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Electrochemical in battery polymerization of poly(alkylenedioxythiophene) over lithium iron phosphate for high-performance cathodes

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Molecular wiring concept was induced in LiFePO_4 cathodes by in battery polymerization methods. This was performed by the addition of alkylthiophene monomers over the LiFePO_4 -based cathode during the first charging step in lithium test cells. The driving force for the in battery polymerization of the monomers was supplied by the oxidizing current and by the physical contact of monomers with delithiated $\text{Li}_{1-x}\text{FePO}_4$ formed during the charging of the battery. The resulted molecularly engineered cathodes give higher initial capacity, superior rate capability and improved cycleability compared to the pristine LiFePO_4 compound. Further to observe changes in the oxidation state of iron, Mössbauer spectroscopy was employed and the results were correlated with impedance spectroscopy, which reveal a significant increase in conductivity during charging. The presented methods allow simple yet effective routes to manufacture efficient cathode materials at room temperature, without the need of additional oxidizing compounds to carry out the polymerization process and to rival high temperature based carbon coatings.

1. Introduction

Electricity generation through energy conversion is a discontinuous process and requires energy storage at cost effective rate. In this scenario, electrochemical systems play a crucial role as they have proven to be highly efficient for storing and converting energy, and major technological solutions are considered to be in the use of batteries and supercapacitors. Currently, lithium ion batteries are seen as one of the most mature technologies available for powering portable electronic devices and have found niches in electric vehicles and stationary applications. Materials used in electric vehicles should provide fast charging/discharging rates, high energy density and cycle life, be safe and producible at low cost. The key component in lithium ion batteries is the cathode and it imposes performance and costs limitations to the widespread implementation of this technology.^{1,2}

After the seminal work of Padhi et al., on olivine structured lithium transition metal phosphates (LiMPO_4) as cathode materials, significant efforts were made, in particular for LiFePO_4 (LFP), due to its attractive features of being cost effective, environmentally friendly, electrochemically and thermally stable.³ However, LFP and related cathode materials suffer from disadvantages, such as low ionic and/or electronic conductivities, which makes the task for the

lithiation/delithiation processes uneasy, while making electron transfer to active sites cumbersome.⁴ In these direction different approaches have been explored to increase the conductivity of LiFePO_4 , for example: blending with metal particles, aliovalent ion doping and reducing the particle size down to the nanoscale.⁵⁻⁸

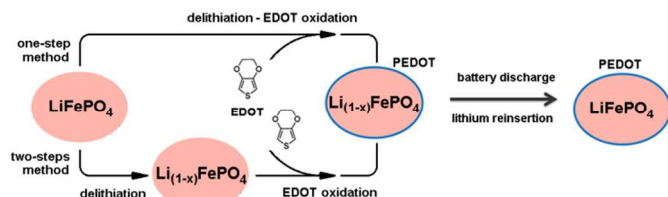
To date, the most common approach adopted to increase conductivity of LiFePO_4 is the formation of homogeneous carbon coatings over the active material particles, which can be achieved by calcination of sugars or surfactants at 500-700°C.^{9-11a-c} However, apart from the high energy consumption, the decomposition of the organics generates contaminants that pose severe environmental hazards. Thus the electrochemical and mechanical performance of electrodes can be further improved by using carbon or polymer as additives to form conducting networks.¹² On the contrary, these electrochemically inactive additives entail a decrease of the practical energy/power density, as the additives do not contribute to the electrode capacity.

Earlier it was shown that conducting polymers like polypyrroles and polythiophenes can enhance the performance of LiFePO_4 and other cathode active materials.¹³ In particular, poly(3,4-ethylenedioxythiophene) [PEDOT] has drawn special attention due to its high electronic conductivity in the doped state,

contribution to the electrode discharge capacity and the ability to improve Li-ion transport due to its highly nanoporous structure, which provides deep accessibility to ions into the inner matrix of the polymer layer.¹⁴

Therefore, different methods have been used to make LiFePO_4 -polymer, including blending with chemically synthesized conducting polymer¹⁵⁻¹⁷ chemical polymerization in presence of LiFePO_4 or $\text{Li}_{1-x}\text{FePO}_4$ ¹⁸ or by electropolymerization over substrates containing LiFePO_4 .^{19,20} For such LiFePO_4 /polymer, it is expected that, upon charging, conjugated polymer delivers the charge to the LFP particles by intermolecular hopping, leading to reversible Li^+ extraction, while the process can be reversed on discharge. Additionally the redox polymer can also act as binder, which offers the possibility to reduce further the use of electrode additives and produce higher energy density batteries.

Within this context, we applied the molecular-wiring concept to improve the conduction in the insulating LFP material by in battery electropolymerization of thiophene-based monomers directly over LFP-based electrodes under battery operation conditions (scheme1), and eliminating the need of any external chemical oxidant. The use of a set of electrochemical and spectroscopic techniques allowed us to confirm the effective electronic communication between the redox polymer and LFP, as the resulting composite electrodes show higher initial capacity, superior rate capability and improved cycleability than the pristine LFP material.



Scheme 1: Illustrating the one or two step polymerization method adopted for inducing molecular wiring approach.

2. Results and discussion

2.1. In battery polymerization process

Figure 1 presents the plot of the two first charge/discharge cycles for the one-step in battery formation of LFP/PEDOT and LFP/poly(3,4-propylenedioxythiophene) [PProDOT]. In both systems, the initial part of the profile shows a first stage involving the oxidation of Fe^{2+} to Fe^{3+} , linked to the delithiation of LFP, with the characteristic charge plateau at ca. 3.5 V. As the galvanostatic charging proceeds, the oxidative polymerization of EDOT and ProDOT monomers appears as a pseudo plateau above 3.8 V. Compared to EDOT, the higher oxidation potential of ProDOT relates to the influence of the extra methylene group on the conjugated ring, which decreases the π -overlap along the backbone, leading to an increase of the bandgap.²¹ In the first discharge, the profile for both LFP/PEDOT and LFP/PProDOT shows the characteristic plateau at ca. 3.4 V, attributed to the Fe^{3+} to Fe^{2+} reduction and reinsertion of lithium ions. Independently of the monomer, the

discharge capacities are higher than the charge capacities measured near 3.8 V before the beginning of the polymerization. Suggesting that de-lithiation of LFP takes place simultaneously with the formation of PEDOT and PProDOT during the first charging step up to 4.2 V. This will be discussed in detail with our ^{57}Fe Mössbauer results in next section.

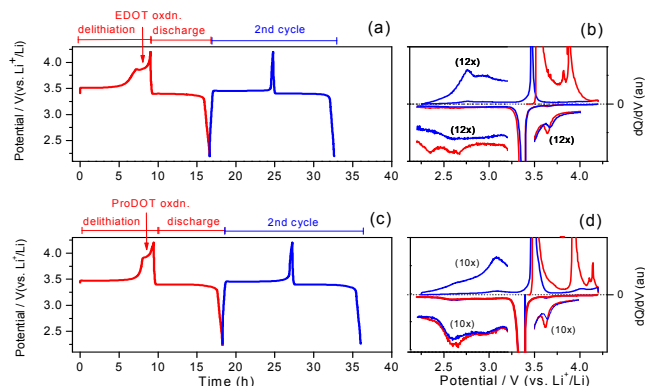


Figure 1. Initial charge/discharge and differential capacity plots for the one-step in battery formation of composites from a-b) PEDOT and c-d) ProDOT.

For both monomers, the second cycle presents flatter charge/discharge plateaus having lower polarization and increased capacity, thus pointing towards the better active material utilization and revealing the positive effect of PEDOT or PProDOT on the conductivity of the fabricated cathodes. At the end of the second charge, the oxidation of both monomers is almost complete, as evidenced by the remnant trace above 3.8 V and by the lower intensity of the respective polymer oxidation peaks in the differential capacity plots (Figure 1b and 1d). For subsequent charge/discharge cycles, the pseudo plateau near 3.8 V vanishes, indicating the end of the oxidative polymerization.

The voltammogram for EDOT and ProDOT monomers (Figure S1) dissolved in the LiPF_6 -based electrolyte, shows the signals ascribed to the initial oxidation of monomers, followed undoping and reduction of deposited polymer.²² It is evident (Figure 1b and 1d) that the redox processes of the polymer occur over the LFP electrode in the range from ca. 4.0 to 2.5 V, which lies within the potential window used to cycle LFP (4.2 - 2.2 V). These signals arising from the polymer are minute. Therefore the contribution from PEDOT and PProDOT to the total discharge capacity in successive cycles is negligible as compared to the capacity from LFP active material.

Figure 2 presents the first and second charge/discharge cycles for batteries with monomers polymerized over delithiated LFP via the two-steps method. The observed profiles are in accordance to those for the one-step method (Figure 1), except for the first charging/delithiation step, which was carried out in the absence of a polymerizable monomer. After the first charging step, the cell was open and the monomer was added to the cathode. In a second step, the re-assembled battery was charged to induce the electropolymerization of the monomers over delithiated LFP. As shown in Figure 2, for the second charge step, there is a minimal initial contribution coming from

Fe^{2+} to Fe^{3+} oxidation near 3.5 V indicating that the Fe^{2+} to Fe^{3+} oxidation was almost completed at the end of the first charge step. Due to the rise in potential (>3.8 V), polymerization of EDOT or ProDOT monomers takes place and continues up to the cut-off voltage at 4.2 V. The lower polarization in the second cycle observed for this two-step method suggests an improvement in the conductivity of the resulting LFP-Polymer cathode.

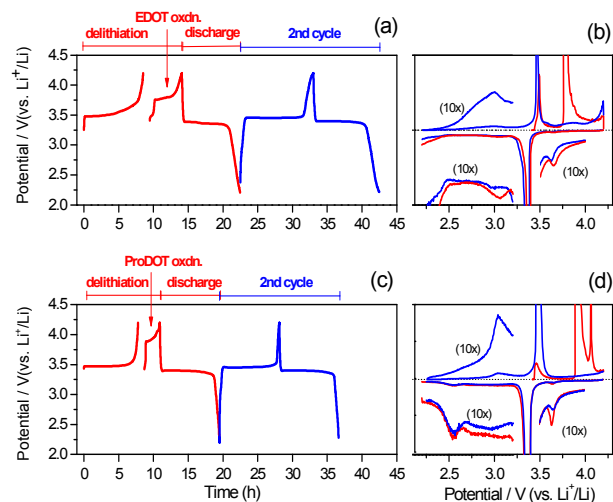


Figure 2. Initial charge/discharge and differential capacity plots for the two-steps in battery formation of composites from a-b) PEDOT and c-d) ProDOT

Figure 2b and 2d show the inverse derivative of the capacity as a function of potential. Additional to the main signals coming from LFP (3.4 and 3.5 V on charge and discharge, respectively), the other oxidation and reduction signals can be attributed to the redox processes of PEDOT and PProDOT previously described for the one-step method.

Figure 3 presents scanning electron microscopy images of the surface of the LFP-based cathode including binder and conductive additives as a function of the charge potential. Figure 3a shows irregular individual particles of pristine LFP. At 3.7 V, the partially delithiated cathodes with EDOT or ProDOT monomers displayed no variation with respect to the pristine LFP cathode. Contrary to this, the surface of the electrode at 4.2 V shown in Fig. 3b, illustrates the characteristic globular structure of PEDOT grown in close contact with the LFP particles, yielding a material with enhanced mechanical and conductive communication between the active particles. These features were also observed in case of LFP-PProDOT. The polymers prepared electrochemically in the absence of LFP (Fig. 3c) show a completely different texture^{14c,d}, which emphasizes the role of LFP in the formation of the polymer by the in battery method.

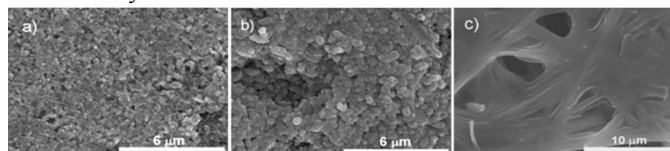


Figure 3. SEM pictures of the cathode surface as a function of charge potential. a) pristine LFP, b) LFP + EDOT charged at 4.2 V and c) PEDOT.

2.2. Mössbauer analysis

In order to elucidate the delithiation process of LFP in the presence of EDOT and ProDOT monomers, Mössbauer spectra were recorded at different depth of charge/discharge corresponding to different stages of the in battery polymerization process. Figure 4 shows the experimental and calculated ^{57}Fe Mössbauer spectra of the LFP active material, both in absence and in presence of EDOT monomers at different charge/discharge potentials. Table S1 provides the hyperfine parameters obtained from the fitting of the spectra.

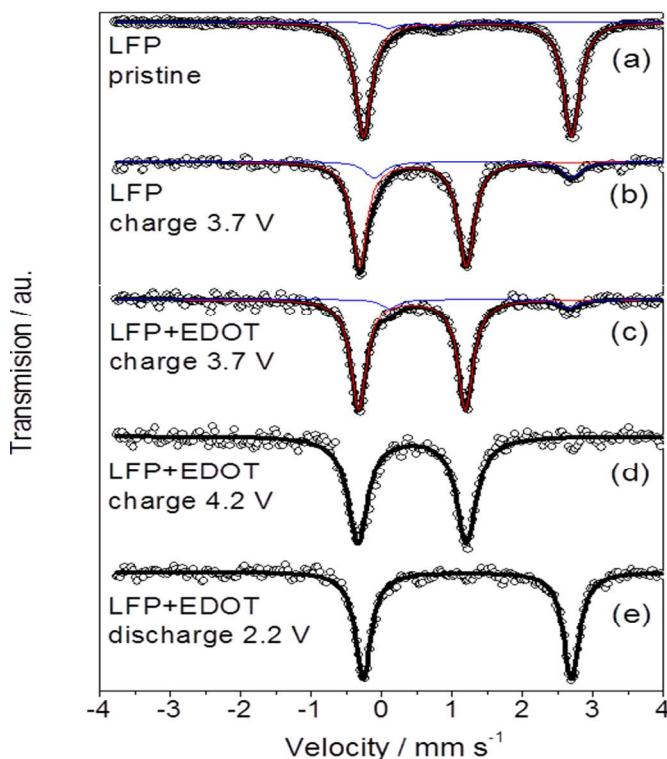


Figure 4. Mössbauer spectra at different potentials for a-b) LFP and c-e) LFP with EDOT.

The spectrum of pristine LFP shows a main doublet with isomer shift (IS) value of 1.22 mm/s and a quadrupolar splitting (QS) of 2.96 mm/s. These values are characteristic of Fe^{2+} ions in high spin configuration, distorted octahedral coordination, as found in LFP. Additionally, a second doublet of lower intensity with IS = 0.48 mm/s and QS = 0.79 is ascribable to Fe^{3+} . The hyperfine parameters allow assigning this signal to FeP impurities.²³ This signal has been previously described in the literature, and is commonly found in samples prepared under carbothermal reducing conditions.²⁴ In our sample, this impurity accounts for ca. 5-7 % of the total iron content. It has been firmly demonstrated that iron phosphide impurities for less than 10 % decrease the capacity of the LiFePO_4 but enhance the utilization efficiency at high discharge rate, due to the high electron conductivity Fe_2P .^{25,26}

Pristine LFP was charged galvanostatically at 3.7 V. At this potential the main signal consists of a doublet with IS = 0.44 mm/s and QS = 1.51 mm/s. These values are consistent with Fe^{3+} phosphate in high spin configuration, distorted octahedral coordination. Additionally, the contribution of the signal previously assigned to Fe^{2+} strongly decreases. These observations provide evidence of the progressive oxidation of Fe^{2+} to Fe^{3+} linked to the extraction of Li^+ to form FePO_4 . At this potential ca. 16 % of the total iron remain unoxidized, corresponding to a fraction $x = 0.84$ of lithium extracted from LFP.

The Mössbauer analysis for the LFP sample in presence of PEDOT and charged at 3.7 V shows that the amount of unoxidized Fe^{2+} decreases to ca. 9 %. This indicates that the use of the monomer in the battery results in a higher efficiency for the lithium extraction, compared to the LFP without monomer/polymer. We speculate the observed improvement is related to an enhanced conductivity of the materials, which is in agreement with our impedance analysis. After charging to 4.2 V, the Mössbauer spectrum of the LFP/PEDOT composite showed only one doublet ascribable to Fe^{3+} , indicating the full delithiation and transformation of LiFePO_4 into FePO_4 . The further discharge of the battery down to 2.2 V results in the full reduction of Fe^{3+} into Fe^{2+} and resinsertion of Li^+ , as evidenced by the signal in the Mössbauer spectrum ascribable to Fe^{2+} , similar to that observed for the pristine LFP.

2.3. Battery cycling

The charge/discharge profiles, at C/10 and 1C rates, for LFP and the composites with PEDOT and PProDOT are shown in Figure 5. In the following discussion, the presented data correspond to the average results from 10 cycles at each rate. The profiles for all the samples present the characteristic charge/discharge plateaus centred near 3.4 V. At C/10, pristine LFP shows the lowest performance with a discharge capacity of ca. 130 mAh g^{-1} , which represents 76 % of the theoretical value for LFP (Qtheo ca. 170 mAh g^{-1}). Higher capacities were found for the cathode with PEDOT or PProDOT, confirming an improvement arising from incorporation of the polymers. For PEDOT based cathode, the capacity value obtained via one-step method was 132 mAh g^{-1} , whereas the two-step method gave an unprecedented, higher capacity of 165 mAh g^{-1} (25% increase), very close to the theoretical value. On the contrary, the inverse situation was observed for PProDOT, as the capacity value obtained via the one-step method (148 mAh g^{-1}) is slightly higher than the value measured for the composite obtained by the two-step method (144 mAh g^{-1}). This indicates that the different properties of the monomers – structure and redox potentials– influence the formation of the composites under similar preparation conditions. Although the performance at 1C rate is lower than at C/10, all the samples with PEDOT and PProDOT display enhanced capacity and notably lower charge/discharge polarization, when compared to pristine LFP. Figure 6a presents the discharge capacity as a function of the cycle number at different rates for all the composites. All the samples with polymer outperform the pristine LFP in terms of

capacity at increasing rates. Apart from this, the incorporation of PEDOT and PProDOT polymers allows the recovery of more than 95% of the initial capacity at C/10 after 60 cycles.

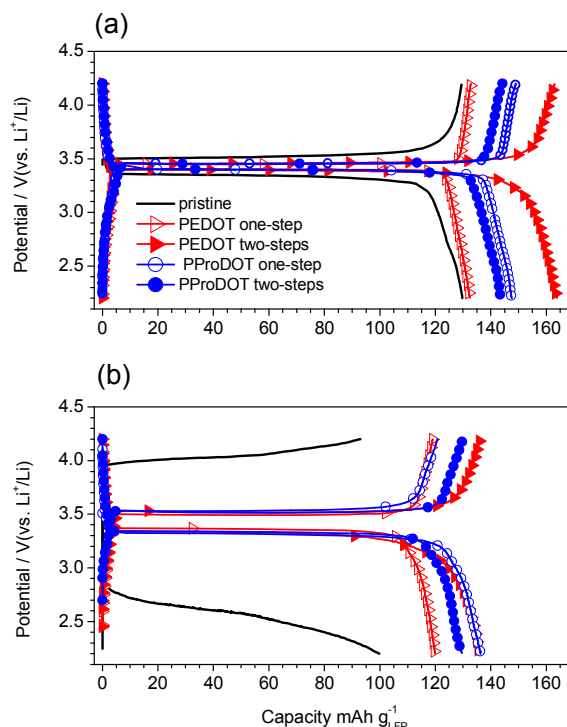


Figure 5. Charge/discharge plots for the different composites at a) C/10 rate and b) C rate.

Figure 6b presents the results for the evaluation of the capacity retention at C/2 for 50 cycles. Prior to the capacity retention test, all the samples were subjected to three charge/discharge cycles at C/10 in order to form the LFP/polymer and to activate LFP. It is evident that pristine LFP not only shows lower initial capacity, but also marked capacity fade of nearly 60% after 30 cycles. On the contrary, the capacity fading of our engineered LFP/polymer cathodes was less than 4 % of the initial capacity at C/2 rate, giving rise to longer and more practical cycle life. The best electrochemical results were obtained for PEDOT based sample by the 2-step preparation. This behaviour has a two-fold origin. First, the conductivity of PEDOT is significantly higher as compared with ProDOT,²¹ which is in accordance with our EIS data. On the other hand, a first activation for the polymerization process was achieved by adding the monomer to a previously charged electrode, which constitutes the basis of the two-step procedure.

2.4 EIS analysis

We explored the variation of the total resistance of the cathode as a function of the charge and discharge potential by means of EIS spectra. Fig. 7a compares the spectra at a particular potential of 4.2 V at which polymerization has occurred. We fitted the experimental spectra to an equivalent electrical circuit described previously for LFP-based electrodes.²⁷ The circuit consists of a high and a medium-to-low frequency semicircles,

the former corresponding to the lithium ion migration resistance in the solid electrolyte interface (SEI) while the later to the charge transfer resistance.

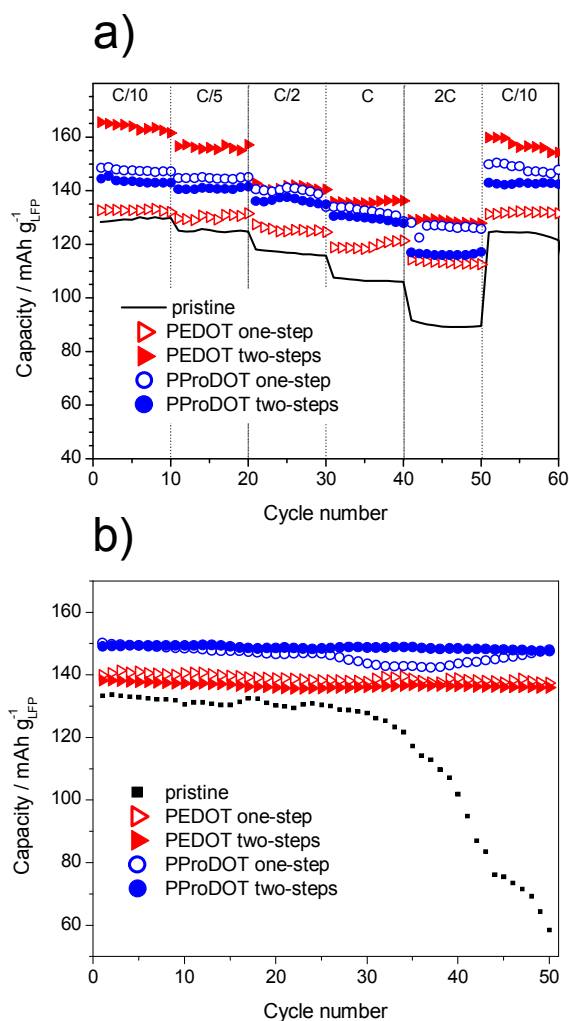


Figure 6. a) Cycleability for the different samples at different rates. b) Capacity retention tests at C/2 rate.

Semi-infinite diffusion and differential intercalation capacity are usually fitted by a series of constant phase elements and a Warburg element in the low frequency region. Besides, the equivalent circuit includes an inductor and a resistor to account for the cables inductance and the contact resistances in the cell (inset Figure 7a). It is worth to mention that during battery charging the total resistance progressively drops as the monomers oxidizes over the cathode (Fig. 7b). Charging the battery until 4.2 V can lead to p-doped, highly conducting forms of PEDOT and PProDOT that favour the discharge performance of LFP.

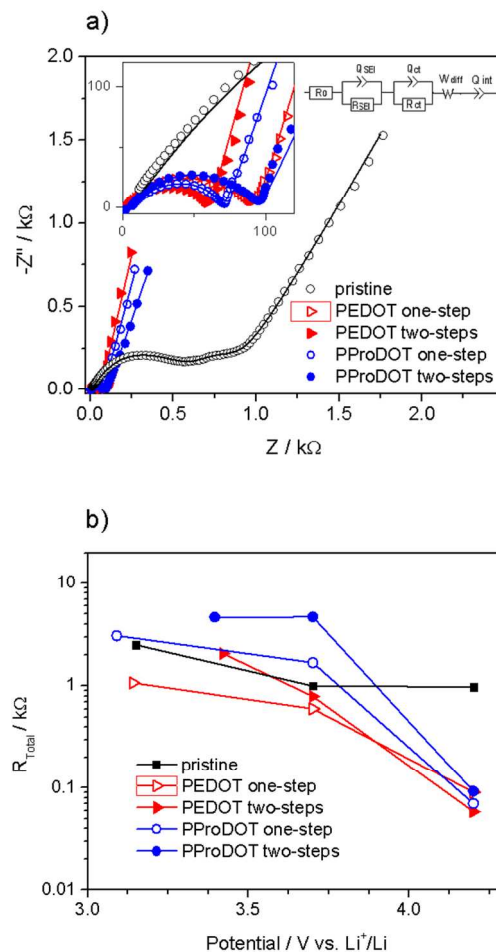


Figure 7. a) Impedance spectra of the composites at the first charge/discharge cycle at 4.2 V. b) Variation of the total resistance of the cell for the first charge/discharge cycle.

4. Experimental Section

$LiFePO_4$ was synthesized as described elsewhere²⁴. The battery electrolyte consisted of conventional 1M $LiPF_6$ dissolved in ethylenecarbonate:diethylcarbonate (EC:DEC, 1:1 volume ratio). 3,4-ethylenedioxythiophene monomer (EDOT) and 3,4-propylenedioxythiophene (ProDOT) monomer were purchased from Aldrich and used as such. Electrodes were prepared by mixing the LFP active material with carbon black and polyvinylidene fluoride (85:8:7wt.) in *N*-methyl pyrrolidone. The mixture was sonicated and the obtained ink was deposited over an aluminum disk (0.64 cm²) and dried at 80°C under vacuum for 12 h. The average amount of LFP in the electrodes was estimated to 5 mg cm⁻².

LFP test batteries without monomers were assembled in two-electrode Swagelok-type cells using the cathode as working electrode, Whatman glass-paper separator soaked with electrolyte, and 1.5 mm thick lithium metal foil as reference/counter electrode. All the cells were assembled inside a glove box under controlled argon atmosphere.

Galvanostatic cycling at different C-rates ($C = 1 \text{ Li h}^{-1} \text{ mol}^{-1}$) was carried out at room temperature using a Biologic VMP or

MPG station. The cut-off potential for charge and discharge were set at 4.2 and 2.2 V (vs. Li^+/Li), respectively.

The modified cathodes of LFP with conducting polymer were prepared inside test batteries by polymerization of EDOT and ProDOT monomers, using two different methods. The first method consisted in assembling the battery with a pristine LFP cathode covered by a solution of monomer (0.02 M in battery electrolyte) and applying a single charging step to the battery, in order to perform the cathode delithiation and the polymerization of the monomers in one step. The composites prepared by the single charging step are referred as “one-step”. The second in battery method consisted in charging a test battery with a pristine cathode at C/10, in order to delithiate LFP. Afterwards, the battery housing the delithiated cathode was opened inside the glove box and monomers were added over the cathode surface. Polymerization of the monomers was carried out by applying a second galvanostatic charge at C/10. LFP/polymer cathodes prepared by the two charging steps are referred to as “two-steps”. The amount of added monomer was 3.6 wt. % of the total electrode mass. To estimate the contribution of the resulting conductive polymer to the total discharge capacity of the composite electrodes, the electroactivity (reversible doping) of the polymer was determined by measuring the capacity associated to the peak at 3.75-3.60 V during cell discharge, and referred to the capacity of LFP. The result was less than 1 %, and thus it was not considered further.

Cyclic voltammetry of the battery electrolyte, EDOT and ProDOT monomers was performed in a three-electrode cell at room temperature at a scanning rate of 1 mV/s from 2.2 - 4.2 V. Platinum wire was used as working electrode fitted between two glass fiber separator wetted with the electrolyte and solution of monomers. Two lithium disks acted as reference and counter electrodes.

Electrochemical impedance spectra of the cathode materials were made with the help of Biologic SP-150. The measurements were carried out in three-electrode Swagelok cells with the LFP-based composite as working electrode, lithium metal counter electrode and lithium reference electrode. The applied sinus amplitude was fixed at 5 mV and the frequency was scanned from 1 MHz to 1 mHz.

^{57}Fe Mössbauer spectra were recorded at room temperature with an EG&G spectrometer at constant acceleration and transmission mode. The gamma radiation source was ^{57}Co (Rh matrix). The velocity scale was calibrated from the sextet lines recorded for high-purity iron foil. The spectra were fitted to Lorentzian profiles by a least square method using WinISO software. Scanning electron microscopy (SEM) images were obtained in a JEOL JSM63000 microscope.

Conclusions

A simple and cost effective method is proposed to improve the performance of LFP electrodes, by using in battery polymerization of alkylthiophenes (ProDOT preferably EDOT) in one- or two-steps. The procedures differ in the addition of

the monomer, prior or after in battery electrochemical delithiation of the phosphate cathode. The latter is particularly attractive as it allows capacities close to the theoretical limit, low polarization, low cycling losses, excellent rate performance, and improved capacity retentions after 50 cycles. ^{57}Fe Mössbauer spectroscopy reveals that the oxidation of Fe^{2+} to Fe^{3+} takes place during the polymerization-doping step. The enhanced electronic conduction in the materials, particularly when using the two-step procedure is the main origin of the improved performance.

Acknowledgements

UCO group is indebted to MES (Contract MAT2011-22753) and Junta de Andalucía (FQM288).

Notes and references

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Electronic Supplementary Information (ESI) available: Cyclic voltammogram of monomers and Mössbauer spectra fitting table]. See DOI: 10.1039/b000000x/

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