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Electron/Ion Transport Enhancer in High Capacity Li-Ion Battery Anodes

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ABSTRACT: Magnetite (Fe₃O₄) was used as a model high capacity metal oxide active material to demonstrate advantages derived from consideration of both electron and ion transport in the design of composite battery electrodes. The conjugated polymer, poly[3-(potassium-4-butoanoate) thiophene] (PPBT), was introduced as a binder component, while polyethylene glycol (PEG) was coated onto the surface of Fe₃O₄ nanoparticles. The introduction of PEG reduced aggregate size, enabled effective dispersion of the active materials and facilitated ionic conduction. As a binder for the composite electrode, PPBT underwent electrochemical doping which enabled the formation of effective electrical bridges between the carbon and Fe₃O₄ components, allowing for more efficient electron transport. Additionally, the PPBT carboxylic moieties effect a porous structure, and stable electrode performance. The methodical consideration of both enhanced electron and ion transport by introducing a carboxylated PPBT binder and PEG surface treatment leads to effectively reduced electrode resistance, which improved cycle life performance and rate capabilities.

INTRODUCTION

The high energy/power density associated with Li-ion batteries serves as a driving force for intensive research related to high capacity anode materials. The main obstacles which retard the practical implementation of high-capacity electrochemically active particles including metal oxides, Si, Sn and their derivatives (Table 1), stem from large volume changes associated with Li insertion/extraction and the resultant electrical contact loss, thereby leading to poor cycling performance.^{1–6} Efforts have been made to circumvent the breakdown of electronic pathways through the introduction of electrically conducting functionalities such as carbon coatings^{3–9} and conductive polymeric binders onto the surface of the active materials;^{2,10,11} or the fabrication of stable battery anodes using an electrically inactive polymeric binder that facilitates retention of electrode integrity.^{12–15} While these approaches are quite effective, consideration should also be given to ion transport. In that regard, a composite electrode designed with porous ion transport channels in addition to electron transport pathways should afford improved performance.

Table 1. Comparison of electroactive anode materials for Li-ion batteries

Material	Theoretical capacity ¹⁶ (mAh g ⁻¹)	Reaction Potential ^a (V vs. Li/Li ⁺)	Volume change ^b (%)
Graphite	372	0.05 ± 0.2	10 ¹⁸
Si	4200	0.05 ± 0.5	420 ¹⁸
Sn	994	0.4 ± 0.8	260 ¹⁸
Metal oxides (Fe ₃ O ₄)	500 – 1 (926)	- (0.5 – 0.8) (200 ^{19,20,21})	- (200 ^{19,20,21})

^a Based on lithiation/delithiation peaks in the cyclic voltammetry.

^b Volume change during lithiation/delithiation processes.

In principle, the electrochemical reactions that occur in an electrode when a Li ion encounters an electron within an active site determine the electrode's intrinsic energy capacity.²² Both electron and ion transport are critical factors that determine the internal resistance of electrodes, which is the primary influence on electrochemical performance. Despite their importance, research that considers both factors is rarely reported.

Here, we report a facile strategy to enhance both electron and ion transport within high capacity anode systems. Magnetite (Fe₃O₄) was used as the electroactive component because it is readily available and has a high theoretical capacity (~926 mAh g⁻¹), which derives from the possibility to induce the transfer of multiple electrons from the lithiation and conversion processes.²³ Fe₃O₄ also exhibits low conductivity that induces poor cycling.⁹ Further, studies pertaining to the use of the semiconducting polymer, poly(3-hexylthiophene) (P3HT), in conjunction with Fe₃O₄-based electrodes to enhance electrode electrical performance, demonstrated that in addition to electron transfer, consideration of ion transport in the design of a composite electrode was essential.²⁴

The approach presented here introduces poly[3-(potassium-4-butoanoate) thiophene] (PPBT) — a water-soluble, carboxylate substituted polythiophene — as a binder component and a polyethylene glycol (PEG) surface coating for the active material. Conjugated polythiophenes have relatively high electronic conductivity (10⁻² – 10⁻⁴ S cm⁻¹; i.e. P3HT)²⁴ and undergo electrochemical doping — provided that the applied potential drives the reduction of the conjugated polymers within the operating voltage of anode applications^{25–27} — enabling more rapid

electron transport and developing electrical bridges between the active materials and carbon additives. Additionally, the side chain carboxylic moieties present in PPBT could facilitate the formation of porous, stable electrodes. PPBT is soluble in water, which has high surface tension and thus may be expected to inhibit perfect coverage of the material surface.²⁸ In turn, this may support pore formation during the evaporation process. Chemical interactions between the PPBT COO⁻ moieties and metal oxide surface (–OH) are expected to favorably impact electrode stability.^{12–15,29} The PEG coating on the Fe₃O₄ surface is likely to reduce the size of aggregates, improve their dispersion,³⁰ and thereby shorten the Li ion diffusion path and enable homogeneous current distribution over the electrode.³¹ In addition, PEG is expected to facilitate Li ion conduction to the active sites from the surrounding electrolyte.³²

The introduction of PPBT as a binder and PEG as a coating on the Fe₃O₄ active particle surface demonstrates the opportunities afforded by consideration of both electron and ion transport processes in the design of high performance composite electrode materials. Synergetic effects derived from using a conjugated polymer for enhanced electron transport with the PEG surface coating that supports ion transport lead to reduced electrode resistance, stable cycling performance and improved rate capabilities.

EXPERIMENTAL SECTION

Materials. Fe₃O₄ nanoparticles (~10 nm) were synthesized by a previously reported co-precipitation process, using aqueous solution of iron(III) chloride hexahydrate, iron(II) chloride hexahydrate, and triethylamine.^{33,34} For preparation of Fe₃O₄ particles coated with PEG (PEG-Fe₃O₄), 1 g of Fe₃O₄ powders in 10 g water were sonicated for 1.5 min at room temperature with an ultrasonic probe (3 pulse of 30 sec each, operated at around 3

W). 2 mL of PEG 1500 solution (Sigma-Aldrich) was added with sonication for 30 sec, and this process was repeated four times until that the total amount of PEG 1500 is 8 mL. The PEG-Fe₃O₄ powders were washed and extracted by centrifuge separation using acetone with speed of 6000 rpm for 5 min for 3 times. PPBT (*M_w*: 16 kDa, polydispersity: 2.2, the head to tail regioregularity: 89%) was purchased from Rieke Metals Inc..

Electrode Fabrication. The slurries for the PPBT-based electrode were prepared by mixing of Fe₃O₄ (or PEG-Fe₃O₄), carbon additives, and PPBT in a solvent of water, and in case of PVDF-based electrode, *N*-methyl-2-pyrrolidone (NMP) solvent was used (weight ratio of Fe₃O₄:carbon:polymer = 71.4:14.3:14.3). The solid content was 3.4 wt% for spin coating, and 27 wt% for blade coating. The composite films for the measurement of optical microscopy (OM) were prepared by spin-coating (WS-6500MZ-23NPP, Laurell) the slurries onto substrates at the spin rate of 1500 rpm for 60 sec in air. The electrodes for field-emission scanning electron microscopy (FE-SEM) measurement, electrochemical evaluation and spectroscopy characterization were produced by blade coating

(doctor blade, MTI corp). These prepared electrodes were pre-evaporated at the room temperature for 2 hr and completely evaporated at 110 °C for 12 hr in a vacuum oven. In case of PVDF-based electrode, NMP solvent was pre-evaporated at 70 °C for 1 hr, and the other fabrication procedures were the same as that of PPBT-based electrodes.

Electrochemistry. 2032-type coin cells were used for electrochemical measurements. Lithium metal was used as a counter electrode and 1M LiPF₆ in ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 by weight) was adopted as electrolyte. Before electrochemical testing, all the coin cells were charging and discharging with the current density of 40 mA g⁻¹ (~0.05 C) to confirm their capacity. The tests were then proceeded for cycling and rate capability. Cyclic voltammetry (CV) was performed in the potential range of 0.01

3.5 V at the rate of electrochemical impedance spectroscopy (EIS) measurements were conducted in the frequency range from 1 MHz to 0.1 Hz.

Microscopic Characterization. OM measurements were conducted on the composite films spin-coated on the glass substrate using Olympus MX61 Microscope. FE-SEM images were observed on the surface/cross-sectional view of the electrodes using Zeiss Ultra-60 FE-SEM with an accelerating voltage of 5 kV using the high vacuum mode at room temperature.

Spectroscopic Characterization. The electrode samples for the spectroscopic measurements were prepared by scraping powder samples from the prepared electrodes to closely investigate the chemical interactions between Fe₃O₄ and PPBT inside the electrodes. Fourier transform infrared (FT-IR) spectra were recorded using KBr pellets of the materials and a Nicolet 8700 FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) characterization was performed using a Thermo K-Alpha XPS system. The instrument was equipped with a monochromatic Al-K x-ray source. XPS spectra were collected using the flood gun and an x-ray spot size of 400 μm. Survey scans were collected with pass energy of 200 eV with 1 eV increments. High resolution scans (for specific elements) were collected with pass energy of 50 eV with 0.1 eV increments

Solubility tests for Hansen solubility parameter (HSP). 5 mg of polymer such as PEG and PPBT were placed into a vial with 2 mL of a test solvent. The vial was heated at 70 °C for 3 hr and sonicated for 60 min and after then the vials were permitted to stand and observed for 6 hr in ambient temperature. The solubility was examined by these solutions via visual observation. In case of polymer, solvents would be considered as poor if they were unable to dissolve the polymer after dissolving process and good if they were able to dissolve it. Based on the visual examination, HSPs (δ_D , δ_P and δ_H) and the radius value (R_o) of the sphere of interaction were calculated and fitted by HSPiP software (Hansen Solubility Parameters in Practice third edition).

RESULTS AND DISCUSSION

To characterize the basic electrochemical behavior of poly[3-(potassium-4-butanoate) thiophene] (PPBT), cyclic voltammetry (CV) experiments were performed in the potential window of 0.01 V to 3 V versus Li/Li⁺ (Figure 1a). An electrode fabricated with a thin polymer film for electrochemical testing was prepared by spin coating the solution onto a Cu foil substrate. Thick polymer films tend to respond more slowly due to ion transport limitations, which lead to resultant lower capacities and energy/power density.^{26,27} Poly(vinylidene difluoride) (PVDF) was used as the standard reference, owing to its wide utilization as a binder in Li-ion battery electrodes. The first CV profile of PPBT shows two distinctive reduction peaks at 0.32 V and 1.1 V and two oxidation peaks at about 1.1 V and 2.2 V. After the 2nd cycle, one reduction peak at ~1.5 V and broad reduction region below 1 V in contrast with PVDF were observed, and one oxidation peak appears at ~1.1 V. This result indicates electrochemical doping could take place within the operating potential window, possibly boosting electron transport along the PPBT backbone and building the requisite electrical bridge between active particles, carbon additives, and current collector.

voltage might suggest the existence of electrochemical doping in the PPBT backbone during electrochemical testing. In Figure 1b, applied potential was sequentially lowered from 3 V to 0.01 V, and then sequentially increased to 1.5 V and 3 V. When the applied voltage decreased, R_{ct} of both PPBT and PVDF decreased. Notably, the hysteresis in R_{ct} at 1.5 V and 3 V was distinctly different for PPBT and PVDF. R_{ct} of PVDF almost recovered to the initial value at each applied voltage step, whereas R_{ct} of PPBT showed large hysteresis, with a difference of 672 Ω at 1.5 V and 926 Ω at 3 V between the initial and final measurements at those voltages. PVDF itself is an electronic/ionic insulator ($\sim 10^{-8}$ S cm⁻¹, Figure 1c), but well-known to possess high ionic conductivity in the electrolyte environment ($\sim 10^{-3}$ S cm⁻¹).³⁶ Considering R_{ct} recovery and low initial resistance at 3V in the PVDF system, ionic conducting properties would be a dominant factor for determining its R_{ct} value. PPBT, however, might be primarily governed by the electronic characteristics and its distinctive behavior could be ascribed to electrochemical doping.

In addition, PPBT and PPBT composites with carbon

Figure 1. Electrochemical characterization of PPBT binder. (a) CV profiles of PPBT binder in the potential window of 0.01 to 3 V versus Li/Li⁺ collected at the rate of 0.5 mV s⁻¹ (inset: PPBT vs. PVDF at 1st cycle). (b) Trend of charge transfer resistance with the change of applied voltage measured by EIS in the frequency range from 1 MHz to 0.1 Hz. (c) Comparison of electronic conductivity between PVDF and PPBT system. (d) Illustration of electrochemical doping: PPBT electronic and chemical

As shown in Figure 1b, electrochemical impedance spectroscopy (EIS) studies were performed with different applied voltages to confirm the possibility of electrochemical doping of PPBT. Typically, the semi-circle in the EIS response profile corresponds to the charge transfer resistance (R_{ct}) at the electrode/electrolyte interface. The electronic resistance and ionic resistance have direct influence on the behavior of R_{ct} .³⁵ The electronic resistance reflects the resistance to bring electrons to the surface reaction sites and the ionic resistance is associated with the transfer of ions across the polymer/electrolyte interface. The investigation of R_{ct} with a change of applied

exhibit relatively high electronic conductivity compared to the PVDF system (Figure 1c). Though PPBT binder is not intrinsically conductive in a pristine state, electrochemical doping enables the formation of electron pathways along its backbone, therefore leading to enhanced electron transport under the reducing environment for anodes. Figure 1d illustrates a proposed PPBT doping mechanism during reduction (n-doping).²⁶ In the case of electrochemical doping, an applied potential induces reduction of the conjugated polymer. Diffusion of a dopant counterion (Li⁺) into PPBT from the surrounding electrolyte compensates for the formal negative charge (negative

polaron) created on the polymer backbone.²⁵ Furthermore, the formation of a lamellar structure via π - π interchain stacking of polythiophenes could facilitate intermolecular charge transport, leading to enhanced electron conduction within the PPBT binder in the composite electrode.^{37,38}

In an effort to reduce aggregate size and improve particle dispersion within the electrode, polyethylene glycol (PEG) was physically introduced onto the Fe_3O_4 particle surface (**Figure 2a**). PEG was selected as a coating material because it is known to be permeable to ions and it has high physical affinity to the PPBT binder. Hansen solubility parameter (HSP) analysis and estimation of the Hansen spheres of interaction provided supporting evidence²⁴: 98.3% of the intersection volume portion ($\%V_{\text{int}}$) indicates high physical compatibility between the two components (**Figure 2b**; the results of solubility tests in a wide range of solvents for HSP analysis is summarized in Supporting Information). Closer physical affinity induces better mixing or dispersion. It is anticipated that the resultant electrodes may experience more homogeneous current distribution over the composite electrode during electrochemical testing.

As illustrated in **Figure 2a**, Fe_3O_4 particles were coated with PEG 1500 in aqueous medium via a simple probe-type ultra-sonication process without any stringent control over the conditions.³⁰ The sonication-assisted PEG coating process limited the growth of aggregates (**Figure 2c**) which is expected to facilitate access to active sites by both Li ions and electrons. Thermogravimetric analysis (TGA) showed that the PEG- Fe_3O_4 particles were comprised of 10 wt% PEG, and dynamic light scattering (DLS) analysis demonstrated that the average particle size was ~ 303 nm (**Figure S1**). To visualize PEG- Fe_3O_4 particle dispersion within the PPBT binder, optical microscopic

(OM) characterization was performed as shown in **Figure 2d**. The uniform morphologies induced by spin-coating demonstrate that the PEG- Fe_3O_4 particles with smaller aggregate dimensions were well-dispersed in the PPBT binder medium with no apparent re-aggregation.

A standard electrode preparation procedure was followed: Fe_3O_4 powders were mixed with carbon additives and a polymeric binder dissolved in a solvent, and then the as produced slurry was blade-coated onto the Cu foil current collector, and finally dried. The resultant electrodes were characterized with field-emission scanning electron microscopy (FE-SEM) to confirm materials dispersion in a vertical/horizontal direction. The SEM images (**Figure 2e,f**) show that PEG- Fe_3O_4 with relatively small aggregate size (~ 0.5

μm) was well-dispersed in the PEG- Fe_3O_4 /carbon/PPBT electrode, compared to a Fe_3O_4 /carbon/PPBT electrode with large aggregates over $\sim 5 \mu\text{m}$ (the inset of **Figure 2e**). The PVDF-based electrode exhibits similar morphology to the PPBT-based system with no PEG coating (**Figure S2**). In addition, SEM characterization demonstrates that the water-soluble PPBT binder system might be favorable to pore formation within the electrode during solvent evaporation, which is expected to facilitate ion transport from the liquid electrolyte environment.

To evaluate the electrochemical performance, coin cells with a Li metal counter electrode were utilized and all of the electrodes were prepared with Fe_3O_4 -based active particles, carbon additives, and a polymeric binder in a 71.4:14.3:14.3 mass ratio. The Fe_3O_4 mass loading in the present study was typically $2\text{--}3 \text{ mg cm}^{-2}$. The electrolyte was a solution of 1 M LiPF_6 in EC/DEC (1 : 1 by weight).

CV analysis was performed to elucidate electrochemical behavior of the PEG- Fe_3O_4 /PPBT binder-based electrode (**Figure 3a**). In the reduction process at the first cycle, the

Figure 2. Effect of PEG coating on the Fe_3O_4 surface. (a) Schematics of PEG 1500 coating on the Fe_3O_4 surface through an ultrasonic probe. (b) Hansen solubility parameter (HSP) spheres of interaction for PEG and PPBT. (c) SEM images of PEG- Fe_3O_4 particles compared to bare Fe_3O_4 (inset). (d) Optical microscopy (OM) images of PEG- Fe_3O_4 /PPBT and Fe_3O_4 /PPBT composites (inset) prepared by spin coating on the glass substrate. (e) SEM images (cross-sectional view) of PEG- Fe_3O_4 /carbon/PPBT electrode and Fe_3O_4 /carbon/PPBT electrode (inset). (f) SEM image (surface view) of PEG-

cathodic peaks at 1.47 V and 0.79 V correspond to the structure transition induced by lithium intercalation ($\text{Fe}_3\text{O}_4 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Fe}_3\text{O}_4$) and the cathodic peak at 0.5 V is attributed to further reduction by the conversion reaction ($\text{Li}_x\text{Fe}_3\text{O}_4 + (8-x)\text{Li}^+ + (8-x)e^- \rightarrow \text{Fe}^0 + 4\text{Li}_2\text{O}$) along with formation of the SEI layer.^{9,39–42} The region below 0.5 V has a significant contribution from lithiation of the carbon additives.⁴³ The subsequent oxidation process at the first cycle shows a broad anodic peak at ~1.72 V, ascribed to oxidation of Fe to $\text{Fe}^{2+}/\text{Fe}^{3+}$. In the subsequent cycles, a broad peak between ~0.72 V and ~1.83 V appeared during the reduction and oxidation process, respectively, due to the electrochemical redox reaction ($\text{Fe}_3\text{O}_4 \leftrightarrow \text{Fe}^0$) through Li insertion/extraction.³⁹ The results obtained for the PEG- Fe_3O_4 /PPBT binder-based electrode are in close agreement with previous studies for Fe_3O_4 /PVDF systems.^{40,41}

formed in the frequency range of 1 MHz to 0.1 Hz before cycling at 3.0 V and after 50 cycles at their open-circuit voltage (OCV). The superior battery performance associated with the PEG coated active material and PPBT binder system may originate from decreased electrode resistance: in comparison to the PVDF standard, PEG coating/PPBT binder system charge transfer resistance (R_{ct} , $\approx$ estimated diameter of the semicircle) was effectively reduced both before cycling and after 50 cycles. This strongly points to positive synergistic effects associated with using both the PEG coating and conjugated polymer binder to improve electron and ion transport phenomena in the electrode. Coating the Fe_3O_4 active material surface with PEG to limit growth of aggregates and facilitate their dispersion is expected to enhance ion transport. With respect to electron transport, the semiconducting PPBT binder may function as an ‘electrical bridge’ between

Figure 3. Electrochemical performance of Fe_3O_4 -based electrodes. (a) CV profiles of PEG- Fe_3O_4 /carbon/PPBT electrode in the potential window of 0.01 to 3 V versus Li/Li^+ collected at the rate of 0.5 mV s^{-1} (the inset shows the galvanostatic charge-discharge profiles in the potential window of 0.01 to 3 V versus Li/Li^+ at a constant current density of 80 mA g^{-1} , comparable to CV profiles). (b) Cycling performance (=capacity retention as function of cycle number) collected for the current density of 240 mA g^{-1} ($\sim 0.3 \text{ C}$) between 0.3 and 3 V. (open circles: Li-insertion capacity, filled circles: Li-extraction capacity) (c) The impedance spectra measured at 3 V before cycling (bottom graph) and at open-circuit voltage (OCV) after 50 cycles (upper graph) in the frequency range from 1 MHz to 0.1 Hz. (d) Cycling performance between 0.01 and 3 V. (e) Delithiation rate capability, where cells were lithiated at a constant current density of 80 mA g^{-1} and delithiated at different current densities between 0.01 and 3 V. (open symbols: capacity retention, filled symbols: Li-extraction capacity) (f) Cell polarization as a func-

Charging-discharging cycling (**Figure 3b**) at the current density of 240 mA g^{-1} ($\sim 0.3 \text{ C}$) demonstrated that the PPBT binder system allowed for noticeably improved capacity retention, and that the PEG coating on the Fe_3O_4 surface afforded more stable cycling than that obtained with only PPBT as a binder. These results are in contrast to Fe_3O_4 anodes fabricated with either PVDF or carboxymethyl cellulose (CMC) binders. EIS analysis in **Figure 3c** supports this observation. The coin cells used in the EIS study correspond to those cycled between 0.3 V and 3 V as shown in **Figure 3b**. This impedance test was per-

Fe_3O_4 active particles and carbon additives (or current collector), thereby facilitating electron transport via the PPBT pathway induced by electrochemical doping during battery cycling (**Figure 1d**).

In order to investigate PPBT binder electrochemical doping effects, newly fabricated coin cells were further lithiated by lowering the cut-off voltage from 0.3 V to 0.01 V. In other words, the cycling test was performed between 0.01 V and 3 V. **Figure 3d** presents the charging-discharging performance at a current density of 240 mA g^{-1} . Despite the harsher lithiation conditions, both PEG-

Fe_3O_4 /PPBT binder- and PPBT binder-based electrode capacity retention appeared more stable than observed under the 0.3 V cut-off conditions. The PEG coating/PPBT binder system, in particular, exhibited 91.2 % capacity retention at 50 cycles, compared to the PVDF control showing only 25.9 % retention.

Conceivably, electrochemical doping positively impacts the low voltage region exhibited a broad reduction peak at about 0.32 V that is believed to be due to electrochemical doping (Figure 1a). Moreover, the beneficial effect of the PEG/PPBT approach was also seen in the rate capability experiments (Figure 3e). Under a constant lithiation current density of 80 mA g^{-1} (~ 0.1 C), a PEG- Fe_3O_4 /PPBT binder-based electrode shows much higher delithiated capacity than the PVDF control over a wide range of delithiation current densities (80–1600 mA g^{-1}) at a voltage range of 0.01–3 V, which conveys its superior rate capability. Figure 3f summarizes a quantitative analysis of the ohmic polarization as a function of the applied current density, where the polarization was examined by measuring the difference in initial voltage between the current density of 80 mA g^{-1} (~ 0.1 C) and a given current density.⁴⁴ A comparison of voltage profiles provides for a cell polarization which provides an indication of the electrochemical kinetics taking place in the electrode. Specifically, in the PEG/PPBT system, PPBT and conductive carbon-mediated electron networks and PEG-induced Li ion accessibility are, presumably, the crucial factors determining the kinetics. The PEG/PPBT approach exhibited a polarization value that was noticeably lower than that of the control, resulting in improved battery performance.

From a mechanistic perspective, molecular interactions between the PPBT carboxyl group and either Fe_3O_4 or PEG- Fe_3O_4 particles may enable electron and ion transport. Fourier transform infrared (FT-IR) spectroscopy studies (Figure 4a) revealed sharp C–H and C–O stretching bands at 1105 cm^{-1} and 2860 cm^{-1} , respectively for PEG- Fe_3O_4 powders, which confirmed Fe_3O_4 surface coordination. With PPBT, PPBT carboxylic moieties exhibit peaks at 1556 cm^{-1} and 1400 cm^{-1} which correspond respectively to O–C–O asymmetric and symmetric stretching.¹⁵ After electrode formation, FT-IR test samples were prepared by scraping powdered samples from the electrodes. In comparison to the raw materials, all PPBT-based electrodes, fabricated with either Fe_3O_4 or PEG- Fe_3O_4 particles, showed strong bands centered at 1556 cm^{-1} and 1400 cm^{-1} associated with free carboxylate anions. In addition, new, lower intensity peaks that were not apparent in the parent samples were observed at 1530 cm^{-1} and 1766 cm^{-1} . As depicted in Figure 4b, the peak at 1766 cm^{-1} is associated with Fe-carboxylate bond C=O stretching. The shoulder observed at about 1530 cm^{-1} (split from the 1556 cm^{-1} band) suggests coordination of carboxylate functionalities with Fe_3O_4 surface: the shift to lower frequency arises from weakening of the O–C–O vibration due to Fe-carboxylate bonding.^{29, 45–47} The FT-IR results provide evidence of PPBT- Fe_3O_4 chemical interactions. Spectroscopically, the PEG- Fe_3O_4 /PPBT and Fe_3O_4 /PPBT electrodes are very similar, strongly suggesting that the PEG coating on Fe_3O_4 is readily displaced by PPBT carboxylate groups which can chemically bond with Fe_3O_4 surface hydroxyl functionalities.^{48–49} While such strong interactions between a binder and the surface of high

Figure 4. Spectroscopy characterization of the Fe_3O_4 , PEG- Fe_3O_4 , PPBT and electrodes prepared by mixing PEG- Fe_3O_4 (or Fe_3O_4) with PPBT binder. (a) FT-IR spectra of materials (bottom lines: Fe_3O_4 , PEG- Fe_3O_4 , PPBT) and electrodes (upper lines: Fe_3O_4 /PPBT, PEG- Fe_3O_4 /PPBT). (b) The possible binding modes of complexes on the Fe_3O_4 surface. (c) and (d) XPS spectra of materials (Fe_3O_4 , PEG- Fe_3O_4 , PPBT) and electrodes (Fe_3O_4 /PPBT, PEG- Fe_3O_4 /PPBT).

capacity active materials have been reported to be one of the most critical factors influencing electrode stability, previous experimental results have been limited to Si anodes.^{12–15}

The x-ray photoelectron spectroscopy (XPS) spectra of the C 1s and Fe 2p core levels further substantiate the presence of chemical interaction between PPBT and the Fe₃O₄ surface. In **Figure 4c**, the C 1s peaks at ~285 eV are ascribed to carbon atoms associated with the C–O bond; note the chemical shift to lower binding energy with an increase in interatomic distance which results from additional bonding between PPBT and Fe₃O₄.^{50,51} The C 1s peak at 287.88 eV for PPBT is indicative of a C=O bond. The remaining C 1s peaks for PPBT at 293.48 eV and 295.88 eV are associated with satellite peaks, which result from the extended delocalized electrons in the sample and provide evidence of interchain PPBT π - π * stacking.⁵² This molecular packing formation may induce charge transport along the π - π stacking direction and improve the electrical properties of the PPBT binder system. C 1s peaks at 288.78 eV for Fe₃O₄/PPBT and PEG-Fe₃O₄/PPBT are attributed to carboxylate (COO⁻),⁵⁰ as seen in the proposed chemical structure in **Figure 4b**. When analyzing the Fe 2p core-level peaks (**Figure 4d**), the binding energy shifts to about 712 eV and 724 eV for Fe₃O₄/PPBT and PEG-Fe₃O₄/PPBT might be attributed to the Fe-carboxylate bond.⁵³ In addition, the Fe³⁺ associated with both systems exhibits a distinct satellite peak at ~718 eV.⁵⁴ Their absence for Fe₃O₄ and PEG-Fe₃O₄ confirms a pure magnetite phase. The presence of the satellite peak for Fe₃O₄/PPBT and PEG-Fe₃O₄/PPBT, further illustrates the chemical interaction between PPBT carboxylic moieties and the hydroxylated Fe₃O₄ surface.

Figure 5. Schematic illustrations depicting electron and ion transport in the electrode.

Figure 5 presents a schematic diagram that elucidates the electron and ion transport phenomena associated with the PEG/PPBT based electrode versus its PVDF counterpart. Within the PVDF control, the individual components (including active materials, carbon additives, and even the PVDF binder) comprising the electrode are expected to exhibit a significant level of aggregation due to their different physical affinities²⁴ (**Figure S2**). PVDF is an electronic insulator, thus blocking electron transport between active materials and carbon additives (or current collector). The PEG/PPBT system, however, enables the creation of electron and ion pathways in the Fe₃O₄ surroundings to enhance the conducting characteristics which help battery performance. Moreover, the smaller-

sized aggregates arising from the introduction of PEG onto the Fe₃O₄ surface are also expected to contribute positively to the electrochemical processes, which may be facilitated by improved dispersion between the active material and carbon additives.⁵⁵

Importantly, however, when considering materials dispersion within a polymer composite electrode, a porous structure must be maintained if a given binder is not permeable to electrolyte molecules.¹⁵ In other words, a binder should either cover only a portion of active material surface or remain permeable to Li ions. In this work, since PPBT is not permeable to Li ions, polymer wrapping on a carbon or active particle through the use of chemical or physical methods, may expedite the process whereby pores become blocked, yielding poor electrochemical results (**Figure S3** and **S4**). Therefore, it is critical to consider transport processes in conjunction with molecular/chemical structure and possible physical or chemical interactions. Here, the possible synergies obtained from the combined use of the semiconducting polymer, PPBT as a binder and PEG as a surface coating for Fe₃O₄ active particles were considered in terms of the above requisites, effecting improved electrochemical behavior.

CONCLUSIONS

We demonstrated methodical consideration for both ion and electron transport by introducing a carboxylated PPBT binder and facile PEG surface treatment, which remarkably enhanced the performance of Fe₃O₄ high-capacity anodes. PPBT with pendant carboxylic moieties facilitated electron transport along the polymer backbone via electrochemical doping, building necessary electrical linkages between carbon and Fe₃O₄ particles. Additionally, Fe-carboxylate bonding positively affected high-capacity anode stability. Generally, the poor cycling performance of high-capacity electrode materials lies in difficulties related to substantial volume changes in the active material and resultant loss of electron transport pathways. The results and mechanistic insight presented here suggest a new approach that can provide for high-capacity energy materials with feasible process methodologies for their practical use in the near future.

ASSOCIATED CONTENT

Supporting Information. Thermogravimetric analysis (TGA) of PEG-Fe₃O₄ particles; field-emission scanning electron microscopy (FE-SEM)/optical microscopy (OM) images of PVDF binder system; material dispersion effects using chemical and physical dispersion process; solubility tests for Hansen solubility parameter of PPBT and PEG 1500. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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Table of Contents

Supporting Information

Electron/Ion Transport Enhancer in High Capacity Li-ion Battery Anodes

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Figure S1. PEG-Fe₃O₄ particles: (a) TGA profile of PEG coating, which is carried out in nitrogen in the temperature range of 25–600 °C at a heating rate of 20 °C/min. (b) Dynamic light scattering (DLS) particle size distribution of PEG-Fe₃O₄ particles. DLS was performed using a Malvern Zetasizer NANO ZS instrument (Malvern instruments). PEG-Fe₃O₄ particles were dispersed in aqueous medium through bath-type sonication for 30 min (1mg particles/1mL deionized water).

Figure S2. PVDF binder system. The SEM images of (a) surface view and (b) cross-sectional view of Fe₃O₄/carbon/PVDF electrode. (c) OM image of carbon/binder composites (50:50 in a mass ratio) prepared by spin coating on the glass substrate.

Figure S3. Effects of material dispersion using chemical/physical dispersion process. (a) OM image of PEG-Fe₃O₄/carbon /PPBT composites spin-casted on the glass substrate after probe-type ultra-sonication (physical dispersion). (b) Hansen solubility parameter analysis of PEG 1500, PPBT and carbon: physical affinity of carbon additives were deviated from Hansen sphere of PEG 1500 and PPBT. SDBS surfactant was used for the carbon dispersion (chemical dispersion). (c) Cycling performance (= capacity retention as a function of cycle numbers) of PEG-Fe₃O₄/carbon/PPBT, PEG-Fe₃O₄/carbon/SDBS/PPBT, and PEG-Fe₃O₄/carbon/PPBT prepared by probe-type ultra-sonication. (d) EIS results of coin cell measured before cycling and after 50 cycles. The chemical/physical dispersion process both has largely increase in R_{ct} before cycling, which affects the resulting poor cycling, especially for the sonication dispersion process.

Figure S4. SEM images of (a) PEG-Fe₃O₄/carbon/PPBT, (b) PEG-Fe₃O₄/carbon/SDBS/PPBT and (c) PEG-Fe₃O₄/carbon/PPBT prepared by probe-type ultra-sonication. The electrodes with no treatment show the well-constructed porous structure, whereas the electrodes with SDBS surfactant and the electrodes prepared by ultra-sonication appear covered with PPBT binder. These morphologies might be attributed to substantially high degree of reaction of PPBT carboxylic moieties with hydroxyl group of Fe₃O₄ and carbon, inducing the polymer wrapping/covering. This strongly indicates the material dispersion by polymer wrapping on the surface of Fe₃O₄ active materials enables the prevention of the pore formation during the solvent evaporation, which rather hinders ion and electron transport.

Table S1. Good and bad solvents in tests of PPBT surface affinity and their RED values. (δ_D =18.73 MPa^{1/2}, δ_P =26.45 MPa^{1/2}, δ_H =26.61 MPa^{1/2}, R_o = 19.9 MPa^{1/2}, Data fit 0.976)

Solvent	δ_D (MPa ^{1/2})	δ_P (MPa ^{1/2})	δ_H (MPa ^{1/2})	Surface affinity	RED
1,2,4-Trichlorobenzene	20.2	4.2	3.2	Bad	1.629
Acetone	15.5	10.4	7	Bad	1.314
Chlorobenzene	19	4.3	2	Bad	1.664
Chloroform	17.8	3.1	5.7	Bad	1.578
Ethanol	15.8	8.8	19.4	Bad	1.002
Hexane	14.9	0	0	Bad	1.924
Tetrahydrofuran	16.8	5.7	8	Bad	1.414
Toluene	18	1.4	2	Bad	1.766
Trichloroethylene	18	3.1	5.3	Bad	1.59
Diethylene Glycol	16.6	12	19	Good	0.848
Dimethyl Formamide	17.4	13.7	11.3	Good	1.01
Dimethyl Sulfoxide	18.4	16.4	10.2	Good	0.967
Ethylene Glycol	17	11	26	Good	0.796
Water	15.5	16	42.3	Good	1.001

Table S2. Good and bad solvents in tests of PEG1500 surface affinity and their RED values. (δ_D =19.06 MPa^{1/2}, δ_P =24.92 MPa^{1/2}, δ_H =27.12 MPa^{1/2}, R_o = 19.0 MPa^{1/2}, Data fit 1.000)

Solvent	δ_D (MPa ^{1/2})	δ_P (MPa ^{1/2})	δ_H (MPa ^{1/2})	Surface affinity	RED
1,2,4-Trichlorobenzene	20.2	4.2	3.2	Bad	1.67
Acetone	15.5	10.4	7	Bad	1.359
Chlorobenzene	19	4.3	2	Bad	1.711
Chloroform	17.8	3.1	5.7	Bad	1.615
Dimethyl Formamide	17.4	13.7	11.3	Bad	1.036
Ethanol	15.8	8.8	19.4	Bad	1.002
Hexane	14.9	0	0	Bad	1.988
Tetrahydrofuran	16.8	5.7	8	Bad	1.447
Toluene	18	1.4	2	Bad	1.815
Trichloroethylene	18	3.1	5.3	Bad	1.628
Diethylene Glycol	16.6	12	19	Good	1
Dimethyl Sulfoxide	18.4	16.4	10.2	Good	0.767
Ethylene Glycol	17	11	26	Good	0.844
Water	15.5	16	42.3	Good	1