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Improving the cycling performance of $LiFePO_4$ cathode material by poly(3,4-ethylenedioxythiopene) coating

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$LiFePO_4$ composite cathode materials with PEDOT [poly(3,4-ethylenedioxythiopene)] were prepared by electropolymerization or by blending methods. The cycling performance of these composites in lithium test cells were then evaluated and compared with bare and carbon-coated $LiFePO_4$. The electrodes were further fined tuned by optimizing the materials and different preparative methods adopted. It was found that the $LiFePO_4$/PEDOT composite obtained by direct electropolymerization over the cathode shows better cycling performance in terms of capacity (110 mAh/g_{LFP} at 2C) and capacity retention (125 mAh/g_{LFP} after 50 cycles at C/2). We attribute the improved performance to an enhanced conductivity, as evidenced by the initial impedance of the cathodes and low charge/discharge polarization during cycling.

1. Introduction

Lithium-ion batteries incorporating $LiFePO_4$ or other $LiMPO_4$ (M=Mn,Co,Ni) olivine-related compounds are attractive in terms of safety, energy and power density, general performance and cost.[1-3] However these compounds possess low electronic conductivity and poor ionic diffusivity, which ultimately result in poor cycling performance for Li-ion batteries.[4] Strategies to improve the electronic conductivity of the active material include coating with carbon or conducting polymers,[5-7] the control of the particle size and morphology, blending with metallic additives, ionic doping or substitution in the crystalline lattice, among other approaches that have been adopted.[8-9]

To overcome the current bottleneck in these materials the electronic and ionic wiring of the active material is one of the strategies which can be applied to increase the rate performance and mechanical stability of the electrode. For this electron-conducting additives and polymeric binders are usually incorporated to the formulation. In the past various kinds of carbon black and fluorinated polymers have been used as common additives; however, such materials do not contribute to the electrode capacity and thus reduce the energy and power density of the battery.[10] In this scenario the incorporation of conducting polymers to the electrode formulation is an attractive option, as it can act in two folds. First as electron conducting additive and as binder, and secondly to provide enhanced electrochemical performance, apart from improving the mechanical properties of the electrodes, and protecting the battery electrolyte from decomposition by the formation of protective layers.[11-12]

The role of polypyrrole, polyaniline and poly(3,4-ethylenedioxythiopene)[PEDOT] on the performance of $LiFePO_4$ in lithium batteries has been investigated during recent years.[2,6,7,11,13] Composite electrode materials with PEDOT are especially attractive in terms of high electronic conductivity, contribution to the electrode capacity and the ability to improve Li-ion transport.[12a] PEDOT has low band gap, chemical stability and can withstand cycling for practical applications and was also shown to be efficient cathode in dye sensitized solar cells for the reduction of redox electrolyte.[12b,12c]Various methods have been proposed to prepare $LiFePO_4$/conducting polymer composites, including blending with a chemically synthesized polymer,[14-16] chemical polymerization in the presence of $LiFePO_4$ or $Li_{1-x}FePO_4$,[13] potentiostatic or potentiodynamic electropolymerization of monomers to form a deposit in the presence of $LiFePO_4$,[6-7] among other approaches. It is well known that a different synthetic procedure leads to different stoichiometry and microstructure that largely influence the physico-chemical properties of the material. In order to further improve the cycling performance of $LiFePO_4$, synthetic approach was fine tuned to incorporate PEDOT into $LiFePO_4$ by electropolymerization or by mechanical blending. The results presented here are obtained from moderate-performance $LiFePO_4$, which allows evaluating more clearly the response of the composites. To understand the performance of different preparative methods adopted, a comparative study of PEDOT-coated $LiFePO_4$ (LFP) has been carried out which was hereto unreported. This is paramount to choose the right chemistry, to yield higher performance materials.

2. Results and Discussion

2.1 Characterization of LFP and LFP/C

X-ray powder diffraction (XRD) patterns were obtained from a Siemens D5000 diffractometer using Cu Kα radiation in the 2θ range from 15 to 80° in steps of 0.04° at 20 s/step. The XRD patterns of LFP and LFP/C pristine materials (supporting info) showed the characteristic reflections for the orthorhombic structure of $LiFePO_4$ (JCPDS 40-1499), except for very weak signals in the 2θ interval from 22.3 to 34.3º, attributed to Li_3PO_4 (JCPDS 15-0760). These reflections are almost undetectable in the pattern of the carbon-coated sample. The refinement of the lattice parameters for LFP with space group *Pnmb* provided the values a = 6.004(1) Å, b =10.322(4) Å, c = 4.691(1) Å, which is in accordance with previous reports.[18] However refined unit cell parameters for LFP/C showed no significant difference.

2.2 Electrochemical Properties

2.2.1 Initial charge/discharge performance

Fig. 1 compares the initial charge/discharge profiles at C/10 for the LFP and LFP/C samples and their composites with PEDOT. The LFP and LFP/C samples show the typical profiles with a potential plateau at ca. 3.4-3.5 V, characteristic of the two phase transformation of $LiFePO_4$ into iso-structural $FePO_4$ upon lithium extraction/re-insertion. The charge capacity for the bare sample reaches 91 mAh g^{-1} and in discharge the cell delivers a reversible capacity of only 77 mAh g^{-1}. To mention here in this article the reported capacities are referred to the total weight of the composite electrode, including LFP active material and additives. For benchmark purposes, common loadings of active material range from 70-85% wt., which would correspond to capacity values of ca. 130 mAh g^{-1}. The carbon-coated sample shows higher capacity than the bare sample, reaching 134 mAh g^{-1} in charge and 110 mAh g^{-1} in discharge. In spite of the improvement in the discharge capacity observed for the carbon-coated sample, this composite illustrates irreversible capacity, while also contains electrochemically inactive carbon black (CB) and polymeric binder (polyvinylidene fluoride [PVDF]) additives.

Recently, Trinh et al.,[6] adapted a dynamic three phase interline electropolymerization to produce cathode films that incorporate PEDOT and LFP without the need of carbon black and PVDF additives, thus improving the power and energy densities. We have adopted the three phase (3phase) method to prepare LFP-PEDOT composites and extended it for preparing LFP/C-PEDOT composites, designated, respectively, as LFP-3phase and LFP/C-3phase. Fig. 1a displays the initial charge and discharge profiles for the LFP-3phase composite. The charge and discharge profiles present the characteristic voltage plateaus for LFP at nearly 3.45-3.37 V. In charge, a particular feature for this sample is the abrupt change of slope at ca. 4.0V, in the region where de-lithiation of active $LiFePO_4$ has taken place. To further investigate the abnormal profile above 4.0 V, we performed a linear voltammetry test for the EDOT monomer in the battery conditions over a platinum electrode. The voltammetry test (supporting info) revealed an oxidation onset potential at nearly 4.0 V and a current peak at 4.13 V(vs. Li^+/Li), in agreement with previous reports[12]. Therefore we attribute the 4.0 V signal in the charge profile of the LFP-3phase composite to the oxidation of unreacted EDOT monomers or oligomeric species trapped within the LFP-3phase composite during its preparation. In discharge, the potential profile for the LFP-3phase composite is similar to that of the LFP sample and the discharge capacity reaches ca. 53 mAh g^{-1} a value that is close compared to the reported[6] (ca. 45 mAh g^{-1}).

Fig. 1b shows the charge/discharge profiles for the LFP/C-3phase composite. The charge profile for this sample presents a smooth increase in potential from the open circuit potential to the characteristic plateau at ca. 3.45V. The potential then continues to rise up to a capacity of 216 mAh g^{-1} (off-scale) at the cut-off potential. In discharge, the LFP/C-3phase composite shows a short plateau at ca. 3.4 V, with further potential decrease until reaching the cut-off potential and a total discharge capacity of ca. 91 mAh g^{-1}. The poor discharge capacity in the 3.4 V plateau region for the LFP-3phase and particularly for the LFP/C-3phase samples reflects the difficulties for incorporating active LFP into the composite. Contrary to the report,[6] we have found it was fragile composites, which required additional reprocessing to form an electrode. Considering these obstacle, the sample (LFP/C-3phase) was not chosen to study further.

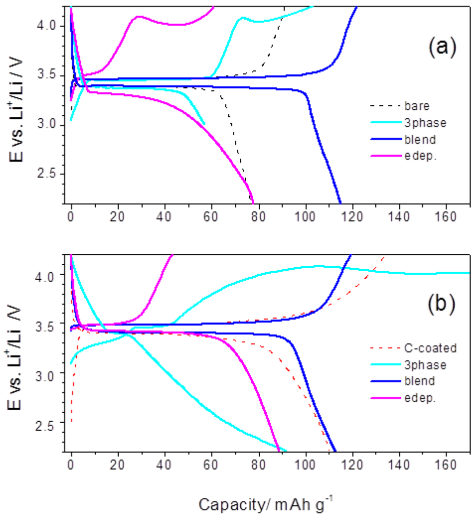

Fig. 1 Initial charge/discharge profiles at C/10 for (a) LFP-PEDOT composites and (b) LFP/C-PEDOT composites.

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Tabe 1. Characteristics of the different composite cathodes

Sample	Preparation details	LFP content (%)	PEDOT content (%)	LFP:PEDOT weight ratio	Additives CB + PVDF (8:7 wt.) content (%)
LFP	LFP cathode with CB and PVDF additives	85	0	100:0	15
LFP-3phase	Three phase electropolymerization in presence of LFP	70	30	70:30	0
LFP-blend	LFP blended with PEDOT obtained by three phase electropolymerization	80	20	80:20	0
LFP-edep.	Electrodeposition of PEDOT over preformed LFP cathode	66	19	78:22	15
LFP/C	LFP/C cathode with CB and PVDF additives	85 (2 % wt. C)	0	100:0	15
LFP/C-3phase	Three phase electropolymerization in presence of LFP/C	50 (2 % wt. C)	50	50:50	0
LFP/C-blend	LFP/C blended with PEDOT obtanained by three phase electropolymerization	83 (2 % wt. C)	17	83:17	0
LFP/C-edep.	Electrodeposition of PEDOT over preformed LFP/C cathode	82 (2 % wt. C)	3	97:3	15

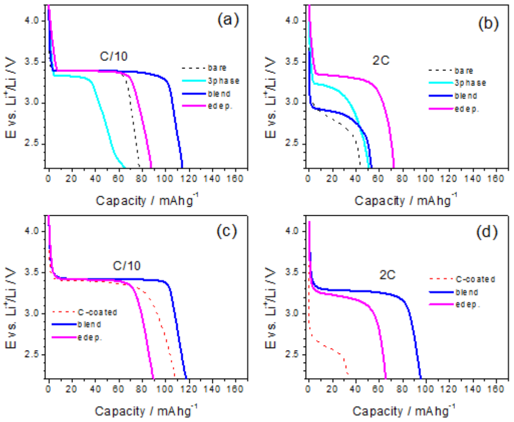

Fig. 2 Discharge curves at C/10 and 2C for (a-b) LFP-PEDOT composites and (c-d) LFP/C-PEDOT composites.

To control better the amount of PEDOT in the composite and improving its electrochemical performance, EDOT was electro-polymerized using the 3phase method[6,17] and then blended with LFP or LFP/C active materials. Fig. 1 shows the charge/discharge profiles for the LFP-blend and the LFP/C-blend samples. The charge/discharge profiles for the LFP-blend sample (Fig. 1a) show flat potential plateaus at ca. 3.47-3.38 V. The charge capacity for this sample reaches ca. 122 mAh g^{-1} and eliminate any profile abnormality near 4.0 V, which was observed for the LFP-3phase composite. These finding suggests an enhanced stability of the polymer against further oxidation, in the absence of LFP during the electropolymerization using three-phase method. While in discharge, the LFP-blend sample delivers a total capacity of 115 mAh g^{-1}, which is close to the benchmark capacity of 130 mAh g^{-1}. These results indicate a notable improvement in performance compared to those obtained for LFP-3phase, and show the importance of incorporating PEDOT with higher degree of polymerization to the active LFP material. In Fig. 1b, the charge/discharge profiles of LFP/C-blend present the plateau at ca. 3.48-3.40 V and capacities of 119 and 113 mAh g^{-1} in charge and discharge, respectively, which are very close to the capacity values obtained for the LFP-blend composite. Charge/discharge profiles of the samples obtained by direct electrodeposition (edep.) of PEDOT on cathodes are shown in Fig.1. In charge, the LFP-edep composite (Fig. 1a) show a short plateau at 3.5 V, followed by an increase in potential and an abrupt change of slope at c.a. 4.0 V, yielding charge capacity at the cut-off potential close to 61 mAh g^{-1}. The charge profiles for the LFP-edep and the LFP-3phase samples are similar, showing that the electropolymerization of EDOT monomers over LFP cathode was incomplete and produced redox active oligomeric species. The LFP-edep composite has the lowest discharge potential and a capacity of ca. 78 mAh g^{-1}. While the LFP/C-edep sample (Fig. 1b) indicates that the charge profile lacks the potential abnormality observed for the LFP-edep composite. This was accordance to our understanding, as the extent of electrodeposition will be higher over more conducting surface (carbon-coated LFP particles). The fact that the discharge capacity for both LFP-edep and LFP/C-edep samples was higher than their corresponding charge capacity indicates simultaneous delithiation of LFP and oxidation of EDOT monomers during the preparation of the composites by the electrodeposition method.

2.2.2. Slow vs. moderate rate performance

Fig. 2 shows average discharge curves at C/10 and 2C for the standard LFP and LFP/C and their different composites with PEDOT. Comparison between slow and moderate rate indicates that both standard LFP and LFP/C samples show capacity loss and potential drop with the increase in rate. The performance of the LFP-3phase composite is inferior among all the samples at C/10 (Fig. 2a), however, at higher rate (Fig. 2b) it retains 80% of its capacity at C/10 and is free from large potential drop found for the LFP and LFP/C. The performance of the LFP-blend composite also deteriorates considerably at 2C, losing more than 50 % of its low rate capacity and suffering considerable drop in potential.

The lower performance of the LFP-blend at 2C (Fig. 2b) contrasts with the better performance of the LFP/C-blend at similar rate (Fig. 2d). Earlier it was found that carbon materials are compatible with conducting polymers and give synergistic results in electroactive composites.[22] We believe that the chemical affinity to TEABF$_4$-doped PEDOT and the carbon coating of LFP/C particles favors the anchoring of PEDOT. Therefore, a more extended conducting polymer matrix is expected to form when both the inorganic and organic materials are blended. Improved performance, compared to parent LFP, was also observed for the cathode materials prepared by the electrodeposition method, especially at 2C. Thus, the LFP-edep sample shows a reversible capacity of ca. 87 mAh g^{-1} and 72 mAh g^{-1} at C/10 and 2C, respectively, with a voltage drop of less than 100mV.

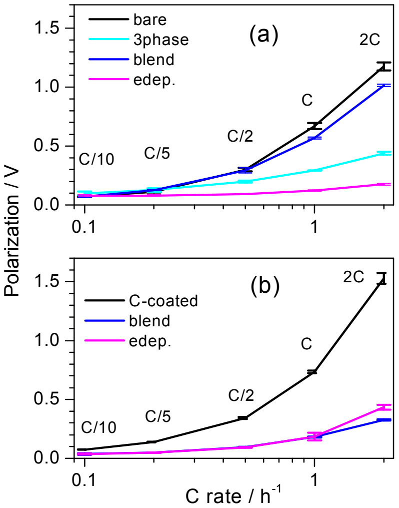

Fig. 3 Charge-discharge polarization plots for (a) LFP-PEDOT and (b) LFP/C-PEDOT composites.

2.2.3. Charge/discharge polarization and cathode impedance

Fig. 3 shows polarization graphs for the standard samples and with PEDOT composites. As expected, composites with polymer show lower charge/discharge polarization than the standard samples. Particularly, the composite prepared by electrodeposition over the LFP cathode show the lowest polarization, which reflects its increased conductivity and reactivity for extraction-reinsertion of lithium ions in the active material. Comparison against the polarization of LFP/C-edep composite (Fig. 3b) suggests that carbon coating is not necessary for the LFP-ed composite. Electrochemical impedance spectroscopy (EIS) was employed to investigate the effect of PEDOT on the conducting properties of the composite cathodes. In the past EIS studies on LFP cathode materials was reported[21], and the spectra can be fitted by using an equivalent electrical circuit consisting of a high and a medium-to-low frequency semicircles (R-Q elements), the former corresponding to the lithium ion migration resistance in the SEI and the later to the charge transfer resistance. Semi-infinite diffusion and differential intercalation capacity are usually fitted by a series capacitance 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. Fig. 4a presents the experimental and fitted spectra by using the above mentioned equivalent circuit. The resistance values obtained from the fitting procedure are listed in Table 2. It is evident from Fig. 4 that the charge transfer resistance values for the LFP-PEDOT composites are lower than for the parent LFP. In particular, the lowest resistance values were found for the LFP-edep. composite, which translates into a lower polarization and a higher cycling performance. The low impedance value was found for the composite prepared by electrodeposition, which suggests that the polymerization over LFP active material particles favors the growth of a highly conducting polymer that improves the electrical wiring between LFP particles. The impedance data of the C-coated samples shows the improvement in the total conductivity for the sample prepared by electrodeposition. However, the sample prepared by blending C-coated LFP and PEDOT give the high value of impedance. This observation can be explained in therms of formation of poorly conducting PEDOT that requires activation in order to reach an ideal polymerization degree and doping. The higher resistance for blend samples can also be related to the textural properties of the composites (Fig. 6). For PEDOT bearing samples, the information provided by SEM showed that the particles are visible after PEDOT addition. However, for blend samples the surface is more abrupt indicative of a less uniform distribution of the polymer.

2.2.4 Extended cycling

Fig. 5 presents the cycling performance of the standard samples and the different LFP-PEDOT and LFP/C-PEDOT composites. During the first 50 cycles, the capacity of all samples decreases progressively as rate increases. After 50 cycles, all the samples, except for the LFP-3phase and LFP-blend (Fig. 5a), recover at least 90% of their initial capacity at C/10 rate. The best performance, in terms of capacity values and capacity retention at C/2 during the first 50 cycles, was found for the LFP-edep. sample. After 110 cycles at variable rates, only the LFP-edep. sample recovers ca. 99% of its initial capacity at C/10, which confirms its remarkable cycling performance. The enhanced cycleability obtained for the LFP-edep. cathode materials suggests that the PEDOT obtained by this method is more chemically and mechanically stable (tethered) over LFP in the battery environment. Fig. 5b presents the cycling performance of two LFP/C-PEDOT composites. During the initial cycles at low rates (C/10-C/5), only the LFP/C-blend composite outperforms the LFP/C sample. At moderate rates (C/2-2C), both LFP/C-blend and LFP/C-edep. composites outperform the LFP and the LFP/C samples. After 50 cycles, both LFP/C-PEDOT composites recover almost 99% of its initial capacity at C/10, and show good capacity retention at C/2 and after 110 cycles both LFP/C-PEDOT samples recover more than 95% of the initial capacity. Comparing the performance of the composites prepared by the blending method, the carbon coating in the LFP/C active material could provide a good substrate that favors the formation of a more extended conducting polymer matrix. In electrodeposition, the higher electrodeposition time for the LFP-edep. allows better wetting of the LFP active material by EDOT monomers, promoting a more quantitative PEDOT electrodeposition.

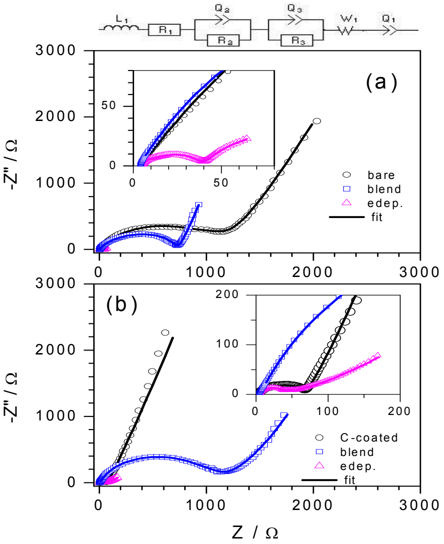

Fig. 4 AC impedance spectra of pristine composites. a) LFP-PEDOT and b) LFP/C-PEDOT

Table 2. Data of the fitting of the EIS spectra shown in Fig. 4

Material	Ro (Ω)	R_{SEI} (Ω)	R_{ct} (Ω)	R_{Total} (Ω)
LFP	4.1	781	258	1043
LFP-blend	3.1	626	102	731
LFP-edep.	4.7	33	8	45
LFP/C	3.9	52.5	12	68
LFP/C-blend	4.7	889	242	1136
LFP/C-edep.	5.0	25	16	47

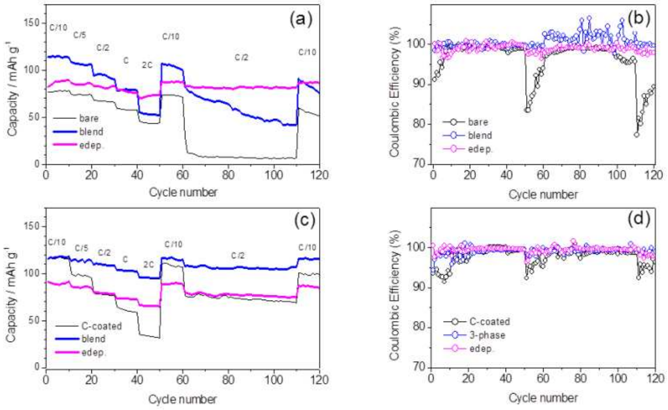

Fig. 5 Cyclability at different rates for (a) LFP-PEDOT and (b) LFP/C-PEDOT composites.

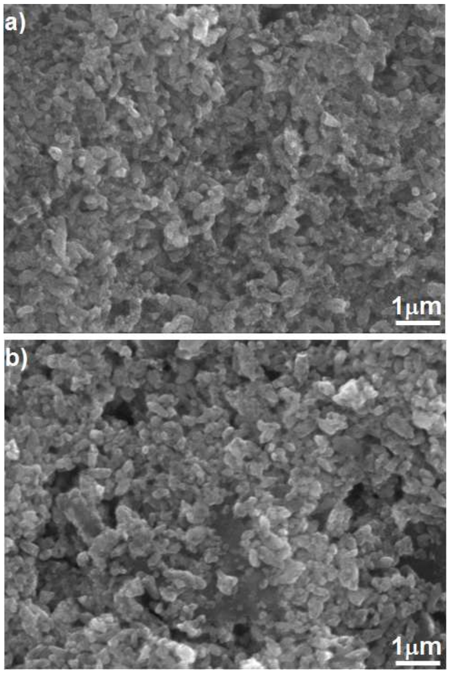

Fig. 6 Scanning Electron Micrographs of composites (a) electrodeposition and (b) blend based on $LiFePO_4$.

3. Conclusions

A comparative study of LFP-PEDOT and LFP/C-PEDOT composites prepared by different methods such as electropolymerization and blending methods were carried out. The $LiFePO_4$/PEDOT composite obtained by direct electrodeposition over the cathode showed the best cycling performance, with a reversible capacity of ca. 110 mAh/g_{LFP} at 2C, a notable capacity retention at C/2 (125 mAh/g_{LFP} after 50 cycles) and low charge/discharge polarization. The improved performance is ascribed to an enhanced overall conductivity of the electrode (active material plus additives) emerging from the conductive nature of polymer. PEDOT alone can well improve the performance of phosphate materials and thus the combination of carbon and PEDOT coating is not necessary to improve the performance of the phosphate.

4. Experimental Section

4.1 Electrode preparation and Materials

$LiFePO_4$ and carbon-coated $LiFePO_4$ (LFP/C) active materials were obtained as described elsewhere.[20] LFP and LFP/C electrodes were prepared by mixing the active material with carbon black (CB) and PVDF additives (85:8:7 wt. %) in *N*-methyl pyrrolidone to form slurry. The slurry was ultrasonicated, deposited over an aluminium disk (0.64 cm^2) and dried at 80°C under vacuum for 12 h. The average amount of active material ranges from 3-5 $mgcm^{-2}$. 3,4-ethylenedioxythiopene (EDOT) and tetraethylammoniumtetrafluoroborate ($TEABF_4$) were obtained from Aldrich, while poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) dispersion (PEDOT:PSS) was procured from Bayer GmbH, and were used without any further treatment. The preparative methods used to obtain the composites with PEDOT and LFP or LFP/C active materials are described below.

4.2. Materials synthesis

Three phase electropolymerization (3phase) consisted in the potentiostatic electropolymerization of PEDOT was formed potentiostatically in the presence of LFP or LFP/C through interphasial electropolymerization.[6]The three-phase reaction medium contained $TEABF_4$ (0.1M) dissolved in water, EDOT (0.1M) dissolved in dichloromethane and the active material spread over the aqueous/organic phase boundary. The experiment was carried out in a three-electrode cell with platinum wire as working electrode situated across the interphase, a carbon rod as counter electrode and an Ag/AgCl (3M KCl, AgCl sat.) as reference electrode, both electrodes immersed in the aqueous phase. The electropolymerization of EDOT monomer took place over platinum at the aqueous/organic interphase when a potential difference of 1.3 V was applied. The obtained composite film was grinded, washed with deionised water followed by acetonitrile, and dried for 12 h under vacuum at 60 ºC. The dry product was dispersed in NMP and deposited on an aluminium current collector, finally it was dried for 12 h under vacuum at 80 ºC. Composites prepared by this method with LFP or LFP/C will be now referred as LFP-3phase and LFP/C-3phase, respectively.

The blending method consisted of mixing PEDOT, prepared by 3phase electropolymerization,[17]and the active material (without CB and PVDF additives) in *N*-methyl pyrrolidone to form slurry. The slurry was ultrasonicated, deposited over an aluminium disk and dried at 80-100° C under vacuum for 12 h. Composites prepared by this method will be henceforth referred to as LFP-blend or LFP/C-blend.

Electrodeposition of PEDOT was performed on LFP and LFP/C cathodes as the substrate. The electrodeposition was carried out using the cathode as working electrode in a three electrode cell with an aluminium disk as counter electrode and Ag/AgCl (3M KCl, AgCl sat.) as reference electrode. The reaction medium consisted of a 0.1 M EDOT, 0.1 M $TEABF_4$solutions in acetonitrile. The electropolymerization over the LFP and LFP/C electrodes was performed potentiostatically at 1.3 V (Ag/AgCl) during 30 and 3 min, respectively. After electropolymerization, the composite electrode was washed with acetonitrile and dried at 80 °C under vacuum for 12 h. The samples prepared with LFP and LFP/C will be henceforth referred to as LFP-edep and LFP/C-edep, respectively. Table 1 summarizes the characteristics of the different LFP-PEDOT and LFP/C-PEDOT composites.

4.3 Battery testing

Batteries were assembled in two-electrode Swagelok-type cells, using the cathode as working electrode, 1 M $LiPF_6$ (EC:DEC, 1:1 volume ratio) electrolyte (SelectiLyte LP40, Merk), with Whatman glass-paper as separator and 1.5 mm thick lithium metal foil as reference/counter electrode. The cells were assembled in a glove box under controlled argon atmosphere (H_2O, O_2< 1 ppm). Galvanostatic cycling at different C-rates (C = 1 Li h^{-1} mol^{-1}) was carried out at room temperature using a Biologic MPG station. The cut-off potential for charge and discharge were set at 4.2 and 2.2 V (vs. Li^+/Li), respectively. All the capacity values are reported considering only the weight of the LFP active material. Extended cycling was performed in order to evaluate the rate capability, the capacity recovery and the capacity retention of the different samples. Rate capability was assessed by repeated and progressive cycling at rates of: C/10, C/5, C/2, C and 2C (10 cycles each). Afterwards, a first evaluation of the capacity recovery at C/10 (10 cycles) was carried out. The capacity retention was evaluated at C/2 for 50 cycles. At the end of the capacity retention test, a second capacity recovery test was carried out by cycling at C/10 for 10 cycles. Electrochemical impedance spectra were recorded for the cathode materials in an Autolab PGSTAT12 station. Measurements were done in three-electrode Swagelok cells housing LFP-based composites as working electrode, lithium metal counter electrode and a perpendicularly aligned lithium reference electrode. The applied ac voltage was 10 mV and the frequency was varied in the range from 1MHz to 10 mHz.

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