High-Rate $LiFePO_4$ Lithium Rechargeable Battery Promoted by Electrochemically Active Polymers

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Received May 5, 2008. Revised Manuscript Received October 14, 2008

$LiFePO_4$ is a promising cathode material for the next generation of a lithium-ion rechargeable battery because of its low-cost, safety, excellent cyclability, and large capacity. Moreover, its voltage, 3.45 V versus lithium, is compatible with the window of a solid-polymer Li-ion electrolyte. Of particular interest for commercial applications is its safety and energy capacity at high power output and at short recharge times. We report here a systematic investigation of the enhancement of capacity at high rates of charge and discharge by substitution of a conductive, electrochemically active polymer for some or all of the deadweight conductive carbon and binder used conventionally to enhance performance of a secondary battery. Polypyrrole (PPy) and polyaniline (PANI) were used as the conductive polymers; two methods, electrochemical deposition and simultaneous chemical polymerization, were used to prepare the $LiFePO_4$/polymer composite cathodes. Our results show that significantly improved capacity and rate capability can be achieved in such composite cathodes and that the electrodeposited carbon-coated $LiFePO_4$/PPy composite exhibits the best performance.

Introduction

The low-cost, environmentally friendly system $FePO_4-LiFePO_4$ has proven to be a safe cathode material for a lithium-ion rechargeable battery.[1] It gives excellent cyclability and large capacity at high rates of charge and discharge if small oxide particles are coated with carbon,[2] which makes possible the realization of high-power batteries for such applications as electrical-energy storage and plug-in hybrid automobiles. $LiFePO_4$ has the olivine structure. Although this structure has only 1D channels for Li extraction, the theoretical capacity of 170 mA h g^{-1} of the $FePO_4-LiFePO_4$ system can be realized for small particles, particularly if the active $LiFePO_4$ particles are coated with carbon.[3,4] We designate the carbon-coated $LiFePO_4$ particles as C-LFP. Due to a small distortion of the $FePO_4$ structure, the open-circuit voltage of 3.45 V versus lithium is flat over almost the entire $FePO_4-LiFePO_4$ compositional range, which means little mixed valence and therefore electronic conductivity in the two end-member phases. However, the carbon coat is permeable to the Li^+ ions and provides electrons that move with the Li atoms into/out of the oxide. The particles are in the shape of flat plates with the 1D Li channels perpendicular to the plates;[5] and the 1D channels of the thin plates are not blocked in the absence of impurity phases.

Although polypyrrole (PPy) has been introduced into $LiMn_2O_4$, V_2O_5, and $LiFePO_4$ oxide/C/PTFE composite cathodes, this strategy has given only a modest enhancement of performance.[6−12] Pasquier et al.[7] have also coated $LiMn_2O_4$ particles with PPy to protect the cathode from capacity fading due to dissolution of manganese into the electrolyte. However, the concept of substituting the inactive C and Teflon (PTFE) binder of a composite cathode with an electrochemically active polymer like PPy or polyaniline (PANI) has only been reported in connection with a preliminary study of electrochemically codeposited PPy/C-LFP composite cathodes.[13,14] We present here a systematic comparison of the electrochemical performance of C-LFP composite cathodes prepared electrochemically and chemically with polymers PPy or PANI. This strategy is shown to

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10.1021/cm8012304 CCC: $40.75

work where, as for C-LFP, the electrochemically active energies of the polymers overlap the energy of the working redox couple of the oxide and a carbon coat of the oxide provides a good electrical contact between the oxide particles and the current collector through the polymer. The electrochemical deposition of PPy gave a better performance than the chemically prepared composites.

Experimental Section

Carbon-coated $LiFePO_4$ (C-LFP) powder was provided to us by Phostech Lithium, Inc., Montréal, Canada. Electrodeposition onto a stainless-steel mesh from a suspension containing C-LFP particles and pyrrole in acetonitrile via cyclic voltammetry yielded a C-LFP/PPy composite cathode as described elsewhere.[13,14] Deposition was performed by cyclic voltammetry with an EG&G potentiostat/galvanostat model 273 over 20 cycles from 0 to 1.3 V at a scanning rate of 100 mV s^{-1} in an argon atmosphere.

Chemically synthesized C-LFP/polymer composites were obtained by a simultaneous chemical polymerization of monomers of pyrrole or aniline in the presence of a C-LFP suspension. PPy was polymerized from pyrrole with ammonium peroxydisulfate $(NH_4)_2S_2O_8$ as oxidizer in deionized water; sodium p-toluenesulfonate was used as dopant because of the good electrochemical stability of toluenesulfonate-doped PPy.[16] The polymerization was carried out at 0−5 °C for 6 h. C-LFP/PANI composites were synthesized via simultaneous chemical polymerization of PANI in the presence of fine C-LFP particles in aqueous suspension. First, a C-LFP aqueous suspension was sonicated for 10 min; then the aniline monomer was dissolved in the suspension and stirred magnetically at room temperature for 0.5 h. A precooled aqueous solution of $(NH_4)_2S_2O_8$ that acts as an oxidant was added into the above solution together with a small amount of hydrochloric acid. The mixture was reacted for 6 h at 0−5 °C. The precipitate was washed several times with deionized water and ethanol, separately, and finally dried overnight in a vacuum at room temperature.

The weight ratio of the polymer in the composite was analyzed by thermogravimetric analysis (TGA, Perkin-Elemer). Electrochemical measurements were carried out between 2.5 and 4.1 V vs Li^+/Li^0 with CR2032 coin cells. The electrodeposited C-LFP/polymer films were used directly as the cathode without addition of either C or PTFE. The chemically synthesized composites were mixed with C black and PTFE (75:20:5 wt %) to fabricate the cathodes. In the coin-cell tests, metallic lithium foil was used as the counter and reference electrodes; the electrolyte was 1 mol/L $LiPF_6$ in a 1:1 solvent mixture of ethylene carbonate and diethyl carbonate (EC/DEC).

Results and Discussion

The method of preparation, which is critical for cell performance, differs for each polymer. With the electrodeposition route, C-LFP/PPy composite films were shown to exhibit an enhanced capacity and an excellent rate capability. Additionally, the carbon coated onto the LFP particles was proven to be necessary for composite cathodes with good performance. However, our repetitious experiments have shown that the electrodeposition method is not available for C-LFP composites with PANI. To obtain good quality composites with PANI, some strong inorganic acids (e.g., sulfuric, oxalic, or perchloric acids) or organic acids (e.g., trifluoroacetic or trichlroacetic acids) are needed in the precursor solution.[15−17] The acid not only acts as an initiator for polymerization but also promotes proton transfer to the PANI to enable the formation of an electroactive polymer. The presence of the acid could destroy the core−shell structure of the C-coated LFP particles, which may be the main reason we were not able to obtain a good C-LFP/PANI composite film via electrochemical polymerization.

With chemical polymerization of the polymer in the presence of fine C-LFP particles, both C-LFP/PPy and C-LFP/PANI composites can be successfully attained. Figure 1 shows SEM images of PPy, PANI, C-LFP/PPy, and C-LFP/PANI. Both PPy and PANI polymers are amorphous. From images C and D in Figure 1, we can see that the polymers are incorporated with the C-LFP particles. Most of the particles congregate with each other, which may be due to the connection of sticky polymers. Because the primary LFP particles were first coated with carbon and then some of them were incorporated with the polymer, it is difficult to distinguish LFP from carbon and polymer particles. Estimated by SEM, the size of the aggregated particles are mostly distributed from 2 to 5 μm. Figure 2 displays thermogravimetric curves for C-LFP/PPy and C-LFP/PANI composites in Ar. The weight loss from room temperature to around 100 °C is due to the release of a small amount of adsorbed water. Both PPy and PANI begin to decompose around 300 °C and completely decompose at 500−550 °C. Presumably, heating the polymers in Ar will lead to some residual carbon; however, their weights drop to zero after 550 °C, which shows that the possibly formed carbon may go away with the flowing Ar gas. In the composites, PPy completely decomposes at 550 °C and PANI at 650 °C. Because C-LFP is stable in Ar under 800 °C and the weight of residual carbon formed by decomposition of the polymers can be ignored, the weight content of the polymer can be calculated from the weight loss of the composite in the thermogravimetric curve.

Figure 3 shows cell voltage vs specific capacity for the C-LFP/polymer composite cathodes. The specific capacity is defined as the capacity per gram of the active cathode material. To compare with the conventional C-LFP/C/PTFE cathode conveniently, the specific capacity was calculated by the total mass of C-LFP and polymer for the chemically synthesized C-LFP/polymer composites, whereas it was calculated by just the mass of C-LFP for the electrodeposited composites. The charge−discharge curves show that the polymers are both electrochemically active at the operating voltage of the cell. Compared with the C-LFP/C/PTFE cathode, C-LFP/PPy and C-LFP/PANI composites both exhibit enhanced capacity. Polymers PPy and PANI themselves are electroactive in the range of 2.0−3.8 V with specific discharge capacities of 62 and 67 mA h g^{-1}, respectively. From the charge−discharge curves of the composites, we can see clearly the electrochemical contribution from PPy and PANI. Specific discharge capacities

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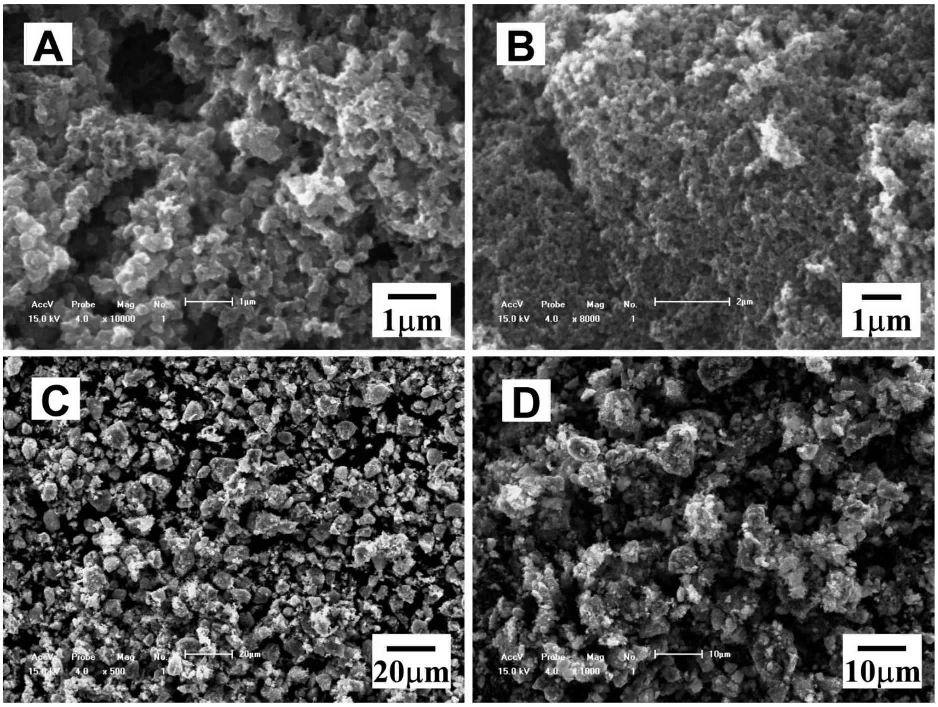

Figure 1. SEM images of (A) PPy, (B) PANI, (C) LFP/PPy, and (D) LFP/PANI.

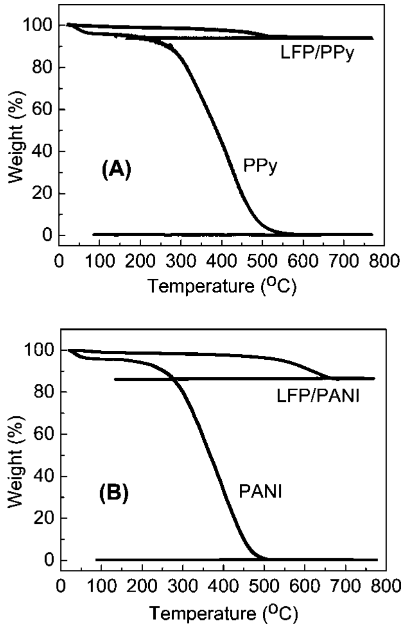

Figure 2. Thermogravimetric curves for (A) LFP/PPy and (B) LFP/PANI composites in argon.

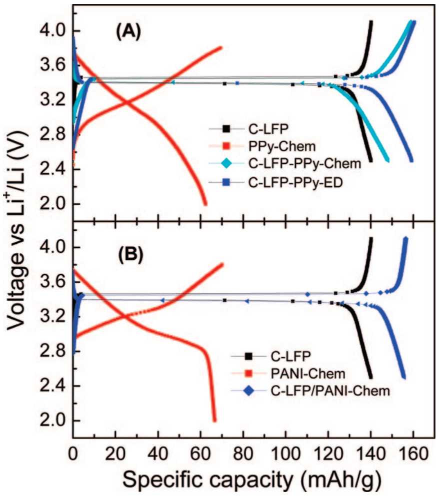

Figure 3. Cell voltage as a function of composite specific capacity for C-LFP/polymer composite cathodes: (A) C-LFP, PPy, C-LFP/7%PPy-Chem, and C-LFP/16%PPy-ED; (B) C-LFP, PANI, and C-LFP/7%PANI-Chem. “ED” refers to “electrodeposited”, “Chem” to “polymerized chemically”. All cells were charged and discharged at 0.1*C*.

obtained at various rates for typical chemically synthesized composite cathodes, 93 wt % C-LFP/7 wt % PPy and 93 wt % C-LFP/7 wt % PANI, are displayed in Figure 4. Compared with C-LFP, the specific capacity is greatly enhanced at rates from 0.1*C* to 10*C*, especially at high current rates. A significantly improved rate capability is clearly achieved in the C-LFP-based composite cathodes with PPy and PANI. The improved rate capability can be ascribed to a kinetic effect. PPy and PANI serve as a host for Li-ion intercalation and extraction and provide, particularly with electrodeposition, good electronic contact between the particles and the current collector. Furthermore, the coating with conducting polymer was proved by impedance measurement to increase the electrical conductivity between $LiFePO_4$ particles.[9]

The C-LFP/polymer composites with different PPy or PANI contents were fabricated and electrochemically tested. The weight contents of PPy and PANI in the composites are important to the charge/discharge properties. Figure 5 compares the rate capability of the chemically polymerized $(C\text{-}LFP)_{1-x}(polymer)_x$ composite cathodes with different polymer weight content x. All cells were charged and discharged at the same rates: 0.1−10*C*. For the chemically synthesized C-LFP/PPy composites, the $x = 3\%$ composite shows almost the same rate capability as the parent C-LFP, indicating that incorporation of 3% PPy is not enough to improve the performance, and 15% PPy in C-LFP degrades

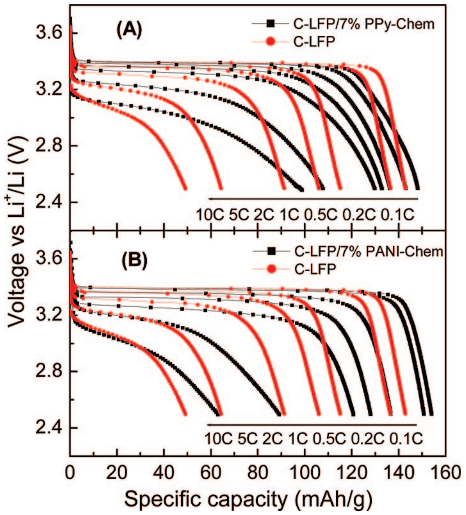

Figure 4. Cell voltage vs composite specific capacity obtained by being discharged at various rates while being charged at 0.1*C* for (A) C-LFP/7%PPy-Chem and (B) C-LFP/7%PANI-Chem. The performance of C-LFP is compared.

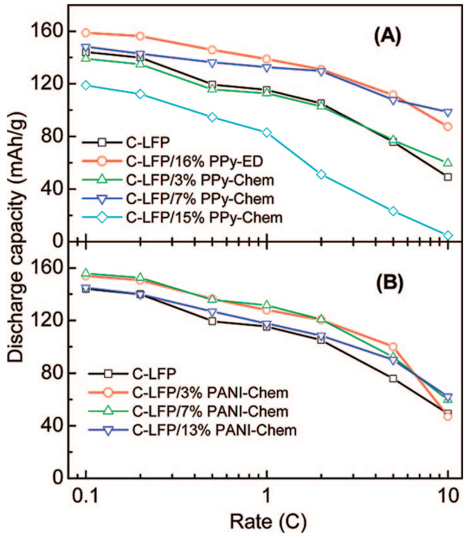

Figure 5. Comparison of discharge rate capability for the C-LFP-based composite cathodes with PPy and PANI. The data were obtained by discharging at various rates after charging at 0.1*C*.

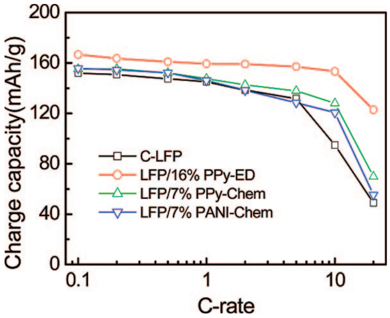

Figure 6. Comparison of charge rate capability for C-LFP, C-LFP/16%PPy-ED, C-LFP/7%PPy-Chem, and C-LFP/7%PANI-Chem. The data were obtained by charging at various rates after discharging at 0.1*C*.

the capacity. The composite with around 7 wt % PPy exhibits the best rate capability. For the $x = 7\%$ composite, the capacity can be charged and discharged up to 110 mA h g^{-1} at 10*C* (6 min), i.e., retaining almost 70% of the theoretical capacity. It should be mentioned that the cell can be simultaneously charged and discharged at a high current density. Similarly, all the tested $x = 3$, 7, and 13% chemically polymerized C-LFP/PANI composites exhibit a superior rate capability compared to the parent C-LFP. However, the best performance still occurs at $x = 7\%$. For the electrodeposited $(\text{C-LFP})_{1-x}(\text{PPy})_x$ composite cathodes, the PPy content with the maximum capacity and optimal rate capability is around $x = 20\%$.[13] As shown in Figure 5(A), the chemically synthesized $x = 7\%$ composite has a performance at high rates comparable to that of the electrodeposited $x = 16\%$ composite. The higher PPy content for the maximum capacity in the electrodeposited $(\text{C-LFP})_{1-x}(\text{PPy})_x$ composites shows that more PPy is needed to act as conductor and binder where there is no further addition of carbon black and PTFE in the cathode. For the chemically synthesized composites, 15−25 wt% additive of carbon black and PTFE is still necessary to achieve improved performance. Zaghib et al.[18] have shown that in the absense of a polymer, the best capacity and power density at high rates is achieved with an optimal weight content of carbon black.

Charge rate capabilities for several typical cathodes, C-LFP, C-LFP/16% PPy-ED, C-LFP/7% PPy-Chem, and C-LFP/7% PANI-Chem, are compared in Figure 6. The data were obtained by charging at various rates from 0.1*C* to 20*C* while discharging at low rate 0.1*C*. Compared with C-LFP, all the composite cathodes show an enhanced charge rate capability especially at high rates. Within 6 min (10*C*), the capacity can reach 62.3, 92.0, 82.5, and 77.5% of the capacity at 0.1*C* for C-LFP, C-LFP/16% PPy-ED, C-LFP/7% PPy-Chem, and C-LFP/7% PANI-Chem, respectively. The electrodeposited C-LFP/16% PPy exhibits the fastest charging performance; it can be charged up to 92% of full capacity within 6 min.

We further investigated the charge−discharge properties for the typical chemically synthesized C-LFP/PPy and C-LFP/PANI composites with $x = 7\%$. The cells were tested in three different modes: (A) charged at 0.1*C*, discharged at 0.1−20*C*; (B) charged at 0.1−20*C*, discharged at 0.1*C*; and (C) charged and discharged both at 0.1−20*C*. For the $x = 7\%$ C-LFP/PPy composite, the capacity can be charged up to 145 mAh/g at 5C and 131 mA h g^{-1} at 10*C* with mode A; to 138 mA h g^{-1} at 5*C* and 128 mA h g^{-1} at 10*C* with mode B; and to 125 mA h g^{-1} at 5*C* and 111 mA h g^{-1} at 10*C* with mode C (see Figure 7). Even with simultaneous fast charge and fast discharge within several minutes, the capacity of the C-LFP/PPy composite cathode can still reach more than 70% of full capacity. Similar charge/discharge performances were also observed for the $x = 7\%$ C-LFP/PANI composite cathode; Figure 8 shows improved rate capability with both fast charge and fast discharge modes. The capacity was charged to 108 mA h g^{-1} at 5*C* and 86 mA h g^{-1} at 10*C* with mode A; to 128 mA h g^{-1} at 5*C* and 121 mA h g^{-1} at 10*C* with mode B; and to 111 mA h g^{-1} at 5*C* and 64 mA h g^{-1} at 10*C* with mode C. The rate capability of C-LFP/PANI is significantly enhanced compared with C-LFP/C/PTFE and is almost comparable to that

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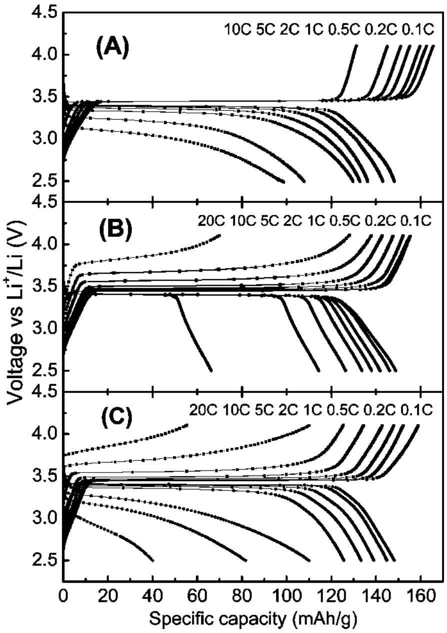

Figure 7. Composite specific capacity for a typical C-LFP/7%PPy composite cathode prepared with simultaneous chemical polymerization: (A) charged at 0.1*C*, discharged at 0.1−10*C*, (B) charged at 0.1−20*C*, discharged at 0.1*C*, and (C) charged and discharged both at 0.1−20*C*.

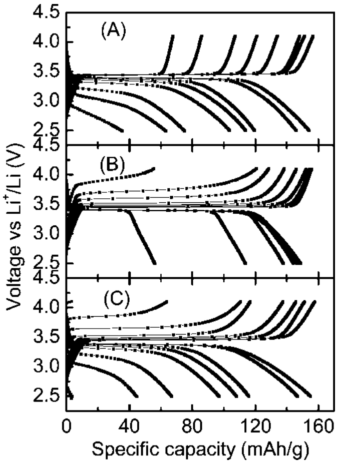

Figure 8. Composite specific capacity for a typical C-LFP/7%PANI composite cathode prepared with simultaneous chemical polymerization: (A) charged at 0.1*C*, discharged at 0.1−20*C*, (B) charged at 0.1−20*C*, discharged at 0.1*C*, and (C) charged and discharged with the same rate at 0.1−20*C*.

of C-LFP/PPy. Therefore, our experiment indicates that the C-LFP-based composites are excellent cathode materials for fast-charging lithium batteries.

Moreover, the composite cathodes show a good cyclability. Figure 9 illustrates specific capacity vs cycle number on being charged and discharged at the same rates for a total of 120 cycles for the chemically synthesized $x = 7\%$ C-LFP/PPy composite cathode. The fade in discharge capacity is 0.7, 0.8, 0.9, 0.8, 2.4, and 10% after each 20 cycles with 0.1*C*, 0.5*C*, 1*C*, 2*C*, 5*C*, and 10*C*, respectively. The fade is very low when the rate is less than 5*C*. This result demonstrates that the structure of the composite is very stable and the electrochemical Li^+-ion insertion/extraction process is quite reversible even at high rates.

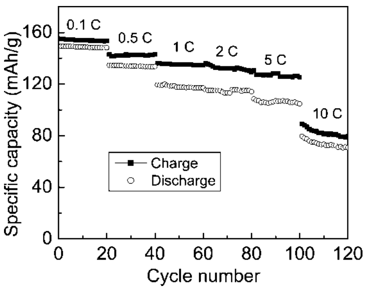

Figure 9. Composite specific capacity vs cycle number for the C-LFP/7%PPy composite cathode prepared with simultaneous chemical polymerization.

Conclusions

Where the electrochemically active energies of a conductive polymer overlap the energy of the working redox couple of a carbon-coated oxide insertion compound, as occurs with PPy or PANI and C-$LiFePO_4$, replacement of some or all of the inactive carbon and PTFE binder by the polymer, which also serves as a host to Li^+-ion insertion/extraction, has been shown to enhance the capacity and rate capability of the electrode. Chemically synthesized composite polymer/C-$LiFePO_4$ electrodes with PPy or PANI as the polymer have been demonstrated, and the performances of these composite electrodes have been compared with that of PPy/C-$LiFePO_4$ composites prepared electrochemically. Electrochemical synthesis of PANI/C-$LiFePO_4$ composites was not achieved. The chemically prepared PPy/C-$LiFePO_4$ and PANI/C-$LiFePO_4$ composites gave similar performance. In contrast, the electrodeposited PPy/C-$LiFePO_4$ composites required no additional carbon or binder and gave a superior capacity at high rates. Electrodeposition ensures good electrical contact between particles and current collector as well as between particles. This strategy may be unsuccessful where the electroactive range of the polymer does not overlap the operative redox couple, as would be the case with PPy and PANI and an oxide giving 4 V versus lithium.

Acknowledgment. We thank K. Zaghib and N. Ravet for supplying us with C-$LiFePO_4$ powder and the Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy under Contract DE-AC03-76SF00098 and the Robert A. Welch Foundation for financial support. Y.H.H. acknowledges support from the National Science Fund for Distinguished Young Scholars of China (50825203).

CM8012304