



## PPy doped PEG conducting polymer films synthesized on LiFePO<sub>4</sub> particles

Andrea Fedorková<sup>a,\*</sup>, Renáta Oriňáková<sup>b</sup>, Andrej Oriňák<sup>b</sup>, Ivan Talian<sup>a</sup>, Andreas Heile<sup>c</sup>, Hans-Dieter Wiemhöfer<sup>d</sup>, Dušan Kaniansky<sup>a</sup>, Heinrich F. Arlinghaus<sup>c</sup>

<sup>a</sup> Department of Analytical Chemistry, Faculty of Science, Comenius University, Mlynská Dolina, SK-84215 Bratislava 4, Slovak Republic

<sup>b</sup> Institute of Chemistry, Faculty of Science, P.J. Šafárik University, Moyzesova 11, SK-04154 Košice, Slovak Republic

<sup>c</sup> Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, D-48149 Münster, Germany

<sup>d</sup> Institute of Inorganic and Analytical Chemistry, Westfälische Wilhelms-Universität Münster, Correnstrasse 30, D-48149 Münster, Germany

### ARTICLE INFO

#### Article history:

Received 9 September 2009

Received in revised form

20 December 2009

Accepted 3 January 2010

Available online 11 January 2010

#### Keywords:

Polypyrrole

Polyethylene glycol

LiFePO<sub>4</sub>

TOF-SIMS

Li-ion batteries

Cathode material

### ABSTRACT

In this work, polyethyleneglycol (PEG) is introduced into polypyrrole (PPy) film coated on LiFePO<sub>4</sub> powder particles to promote the properties of cathode material for lithium-ion batteries. The enhancement of the electrochemical activity by the substitution of a carbon with electrochemically active polymer is investigated. Films of the PPy doped with the PEG were prepared by the chemical oxidative polymerization of pyrrole (Py) monomer. PEG has been added as an additive during polymerization process to improve mechanical and structural properties of the PPy in final PPy/PEG–LiFePO<sub>4</sub> cathode material. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge/discharge measurements were employed to characterize the electrochemical properties of PPy/PEG–LiFePO<sub>4</sub> material. The electrochemical performance of PPy–LiFePO<sub>4</sub> electrodes was greatly improved by introduction of PEG into the PPy films. Charge/discharge measurements confirmed the increase in capacity when applying PEG in PPy. The morphology and particle sizes of the prepared cathode powder material were investigated by scanning electron microscopy (SEM) and particle size analysis (PSA). Distribution of PPy and PPy/PEG films onto the LiFePO<sub>4</sub> particles surface was studied by time of flight secondary ion mass spectrometry (TOF-SIMS). In addition to polymeric coating layer on the surface of PPy–LiFePO<sub>4</sub> composite particles, some PPy unequally distributed between the particles was found. The median diameter value is 4.92 μm for PPy–LiFePO<sub>4</sub> sample. TOF-SIMS measurements and SEM images confirmed that thickness of polypyrrole coating on LiFePO<sub>4</sub> particles is about 100 nm.

© 2010 Elsevier B.V. All rights reserved.

### 1. Introduction

Olivine LiFePO<sub>4</sub> has received much attention recently as a promising storage compound for cathodes in Li-ion batteries. It has an energy density similar to that of LiCoO<sub>2</sub>, the current industry standard for cathode materials in Li-ion batteries, but with a lower raw material cost and an increased level of safety. This compound has a theoretical capacity of 170 mAh g<sup>-1</sup> and a constant open-circuit voltage of 3.4 V vs. Li/Li<sup>+</sup> that is matched to polymer electrolytes [1]. Due to these properties, this material has become an important candidate for cathodes of low-power, rechargeable lithium batteries [2]. Only one limitation of LiFePO<sub>4</sub> is low intrinsic electronic conductivity which limits its application in commercial systems. Bare LiFePO<sub>4</sub> is an insulator with electrical conductivity of about  $\sim 10^{-11}$  S cm<sup>-1</sup>. One of the possibilities how to increase electrical conductivity of LiFePO<sub>4</sub> is coating with conducting polymers [3,4]. It was reported, that LiFePO<sub>4</sub>-carbon composites show

higher discharge capacity than pure LiFePO<sub>4</sub> and an excellent rate property [5]. The particle size also greatly influences the capacity and rate performance of LiFePO<sub>4</sub> due to the short diffusion length of lithium ions [6,7], but too small particles will reduce the tap density and energy density [8]. Therefore, appropriate particle size with good electronic conductivity is important for LiFePO<sub>4</sub> material to reach the best electrochemical properties [5]. The various methods employed involved reaction with carbon [9–11], reaction with sugar [8], and using metal nanoparticles in a sol-gel reaction [12]. A problem with using these conductive additives is that it necessitates many extra steps in the electrode production process, increasing amount of time and cost involved in the electrode preparation.

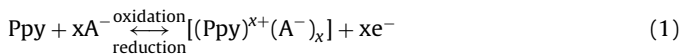
Polypyrrole (PPy) is one of the conducting polymers which can be used in Li-ion batteries in combination with LiFePO<sub>4</sub> as a base. PPy, for instance, can act as a host material for Li<sup>+</sup>-ion insertion/extraction in the voltage range of 2.0–4.5 V vs. Li/Li<sup>+</sup>, with a theoretical capacity of 72 mAh g<sup>-1</sup>. Therefore, PPy is a possible additive which can be used both as a conductive agent as well as a polymeric cathode material [13]. Films of PPy were prepared by simple chemical oxidative polymerization of pyrrole (Py) monomer

\* Corresponding author. Tel.: +421 55 2342327; fax: +421 55 6222124.

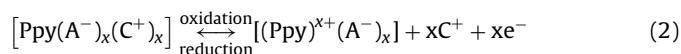
E-mail address: [fedorkova@fns.uniba.sk](mailto:fedorkova@fns.uniba.sk) (A. Fedorková).

directly on the surface of LiFePO<sub>4</sub> particles. It was also reported that the addition of polyethylene glycol (PEG) during Py polymerisation leads to enhanced electronic conductivities [14]. Blending with insulating polymer PEG is an attractive route to improve mechanical properties of PPy without losing electronic conductivity of the resulting composite polymer [15].

It was found [16] that insertion and extraction of anions to electrolyte solution is accompanying the electrochemical activity of PPy:



where A<sup>-</sup> is a dopant anion to compensate positive charges generated during the oxidation process and *x* is the doping level. However, the insertion of cations into the film, during the cathodic process has been described as:



It is interesting to know that at lower PEG concentration the main process of charge transfer would be associated with the anionic exchange, according to Eq. (1), although PEG is a cationic conductor. Insertion of cations into the PPy film is a secondary step in charge-transfer process. However, when the PEG concentration increases, a large amount of PEG is incorporated into the PPy and a more compact structure is attained, which hinders the ejection of anions and the process associated with the Eq. (1) becomes favoured.

A detailed study on the influence of the PEG introduction into PPy film synthesised on LiFePO<sub>4</sub> powder particles on the electrochemical behaviour, surface morphology and polymeric film distribution is presented in this work, in order to optimise its performance in Li-ion batteries.

## 2. Experimental

### 2.1. Preparation of PPy/PEG coated particles

1 g of pyrrole monomer (Aldrich Chemicals Co.) and 1 g of commercial battery-grade, carbon coated (C-coated) LiFePO<sub>4</sub> (Südchemie) were placed in a 100 ml round-bottom flask. The (C-coated) LiFePO<sub>4</sub> powder was used for all samples as base material in this study. Additional 1.42 g of FeCl<sub>3</sub> (99.9% Aldrich), used as oxidation agent, was dispersed in an aqueous solution of 0.1 mol l<sup>-1</sup> HCl (50 ml) and added to the flask with LiFePO<sub>4</sub> powder. Then the PEG was added in weight ratio PPy:PEG = 33:1. 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<sub>4</sub> powder was isolated by filtration, washed with water and acetone and subsequently dried in an oven (~70 °C) up to a constant weight.

### 2.2. Preparation of samples for TOF-SIMS

A slurry was made by mixing the PPy-LiFePO<sub>4</sub> (PPy/PEG-LiFePO<sub>4</sub> or pure PPy/PEG) as the active material with poly(vinylidene fluoride) (PVDF). PVDF was dissolved in N-methyl-2-pyrrolidone (NMP). A weight ratio of active material and PVDF was 90:10. The slurry was then coated onto aluminum foil as current collector using the doctor-blade technique and subsequently dried in a vacuum oven at 80 °C for 18 h (NMP was than evaporated). Circular samples with 12 mm diameter were cut out of the coated foil, with an area about 1.13 cm<sup>2</sup> and total mass of 1.5–2 mg on a substrate of Al foil.

### 2.3. Methods

Properties of cathode materials were analyzed by time of flight secondary ion mass spectrometry (TOF-SIMS). TOF-SIMS experiments were performed with a TOF-SIMS IV equivalent instrument built at the University of Münster which used a 25 keV Bi<sup>3+</sup> primary ion-gun (ION-TOF GmbH). The primary ion beam was rastered on 10 μm × 10 μm areas with a current of 0.12 pA. The removal rate was about 10 nm s<sup>-1</sup>.

For electrochemical measurements we used samples prepared by the same procedure as for TOF-SIMS measurements. These electrodes were assembled (in Swagelok T-cell) with Li counter and reference electrodes, with a layer of separator (fiber glass separator Wattman GF/D) to make the test cells. The cells were assembled in an argon filled glove box (Mbraun, Unilab, Germany). 1 mol l<sup>-1</sup> LiPF<sub>6</sub> in ethylene carbonate/ethylmethyl carbonate (EC/EMC) 1:1 by volume was the electrolyte used in the experiments.

Cyclic voltammetry (CV) measurements were performed using EG & G scanning potentiostat (Mod. 273). Voltage range was 2.8–4.2 V and scanning rate was 0.05 mV s<sup>-1</sup>. DC potential was 3.83 V.

AC impedance measurements were carried out in the frequency range 10<sup>5</sup> to 0.1 Hz with amplitudes of ±10 mV.

Constant current charge/discharge experiments were performed in a three-electrode cell between 2.5 and 4.5 V vs. Li<sup>+</sup>/Li at room temperature. The charge/discharge rate used for our experiments was C/5.

Scanning electron microscope Quanta 200 ESEM FEG was used to study the morphology of samples.

Cilas 1064 particle size analyser was used to determine size of the LiFePO<sub>4</sub> particles with and without polymer coating.

## 3. Results and discussion

The influence of PPy and PPy/PEG coating film on electrochemical properties of the LiFePO<sub>4</sub> based electrodes was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. Fig. 1 shows the cyclic voltammograms of electrodes from PPy-LiFePO<sub>4</sub> and from PPy/PEG-LiFePO<sub>4</sub> measured at room temperature. The pair of anodic and cathodic peaks was observed between 3.3 and 3.5 V vs. Li/Li<sup>+</sup>. This is the expected potential range for the reaction:

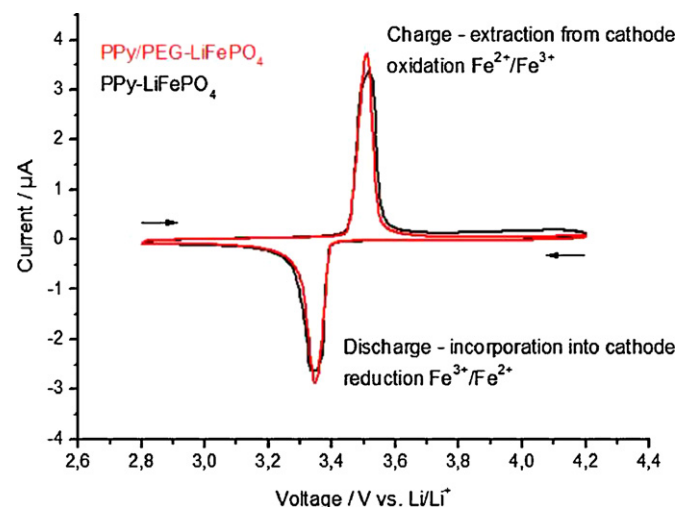


Fig. 1. Cyclic voltammograms (3rd cycle) of PPy-LiFePO<sub>4</sub> and PPy/PEG-LiFePO<sub>4</sub> electrodes measured at room temperature and 50 μV s<sup>-1</sup>.

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/PEG–LiFePO<sub>4</sub> electrode sample is more active as compared to the untreated PPy–LiFePO<sub>4</sub>. Cathodic peak is somewhat smaller than the peak of the anodic reaction. This may be due to irreversible reaction products formed by going up a maximum cathodic potential of 4.2 V vs. Li/Li<sup>+</sup> which gives rise to a gradual lowering of peak height with increasing number of cycles. CV profiles reflect not just the electrochemical properties of the active material but also those of the entire electrode. Note that the reaction is a phase change (FePO<sub>4</sub> → LiFePO<sub>4</sub>) coupled with in-diffusion of Li. Therefore, it is coupled to diffusion inside the solid. It is not a single electrode reaction limited to the electrode surface. There will be superposition of transport overvoltage.

AC impedance measurements were performed with the PPy–LiFePO<sub>4</sub> and with the PPy/PEG–LiFePO<sub>4</sub> composite electrodes. Fig. 2 shows typical Nyquist plots for our samples. Impedance on the Z' at high frequency region represents the ohmic resistance—the resistance of the electrolyte and electrode. Impedance of the semicircle represents the migration of the Li<sup>+</sup> ions at the electrode/electrolyte interface through the SEI layer (high frequency) and charge-transfer process (middle frequency). 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  $\pi/2$ ). Diffusion of the lithium ions into the bulk of the electrode material represented by Warburg element (straight line) is typical for porous electrodes [17]. The low-frequency region is characterized by a step 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. 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. The CPE is commonly used to describe the depressed semicircle that results from a porous electrode. The PPy/PEG coating increased the electrical conductivity between LiFePO<sub>4</sub> particles and it promotes charge-transfer reaction in electrodes.

Fig. 3 shows the discharge capacity of LiFePO<sub>4</sub> in combination with different polymer compound. Specific discharge capacities vs. number of cycles at a C/5 rate within the voltage range 2.5–4.5 V

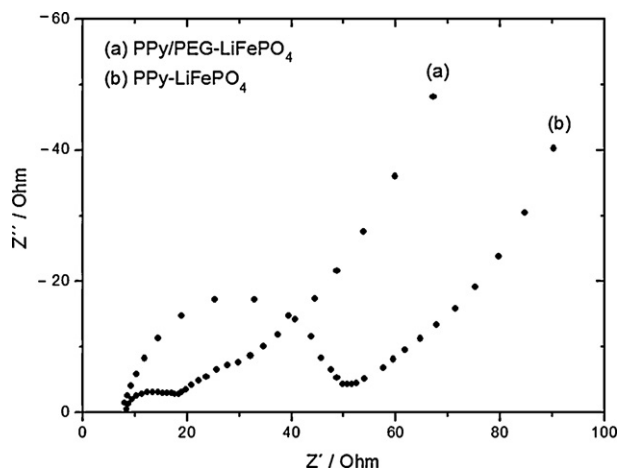


Fig. 2. AC impedance spectra of (a) PPy/PEG–LiFePO<sub>4</sub> and (b) PPy–LiFePO<sub>4</sub> electrodes. Frequency range 10<sup>5</sup> to 0.1 Hz.

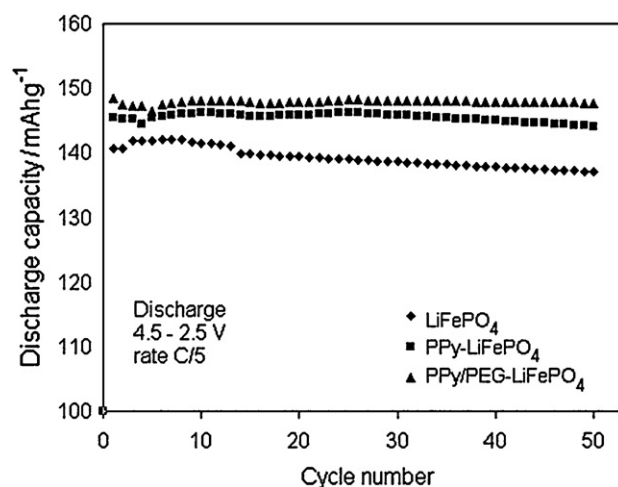


Fig. 3. Discharge capacity vs. cycle number for LiFePO<sub>4</sub>, PPy–LiFePO<sub>4</sub> and PPy/PEG–LiFePO<sub>4</sub> samples taken at a rate of C/5.

for LiFePO<sub>4</sub>, PPy–LiFePO<sub>4</sub> and PPy/PEG–LiFePO<sub>4</sub> samples are represented. With increasing cycle number, the capacity increased during the first few cycles and then reached a stable value, which indicates excellent stability. Bare LiFePO<sub>4</sub> in comparison with LiFePO<sub>4</sub> composites shows lower stability during cycling. This behaviour can be explained by the existence of polymeric coating which enhances the electronic conductivity of bare LiFePO<sub>4</sub> and provides inter-grain connectivity to the hybrid electrode. In the case of LiFePO<sub>4</sub> discharge capacity was 138 mAh g<sup>−1</sup> at C/5 rate. The PPy–LiFePO<sub>4</sub> sample gave a capacity of 146 mAh g<sup>−1</sup> and PPy/PEG–LiFePO<sub>4</sub> 148 mAh g<sup>−1</sup>. All samples showed a good cycling stability and the specific capacities remain nearly unchanged within 50 cycles. From Fig. 3, it is evident that PPy/PEG–LiFePO<sub>4</sub> provides best cycling performance and capacity.

Fig. 4a shows the scanning electron microscopy (SEM) image of the typical LiFePO<sub>4</sub> particles. The powder consisted of small particles about 500 nm to 1 μm, some particles formed agglomerates of 1.5–2 μm. Only material with an adequate particle size (not very big, not very small) is useful to produce a powerful LiFePO<sub>4</sub>-cathode based battery system. The LiFePO<sub>4</sub> particles coated with the PPy are shown in Fig. 4b. It is clearly seen that the particles are covered with the layer of polypyrrole. It seems that PPy–LiFePO<sub>4</sub> composite has a PPy-coating layer on the surface of particles and some PPy is unequally distributed between the particles. The layer of PPy/PEG composite polymer is distributed likewise as the layer of pure polypyrrole. The influence of the PEG additive is mainly detectable by the improved electrochemical kinetics of the cathode material. No difference in surface structure was observed for PPy/PEG–LiFePO<sub>4</sub> samples.

The small particles and loosely coupled agglomerates facilitated the penetration of the electrolyte and reduced the lithium diffusion length within the particles. This is helpful to enhance the electrochemical properties of Li/LiFePO<sub>4</sub> batteries.

Because the polymerization of pyrrole takes place in solution, clusters of pure PPy are formed between particles during reaction. The amount and distribution of the PPy clusters could not be identified from the SEM images. Accordingly we examined the particle size range for these samples more closely. The particle size distribution is shown in Fig. 5. It may be seen that while pure LiFePO<sub>4</sub> particles (Fig. 5a) show a very narrow distribution (average distribution 1.64 μm), the range of particle size for PPy–LiFePO<sub>4</sub> (Fig. 5b) is quite different. For the PPy–LiFePO<sub>4</sub> particles (Fig. 5b) three granulometric fractions can be distinguished: 0.1–0.8, 0.8–8 and 8–20 μm. Smallest size fraction comprises the PPy particles



formed during the chemical polymerization of Py in the bulk, not on the surface of  $\text{LiFePO}_4$  particles. A medium granulometric class is formed by the uncoated and PPy coated  $\text{LiFePO}_4$  particles as well by clusters of these particles. The largest fraction consists of aggregates of PPy,  $\text{LiFePO}_4$  and PPy– $\text{LiFePO}_4$  particles. The median diameter value is  $4.92 \mu\text{m}$  for PPy– $\text{LiFePO}_4$  sample.

Since the PPy can act as a cathode material the capacity of coated  $\text{LiFePO}_4$  is higher even if the particle size was increased. Particle size distribution only confirmed formation of PPy on the particle surface and also between the particles. By coating the conductive polypyrrole on the surface of the  $\text{LiFePO}_4$  particles, the electrical conductivity can be significantly improved, which facilitates the charge-transfer reaction. The electrodes with better electrical conductivity should have better capacity. Of course, a big increase in PPy content in the composite would reduce the specific capacity of the composite electrode (capacity of  $\text{LiFePO}_4$  is  $170 \text{ mAh g}^{-1}$  and PPy is  $72 \text{ mAh g}^{-1}$ ). Therefore, the specific capacity of PPy– $\text{LiFePO}_4$  composite electrodes is compromised by the PPy content.

The TOF-SIMS analysis confirms that the ionic residues of PPy were present around the  $\text{LiFePO}_4$  particle or around the agglomerate of few of these particles. These fragments, namely: 39, 41, 128

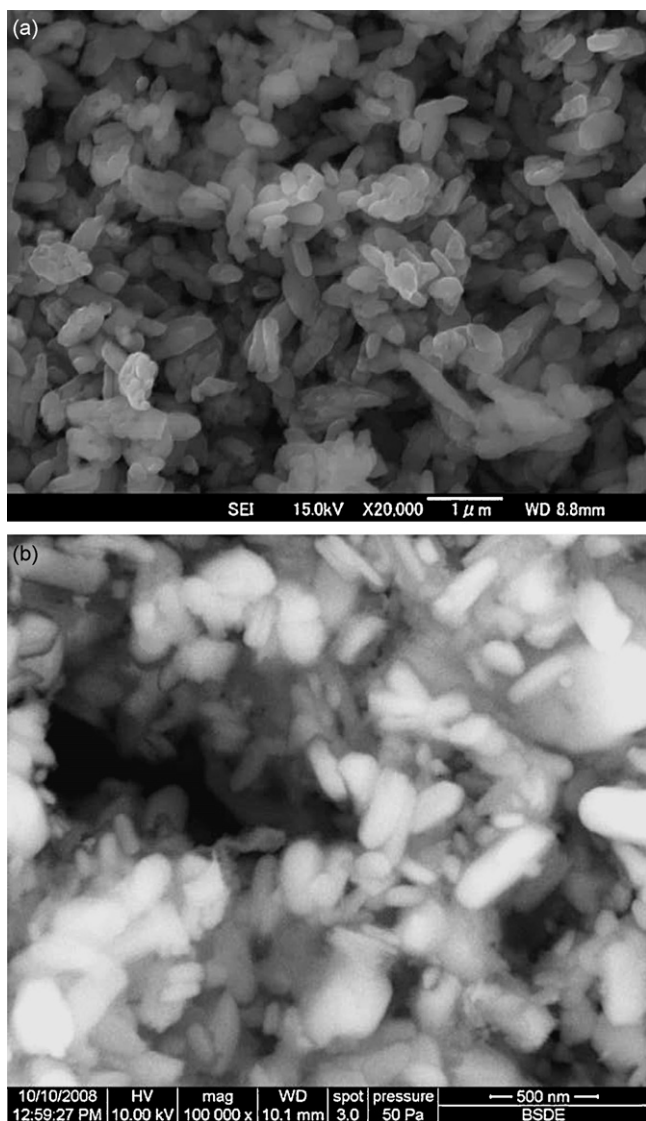


Fig. 4. The SEM image of (a) pure  $\text{LiFePO}_4$  and (b)  $\text{LiFePO}_4$  particles covered with PPy.

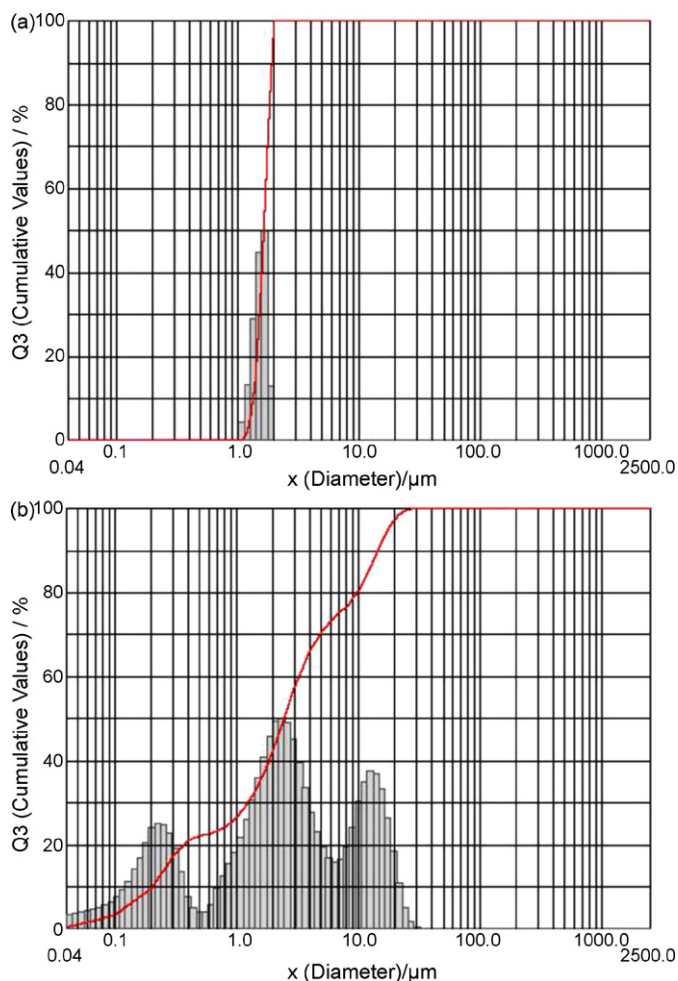


Fig. 5. Particle size distribution of (a) pure  $\text{LiFePO}_4$  and (b) PPy– $\text{LiFePO}_4$  particles.

and 144 corresponding to the  $[\text{C}_3\text{H}_3]$ ,  $[\text{CH}_3\text{CN}]$ ,  $[2\text{CH}_3(\text{CH}_2)_3\text{NH}]$  (e.g.  $[2\text{PPy} + 4\text{H}]$ ) and  $[\text{CH}_3(\text{CH}_2)_3\text{N}(\text{CH}_2)_3\text{CH}_3]$ , respectively, are descended from PPy film. These fragments were obtained also by the thermal decomposition analysis of the pure PPy. The TOF-SIMS image of the  $\text{LiFePO}_4$  particles mixed with the PPy showed good coverage of the  $\text{LiFePO}_4$  particles with the PPy layer (Fig. 6).

The ion with  $m/z = 56$  belonging to  $[\text{Fe}]^+$  originated from the  $\text{LiFePO}_4$  particles. Its distribution over the scanned area in TOF-SIMS maps has clearly the same shape as the fragments originated from the PPy (Fig. 6). The SEM pictures together with the SIMS images of  $\text{LiFePO}_4$  particles coated with the PPy layer confirms the uniformly and homogeneously distributed polymeric film onto the surface of particles. The PPy/PEG– $\text{LiFePO}_4$  particles represent a more active cathode material than bare  $\text{LiFePO}_4$  particles. To ensure a good reproducibility of the measurements and define the properties of prepared composite cathodic material it was necessary to know the thickness of polymeric layer. The SEM picture suggests that the darker thin layer around the lighter  $\text{LiFePO}_4$  particles rises from the PPy coating layer. In this case the layer thickness is about the 100 nm.

This was also confirmed by the TOF-SIMS depth profile (Fig. 7) of the coated particle. Notice the decreasing intensity of the PPy fragments except the  $\text{Fe}^+$  ion the intensity of which is rising with the measured depth. The  $\text{Fe}^+$  ion intensity curve is crossing the  $\text{NH}_4^+$  (resulting from the PPy) intensity curve at about 10 s. The approximate average rate of sputtering beam for sample studied was about  $10 \text{ nm s}^{-1}$ , which corresponds with the thickness of PPy

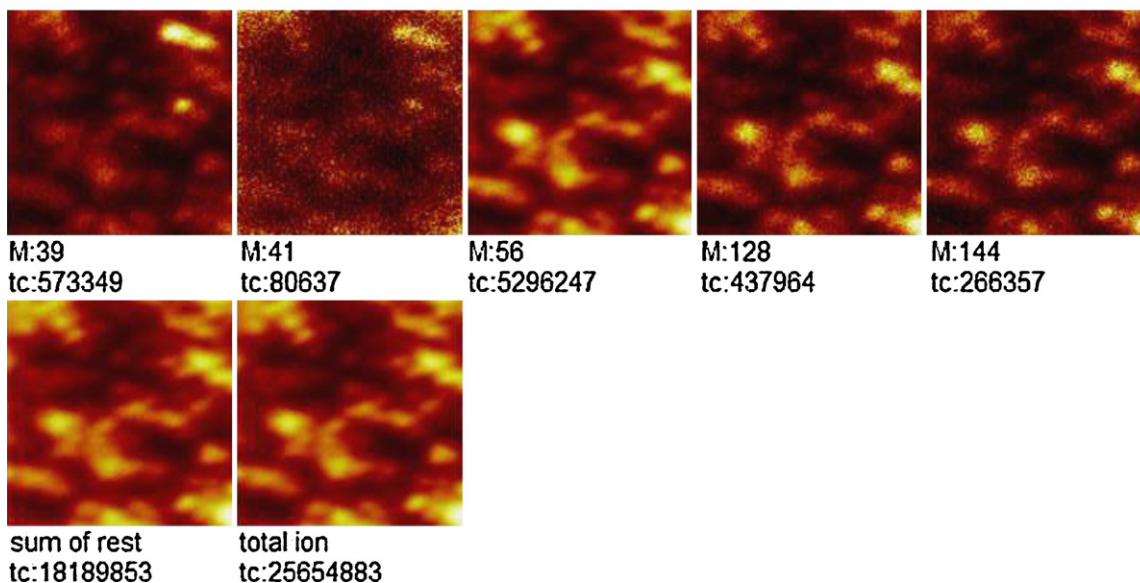
Field of view: 9.8 x 9.8  $\mu\text{m}^2$ 

Fig. 6. TOF-SIMS image showing the distribution of the positive, nitrogen containing fragments with PPY origin coated on Al foil.

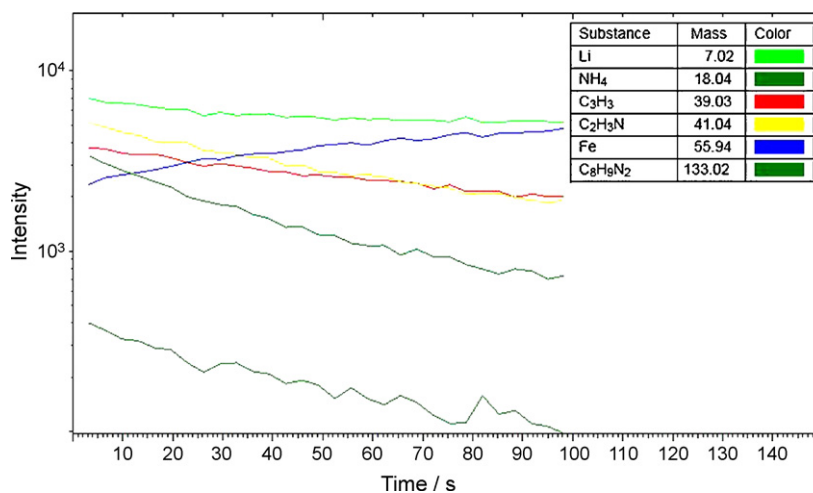


Fig. 7. Depth profile of PPY/PEG-LiFePO<sub>4</sub> material.

circa 100 nm. It should be noted, that the exact value of sputtering beam rate can not be determined, because it changes for different substrate. Moreover, the TOF-SIMS depth profile exhibits the high intensity and flat profile of the Li<sup>+</sup> ion with the increasing depth (Fig. 7). This behavior confirms that the Li<sup>+</sup> cation penetrates from the LiFePO<sub>4</sub> to the PPY layer whereby it facilitates the Li<sup>+</sup> transfer into the PPY/PEG-LiFePO<sub>4</sub> particles. Hence, PPY/PEG-LiFePO<sub>4</sub> is a unique and promising hybrid cathode material for rechargeable Li-ion batteries.

#### 4. Conclusions

The PPY/PEG-LiFePO<sub>4</sub> samples were synthesized by simple chemical oxidative polymerization. The PPY coating improves the conductivity of LiFePO<sub>4</sub> and increases the specific surface area of electrodes. PPY/PEG coating allows easier access of ions and electrons to deeper lying of LiFePO<sub>4</sub> structure. AC impedance and cyclic voltammetry measurements confirmed that PPY/PEG composite polymer improved electrochemical activity and charge-transfer reaction of PPY/PEG-LiFePO<sub>4</sub> cathodes. The initial

discharge capacity of pure LiFePO<sub>4</sub> was about 138 mAh g<sup>-1</sup> whereas for PPY/PEG-LiFePO<sub>4</sub> it was 148 mAh g<sup>-1</sup>. The improved battery performance and cycleability of materials in this study resulted from homogeneous distribution of PPY or PPY/PEG layers. Particle size analysis showed that the PPY-LiFePO<sub>4</sub> particles belonging to three different granulometric classes: (i) single PPY, (ii) uncoated and coated PPY-LiFePO<sub>4</sub> particles and (iii) aggregates formed by all these components. The SEM pictures of LiFePO<sub>4</sub> particles coated with the PPY layer along with the SIMS images indicated the evenly and homogeneously coated particles. Thickness of polypyrrole film on LiFePO<sub>4</sub> particles is about 100 nm. It can be concluded that the hybrid material PPY/PEG-LiFePO<sub>4</sub> reported here is therefore a promising cathode material for lithium-ion batteries, providing a stable and reversible capacity, good performance and rate capability.

#### Acknowledgements

The authors wish to acknowledge the financial support from the Grant Agency of Ministry of Education of the Slovak Republic

(Grant No. 1/0043/08), Slovak Research and Development Agency (project VVCE-00707), from Deutsche Forschungsgemeinschaft (Grant WI 952 within DFG-PAK 177) and from DAAD (Grant No. 03042007/SMS). The authors are grateful to Professor M. Winter and his coworkers for the cell assembly facilities in his laboratory and Süd-Chemie AG for providing the  $\text{LiFePO}_4$ .

## References

- [1] N. Ravet, Y. Chouinard, J.F. Magnan, S. Besner, M. Gauthier, M. Armand, J. Power Sources 503 (2001) 97–98.
- [2] A.K. Padhi, K.S. Nanjundaswami, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188–1194.
- [3] S. Kuwabata, S. Masui, H. Yoneyama, Electrochim. Acta 44 (1999) 4593–4600.
- [4] G.X. Wang, L. Yang, Y. Chen, J.Z. Wang, S. Bewlay, H.K. Liu, Electrochim. Acta 50 (2005) 4649–4654.
- [5] C. Lai, Q. Xu, H. Ge, G. Zhou, J. Xie, Solid State Ionics 179 (2008) 1736–1739.
- [6] K.S. Park, K.T. Kang, S.B. Lee, G.Y. Kim, Y.J. Park, H.G. Kim, Mater. Res. Bull. 39 (2004) 1803–1810.
- [7] D.-H. Kim, J. Kim, Electrochem. Solid-State Lett. 9 (2006) A439–A442.
- [8] Z.H. Chen, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1184–A1189.
- [9] P.P. Prosini, D. Zane, M. Pasquali, Electrochim. Acta 46 (2001) 3517–3523.
- [10] S. Franger, F. Le Cras, C. Bourbon, H. Rouault, Electrochem. Solid-State Lett. 5 (2002) A231–A233.
- [11] S.F. Yang, Y.N. Song, P.Y. Zavalij, Y. Stanley Whittingham, Electrochem. Commun. 4 (2002) 239–244.
- [12] F. Croce, A. D'Epifanio, J. Hassoun, A. Deputa, T. Olczac, B. Scrosati, Electrochem. Solid-State Lett. 5 (3) (2002) A47–A50.
- [13] Y.H. Huang, K.S. Park, J.B. Goodenough, J. Electrochem. Soc. 153 (12) (2006) A2282–A2286.
- [14] A. Fedorková, H.D. Wiemhöfer, R. Oriňáková, A. Oriňák, M.C. Stan, M. Winter, D. Kaniansky, A.N. Alejos, J. Solid State Electrochem. 13 (2009) 1867–1872.
- [15] H.C. Kang, K.E. Geckeler, Polymer 41 (2000) 6931–6934.
- [16] P. Burgmayer, R.W. Murray, in: T.A. Skotheim (Ed.), Handbook of Conducting Polymers, M. Dekker, Inc., New York, 1986, pp. 507–524.
- [17] M.D. Levi, D. Aurbach, J. Phys. Chem. B 108 (2004) 11693–11703.