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Improved lithium exchange at LiFePO₄ cathode particles by coating with composite polypyrrole–polyethylene glycol layers

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Abstract The polypyrrole–LiFePO₄ composites were synthesized by simple chemical oxidative polymerization of pyrrole (Py) monomer directly on the surface of LiFePO₄ particles. Properties of resulting polypyrrole–LiFePO₄ (PPy-LiFePO₄) samples (especially conductivity) are strongly affected by the preparation technique, polymer additives, and conditions during synthesis. For increasing of PPy-LiFePO₄ conductivity, we used polyethylene glycol (PEG) as additive during polymerization. The electrochemical behavior of the samples was examined by cyclic voltammetry and electrochemical impedance spectroscopy. It was found that PPy/PEG composite polymer decreased the particle to particle contact resistance. Impedance measurements showed that the coating of PPy/PEG significantly decreases the charge transfer resistance of LiFePO₄ electrodes.

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Introduction

Electroactive conducting polymers (ECPs) are conjugated polymers that exhibit electronic conduction when partially oxidized or reduced and are capable of undergoing oxidation/reduction reactions [1]. Examples of ECPs include polypyrrole (PPy), polyaniline, polythiophene, and polyphenylene vinylene. Several of these polymers have been tested as cathode materials for lithium batteries. Polypyrrole, for instance, can act as a host material for Li⁺-ion insertion/extraction in the voltage range of 2.0– 4.5 V versus Li/Li⁺ with a theoretical capacity of 72 mAh/g [2]. Therefore, PPy is a possible additive which can be used both as a conductive agent as well as a polymeric cathode material. Some problems for the practical utilization of conducting polymers such as PPy arise from poor mechanical properties like brittleness and bad processability. It has been demonstrated, however, that blending PPy with soft polymers like polyethylene glycol (PEG) is an attractive route to improve their mechanical properties without loosing their good electronic conductivity [3, 4].

During the past few years, LiFePO$_4$ received growing interest as a promising cathode material for low cost lithium batteries with reasonable cell voltage. The material is environmentally benign, inexpensive, nontoxic, and is characterized by a high theoretical specific capacity 178 Ah/kg [5]. Due to these properties, this material has become an important candidate for cathodes of low-power, rechargeable lithium batteries [6]. Bare LiFePO$_4$, however, shows very low ionic and electronic conductivity (electrical conductivity of the order of 10^{-11} S/cm). Therefore, the electrical conductivity is improved in most cases by dispersing high surface area carbon black or generating finely dispersed carbon on the LiFePO$_4$ particle surfaces [7–9]. Further possibilities concern the dispersion of copper/silver powders [10] and, more recently, coating with electronically conducting polymers, in particular with PPy [11, 12]. Particles covered with thin PPy films can be obtained by simple oxidative polymerization in a solution containing suspended LiFePO$_4$ particles [13]. It was also reported that the addition of PEG during PPy polymerization leads to enhanced electronic conductivities. As part of a study of improved LiFePO$_4$-based cathodes for lithium batteries, in this paper, we analyze the effect of PPy and PPy/PEG polymer coatings on LiFePO$_4$ particles and their electrochemical performance in corresponding cathode layers.

Experimental

Preparation of PPy-coated particles

One gram of pyrrole monomer (Aldrich Chemicals) and 1 g of commercial battery-grade, C-coated LiFePO$_4$ (Südchemie) were placed in a 100-mL round-bottom flask. The LiFePO$_4$ powder from Südchemie was used for all samples as base material in this study. Additional FeCl$_3$ (99.9%, Aldrich), used as oxidation agent, was dispersed in an aqueous solution of 0.1 mol/L HCl (50 mL) and added to the flask with LiFePO$_4$ powder. The pyrrole polymerization reaction was allowed to proceed for 6 h. The mixture was kept at ~4 °C and stirred vigorously. A black precipitate formed progressively during the reaction. The resulting PPy-coated LiFePO$_4$ powder was recovered by filtration, washed with water and acetone, and subsequently dried in an oven (~70 °C) up to a constant weight.

### Preparation of cathode layers and test cell

A slurry was made by mixing the PPy–LiFePO$_4$ as the active material with Super P and polyvinylidene fluoride in N-methyl-2-pyrrolidon with a weight ratio of 80:10:10. The slurry was then coated onto aluminum foil as current collector using the doctor-blade technique and subsequently dried in a vacuum oven at 120 °C for 18 h. Circular electrodes with 12 mm diameter were cut out of the coated foil with an area of 1.13 cm^2 and total mass of 1.5–2 mg on a substrate of Al foil. Test cells were assembled using these
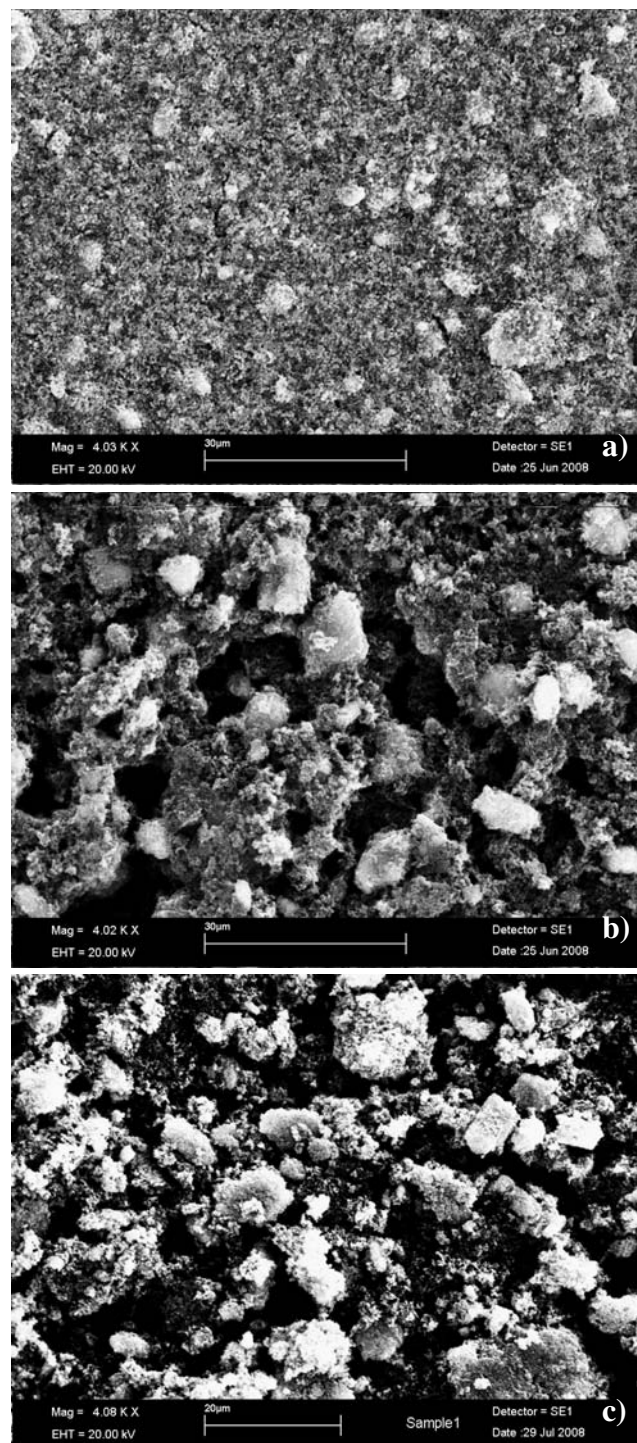
Fig. 1 Aluminum foil coated with slurry prepared **a** from pure LiFePO$_4$, **b** from PPy–LiFePO$_4$, and **c** from (PPy/PEG)–LiFePO$_4$
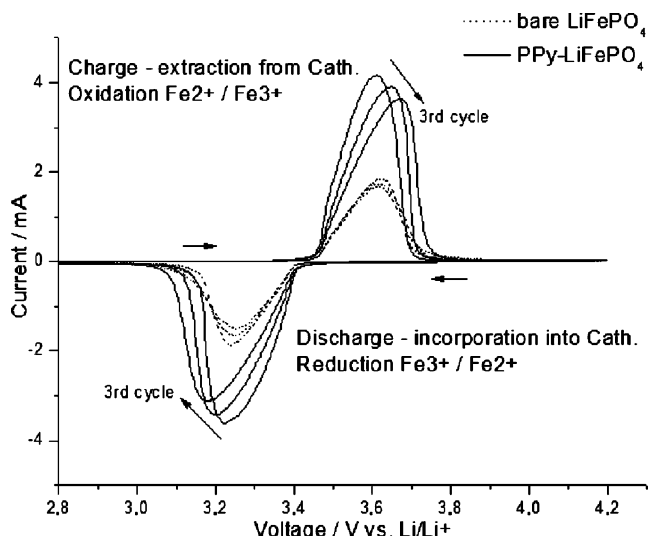
Fig. 2 Cyclic voltammograms (first three cycles shown) of untreated LiFePO$_4$ and PPy–LiFePO$_4$ measured at 23 °C and with a sweep rate of 50 µV/s

cathodes in a Swagelok T-cell together with a counter and a reference electrode made from lithium metal foil and a separator layer (SEPARION® and fiber glass separator Wattman GF/D). All handling was done in an argon-filled dry glove box (MBraun, Unilab, Germany). The electrolyte consisted of 1 M LiPF$_6$ in ethylene carbonate/ethyl methyl carbonate (volume ratio 1:1).

Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed on the test cells using an EG & G scanning potentiostat (Mod. 273) in the voltage range 2.8–4.2 V and with a scanning rate of 0.05 mV/s. AC impedance measurements were carried out in the frequency range 10^5 to 0.1 Hz with amplitudes of ±10 mV. Cycling measurements were controlled with an Arbin instrument system and performed between 2.5 and 4.5 V vs. Li$^+$/Li at room temperature.
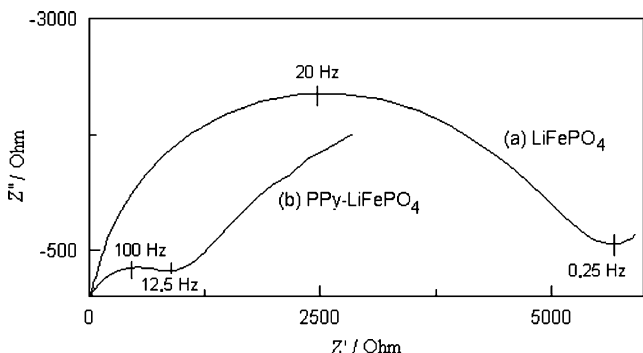
Fig. 3 Cole–Cole plot from AC impedance spectroscopy **a** for an untreated LiFePO$_4$ electrode and **b** for a PPy–LiFePO$_4$ electrode. Frequency range was 10^5–0.1 Hz

Results and discussion

### Electrochemical properties of PPy–LiFePO$_4$ electrodes

The net PPy content of the as-prepared PPy–LiFePO$_4$ composite powders were approximately 10 wt.%. Figure 1 shows the scanning electron microscopy (SEM) images of an aluminum foil coated with slurry prepared (a) in the first case from pure LiFePO$_4$ and (b) in the second case from PPy–LiFePO$_4$ as active material. The SEM image of PPy–LiFePO$_4$ composites clearly shows the higher porosity in comparison to nonmodified LiFePO$_4$. The surfaces of the LiFePO$_4$ particles are coated by the PPy polymers with a tissue-like structure consisting of fibers. The PPy coating is expected to reduce the particle-to-particle contact resistance and facilitates the transport of electrons from the current collector due to its electronic conductivity. In this way, the polypyrrole acts as an electronically conducting network which increases the rate of electron exchange in the depth of the electrode. Another advantage of the PPy coating is the enhanced porosity which acts in favor of an improved access of electrolyte to the cathode particles.

Another advantage of PPy films is the solubility for ions from the electrolyte and the mobility of dissolved ions which is a prerequisite for a fast lithium exchange. The advantageous properties observed for PPy-coated LiFePO$_4$ with PEG admixture may partially be explained by the increased salt solubility of the PPy/PEG composites as PEG is known as a very good solvent for lithium salts. On the other hand, PEG with dissolved salt is also known as a good polymer electrolyte which also contributes to its favorable role in the modified LiFePO$_4$ cathodes. We, therefore, assume that PPy/PEG composites as coatings on LiFePO$_4$ particles improve both the percolative transport of electrons along the resulting polymer network and the surface exchange of lithium ions due to the observed higher porosity and the good salt-dissolving property of PEG.

We investigated the influence of PPy on the conductivity of the PPy–LiFePO$_4$-based electrodes by cyclic voltammetry and electrochemical impedance spectroscopy. Figure 2 shows the cyclic voltammograms of electrodes from untreated LiFePO$_4$ and from PPy–LiFePO$_4$ measured at room temperature. The pair of anodic and cathodic peaks was observed between 3.2 and 3.7 V vs. Li/Li$^+$ with a

Table 1 Parameters obtained from equivalent circuit fitting of impedance spectra (see Figs. 3 and 5) on three differently prepared LiFePO$_4$ electrode layers with the same area (1.13 cm^2)

| Sample	R [Ω]	R_{CT} [Ω]
Bare LiFePO$_4$	14.1	5,890
PPy–LiFePO$_4$	12.3	834
PPy/PEG–LiFePO$_4$	9.9	118
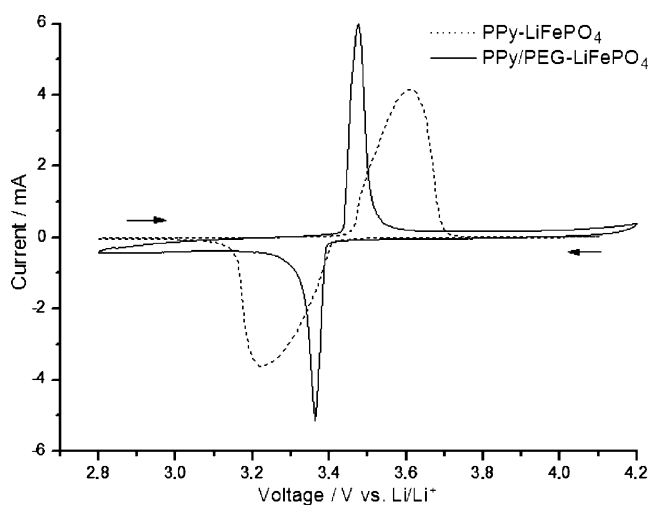
Fig. 4 Cyclic voltammograms (only first cycles shown) of PPy–LiFePO$_4$ and (PPy/PEG)–LiFePO$_4$ measured at ~23 °C and 50 μV/s. The broad peaks of the PEG-free electrode indicates a strong additional ohmic polarization in the cathode structure, presumably due to less ionic conductivity in the particle coatings

center at 3.2 V. This is the expected potential range for the reaction: $Li^+ + e^- + FePO_4 \rightleftarrows LiFePO_4$. The voltammograms indicated that only a single electrochemical reaction occurred during the charge and discharge of our samples. It can be clearly seen that the PPy–LiFePO$_4$ electrode sample is more active compared to the untreated LiFePO$_4$. The peaks are slightly asymmetric as the cathodic peak height is somewhat smaller than that of the anodic reaction. This may be due to irreversible reaction products formed by going up to a maximum cathodic potential of 4.2 V vs. Li/Li$^+$ which gives rise to a gradual lowering of peak height with increasing number of cycles.

AC impedance measurements were performed with the untreated LiFePO$_4$ and with the PPy–LiFePO$_4$ composite electrodes. Figure 3 shows the typical Nyquist plots for our samples. Impedance on Z' at the high-frequency region
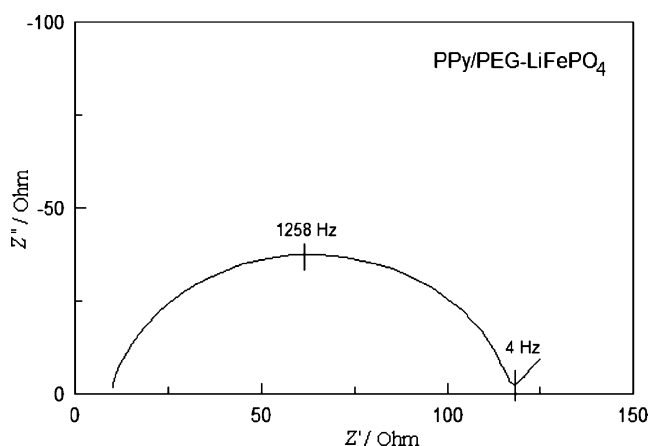

Fig. 5 Cole–Cole plot from AC impedance spectroscopy of a PPy/PEG–LiFePO$_4$ electrode. Frequency range was 10^5–0.1 Hz
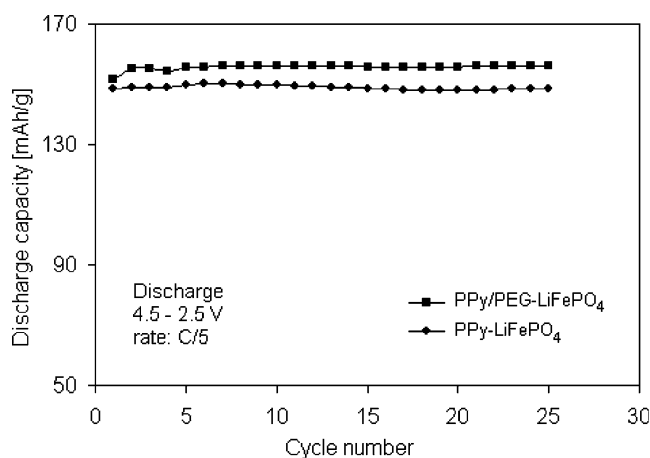
Fig. 6 Discharge capacity versus cycle number for PPy–LiFePO$_4$ and PPy/PEG–LiFePO$_4$ samples taken at a rate of C/5

represents the ohmic resistance—the resistance of the electrolyte and electrode. Impedance of the semicircle represents the migration of the Li$^+$ ions at the electrode/electrolyte interface through the solid electrolyte interface layer (high frequency) and charge transfer process (middle frequency). Diffusion of the lithium ions into the bulk of the electrode material represents Warburg impedance (straight line). Impedance spectra were fitted using an equivalent circuit. The calculated values fit well to the measured values. Parameters obtained from equivalent circuit are shown in Table 1. The resistance of electrolyte/electrode (R) is very similar because of adding Super P (carbon black) into the slurry which enables good conductivity of the electrodes. The charge transfer resistance (R_{CT}) is much lower for the PPy–LiFePO$_4$ sample. The polypyrrole coating increased the electrical conductivity between LiFePO$_4$ particles and promoted the charge transfer reaction in electrodes.
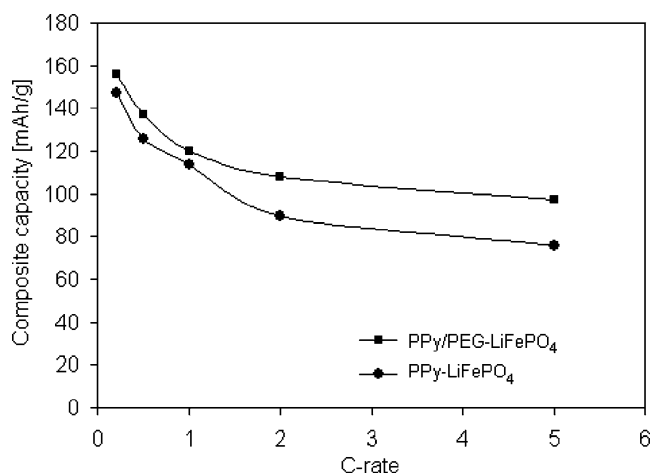
Fig. 7 Comparison of composite capacities of PPy–LiFePO$_4$ and PPy/PEG–LiFePO$_4$ with various C rates (C/5, C/2, 1C, 2C, 5C)

Electrochemical properties of PPy/PEG–LiFePO$_4$ electrodes

The (PPy/PEG)–LiFePO$_4$ electrodes were prepared like PPy–LiFePO$_4$, but at the beginning of the polymerization, additional PEG was added (with a weight ratio PPy/PEG= 33:1). However, we did not determine the resulting final weight ratio of the two polymers in the particle coating after pyrrole polymerization.

Because of the low processability and brittleness of pure polypyrrole, the PEG addition will also add additional elasticity to the resulting coatings which will stabilize the polypyrrole films during the volume changes accompanying the charge–discharge processes. The fiber-like tissue structure of PPy coatings in Fig. 1b changed to an increased roughness after adding the PEG (see Fig. 1c). Thus, the presence of PEG improves the mechanical stability of PPy vs. volume changes and it increases the specific surface area of the resulting particles.

Furthermore, cyclic voltammetry confirmed that (PPy/ PEG)–LiFePO$_4$ electrode layers show enhanced electrochemical activity. Whereas the PEG-free PPy–LiFePO$_4$ electrode shows very broad peaks (see Fig. 4), the (PPy/ PEG)–LiFePO$_4$ electrodes exhibit very sharp redox peaks with nearly theoretical difference of the potentials at the peak maxima. This is a clear indication of the great enhancement in the charge transfer kinetics of the lithium exchange at the electrode surface and for the enhanced transport of lithium ions and electrons within the three-dimensional cathode structure.

The electrochemical incorporation of Li$^+$ ions into the PPy–LiFePO$_4$ structure was slow and occurred only at a potential range 3.1–3.4 and 3.45–3.7 V (wide peaks in Fig. 4). Higher and narrow peaks are the result of the rapid insertion of Li$^+$ ions into the structure of PPy/PEG– LiFePO$_4$ but electrochemical reaction then continues up to 4.2 V (or 2.8 V) causing tailing of the peaks between 2.8– 3.2 and 3.7–4.2 V. The behavior found corresponds to the differences in the structure of PPy–LiFePO$_4$ and PPy/PEG– LiFePO$_4$.

The AC impedance measurements (see Fig. 5) supported the results from the CV technique very nicely. The net charge transfer resistance (R_{CT}) for the (PPy/PEG)–LiFePO$_4$ composite electrode was decreased by a factor of 7 in comparison with the PEG-free PPy–LiFePO$_4$ electrode. An overview of these values for all samples is given in Table 1.

Figure 6 shows the specific discharge capacities versus the number of cycles at a C/5 rate within the voltage range 2.5–4.5 V for PPy–LiFePO$_4$ and PPy/PEG–LiFePO$_4$ samples. With increasing cycle number, the capacity increased during the first five cycles and then reached the stable value, which indicates excellent stability. In the case of PPy–LiFePO$_4$, the discharge capacity was 147 mAh/g at

C/5 rate. The PPy/PEG–LiFePO$_4$ sample gave a capacity of 156 mAh/g. Comparison of composite capacities for both samples with various C rate is shown in Fig. 7. For samples with PEG, capacity loss with increasing C rate was 37.8%; for samples without PEG, it was 48.3%. Samples with PEG were found to have more capacity and better rate capability. This result suggested that PEG improved the electrochemical properties of PPy–LiFePO$_4$ cathodes.

Conclusions

PPy/PEG-modified LiFePO$_4$ cathode particles can be prepared in a simple way by oxidative polymerization in an aqueous dispersion. The PPy coating clearly improves the conductivity of the LiFePO$_4$ cathode film and increases the porosity and specific surface area of as-prepared electrodes. PPy/PEG coating leads to an easier access of both lithium ions and electrons to the three-dimensional LiFePO$_4$-based cathode structure. AC impedance measurements and results of cyclic voltammetry confirmed that PPy/PEG composite polymer improved the charge transfer reaction kinetics which is explained by a good mixed ionic– electronic conductivity of the PPy/PEG composite layer. Charge–discharge measurements confirmed the increase in capacity by using PEG which clearly demonstrates its unique characteristics for use in cathode material. We conclude that the efficiency and the achievable current densities of PPy/PEG–LiFePO$_4$-based lithium cathodes are considerably enhanced in comparison to conventional C-coated LiFePO$_4$ or LiFePO$_4$ modified by PPy alone.

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