

Composite doped emeraldine–polyethylene oxide-bonded lithium-ion nano-tin anodes with electronic–ionic mixed conduction

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Abstract

Mixed-conducting lithium-ion doped emeraldine polyaniline (PAni)–polyethylene oxide (PEO) blends have been developed to achieve an optimal electronic–ionic conductivity balance in nano-tin composite anodes. Electrochemical evaluation was performed on the anodes with differing electrode preparation procedures, doping methods and PEO contents. Results indicate that both good electronic and ionic conductivity in the binder are required for rapid lithium insertion/extraction and low polarization. This doped PAni–PEO polymer blend is an attractive binder for high capacity composite anodes with low polarization.

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1. Introduction

Lithium-alloy anodes for secondary Li-ion batteries have much higher packing densities and capacities than those of carbon-based anodes [1,2]. They have been extensively studied since the feasibility of electrochemical insertion of Li from liquid organic electrolytes was demonstrated in the early 1970s [3].

Lithium-alloy anodes are generally fabricated by binding the active storage materials with flexible polymer composites such as polyvinylidene fluoride

(PVDF), filled with electronically conducting additives, e.g., carbon black or nickel powder [4–7]. An ideal conductive binder should have a high mechanical strength to accommodate the volume change in the active material during Li insertion/extraction, which often causes anode cracking or pulverization [8]. It should also be an electronic conductor to offer conductive pathways bridging active particle-to-particle and particle-to-current collector contact, and at the same time be a Li-ion conductor to provide a high contact area between active particles and the electrolyte, allowing rapid Li insertion/extraction kinetics and low polarization during cycling. In the conventional multi-porosity anodes described above, the flexible polymer and conductive additive, respectively, offer mechanical strength and electronically

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conductive pathways. In addition, liquid electrolyte may penetrate into composite polymer binder microporosity, giving the ionically conducting pathway required for rapid Li insertion/extraction transfer.

However, the volume of electronically conducting additives limits the polymer binder volume fraction present, hence reduces the ability of the binder to handle active material volume changes. In addition, micropores serving as ionically conducting pathways are not effective when solid electrolytes are used, which restricts anode charge rate under such circumstances. It is also difficult to achieve a correct match between electronic and ionic conductivity because both the local microporosity and local ratio of conductive additives to micropores are uncontrollable. Thus, the real properties of polymer binders limit the performance of lithium-in-metal storage anodes.

The polyaniline (PAni)–polyethylene oxide (PEO) polymer blend meets the requirements for an effective anode binder. Incorporation of ionically conducting Li⁺-doped PEO into electronically conducting Li⁺-doped (sometimes incorrectly called pseudoprotonated) emeraldine PAni results in unique conductive structures exhibiting enhanced mechanical properties and improved charge transfer rates compared with those for pure electronically conducting polymers or polymer composites [9,10]. In this paper, PAni is used to designate the lithium emeraldine salt. Nano-tin–PAni–PEO composite anodes containing nano-size tin active material with different PEO mass fractions, different electrode preparation procedures, and different doping methods were prepared and their electrochemical performance was investigated.

2. Experimental

2.1. Electrode preparation

Nano-Sn powder (Argonide, Sanford, FL) of 98 nm mean particle diameter was used as the active material. Emeraldine base PAni (EB, Aldrich Chemical, Milwaukee, WI) with molecular weight of 20,000 Da was doped (see below) with lithium hexafluorophosphate (LiPF₆, Aldrich Chemical) to give the corresponding emeraldine salt (ES), an excellent electronic conductor. The doping mechanism of emeraldine base PAni has been published [11–16]. The

recent paper of Shimano and MacDiarmid [17] is particularly instructive.

The 1-methyl 2-pyrrolidone (NMP) solutions of PAni and PEO containing 0, 10, 15, 25, 35, 50, 65, 75, 85 and 100 wt.% of PAni in the total polymer mass were prepared at room temperature. The nano-Sn powder was added, and the suspension was stirred for 30 min. LiPF₆ was added to the mixture to add positive charges to the PAni, changing it from insulating EB to electronically conducting ES, at the same time providing ionic conductivity to the PEO. The weight ratio of LiPF₆ to the total PAni + PEO mass was 1:1.2, and the nano-Sn content was fixed at 80 wt.%. The mixtures were again stirred, then cast directly onto the copper gauze to form the anodes, which were slowly dried at room temperature overnight, followed by drying in vacuo at 75 °C for 24 h. The area of the electrodes and thickness as prepared were 1 cm² and 200–250 μm, respectively. To investigate the influence of the method of doping on electrochemical performance, doping after anode preparation (without pre-doping as above) was also conducted. In this procedure, undoped as-prepared nano-Sn–PAni–PEO anodes were immersed in the 4:1:3:2 by volume ethylene carbonate (EC)–propylene carbonate (PC)–dimethylcarbonate (DMC)–ethyl methyl carbonate (EMC) solvent containing 1.0 M LiPF₆ (EM Industries, Hawthorne, NY) for 72 h for doping.

As an alternative to casting, hot-pressing was also used for anode preparation. Nano-Sn, PAni, PEO and LiPF₆ were added to NMP, which was stirred for 30 min. Films containing nano-Sn, PAni, PEO and LiPF₆ were obtained by drying the mixtures at 75 °C for 24 h. They were finely ground, and pressed at 100 MPa onto copper gauzes at 210 °C.

2.2. Electrochemical measurement

Charge–discharge behavior was examined in a three-electrode PTFE cell containing excess electrolyte solution described above. Two lithium foils were used as counter and reference electrodes. All potentials given are vs. Li/Li⁺ in this electrolyte. Cells were assembled in an argon-filled glove box. Charge (lithium insertion) and discharge (lithium extraction) were conducted on an Arbin (College Station, TX) automatic battery cycler at current densities of 5.0 mA g⁻¹ with cut-off potentials of 0.05 and 1.5 V.

Electrochemical impedance spectroscopy (EIS) was performed using a Solartron FRA 1250 frequency response analyzer and a Solartron model 1286 electrochemical interface. Before each measurement, the electrodes were first charged galvanostatically at 5 mA g^{-1} to 0.05 V , then left on open-circuit for 5.0 h to allow their potential to stabilize. EIS measurements were then carried out using a 5.0-mV AC voltage signal in the 65 kHz – 10 mHz frequency range in automatic sweep mode from high to low frequency.

3. Results and discussion

3.1. Influence of ionic conductivity on electrochemical performance of composite anodes

In multi-porosity electrodes, liquid electrolyte often penetrates the electrode interior and acts as the ionic conductor to promote interfacial mass transport and hence anode capacity. Fig. 1a shows the potential profiles of the first Li insertion/extraction cycle for nano-Sn–PAni (8:2 by weight) composite anodes with differing preparation procedures. For cast anodes, a homogeneous and compact structure on the micrometer scale is obtained when the electrodes are slowly dried [16], so the liquid electrolyte cannot penetrate the anode interior, and slow interfacial mass transport through the binder hinders Li insertion/extraction to or from the active materials, resulting in low charge and discharge capacities. However, pressed anodes have a multi-porosity microstructure [16], and electrolyte is able to penetrate micropores, so capacities are much larger (Fig. 1a). The EIS data in Fig. 1b show the importance of the electrode–electrolyte interfacial process in determining Li insertion/extraction kinetics. Typical impedance spectra all show one depressed semicircle for the interfacial impedance, which is usually taken to be for interfacial Li charge transfer associated with the formation of the passive surface electrode interface (SEI) film [18–22]. Fig. 1b shows that the interfacial impedance of pressed composite anodes is much lower than that of cast anode, which agrees with the results of charge–discharge testing (Fig. 1a).

Although a multi-porosity structure can accelerate Li insertion/extraction and hence increase capacity, the existence of micropores decreases the total

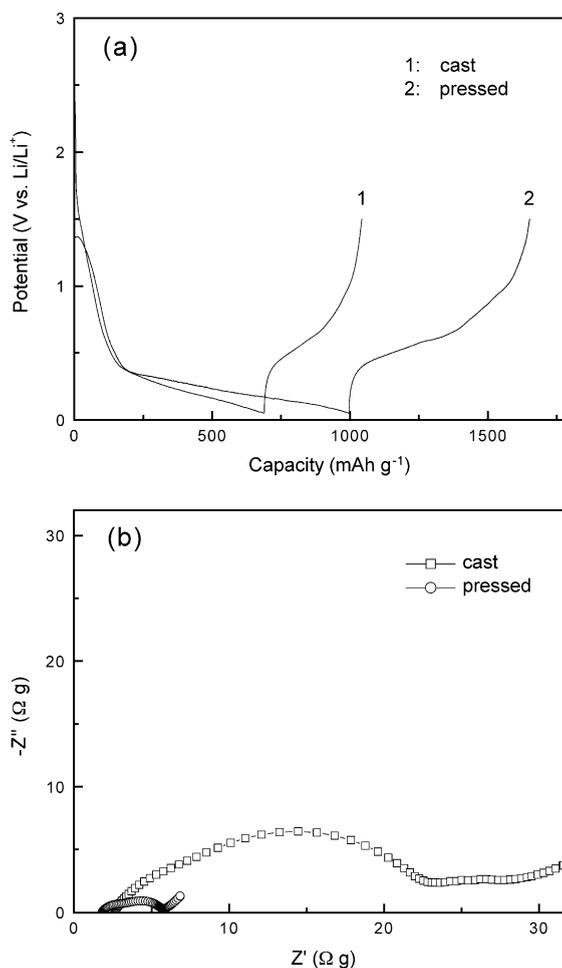


Fig. 1. Charge–discharge curves (a) and electrochemical impedance spectra (b) for nano-Sn–PAni (8:2) composite anodes with differing preparation procedures. Capacities are given with respect to the mass of anode active material.

mechanical strength of anode binders, resulting in poor cycling properties. Furthermore, if immobile solid electrolytes are used, they cannot make use of the multi-porosity structure. Hence, the use of ionically conducting doped PEO enables fast Li insertion/extraction kinetics. Fig. 2a shows the potential profiles and Fig. 2b electrochemical impedance spectra for nano-Sn–PAni–PEO (8:1:1) composite anodes with differing preparation procedures. The capacities for cast and pressed anodes are similar (Fig. 2a), as are their interfacial impedances (Fig. 2b). Therefore, the PEO phase in the blended polymer system operates as

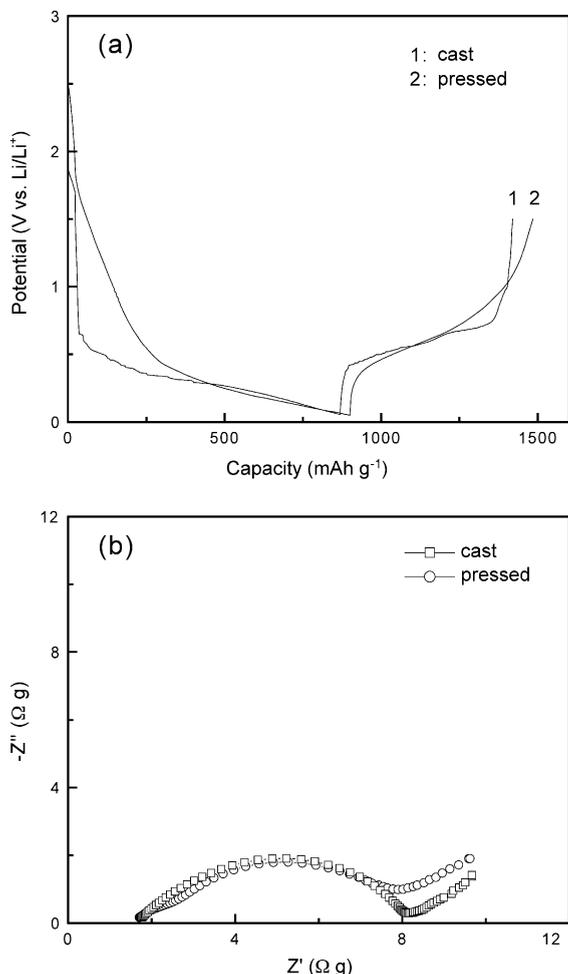


Fig. 2. Charge–discharge curves (a) and electrochemical impedance spectra (b) for nano-Sn–PANI–PEO (8:1:1) composite anodes with differing preparation procedures. Capacities as in Fig. 1.

a liquid electrolyte absorbed in the micropores of a multi-porosity anode. Introduction of the ionically conducting PEO phase overcomes the major defects of the conventional multi-porosity anode, i.e., its deterioration in mechanical strength and the fact that the solid electrolyte cannot use its porosity. To avoid the influence of micropores on performance, the anodes investigated below were fabricated by casting.

3.2. Influence of PEO content

The electrochemical performance of nano-Sn–PANI–PEO composite anodes is greatly influenced by

the electronic–ionic conducting properties of PANi–PEO blends, which are mainly determined by the PANi–PEO ratio. Eleven nano-Sn–PANI–PEO composite anodes with various PEO contents were fabricated. Their potential profiles for the first Li insertion/extraction cycle are shown in Fig. 3. It can be seen that the charge–discharge characteristics of these anodes varies greatly with the variation of electronic–ionic conductivity ratio in the polymer blend binders, which determines the electrode–electrolyte interfacial process. To investigate the influence of the electronic–ionic conductivity ratio of the polymer blend on the capacity of each composite anode, both charge and discharge capacities are shown in Fig. 4 as a function of PEO content. It was found that both the charge and discharge capacities increase with an increase in PEO content up to a maximum value, and then decrease.

The typical impedance spectra in Fig. 5 show that, except for 100% PEO, the interfacial impedance of nano-Sn–PANI–PEO composite anodes increases with a decrease in PEO content, indicating a slower Li insertion/extraction process at low PEO ratios. At low ratios, slow Li insertion/extraction is the rate-controlling step of the charge–discharge process of composite anodes due to their low ionic conductivity. Hence, both charge and discharge capacities first increase with the increase of PEO content. However, the situation in the high PEO ratio region is very

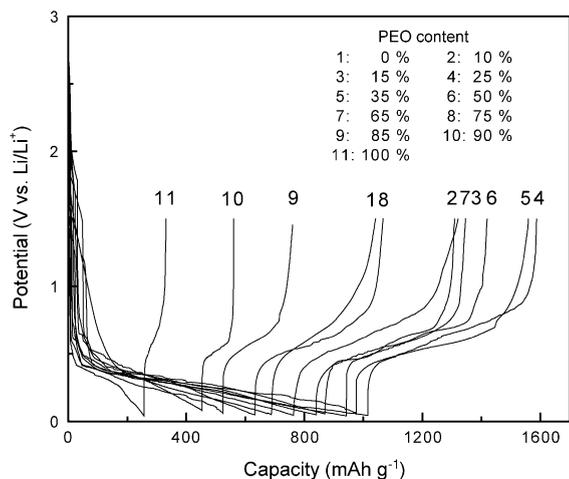


Fig. 3. Charge–discharge curves for nano-Sn–PANI–PEO composite anodes with differing PEO contents. Capacities as in Fig. 1. The PEO wt.% is with respect to the combined masses of PANi and PEO.

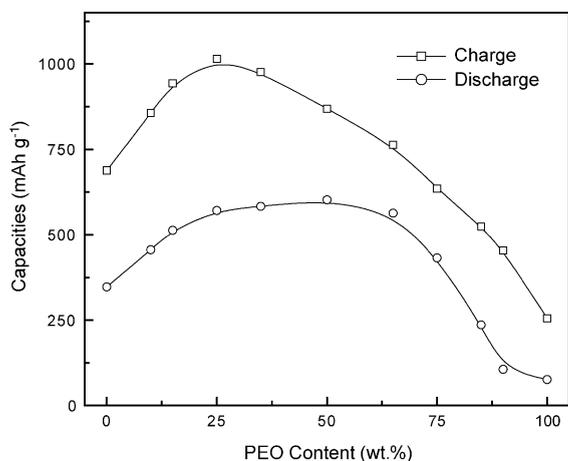


Fig. 4. Charge and discharge capacities for nano-Sn-PANI-PEO composite anodes as a function of PEO content. Capacities as in Fig. 1.

different. The region for high effective electronic conductivity for PANI-PEO blends has been shown to be from 10 to 40 wt.% of PANI content [23], so electronic conductivity is low in the high PEO content region. Thus, the lack of conductive pathways between the active materials and the current collectors make the electrochemical processes slow, giving low capacities. As a result, a balance between the electronic and ionic conductivities is a key issue for PANI-PEO blends.

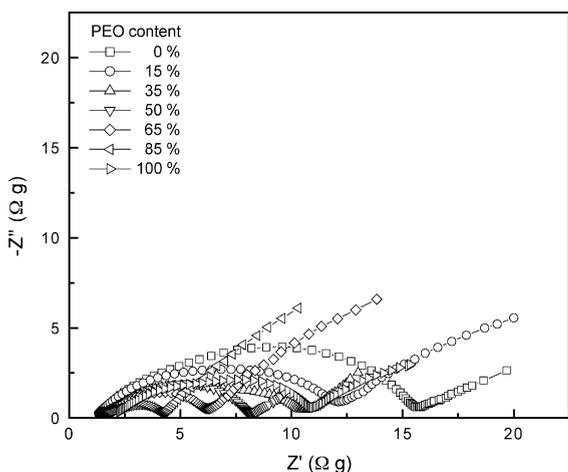


Fig. 5. Electrochemical impedance spectra of nano-Sn-PANI-PEO anodes with differing PEO contents. Before measurements, anodes were first charged at 5 mA g^{-1} to 0.05 V, and then allowed to relax at open-circuit for 5.0 h.

However, the optimized PEO contents for the charge and discharge processes are different (25 and 50 wt.%, respectively). This difference is associated with the different kinetics of Li insertion/extraction into or from the active materials. The Li insertion process leads to their expansion, and is much slower than Li extraction from the kinetic viewpoint. During Li insertion, the rate-controlling step is to overcome the outside obstruction resulting the volume expansion of active material. During discharge, fast Li extraction from the active material requires high ionic conductivity of the blended binder; therefore, the optimized PEO content for discharge is larger than that for charge.

Fig. 6 shows the charge-discharge efficiency of nano-Sn-PANI-PEO anodes as a function of PEO content. It can be seen that the efficiency also increases to a maximum value with the increase of PEO content, and then decreases. The optimized PEO content for anode charge-discharge efficiency is higher than that for discharge capacity at 65%.

3.3. Influence of method of doping

In addition to the PEO content, the method of doping used for the PANI-PEO blend has a major effect on the electrochemical performance of the composite anode. Fig. 7 shows potential profiles of the first insertion/extraction cycle for nano-Sn-PANI-PEO (8:1:1 by weight) anodes with differing methods of doping. The morphologies of PANI-PEO blends have

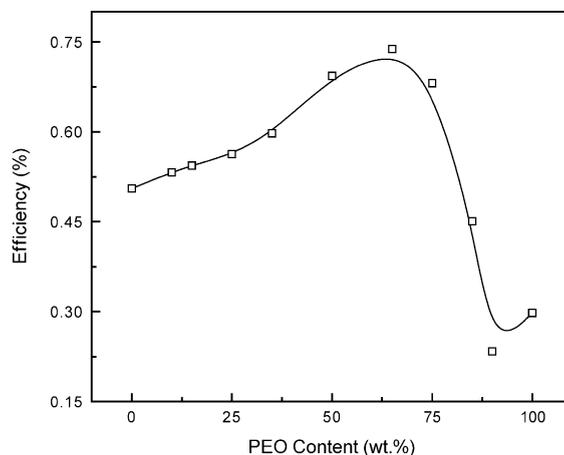


Fig. 6. Charge-discharge efficiencies for nano-Sn-PANI-PEO composite anodes as a function of PEO content.

been studied, and it is found that they contain the PEO phase in the form of spheres dispersed in the polymer blend matrix [23,24]. In consequence, no further comments on their morphology are given here. It suffices to say that sufficient adsorption of lithium salt from the doped PEO and experimental liquid electrolytes to give high ionic conductivity in the blended phase does not occur. As a result, the Li insertion/extraction into or from the host material is very slow and occurs with high polarization, giving small charge and discharge capacities. Lithium insertion in fact starts at 0.30 V, below the equilibrium plateau potential (0.38 V) for $\text{Li}_{4.4}\text{Sn}$ formation [25,26].

Anodes doped as part of preparation by adding LiPF_6 to NMP solution of PANi and PEO allows rapid and complete absorption of salt during preparation, giving a high ionic conductivity PEO phase which allows rapid Li insertion/extraction with low polarization (Fig. 7). For these anodes, Li insertion starts at 0.45 V.

3.4. Onset potential

The onset potential may be defined as the potential where an inflection is observed in the charge–discharge curve, i.e., where significant Li insertion or extraction begins (Fig. 8). It is a function of the polarization of the composite anode, which

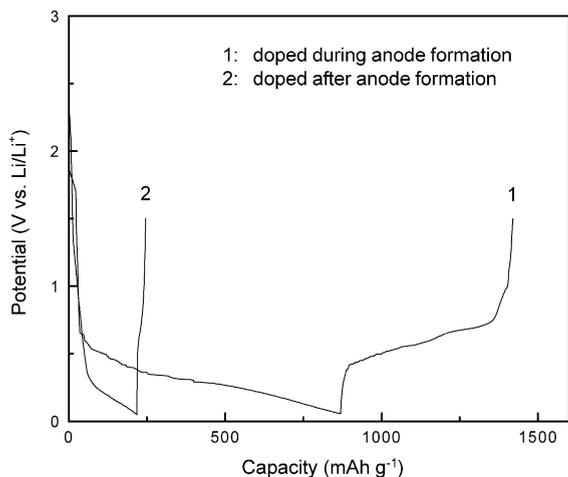


Fig. 7. Charge–discharge curves for nano-Sn–PANi–PEO (8:1:1) composite anodes with differing methods of doping. Capacities as in Fig. 1.

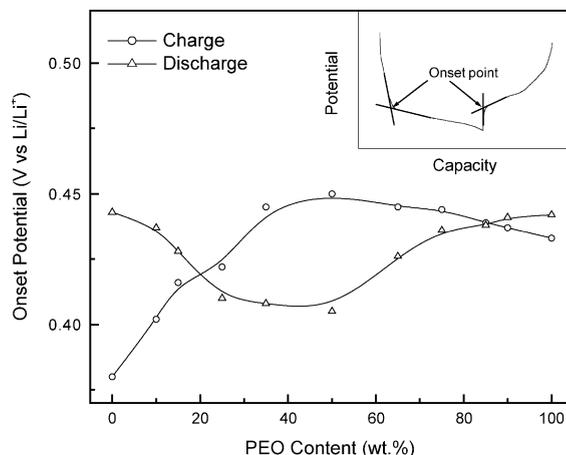


Fig. 8. Onset potentials for nano-Sn–PANi–PEO composite anodes as a function of PEO content.

should always be minimized during charge–discharge cycling. A low onset potential during discharge indicates low polarization, i.e., optimized anodes, while the reverse is true on charge. The onset potentials for nano-Sn–PANi–PEO composite anodes as a function of PEO content are shown in Fig. 8. Increasing PEO content first increases the onset potential on charge to a maximum value, which is followed by a decrease. Similarly, during discharge it first decreases then increases. The highest and lowest onset potentials on charge and discharge are observed at 50 wt.% PEO. As for the charge–discharge capacities, insufficient electronic or ionic conductivity in the polymer binder both result in severe polarization. The lowest polarization for the nano-Sn–PANi–PEO composite anodes is only observed when an optimum balance between electronic and ionic conductivity is obtained in the PANi–PEO polymer blend.

4. Conclusions

An electronic–ionic conductivity balance for the polymer binder in composite anodes must be obtained to give fast interfacial Li insertion/extraction and low polarization.

Doped PANi provides high electronic conductivity and requires no conductive additives, whereas doped PEO gives high ionic conductivity allowing fast Li insertion/extraction and low polarization. Use of the

polymer blend as a binder can also give high-strength composite anodes, which can accommodate the volume changes in the active insertion material. Finally, the use of active materials of small particle size may minimize any large absolute volume changes.

This work shows the electronic–ionic conductivity ratio can be controlled to permit rapid Li insertion/extraction at low polarization. Doped nano-Sn–PANI–PEO composite anodes with differing PEO contents, preparation procedures and doping methods were prepared to examine the influence of electronic–ionic conductivity ratio on electrochemical performances.

The ionically conducting PEO phase performs the same function as that of liquid electrolyte absorbed in a multi-porosity anode, but it confers mechanical strength to the anode and may be used with solid electrolytes. Because of the complex two-phase structure for the PANI–PEO blend, anodes doped during preparation have more rapid interfacial Li insertion/extraction kinetics and lower polarization than those doped after the electrode formation.

The electronic–ionic conductivity ratio of the blended polymer binder can be readily controlled by selectively adjusting the PEO content. A lack of sufficient electronic conductivity results in a loss of conductive pathways between the active materials and current collector, giving poor electrochemical performance. Similarly, a lack of sufficient ionic conductivity results in slow Li insertion/extraction kinetics and high polarization. The most satisfactory PEO content range is from 25 to 65 wt.% of total polymer for the system studied. PANI polymer blends with PEO and related solid polymer electrolytes are therefore attractive candidates for composite Li-ion secondary anodes with high capacity, low polarization and long cycle lifetimes.

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