Short communication

High temperature electrochemical performance of nanosized LiFePO$_4$

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ABSTRACT

The electrochemical performance of LiFePO$_4$ was tested at temperatures up to 150 °C for micrometric and nanometric size samples. Among the latter, both highly defective samples obtained by direct precipitation and annealed samples were tested. The comparison of voltage composition profiles for these samples coupled to GITT experiments allowed to conclude that defects seem to be the major factor in inducing the solid solution behaviour at room temperature. Good capacity retention is exhibited upon prolonged cycling at 100 °C in EC LiBOB electrolyte, also for nanosized samples that still maintain 75% of the initial capacity after 170 cycles. These results prove that the enhanced thermal stability of such electrolytes can be extended to temperatures much higher than those usually tested.

1. Introduction

Batteries able to work at relatively high temperature are needed for some specific applications, such as Measurement While Drilling (MWD) tools for the oil drilling market. For instance, Li/CuO primary cells that can operate up to 150 °C are currently being used in down-hole tools in the oil-well logging industry [1,2]. In this context, the development of secondary lithium batteries (rechargeable) able to operate in that temperature range would represent an interesting alternative, even if only moderate cyclability could be attained. The performances of lithium batteries with conventional organic electrolyte solvents were rarely investigated at temperatures higher than 55 °C. Above this value poor storage and cycling behaviours were generally observed [3–5] as a result of severe degradation of the electrode/electrolyte interface, promoted by too high temperatures. Recent studies aimed at finding acceptable lithium ion battery technologies capable of working at temperatures higher than 60 °C proposed the use of LiPF$_6$ salt in EC as the electrolyte with conventional electrode technologies based on "standard" anode and electrode materials [6]. Although remarkable performances were achieved for the first electrochemical cycle, important capacity fading was observed. We recently succeeded in achieving good capacity retention at 100 °C for chromium-rich oxidised stainless steel electrodes cycled in organic-based electrolytes [7].

In this paper, we report on the study of the electrochemical response at various temperatures and with various electrolytes of a much studied material, LiFePO$_4$, with controlled particle size and stoichiometry, inherently very stable upon electrochemical cycling under demanding conditions. The results of the experiments performed allowed us to address in an original way the much debated topic [8–11] on the relative influences of temperature, particle size and defects onto the mechanisms (two-phase vs. single-phase) of Li$^+$ extraction/insertion from/into LiFePO$_4$.

2. Experimental

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Aldrich, ≥99.95%), LiBF$_4$ (Aldrich, 98%) and lithium bis(oxalato)borate (LiBOB, Chemetall, premium battery grade, 99.4%) electrolyte salts were used as received. CsTFSI and KTFSI were prepared from Bis(trifluoromethane)sulfonimide (Fluka, ≥95%) and either CsCO$_3$ or KCO$_3$ (Aldrich, purity ≥99.0%) in dry absolute ethanol (Panreac), according to previously reported procedures [12]. Ethylene carbonate was purchased from Fluka (≥99.0%)) and used to prepare, inside an argon filled glove box, 1 M electrolyte solutions of the corresponding salts. Commercial 1 M LiPF$_6$ in EC:DMC 1:1 (LP30) was purchased from Merck.

Electrochemical experiments at 150 °C were made using a specially designed high temperature electrochemical cell as described in Ref. [13] whereas those carried out at lower temperatures could also be carried out using standard Swagelok cells [14] using Teflon^{TM} gaskets. The working electrode typically consisted of 5 mg of a powder mixture of LiFePO$_4$ and 20% Ketjenblack EC-300J (Akzo

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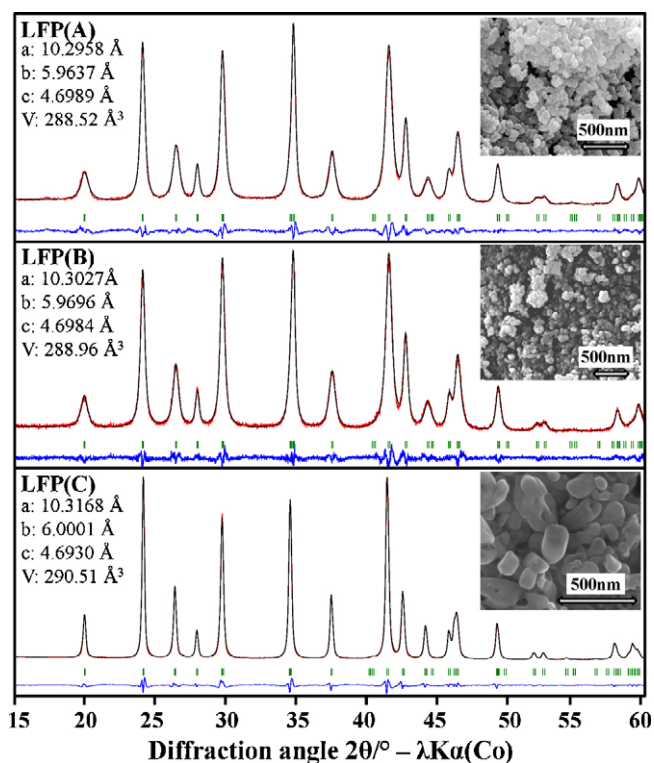
Fig. 1. X-ray diffraction patterns recorded with Co Kα radiation, of three samples of "LiFePO₄" and their respective SEM micrographs.

Nobel). Two sheets of Whattman GF/d borosilicate glass fiber were used as separator, soaked with the electrolyte (ca. 0.5 cm³). The negative electrode consisted of lithium metal foil (0.38 mm thick, Aldrich, 99.9%). Electrochemical cycling experiments were made using either a Mac Pile or a VMP3 potentiostat (Bio-Logic, France). Galvanostatic cycling data were recorded at C/20 rate either in continuous or intermittent (Galvanostatic Intermittent Titration Technique, GITT) modes. For the latter, durations of both pulses and open circuit periods were set at 30 min.

X-ray powder diffraction (XRD) diagrams were collected on a Bruker D8 diffractometer using the Co Kα radiation (at 40 kV, 40 mA), a Göbel mirror and a Braun PSD detector, mounted in a θ–θ configuration. The morphology, size, and elemental compositions of the samples were characterized by scanning electron microscopy (SEM) using a Philips XL30 FEG, equipped with a Link Isis apparatus (Oxford) for energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Description of the LiFePO₄ samples used

Three LiFePO₄ samples were used in this study. Their XRD patterns and calculated lattice parameters are displayed in Fig. 1.

- Sample A, obtained through a precipitation technique as described in Refs. [15–17] is a defective $Li_xFe_yPO_4$ powder (~40–50 nm-size particles) characterized by a typical smaller unit-cell volume (288.5 Å³) than that of stoichiometric LiFePO₄. As extensively discussed in Ref. [11] and further confirmed to a greater extent in [18], this small unit-cell volume is directly related with structural defects (Fe vacancies, Li/Fe anti-site mixing) within the $Li_xFe_yPO_4$ particles which were evidenced through Rietveld refinements using neutron powder diffraction data [11]. "Anti-site" defects were proposed by Fisher and Islam [19] to be the most likely to occur in LiFePO₄ and where there-

after "visualized" very nicely by Chung et al. through STEM [20]. These authors also report that higher temperature annealing of "LiFePO₄" powders resulted in lower amounts of structural defects [20].

- Sample B was obtained by annealing sample A at 300 °C for 10 h in N₂ atmosphere. The slightly larger unit-cell volume ($V = 289$ Å³) when compared to that of sample A, is likely to be associated to structural redistribution, of Li and/or Fe on their respective "normal" crystallographic sites, during the annealing process, as described in Ref. [20]. We recently reported [18] on a clear relationship between the amount of structural defects in "LiFePO₄" and its unit-cell parameters. Annealing at moderate temperature (300 °C) does not induce particle growth and hence the unit-cell volume change must be associated to changes in the structural defects.

- Sample C was obtained by precipitation followed by annealing at 700 °C under N₂ so as to produce a thin carbon coated layer on stoichiometric LiFePO₄ particles. The volume of its unit-cell is much closer to theoretical for fully stoichiometric non-defective LiFePO₄ (291 Å³), the mean particle size being around ~120 nm in size.

3.2. Choice of electrolyte

Electrolyte solvent and salts that could potentially be used in high temperature experiments were chosen taking into account thermal stabilities and voltage operation windows [21,22]. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis (oxalato)borate (LiBOB) and lithium tetrafluoroborate (LiBF₄), were selected as salts. Ethylene carbonate (EC) was chosen as solvent in view of its high boiling point and thermal stability combined with its low degradation at high temperature [23,24]. In addition to those, a molten mixture of LiTFSI, KTFSI and CsTFSI (with respective molar fractions 0.2, 0.1 and 0.7, m.p. 146 °C) was used as electrolyte for tests performed at 150 °C. It has been reported to exhibit a large electrochemical window at this temperature that allowed successful cycling of a Li//LiFePO₄ open flooded cell inside a glove box [25].

With the aim of selecting the most suitable electrolyte, identical cells were built using sample C, which can be considered to be "standard" LiFePO₄ powder, as positive electrode vs. Li. The above-mentioned electrolytes were used for electrochemical cycling in galvanostatic mode at different temperatures (see Fig. 2).

- Efficient cycling at 150 °C was found to be possible only in the molten salt (Li/K/Cs TFSI) electrolyte: Fig. 2a demonstrates indeed a large and reversible capacity attained with an extremely small polarization for this configuration. These new results, obtained in tight-closed cells cycled in an oven are fully comparable with those obtained by Watarai et al. [25] using flooded cells cycled inside a glove box. Prolonged cycling was however tricky to achieve with our experimental setup since the string present in the cell to maintain electric contact forces electrolyte extrusion from the separator. Work is currently in progress to solve this problem.

- All attempts to cycle cells using LiBF₄/EC as the electrolyte at 100 °C were unsuccessful and generally failed in the very first cycles. However, cycling at 80 °C was possible (Fig. 2c) even if a slightly lower capacity and much larger polarization (ca. 250 mV) was observed. This is presumably related to the much lower ionic conductivity of LiBF₄-based electrolytes with respect to LiBOB-based ones [21].

- Successful cycling at 100 °C with large capacity and small polarization (ca. 70 mV) was achieved using 1 M LiBOB in EC as electrolyte (Fig. 2b) thanks to the high thermal stability of the bis(oxalate)borate anion [26]. LiFePO₄//graphite cells operating
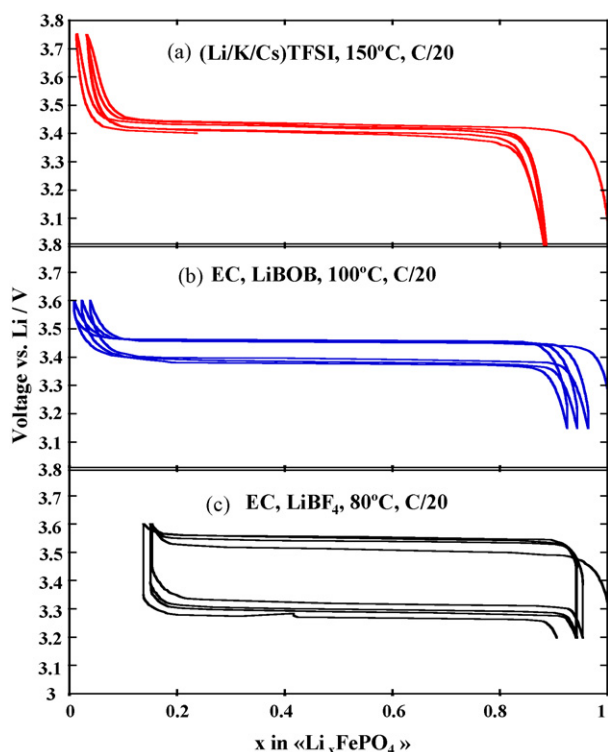
Fig. 2. Galvanostatic cycling at C/20 vs. Li of LFP(C) with diverse electrolytes and at different temperatures.

at 55 °C using 0.7 M LiBOB in EC:PC:DMC (1:1:3) electrolytes have been shown to exhibit much lower capacity fading than the corresponding analogs using LiPF$_6$ due to the suppression of iron dissolution [5]. Such effect has been recently confirmed in large cells that were also exhibiting enhanced safety [27], in agreement with previous ARC studies on the reaction between LiFePO$_4$ and LiBOB in EC/DEC electrolyte [28]. Our results suggest that the beneficial effects of using this electrolyte go far above the 55–60 °C temperature range previously reported, since successful cyclability is attained at 100 °C.

Fig. 3 depicts the voltage vs. composition profile together with the capacity vs. cycle number for LiFePO$_4$(C) cycled at 100 °C in 1 M LiBOB/EC (Fig. 3a) and at 25 °C in LP30 (Fig. 3b) for comparison. Most remarkably, the coulombic efficiency (~100%) and the very stable capacity retention upon cycling at 25 °C using LP30 electrolyte, are still observed at 100 °C using LiBOB in EC. Indeed, these cells were found to exhibit excellent behaviour with less than 3% capacity loss after 30 cycles. This strongly contrasts with the literature results of similar Li//LiFePO$_4$ cells for which a capacity loss close to 20% was reported after 30 cycles at much lower temperatures (60 °C) using 1 M LiPF$_6$ in PC:EC:DMC (1:1:3) [29].

In view of these results, we selected 1 M LiBOB in EC as the most suitable electrolyte for further experiments involving nanometric samples A and B.

### 3.3. Experiments on nanosized "LiFePO$_4$" (A and B)

Galvanostatic cycling experiments (GITT) were performed on cells containing nanosized LiFePO$_4$(A) as the positive electrode material and standard LP30 electrolyte (Fig. 4) so as to address the combined effects of particle size, temperature and defect chemistry on the shape of the voltage–composition curves (two-phase vs. single-phase mechanism). The relatively high initial OCV voltage (3.35 V vs. Li$^+$–Li^0) of the pristine material together with the
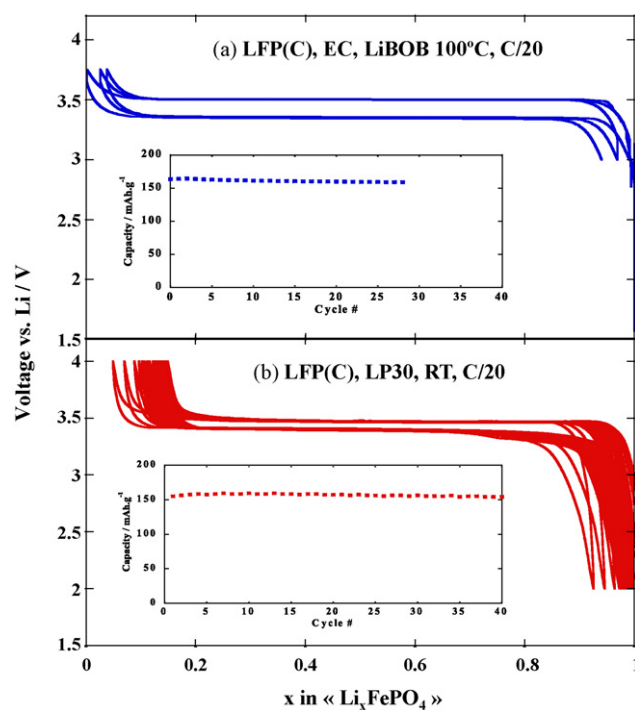
Fig. 3. Prolonged cycling at C/20 vs. Li of LFP(C) using LiBOB at 110 °C (a) compared to more classical data obtained at 298 K with LP30 electrolyte (b).

limited electrochemical capacity ($\Delta x \sim 0.34$) upon the first oxidation is consistent with the presence of significant amounts of Fe^{III} in the sample as a consequence of both vacancies on the Fe crystallographic site and Li/Fe anti-site mixing in the structure [11,18]. This is further confirmed after the first reduction, since it involves a much larger electrochemical capacity ($\Delta x \sim 0.50$) than the first oxidation.

The most interesting feature of the data plotted in Fig. 4 is the continuous decrease of the quasi-equilibrium OCV for the whole composition range, which further confirms the full single-phase
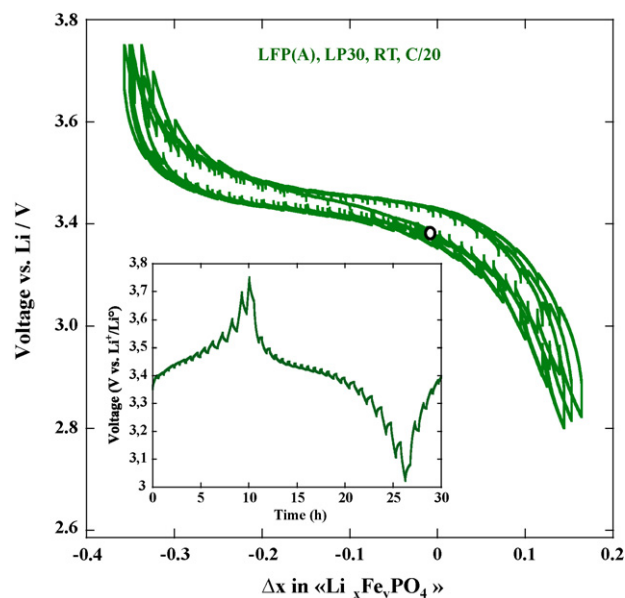
Fig. 4. GITT cycling of nanosized Li$_x$Fe$_y$PO$_4$ vs. Li at 298 K using LP30 as the electrolyte. Note that the OCV prior first charge was of 3.35 V vs. Li, indicated by a small white circle.
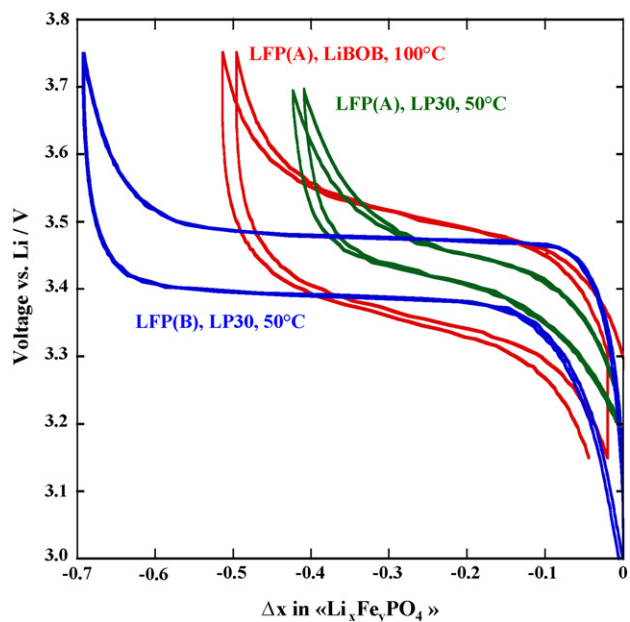
Fig. 5. Galvanostatic cycling at C/20 vs. Li of nanosized (∼40 nm) LFP(A) and LFP(B) electrodes.

Fig. 6. Capacity vs. cycle number for LFP(B) cycled at 100 °C at C/20 vs. Li using LiBOB electrolyte. The inset shows the voltage vs. composition plot for the two first cycles.

solid solution domain already reported earlier [11]. This solid solution process is accompanied by a continuous shift of the X-ray diffraction lines during cycling [11]. We confirmed that this full solid solution range was maintained upon increasing the operating temperature of the cell up to 100 °C using the LiBOB electrolyte yielding ca. 90 mA h g^{-1} with good capacity retention. This non-conventional behaviour of an $LiFePO_4$-based electrochemical cell offers very interesting perspectives in terms of being able to properly monitoring the state of charge of the battery, as opposed to the "classical" two-phase plateau at ∼3.45 V vs. Li commonly observed for "standard" $LiFePO_4$ electrodes.

Fig. 5 compares the electrochemical data for nanosized "$Li_xFe_yPO_4$". Special attention deserves the fact that the sloping voltage vs. composition behaviour observed for LFP(A) (high concentration of defects, $V = 288.5\,\text{Å}^3$) with both LP30 electrolyte at 50 °C and LiBOB electrolyte at 100 °C is no longer observed in LFP(B). The simple thermal treatment of LFP(A) under N_2 at 300 °C to yield LFP(B) does not induce particle growth but is found to drastically change the profile of the voltage–composition curve. In the case of LFP(B) it is characteristic of a two-phase "plateau" reaction between $Li_{1-\delta}FePO_4$ and $Li_\varepsilon FePO_4$. Although we need to fully confirm/measure the concentration of defects (antisites, vacancies, . . .) remaining in the LFP(B) framework, these observations tend to minimize the role of particle size on the existence, or not, of Li_xFePO_4 solid solution at low temperature, contrary to what had been proposed in [9,10].

The larger capacity exhibited by LFP(B) when compared to LFP(A) was also maintained upon prolonged cycling at 100 °C in LiBOB electrolyte (see Fig. 6). Since the increase in the temperature of the experiment favours the single phase mechanism, a slopy trend for the voltage vs. composition profile is observed for LFP(B) at 100 °C. Capacity fading is relatively low, since 75% of the initial value is still maintained after 170 cycles. These results show the feasability of extending the application domain for $LiFePO_4$ based batteries to cover uses involving thermally aggressive environments while at the same time proving that the enhanced thermal stability of LiBOB-EC electrolytes can be extended at temperatures much higher than those tested to date.
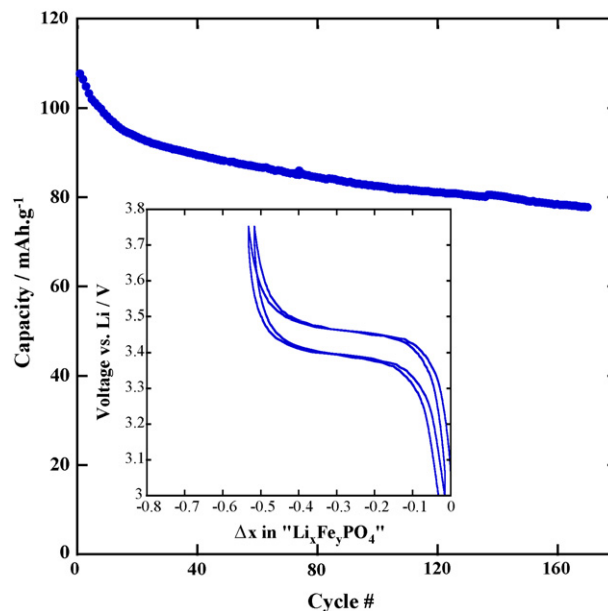
4. Conclusion

The electrochemical performance for nanosized $LiFePO_4$ samples obtained by direct precipitation was tested, both as obtained (i.e. with higher presence of defects) and after annealing at 300 °C. The comparison of voltage composition profiles for these samples coupled to GITT experiments allowed to conclude that defects seem to be the major factor in inducing the solid solution behaviour at room temperature for nanosized $LiFePO_4$. Efforts were also pursued to find electrolytes suitable for use in $LiFePO_4$ based batteries aimed at high temperature operation. LiBOB in EC was found to be particularly adapted for such purpose, nanosized $LiFePO_4$ still maintaining 75% of the initial capacity after 170 cycles at 100 °C, thus showing promise for enlarging the application field of batteries based on this material.

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