

Short communication

Nanoscale battery materials based on the self-assembly of block copolymers

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Abstract

An ionically conducting block copolymer was used as a template for the synthesis and confinement of lithium manganese oxide nanoparticles. The block copolymer functions as a polyelectrolyte and as a composite anode in a lithium battery system. Impedance spectroscopy and galvanostatic testing, X-ray diffraction and transmission electron microscopy were used to characterize the anode and polyelectrolyte. Galvanostatic testing indicates 300 or more cycles were possible without appreciable capacity fade.

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1. Introduction

Research in electronics and power supplies have progressed at a tremendous rate since the 1990s. Work in field of lithium polymer batteries has reached many milestones and performance increases [1–4]. However, reducing the cost and processability of these devices is still an area of current interest. A solid electrolyte would improve the processability of the battery and would provide the desired mechanical properties and good ionic conductivity [5,6]. Composite cathodes which incorporate low molecular weight polyelectrolyte component have been studied [10]. The low molecular weight component was shown to improve cycling performance. Block copolymers have been synthesized which function as a polyelectrolyte and a block copolymer template for metal oxide cathode materials. The block copolymer microphase separates into nanoscale, lamellar domains. The lamellar domains allow equal fractions of ionically conductive domains and domains containing cathode material. Other work using block copolymers as composite cathodes has been performed, but this work used organic cathode materials [11]. More recent work using block copolymers for templating of composite anode materials was

performed [12]. The work presented in this paper deals with cathode materials. The ease of processing at room temperature and casting durable films that comprise the electrolyte and cathode are the main focus of our experimental study.

2. Materials and experimental

2.1. Materials

All syntheses were carried out in an argon-filled MBraun LM100 glovebox or under argon atmosphere using Schlenk techniques unless otherwise noted. Tetrahydrofuran (THF), diethyl ether and pentane were distilled over sodium/benzophenone. CH₂Cl₂ was distilled over calcium hydride. All solvents used were degassed with three successive freeze-pump-thaw cycles. ¹H and ¹³C NMR spectra were recorded on a Bruker AM400 using d-THF or d-CDCl₃ solvent as noted. Ruthenium catalyst, dichloro-bis, [tricyclohexylphosphine] ruthenium benzylidene was purchased from Strem Chemicals and used as received. Triethylene glycol, allyl bromide, lithium trifluorosulfonamide and acetic acid were purchased from Aldrich. *endo*-, *exo*-5-Norbornene-2,3-dicarboxylic acid bis-trimethylsilyl ester was synthesized from published procedures [7]. 1,4,7,10-Tetraoxacyclotetradec-12-ene (TOCD) was synthesized according to work performed by Maynard and Grubbs [8].

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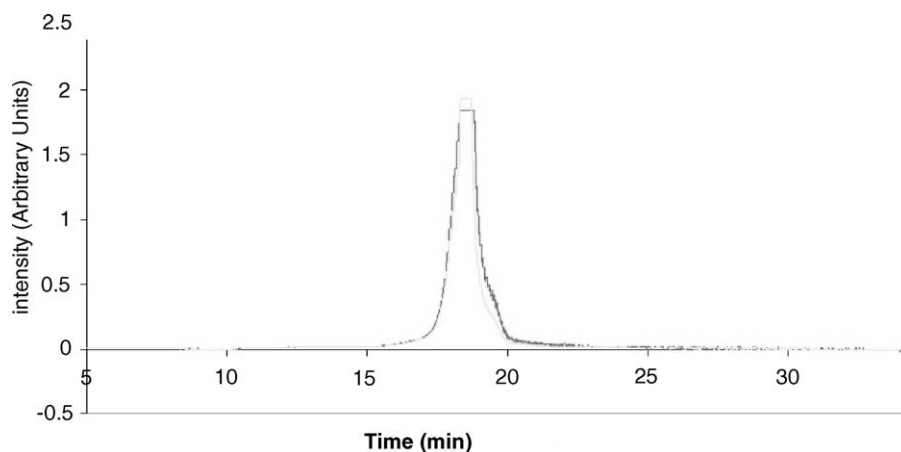


Fig. 1. GPC analysis of NORCOOH₂₀₀TOCD₂₀₀.

2.2. Experimental

The chemical shifts were referenced to internal d-THF or chloroform with tetramethylsilane. Gel permeation chromatography-light scattering (GPC-LS) was performed with a Wyatt Technology *MINI Dawn* in conjunction with a Waters 2410 refractive index detector (Fig. 1). The mobile phase was THF at a flow rate of 1.0 ml/min using two Polymer Laboratories Mixed B columns in series. The columns were calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was performed with a Dupont TA Instruments DSC 2100 with a heating rate of 10 °C/min. Impedance spectroscopy (IS) was performed in an argon-filled portable airlock of our own design. [NORCOOH]₁₅₀/[TOCD]₁₅₀ electrolyte, treated with lithium trifluorosulfonamide (LiTFSI) was placed between two stainless steel blocking electrodes using a Swagelok T cell arrangement [9]. An electrochemical cell with a lithium anode, liquid electrolyte (1 M LiTFSI in propylene carbonate:dimethyl carbonate, 1:1, Aldrich), and a composite cathode of the [NORCOOH]₁₅₀/[TOCD]₁₅₀ diblock doped with LiMn₂O₄ was prepared. An Eco-Chemie AutoLab PGSTAT 30 with a frequency response analyzer (FRA) was used for impedance spectroscopy and cyclic voltammetry. The block copolymer composites were scanned from 2.5 to 4.5 V, with a scan rate of 0.5 mV/s. An Arbin battery tester was used for galvanostatic charge and discharge studies, with voltage limits between 2.7 and 4.3 V at a constant current of 0.1 mA. X-Ray diffraction studies were done using a Bruker C-8 diffractometer with a global area detector. Transmission electron microscopy (TEM) was performed with a Hitachi 600AB microscope operating at 100 kV on microtomed sections of the block copolymer. Microtoming of the block copolymer was performed with a diamond knife using dimethyl sulfoxide (DMSO) as the collection fluid.

The polymerization of the diblock poly-[NORCOOH]₁₅₀/[TOCD]₁₅₀ was achieved with the addition of Grubbs's catalyst into a solution of *endo*-, *exo*-norbornene-2-3-trimethylsilyl carboxylic acid. Next, TOCD was added followed

by termination with ethyl vinyl ether. Precipitation into 100 ml pentane and 10 ml acetic acid gives the diblock.

3. Results and discussion

GPC analysis of the prepared diblock was performed using THF as the mobile phase. The molecular weight was 123 000 and the polydispersity was 1.7. The templating of cathode materials using block copolymers is documented in Fig. 2. This TEM clearly shows the lamellar structure of the block copolymer. Darker areas contain metal oxide

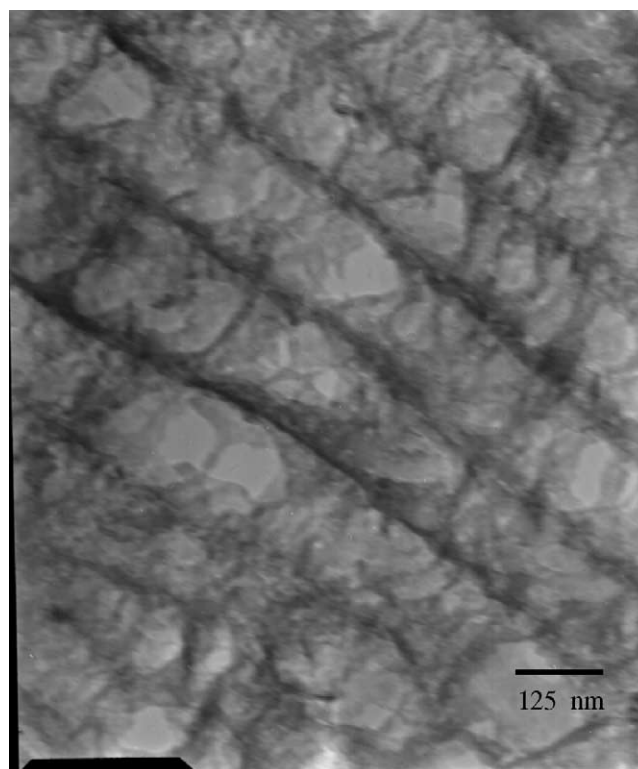


Fig. 2. TEM of LiMn₂O₄ doped copolymer nanocomposite.

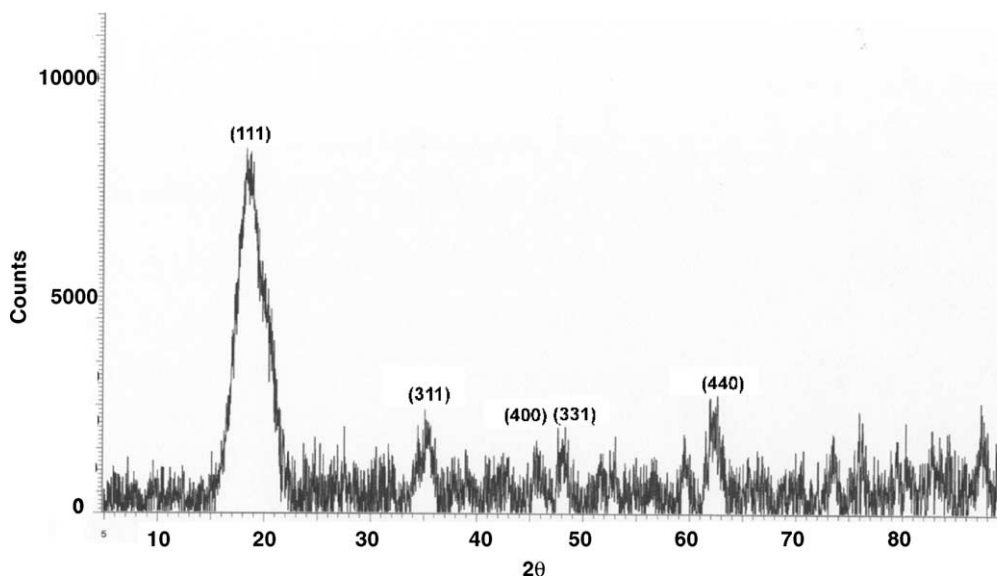


Fig. 3. X-ray diffraction of LiMn_2O_4 doped copolymer nanocomposite.

and are confined within the regions of the more polar norbornene carboxylic acid domains. The lamellae of the metal doped block copolymer are uniformly spaced with the larger areas containing the TOCD domains. The microtomed sections were seen swelling during the collection of the grids in DMSO. The swelling is caused by the TOCD regions dissolving slightly and this swelling led to a larger size structure than is predicted by the copolymer block lengths.

The room temperature, wet chemical technique for metal loading of the block copolymers involves ionically conductive domains interspersed throughout the cathode without blending or other post processing. Simple oxidation with

water washes allows the formation of LiMn_2O_4 clusters. The $[\text{NORCOOH}]_{150}/[\text{TOCD}]_{150}$ polymer was dissolved in THF solution containing Li and Mn acetate salts. The cast film was washed with water and oven-dried at 50°C to remove water, resulting in a dark brown polymer composite. X-ray diffraction of the polymer nanocomposite indicates the formation of LiMn_2O_4 , as seen in Fig. 3. The major peaks have been identified and match literature values. This synthesis was conducted at room temperature.

Testing of the diblock copolymer as a polyelectrolyte was performed with impedance spectroscopy. Lithium trifluor-sulfonamide (LiTFSI), was used as the lithium salt. The room temperature ionic conductivity of the diblock copolymer was found to be $2.22 \times 10^{-6} \text{ S/cm}$. Temperature-dependent ionic conductivity is presented in Fig. 4. This range of ionic conductivity values near 10^{-5} is perceived to be the limit for use in battery applications [13]. Higher temperature ionic conductivity measurement indicates roughly linear behavior with increasing temperature. The high temperature (60°C) ionic conductivity value is $1.05 \times 10^{-4} \text{ S/cm}$. This represents useful ionic conductivities within the operating range of high

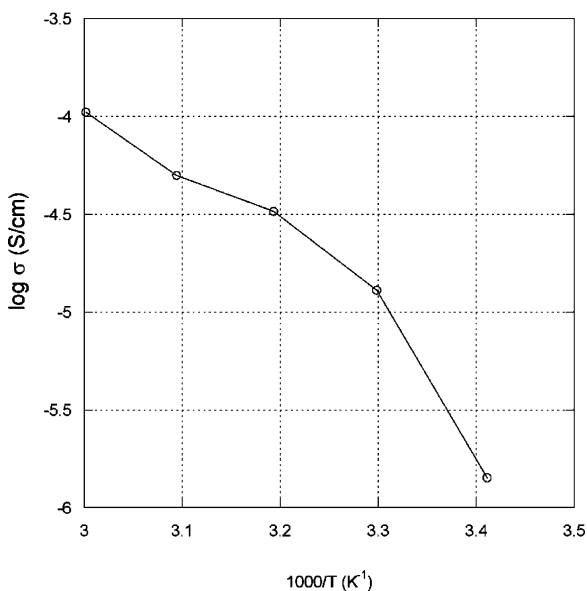


Fig. 4. Impedance spectra of (NORCOOH/TOCD) diblock with LiClO_4 .

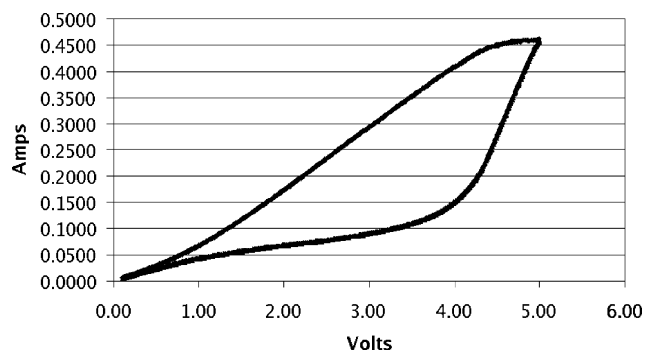


Fig. 5. Cyclic voltammetry of LiMn_2O_4 composite cathode.

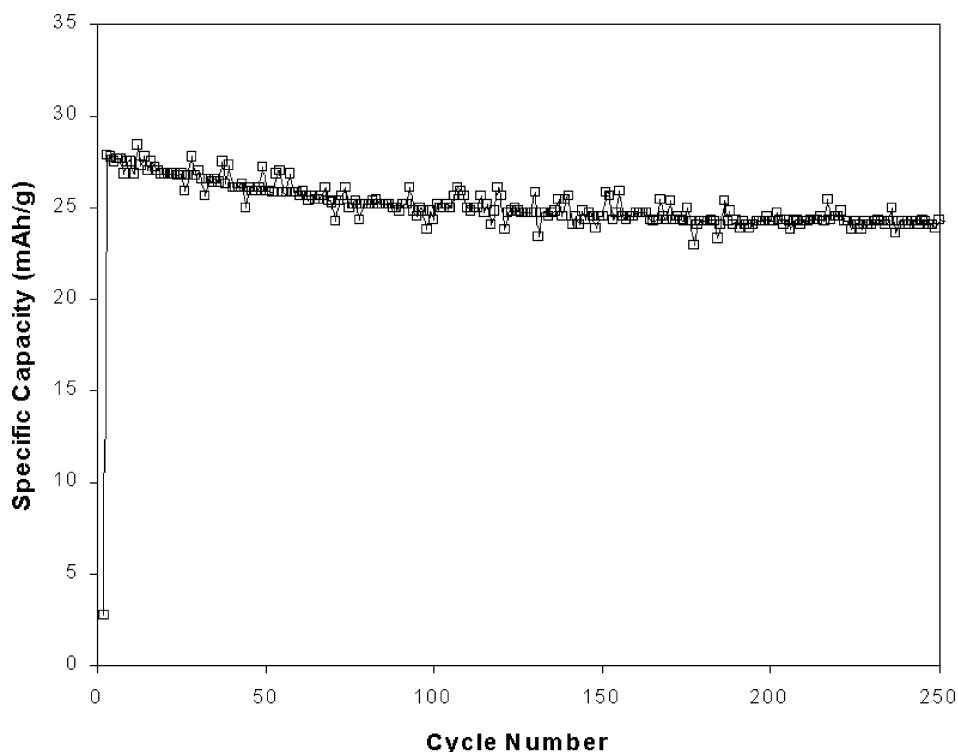


Fig. 6. Galvanostatic testing of lithium battery based LiMn_2O_4 composite cathode.

temperature batteries. Structurally similar diblock polymers self-doped with lithium [13] have ionic conductivity values of comparable magnitude. Good polyelectrolytes generally have a high chain flexibility, with low crystallinity to allow for Li ion migration. The nature of the polymer chain flexibility allows for passage of ions along the polymer. In addition, our diblock copolymer has unsaturated carbon bonds in its backbone, thereby avoiding crystallization, which is observed in saturated backbone PEO-salt complexes. Crystallinity causes decreasing chain flexibility, lowering the ion mobility.

Electrochemical testing results of a Li cell indicate a voltage plateau at 4.0 V. Fig. 5 shows the plateau at approximately 4.0 V. The as-assembled voltage was 3.9 V, closely matching the CV. A second plateau occurs at approximately 2.5 V, which matches the lower limit for recharge voltage of many lithium battery systems. Galvanostatic testing of the battery shows cyclability for up to 300 cycles, with minimal capacity fade. Over 90% of the initial capacity is retained and Fig. 6 indicates the capacity had reached a stable value.

4. Conclusion

Diblock copolymer nanocomposites were synthesized as both composite cathodes and as a block copolymer electrolyte. The phase separation of the metal oxide domains allows an ionically conducting domains to be adjacent to

cathode containing domains. The measured ionic conductivity is suitable for battery applications, however, further studies to improve ionic conductivity are underway. Initial battery cycling tests show cycling capability up to 300 cycles. Ninety percent of capacity is still retained after 300 cycles. These results show the block copolymer has potential as lithium battery materials in both electrolyte and cathode areas.

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