

A soft chemistry approach to conducting polymer coating of LiFePO₄

David Lepage, Christophe Michot, Guoxian Liang, Michel Gauthier and Steen B. Schougaard*

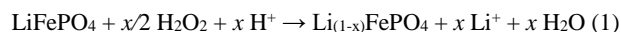
Lithium-ion batteries have an important role to play in reducing atmospheric pollution, by enabling the use of clean energies like solar, hydro, and wind for transportation. Numerous chemistries have been or are being developed for lithium batteries. Particularly interesting for the cathode is *olivine*-LiFePO₄^[1] due to its environmentally friendly and inexpensive constituents, iron and phosphate. However, the use of LiFePO₄ as a cathode requires that its poor electronic conductivity be overcome.^[1-2] Several schemes have been put forth to circumvent this drawback such as metal ion doping of the structure with foreign metal ions^[3], however the most common scheme remains coating with carbon. Coatings are commonly formed by mixing an organic precursor with preformed LiFePO₄ before a heat treatment at high temperature (500-700 °C) in an inert or reducing atmosphere.^[4] The decomposition of the organic constituent leads, in addition to formation of carbon, to the formation of volatile organic compounds (VOC's), CO and CO₂, which pose environmental problems.^[5] More critical for battery applications is however that irregular coating of LiFePO₄ can lead to poor connectivity of the particles and hence performance loss.^[6] It would therefore be an important improvement to the current LiFePO₄ system if low temperature methods could be found to coat LiFePO₄ uniformly without the formation of VOC's, CO or CO₂.

Previously, it has been shown that conducting polymers, including redox polymers^[7] can have a positive effect on the performance of LiFePO₄^[8] and other cathode materials such as Li_{1.03}Mn_{1.97}O₄^[9] and LiCoO₂^[10]. Several means have been used to make polymer/LiFePO₄ composites, including electropolymerization from a suspension of LiFePO₄ particles^[8d], polymerization using a chemical oxidant in the presence of the particle^[8b] or, more recently, formation of a colloidal suspension of the polymer immediately before the introduction of the LiFePO₄ particles^[11].

Herein, we present a methodology that significantly improves the fabrication and use of conducting polymer/LiFePO₄ composites. First, the method relies on the intrinsic oxidation power of Li_(1-x)FePO₄ rather than an external oxidant as the driving force of the

polymerization process. This eliminates the risk of residual oxidant or oxidant by-products leaching from the polymer into the battery electrolyte, which would wreak havoc on the anode electrode process. Second, the propagation of polymerization requires the reinsertion of lithium into lithium iron phosphate, as well as the transport Li⁺ ions and electrons through the excising polymer coating. In turn, these are also the functionality characteristics of an effective conducting coating for LiFePO₄. As such, the propagation reaction intrinsically favours the functionality of the final product. Moreover, compared to the classical carbon coating technology, this approach is devoid of high temperature processing and VOC's, CO and CO₂ formation. Third, an environmentally benign process based on H₂O₂ is used to form Li_(1-x)FePO₄ from the standard *olivine*-LiFePO₄. Finally, the conducting polymer/LiFePO₄ composite made by our method can be used directly in a "no-carbon-added" cathode.

The first processing step is delithiation of LiFePO₄. Several oxidants are known to delithiate LiFePO₄ such as nitronium^[1,12] and Br₂^[13]. However, these cannot generally be considered environmentally benign. Instead inexpensive hydrogen peroxide is used here because its degradation product is water. Importantly, it has previously been shown that LiFePO₄ is stable in water.^[14] The first reaction step is therefore



Once the solid Li_(1-x)FePO₄ is removed from the reaction mixture by filtration, the extracted lithium can be recovered by simple evaporation, thus minimizing the waste.

The second step is the polymerization of ethylenedioxythiophene (edot) by reinsertion of lithium into Li_(1-x)FePO₄. Edot was chosen because the polymerization potential is close to the redox potential of LiFePO₄/FePO₄ and it is known to form stable films with high electronic conductivity.^[15] The lithium source used in (2) is lithium bistrifluoromethanesulfonamide (LiTFSI) since it is a stable salt in ambient environments^[16] and has negligible currents below 4.2V in LiFePO₄ lithium batteries^[17]. In addition, it has been shown that using TFSI as the counter ion for the oxidized state of pedot yields polymers with high conductivity.^[18] The polymerization reaction of edot by the reinsertion of lithium operates without any other source of oxidant or initiator (Figure 1).

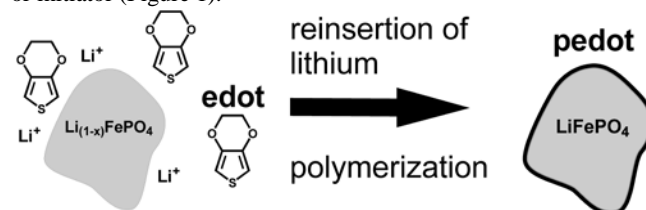


Figure 1. The polymerization reaction. The reinsertion of lithium into Li_(1-x)FePO₄ leads to oxidation of edot, which is deposited on the solid surface as the conducting pedot polymer.

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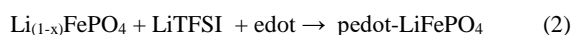
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Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

The reinsertion of lithium in the structure of $\text{Li}_{(1-x)}\text{FePO}_4$ follows equation 2. An excess of LiTFSI is used to maximize the reinsertion of lithium into $\text{Li}_{(1-x)}\text{FePO}_4$.



The X-Ray diffractograms (Figure 2) show the industrial grade *olivine*- LiFePO_4 without carbon coating before and after the oxidation process. The oxidized material, with the average composition $\text{Li}_{(1-0.3)}\text{FePO}_4$, as determined by atomic emission/absorption spectroscopy, is composed of 0.7 *olivine*- LiFePO_4 and 0.3 *heterosite*- FePO_4 (labelled with *). This phase separation is well documented.^[19] The final X-Ray diffractogram (Figure 2c) obtained after the polymerization reaction confirms the reinsertion of the lithium into the olivine structure. The pedot coating is not detected by this technique due to its predominantly amorphous nature.

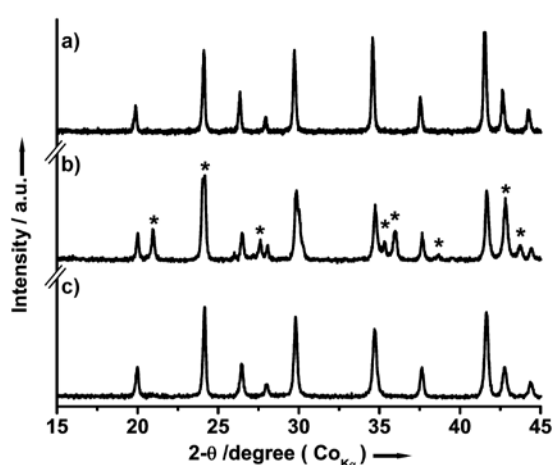


Figure 2. XRD patterns of a) LiFePO_4 , b) $\text{Li}_{(1-0.3)}\text{FePO}_4$, and c) pedot- LiFePO_4 .

The transmission electron microscopy (TEM) micrograph, Figure 3 shows the thickness of the polymer coating can be as thin as two nanometers for isolated particles. In areas where agglomerated particles overlap, the polymer is less uniform and thicker (see Figure S2 in the supporting information).

Confirmation of the presence of the pedot on the surface of LiFePO_4 was achieved by comparison of the IR-spectra of LiFePO_4 , $\text{Li}_{(1-x)}\text{FePO}_4$ and pedot- LiFePO_4 (Figure 4). *Olivine*- LiFePO_4 have three main bands at 979, 1061 and 1136 cm^{-1} caused by the stretching mode of $(\text{PO}_4)^{3-}$. Two others bands at 633 and 647 cm^{-1} stem from the bending modes (ν_2 and ν_4) P-O-P.^[5a] The two new bands at 684 and 1237 cm^{-1} found in the spectrum of $\text{Li}_{(1-x)}\text{FePO}_4$ indicates the formation of *heterosite*- FePO_4 .^[20] After the polymerization reaction, the formation of pedot is confirmed by the C=C ring and C-O-R vibrations at 1181 cm^{-1} and the C-S vibration at 929 cm^{-1} .^[21] The polymer p-doping is indicated by the bands at 1514 and 1320 cm^{-1} .^[22] Thus, the pedot formed is similar to the material polymerized by solution oxidants, which exhibit high electronic and ionic conductivities.^[23] This was further evidenced by the conductivity measurement of pressed powders, where the pedot covered samples showed conductivities in the 0.1 S/cm range, while uncoated samples were below the limit of detection ($<10^{-6}$ S/cm).

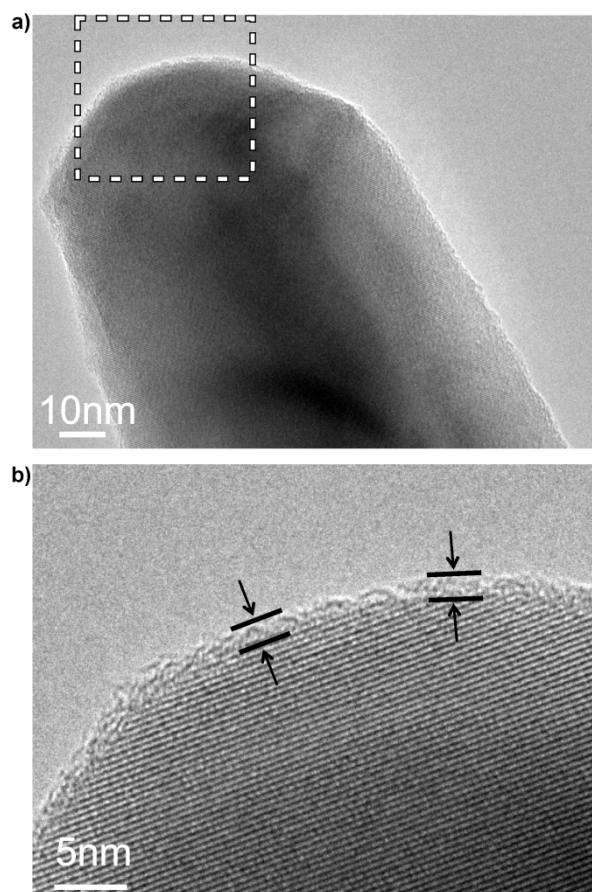


Figure 3. Transmission electron microscopy of a) LiFePO_4 and b) pedot- LiFePO_4

The weight percentage of pedot in the LiFePO_4 -polymer composite was determined by a thermo gravimetric analysis. The differential weight loss of $\text{Li}_{(1-0.3)}\text{FePO}_4$ and pedot- LiFePO_4 was 7.1 % (see Figure S1 in the supporting information).

Electrochemical testing (Figure 5) using coin-type batteries and a constant rate of discharge of ten hours (C/10) showed capacities of 163 mAh g^{-1} , which are in close agreement with the theoretical capacity of LiFePO_4 (170 mAh g^{-1}). At higher rates of discharge, more specifically at 10 C (at constant current for a discharge in 6 minutes) the capacity is 123 mAh g^{-1} i.e. approximately 70 % of the theoretical capacity. Importantly, LiFePO_4 treated in the same manner as the composite, but without the addition of edot, exhibit little practical capacity, thus illustrating the importance of the polymer layer (see supporting information S5). The pedot- LiFePO_4 electrochemical tests were performed on “no-carbon-added” electrodes. This is significant since carbon is used in the standard cathode fabrication as an additive that ensures electronic conductivity throughout the electrode. It is however not electrochemically active and therefore diminishes the practical storage capacity of the electrode.^[4b] In addition, it also increases the tortuous electrolyte conduction path in the electrode.^[24] The ability to replace carbon by a polymeric conductor that conducts both ions and electrons is for these reasons highly advantageous.

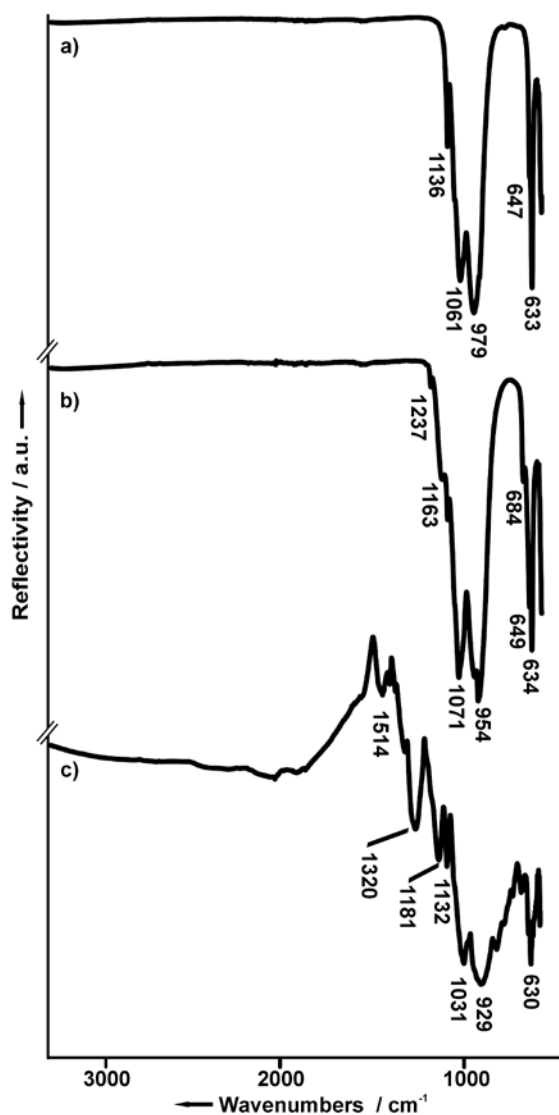


Figure 4. FTIR of a) LiFePO_4 , b) $\text{Li}_{(1-0.3)}\text{FePO}_4$, and c) pedot- LiFePO_4 .

Cycling data at the C/2 rate for 30 cycles at 60°C confirms the stability of the coating in the highly alkaline lithium-ion battery environment (Figure 6).

Using environmentally benign reactants and solvents, we have shown that *olivine*- LiFePO_4 can be oxidized to form a product that is appropriate for polymerization of the conducting polymer pedot. Importantly, the waste products from this oxidation reaction are only water and lithium acetate. The latter can therefore be recuperated at minimal cost. We have further shown that our polymer coating can eliminate the pyrolysis reaction used to form carbon coating on LiFePO_4 without significant electrochemical performance loss. More importantly, we have shown that substituting the standard carbon coating by the conductive polymer leads to a material that can be assembled directly into functional “no-carbon-added” electrodes. Combined, the methodology reported here offers a compelling case for replacing the industrial standard of carbon coating LiFePO_4 , with our soft chemistry polymerization reaction.

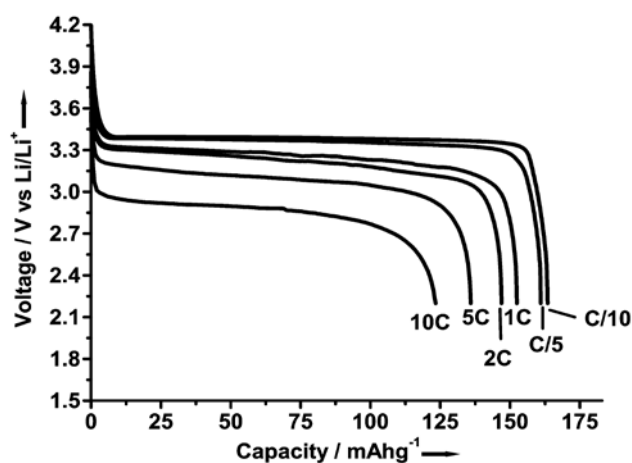


Figure 5. Discharge curves of pedot: LiFePO_4 : PvdF (5.9:86.6:7.5 in wt. %) (Charge conditions are 2.2–4.2 V, versus Li+/Li). The term 1C represent a constant current discharge for 1 hour and C/10 represents a constant current for a discharge in 10 hours.

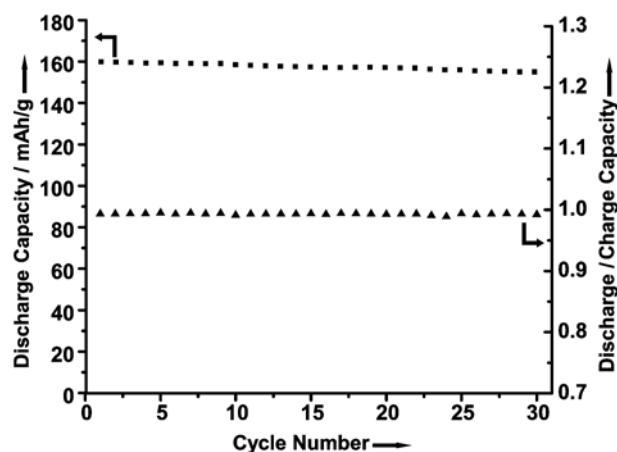


Figure 6. Discharge capacity (squares) and coulombic efficiency (triangles) at the C/2 rate of the pedot- LiFePO_4 composite at 60°C . (pedot: LiFePO_4 : PvdF (10:84:6) in wt. %)

Experimental Section

Formation of $\text{Li}_{(1-0.3)}\text{FePO}_4$:

2 mL glacial acetic acid (Alfa Aesar) and 5 mL of hydrogen peroxide ACS Grade, 29.0–32.0 % (EMD Chemicals) was added to 100 mL of water. Carbon free LiFePO_4 (10.2 g) (Phostech Lithium, Saint-Bruno de Montarville, Canada, prepared according to US Patent 7,807,121 B2) in water suspension (250 mL) was added to the solution. The suspension was vigorously stirred for 15 min, filtered and rinsed with water. The $\text{Li}_{(1-x)}\text{FePO}_4$ was dried at 60°C overnight in vacuum. The supernatant was combined with the washing water and analyzed using a Varian spectrAA 220 FS to determinate the level of deinsertion of lithium and the iron concentration. When compared to a LiFePO_4 sample treated in the same manner, but without the oxidant, no additional iron was found.

Formation of pedot-LiFePO₄:

3.10 g LiTFSI (3M™ Fluorad) was dissolved in 25 mL of methanol in a Petri dish. Hereafter 0.51 g of 3,4-ethylenedioxythiophene (Aldrich) and 4.68 g of Li_(1-0.3)FePO₄ was added to the solution. The Petri dish was placed in an oven at 60 °C for 2 hours. A blue color appeared upon solvent evaporation. The mixture was transferred to a filter and rinsed with methanol and acetonitrile. The pedot-LiFePO₄ was dried at 60 °C overnight in vacuum. The reinsertion of Li into Li_(1-x)FePO₄ was confirmed by atomic absorption/emission: Li:Fe 1.02 ± 0.02 (95 % confidence interval).

Characterization:

The crystal structures were determined using a SIEMENS (D5000) CoK_α diffractometer equipped with a position sensitive detector. TEM images were recorded with Jeol JEM-2100F TEM operating at 200 kV. The FTIR analysis was made with a Nicolet 6700 FTIR Smart Endurance using the Single-Reflection Diamond ATR tool.

The electrochemical properties of pedot-LiFePO₄ were determined from CR2032-type coin cells using metallic lithium as the anode. The cathode was made by coating pedot-LiFePO₄ and a solution of PVDF (Kynar® KF Polymer W#1100) in *N*-methylpyrrolidone (Aldrich) onto carbon coated Al foil (Exopack #2651). The product ratio was pedot:LiFePO₄:Pvdf (8:84.5:7.5 in wt. %). The thickness of the active materials varied between 13 μm to 30 μm. The cells were assembled in an argon atmosphere glove box (H₂O < 1 ppm, O₂ < 1 ppm). The electrolyte was 1 M LiPF₆ in a 1:1 ethylene carbonate and dimethyl carbonate (Novolyte Technologies). Celgard 2500 was used as the separator. Electrochemical testing was completed using constant current cycling, between 2.2 to 4.2 V using a Bio-Logic VMP®3 potentiostat. For room temperature testing a charging rate of C/10 was used, while 60 °C testing required 5 cycles of break in at the C/10 rate (data not shown) before stability cycling at the C/2 rate.

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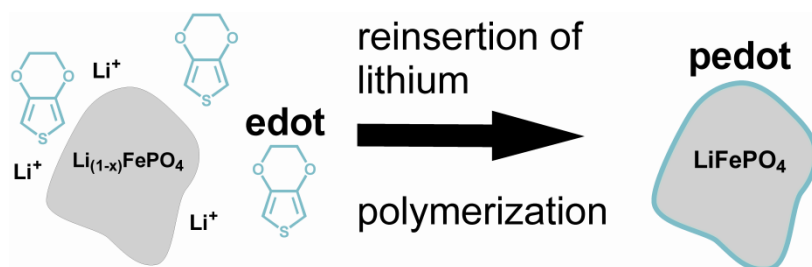
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A soft chemistry approach to conducting
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Using the intrinsic oxidative power of the $\text{LiFePO}_4/\text{FePO}_4$ combined with the reinsertion of lithium ions, we demonstrate the formation of the conducting polymer poly(3,4-ethylenedioxythiophene) (pedot) at the solid surface. The resulting composites are shown to have very promising electrochemical properties in rechargeable lithium batteries, specifically they allow for the elimination of carbon additives.