

Surface treatment of LiFePO_4 cathode material with PPy/PEG conductive layer

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Abstract In this work, we studied LiFePO_4 particles coated with thin films of highly conductive polypyrrole (PPy) and their electrochemical performance in cathode layers of lithium cells. Carbon-free LiFePO_4 particles were synthesized by a solvothermal method. Besides this, a part of the experiments were carried out on commercial carbon-coated LiFePO_4 for comparison. Polypyrrole coated LiFePO_4 particles (PPy- LiFePO_4) were obtained by a straightforward oxidative polymerization of dissolved pyrrole on LiFePO_4 particles dispersed in water. The use of polyethylene glycol (PEG) as an additive during the polymerization was decisive to achieve high electronic conductivities in the final cathode layers. The carbon-free and carbon-coated LiFePO_4 particles were prepared with

PPy and with PPy/PEG coating. The obtained PPy- LiFePO_4 and PPy/PEG- LiFePO_4 powders were characterized by SEM, EIS, cyclic voltammetry, and galvanostatic charge/discharge measurements in lithium-ion cells with lithium metal as counter and reference electrode. Carbon-free LiFePO_4 coated with PPy/PEG hybrid films exhibited very good electrode kinetics and a stable discharge capacity of 156 mAh/g at a rate of C/10. Impedance measurements showed that the PPy/PEG coating decreases the charge-transfer resistance of the corresponding LiFePO_4 cathode material very effectively, which was attributed to a favorable mixed ionic and electronic conductivity of the PPy/PEG coatings.

Keywords Lithium-ion battery · Polypyrrole coating · LiFePO_4 · Cathode particles · Impedance

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Introduction

In the last 15 years, lithium ion and lithium polymer batteries have shown a remarkable and continuous development with respect to both the number of produced units as well as to the efficiency and life time. This progress was fed by the expansion of the market of portable electronic devices leading to lithium batteries with high energy and power density and good cycle life, which tend to replace nickel metal hydride and nickel cadmium batteries [1].

A large influence on the performance and cost of the lithium batteries is due to the properties of the cathode materials. Although lithium cobalt oxide was the most successful commercial cathode material in the past, its disadvantages are the price and the limitation of the cobalt resources. Another disadvantage is the safety problems of lithium cobalt oxide due to the possible formation of free

oxygen at high voltages, during overcharge, or in the case of increasing temperature. LiFePO_4 , on the other hand, does not form free oxygen such as cobalt oxide under those conditions, shows a substantial reversible capacity at around 3.4 V, good capacity of 170 mAh/g, low cost, long cycle life due to small volume changes. Furthermore, it is environmentally benign and well suitable in combination with polymer-based electrolytes [2].

However, the pristine LiFePO_4 has the disadvantage of poor rate performance due to a very low electronic conductivity of about $10^{-9} \text{ S cm}^{-1}$. Therefore, corresponding cathode particles usually are coated with a thin electronically conducting carbon layer, which has to provide a continuous electron transport between the surfaces of the cathode structure and the current collector. In a number of papers, preparation of carbon-included LiFePO_4 has been described and studied [3–5]. The reductive properties of carbon also improve the stability of the lithiated material and avoid formation of the Fe^{3+} oxidation state. Another approach has recently gained interest, which uses a coating by electroactive conductive polymers (ECPs) instead of carbon [6, 7]. Examples of ECPs include polypyrrole, polyaniline, polythiophene, and polyphenylene vinylene. These ECPs contain conjugated polymer chains that show electronic conductivity when partially oxidized or reduced. Hence, they are capable of undergoing oxidation/reduction reactions [8]. In this work, our attention focused on polypyrrole (PPy).

Polypyrrole even can act as a host material for a reversible Li^+ ion insertion/extraction in the voltage range from 2.0 to 4.5 V versus Li/Li^+ , with a theoretical capacity of 72 mAh/g [9]. Therefore, a PPy additive is not only an additive to enhance electronic conduction but also shows a cathodic activity. Usually, the practical utilization of conducting polymers like PPy is limited due to poor mechanical properties like brittleness and low processibility. In this work, however, we demonstrate that blending PPy with suitable soft polymers removes these constraints and yields a stable and elastic polymer network. Fine tuning of polymer properties is a well-established approach in polymer technology [10–12]. Furthermore, the blends with PPy as described here can also take the role of an electrochemically transparent binder with electronic and ionic conductivity. Accordingly, the results of this work show a promising approach towards polymer coated LiFePO_4 -based cathode structures with improved charge/discharge rates and long-time stability.

Experimental

Synthesis of LiFePO_4 particles Carbon-free LiFePO_4 powder was prepared by solvothermal method. Stoichiometric amounts of $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$, $\text{Fe}(\text{CH}_3\text{COO})_2$, and H_3PO_4

were dissolved in 70 ml of ethylene glycol. The liquid reaction mixture was placed in a round-bottom flask, open only at the top. This flask was connected to a condenser and refluxed vigorously for 72 h at 200 °C. The remaining product was filtered off and washed several times with distilled water and ethanol. In a subsequent step, the product was initially preheated at 60 °C for 5 h followed by sintering at 700 °C for 5 h under nitrogen atmosphere. The as-prepared carbon-free LiFePO_4 was used in order to compare the polymer coating approach between our solvothermal material and the carbon-coated commercial LiFePO_4 (Südchemie).

Preparation of LiFePO_4 polymer composites Pyrrole monomer (1.5 g, Aldrich Chemicals Co.) and 1 g of LiFePO_4 , synthesized as previously described, were placed in a 100 ml round-bottom flask. 1.42 g FeCl_3 (99.9% Aldrich) as oxidation agent was dispersed in 50 ml of an aqueous solution of 0.1 mol/l HCl. The resulting solution was added to the flask. The reaction was allowed to proceed for 7 h. During this time, the mixture was kept at ~4 °C and stirred vigorously. A black precipitate formed progressively during the reaction. The resulting polypyrrole- LiFePO_4 (PPy- LiFePO_4) powder was recovered by filtration, washed with water and acetone, and dried in an oven (~70 °C) until a constant weight was reached.

The preparation of PPy/PEG- LiFePO_4 samples with blended polymer coatings was done in the same way, except that polyethylene glycol (PEG 1000, Aldrich) as an additional component, was dissolved in the reaction mixture at the beginning of the polymerization (weight ratio PPy:PEG=33:1).

Materials characterization A slurry was prepared by mixing the active materials PPy- LiFePO_4 or PPy/PEG- LiFePO_4 with poly(vinylidene fluoride) (PVDF, Aldrich). PVDF was dissolved in N-methyl-2-pyrrolidone (NMP, Aldrich). The weight ratio of the active-coated electrode material and PVDF was 90:10. The slurry was then coated onto an aluminum foil (used as current collector) using the doctor-blade technique and subsequently dried in a vacuum oven at 80 °C for 18 h (until NMP was evaporated). Circular samples with 12 mm diameter were cut from the coated foil. Test cells were assembled using these cathodes in a Swagelok T cell together with a counter and a separate reference electrode made from lithium metal foil and a separator layer (SEPARION®, Evonik, 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 mol/l LiPF_6 in ethylene carbonate/ethylmethyl carbonate (EC/EMC, volume ratio 1:1 provided by MERCK, Germany). Cyclic voltammetry (CV) measurements were performed on the test cells using

an scanning potentiostat (EG & G, Mod. 273) in the voltage range from 2.8 to 4.2 V and with a scan 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. The morphology of the electrode samples was studied with a scanning electron microscope (Quanta 200 ESEM FEG).

Results and discussion

The influence of PPy on the conductivity of the PPy-LiFePO₄- and PPy/PEG-LiFePO₄-based electrodes was investigated by cyclic voltammetry, electrochemical impedance spectroscopy, and galvanostatic charge/discharge measurement. Four different sample materials were examined: PPy-LiFePO₄, PPy/PEG-LiFePO₄ (LiFePO₄=carbon-coated base material from Südchemie) and PPy-LiFePO₄, PPy/PEG-LiFePO₄ (LiFePO₄=carbon-free, synthesized in our lab).

Figure 1 shows a typical SEM image of LiFePO₄ particles prepared by solvothermal method. The particles show high crystallinity and the morphology shows various shapes like rods and plates with an average size between 300 and 400 nm. The morphology of the solvothermally synthesized LiFePO₄ materials was described in detail in a previous publication [12].

Figure 2 shows cyclic voltammograms measured at room temperature for electrodes made from PPy-LiFePO₄ (carbon-free LiFePO₄, prepared by solvothermal synthesis)

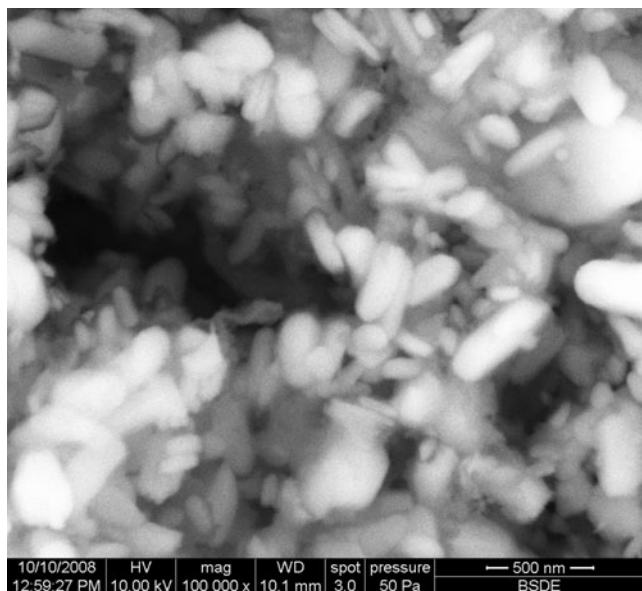


Fig. 1 SEM image of carbon-free LiFePO₄ prepared by solvothermal method

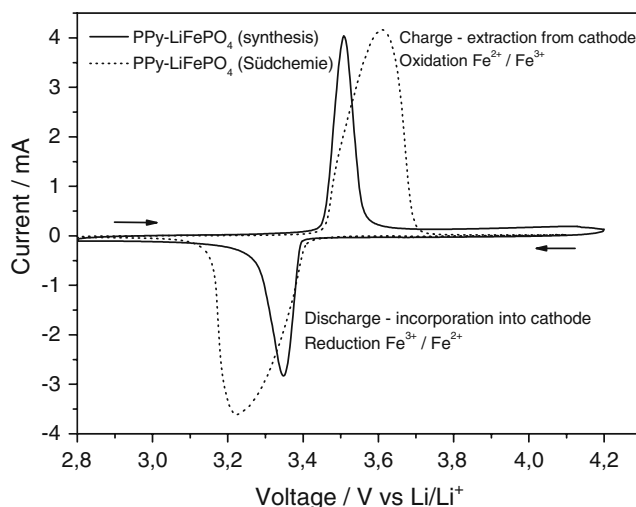


Fig. 2 Cyclic voltammograms (third cycle) of PPy-LiFePO₄ (carbon-free LiFePO₄ prepared by synthesis) and PPy-LiFePO₄ (LiFePO₄+4% carbon from Südchemie) measured at 23°C and with a sweep rate of 50 μV/s

and PPy-LiFePO₄ (LiFePO₄+4% carbon, Südchemie). The voltammograms clearly indicated that a single electrochemical reaction occurred during charging and discharging. The higher amount of carbon (Südchemie samples) resulted in higher electrical conductivity. Moreover, PPy-LiFePO₄ (synthesis) samples shown better reversibility and cyclability due to smaller size of particles and uniform distribution. The peaks of the carbon-free PPy-LiFePO₄ electrodes are much sharper than those of the commercial material. The peak heights of the electrodes from carbon-free LiFePO₄ are slightly unsymmetric, the cathodic reduction peak height being somewhat smaller than that of the anodic peak. This may be due to a higher degree of lithiation in the

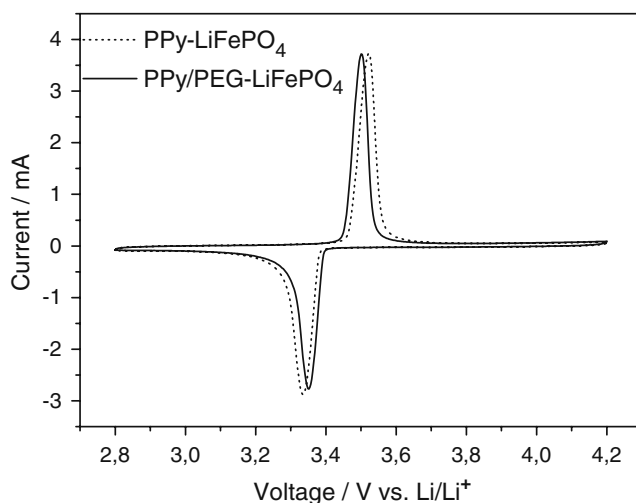


Fig. 3 Cyclic voltammograms (third cycle) of PPy-LiFePO₄ and PPy/PEG-LiFePO₄ (carbon-free LiFePO₄ prepared by synthesis) measured at 23°C and with a sweep rate of 50 μV/s

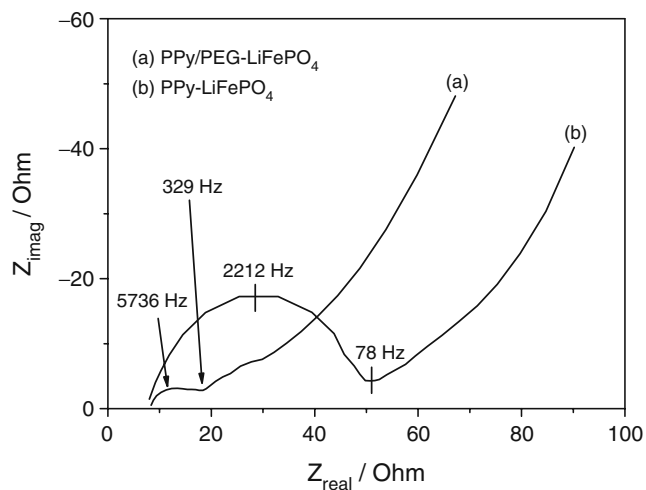


Fig. 4 AC impedance spectra (Nyquist diagram) of PPY/PEG-LiFePO₄ (a) and PPY-LiFePO₄ (b) electrodes (LiFePO₄ base material from Südchemie). The frequency range from left to right corresponds to 10⁵ to 0.1 Hz

solvothermal material (corresponding to a lower lithium deficit x as specified by the formula Li_{1-x}FePO₄). Although extraction of lithium occurs during the anodic peak, the generated empty ion sites at the particle surfaces are slowly filled by diffusion of lithium from the bulk of the particles so that less empty lithium sites are available during the subsequent cathodic peak on the average. This explains a lower cathodic current in a highly lithiated sample.

Figure 3 shows the cyclic voltammograms of PPY-LiFePO₄ and PPY/PEG-LiFePO₄ electrodes prepared from carbon-free LiFePO₄ material. They show reversible peaks centered at 3.5 V associated with the reduction and reoxidation of the LiFePO₄. The difference in the peak potentials (ΔE_p) for PPY-LiFePO₄ cathode is 186 mV and

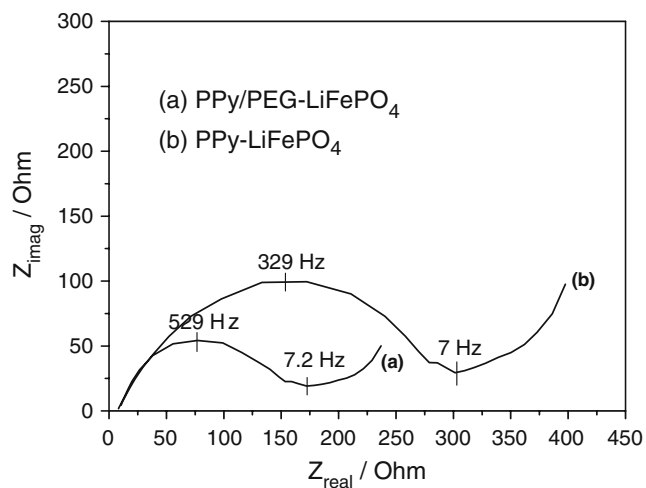


Fig. 5 AC impedance spectra (Nyquist diagram) of PPY/PEG-LiFePO₄ (a) and PPY-LiFePO₄ (b) electrodes (carbon-free LiFePO₄ prepared by solvothermal synthesis). The frequency range from left to right corresponds to 10⁵ to 0.1 Hz

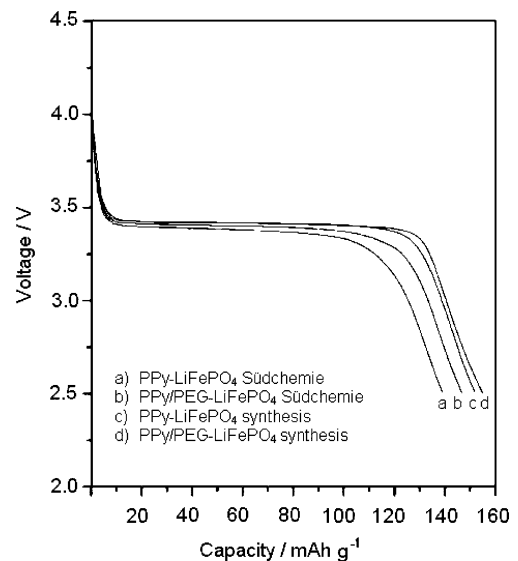


Fig. 6 The initial discharge curves of the LiFePO₄ samples covered by polymer layer in the voltage range of 2.5–4 V at C/10 rate

for PPY/PEG-LiFePO₄ cathode 150 mV. This clearly shows that reversibility and conductivity of PPY/PEG-LiFePO₄ cathodes are better than those without PEG additive.

Comparative AC impedance measurements were performed with the PPY-LiFePO₄ and with the PPY/PEG-LiFePO₄ composite electrodes. Figure 4 shows typical Nyquist plots for samples prepared from the commercial LiFePO₄ material (Südchemie). Figure 5 depicts typical impedance plots of composite LiFePO₄ samples prepared from carbon-free LiFePO₄ particles. The high frequency limiting value of the real part Z_{real} of the impedance represents the ohmic resistance, i.e., the sum of the series resistances due to the electrolyte and the electrode. The depressed semicircle depends on the charge/discharge state with respect to lithium and therefore, is largely determined by the charge-transfer

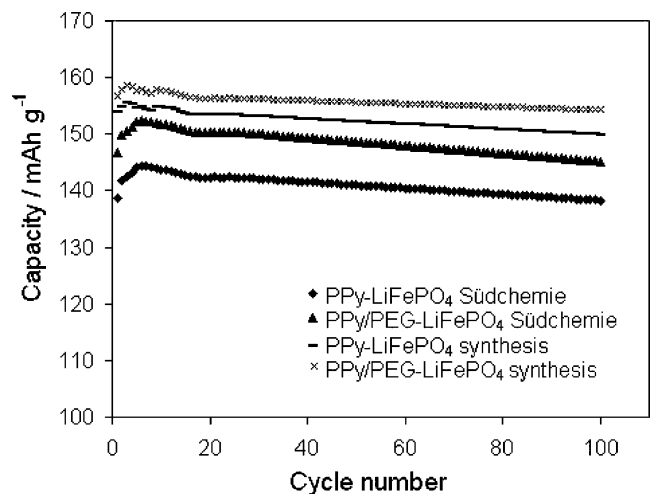


Fig. 7 Discharge capacity versus cycle number for different LiFePO₄ samples taken at a rate of C/10

impedance. It may be represented by a parallel circuit of the transfer resistance and a distributed capacitance of the electrolyte/electrode interface (expressible in the form of a constant phase element with a phase angle smaller than $\pi/2$).

The low-frequency region is characterized by a steep increase of both the real and the imaginary part of the impedance. This is typical for a rate limiting incorporation/extraction of lithium into or out of the electrode particles. Accordingly, it will depend on the coupled transport of electrons and lithium ions within the heterogeneous electrode network. For a homogeneous mixed ion and electron conducting electrode, this would correspond to a rate limitation by chemical diffusion in the bulk giving rise to finite Warburg impedance. Its limiting high-frequency dependence is expected as constant phase element with phase angle $\pi/4$. But in our case, the hybrid electrode has a three-dimensional structure consisting of an electrode/electrolyte network with distributed fast and slow paths for ion and electron transport. Hence, one expects an equivalent circuit with corresponding distributed Warburg impedance elements which will show more complicated frequency dependence.

Therefore, in Fig. 4, the relative increase of the real part of the impedance to the right of the small semicircle in the low-frequency region is mainly indicating a net electronic and ionic transport resistance. Both, this low-frequency transport resistance as well as the charge-transfer resistance (diameter of the semicircle) of our samples, increased from PPy/PEG-LiFePO₄ to PPy-LiFePO₄, which is in contrast with the inverse order of the capacity measurements (Fig. 6). Due to the lower electronic and ionic charge-transfer resistance of PPy/PEG-LiFePO₄ electrode, the electrode reaction kinetics became excellent. This result is most probably explained by a parallel improvement of the electronic and the ionic transport in the adherent PPy/PEG composite films acting as mixed conducting material. The presence of PEG enhances the salt solubility and therefore, increases the concentration of mobile cations and anions. Furthermore, a high p-type conductivity of the PPy needs stabilization by negatively charged anions, which will also be favored by the good solvent properties of the PEG additive. To conclude, the PPy/PEG coatings lead to an improved and balanced electrical conductivity at the surface of the LiFePO₄ particles and, in this way, facilitate charge-transfer reactions of corresponding electrode materials.

The constant-current discharge curves (Fig. 6) for the four composite samples show a flat voltage plateau centered at 3.4 V, which is a characteristic for LiFePO₄ [2, 13, 14]. At the lowest applied discharge rate of C/10, the highest specific capacity in our experiments was 156 mAh/g. It was obtained on PPy/PEG-LiFePO₄ (phosphate from solvothermal synthesis), which also showed an excellent rate capability. Figure 7 shows the specific

discharge capacities for different coatings and LiFePO₄ base materials versus the number of cycles at a rate of C/10 and within a voltage range between 2.5 and 4.5 V. During the first six cycles, the charge/discharge capacity typically increased and finally reached a constant value indicating an excellent stability. In the case of PPy-LiFePO₄ (Südchemie), the discharge capacity was 138 mAh/g (at C/10). PPy/PEG-LiFePO₄ (Südchemie) samples yielded a slightly higher capacity of 146 mAh/g. The data obtained on the carbon-free LiFePO₄ were even slightly better: PPy-LiFePO₄ (carbon free) gave 153 mAh/g and PPy/PEG-LiFePO₄ (carbon free) yielded 156 mAh/g.

Conclusions

A new promising route to prepare high-performance phosphate-based cathode materials for lithium-ion batteries was developed. Bare LiFePO₄ was synthesized by solvothermal method, and the particle size of the resulting material was about 300–400 nm. In order to increase the conductivity of LiFePO₄ particles, PPy or polymer mixture PPy/PEG were studied. The PPy coatings improved the conductivity of LiFePO₄ and increased the specific surface areas of the corresponding electrodes. The hybrid coating with PPy/PEG gave the best results. This was attributed to an optimized access of lithium ions and electrons at the coated LiFePO₄ surfaces. The electrode activity, the charge-transfer rates, and the charging/discharging characteristics were improved with PPy/PEG coatings. It can be concluded that the hybrid material PPy/PEG-LiFePO₄ reported here is a promising cathode material for lithium-ion batteries.

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References

1. Armand M (1994) *Solid State Ionics* 69:309
2. Ravet N, Chouinard Y, Magnan JF, Besner S, Gauthier M, Armand M (2001) *J Power Sources* 503:97
3. Baker J, Saidi MY, Swoyer JL (2003) *Electrochem Solid State Lett* 6:A53
4. Franger S, Le Cras F, Bourbon C, Rouault H (2002) *Electrochem Solid State Lett* 5:A231
5. Chen Z, Dahn JR (2002) *J Electrochem Soc* 149:A1184

6. Kuwabata S, Masui S, Yoneyama H (1999) *Electrochim Acta* 44:4593
7. Wang GX, Yang L, Chen Y, Wang JZ, Bewlay S, Liu HK (2005) *Electrochim Acta* 50:4649
8. Tallman DE, Vang C, Wallace GG, Bierwagen GP (2002) *J Electrochem Soc* 149(3):C173
9. Osaka T, Momma T, Nishimura K, Kakuda S, Ishii T (1994) *J Electrochem Soc* 141:1994
10. Kassim A, Ekarmul Mahmud HNM, Yee LM, Hanipah N (2006) *Pacific J Sci Technol* 7(2):103
11. Fedorková A, Wiemhöfer HD, Oriňáková R, Oriňák A, Stan MC, Winter M, Kaniansky D, Alejos AN (2009) *J Solid State Electrochem* 13:1867
12. Fedorková A, Alejos AN, Gomez-Romero P, Oriňáková R, Kaniansky D (2009) Structural and electrochemical studies of PPy/PEG-LiFePO₄ cathode material for Li-ion batteries. *Electrochim Acta*. doi:10.1016/j.electacta.2009.09.060
13. Croce F, Epifanio AD, Hassoun J, Deptula A, Olczac T, Scrosati B (2002) *Electrochem Solid-State Lett* 5:A47
14. Takahashi M, Tobishima S, Takei K, Sakuri Y (2002) *Solid State Ionics* 148:283