S. Passerini, J.M. Rosolen, B. Scrosati, J. Power Source 45 (1993) 333.
- [9] H.S. Choe, J. Giaccari, M. Alamgir, K.M. Abraham, Electrochim. Acta 40 (1995) 2289.
- [10] D.W. Kim, Y.K. Sun, J. Electrochem. Soc. 145 (1998) 1958.
- [11] D.W. Kim, Y.K. Sun, Solid State Ionics 111 (1998) 243.

- [12] D. Caurant, N. Baffler, B. Garcia, J.P. Pereira-Ramos, *Solid State Ionics* 91 (1996) 45.
- [13] J. Aragane, K. Matsui, H. Andoh et al., *J. Power Source* 68 (1997) 13.
- [14] R. Fong, U. von Sacken, J.R. Dahn, *J. Electrochem. Soc.* 137 (1990) 2009.
- [15] J.M. Tarascon, D. Guyomard, *J. Electrochem. Soc.* 138 (1991) 2864.