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Ultrafast charging of $LiFePO_4$ with gaseous oxidants under ambient conditions†

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Lithium iron phosphate is a lithium-ion battery positive electrode material with widespread use, as well as, unusually complex redox chemistry. Here we report on the discovery of a direct gas–solid delithiation reaction. Unique to this reaction, in addition to the lack of solvent, is remarkably fast kinetics. *In situ* X-ray diffraction, corroborated by elemental analysis, shows for the first time that $LiFePO_4$ bulk diffusion supports nearly complete delithiation/charging of carbon coated $LiFePO_4$ micropowder at ambient temperature in less than 60 seconds.

Introduction

Electric cars are back on the mass market as an environmentally friendly mode of personal transportation. However, current consumers are cautious and have voiced concerns about long charging times which limits autonomy.[1] Importantly, speed of charge is related to slow transport kinetics inside the battery. This is, in turn, often associated with the kinetics of the lithium insertion/deinsertion reaction in the ceramic electroactive solid, since solid-state diffusion generally is slow compared to the liquid and the gas phase.[2] Specifically, $LiFePO_4$ though superior in many aspects to other positive electrode materials, is criticized for low electronic conductivity and bulk lithium diffusivity.[3] Yet, in model systems, $LiFePO_4$ electrode materials repeatedly exhibit a much larger diffusion coefficient (around 10^{-8} cm^2 s^{-1})[4,5] than in $LiFePO_4$ powders designed for application (around 10^{-14} cm^2 s^{-1}).[2] Moreover, a limited number of experimental results have recently shown that commercially relevant $LiFePO_4$ might be capable of much higher charge/discharge rates, than previously thought. For example, Ceder and co-workers published a controversial[6] study on a modified $LiFePO_4$ material with non-stoichiometric composition and amorphous surface layer, with which approximately 75% of the theoretical capacity could be achieved within a one minute discharge.[7] Similarly an electrochemical single particle study by Munakata and co-workers showed about 75% of the initial capacity at a one minute discharge.[8]

At the same time, industry is concerned with the stability of $LiFePO_4$ in ambient atmosphere, as this is of great importance to the storage and handling of commercial $LiFePO_4$ during production. For example, complete transformation of $LiFePO_4$ into the NASICON analogue $Li_3Fe_2(PO_4)_3$ and hematite was observed during exposure to air at 300 °C and above,[9] whereas at temperatures below 120 °C, in humid air, the formation of hydroxide containing compounds has been reported.[10,11] Yet, it remains unclear, why lithium is *not* extracted under oxidative aging conditions, even though this is the dominating mode of oxidation in solution.

To address this question of different reaction modes in air compared to electrolyte, and to shed light on the lithium transport kinetics of these reactions, we have examined the impact of different gaseous oxidants on commercial $LiFePO_4$. Surprisingly, we have found that even though exposure to O_2/O_3 did *not* significantly alter the $LiFePO_4$ materials, NO_2 consistently delithiates $LiFePO_4$ completely within a short period of time according to the following reaction:

$$LiFePO_4(s) + 2NO_2(g) \rightarrow FePO_4(s) + LiNO_3(s) + NO(g)$$

This reaction differs significantly from previous oxidative delithiation transformations, as it does not include a liquid phase that can solvate the lithium ion and transport it away from the surface as the reaction progresses. More importantly, it exhibits unseen fast reaction rates for commercial $LiFePO_4$ materials.

Results and discussion

Characterization

To confirm, that this reaction indeed is comparable to electrochemical charging, the solid reaction products have been characterized using attenuated total reflectance infrared

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spectroscopy (ATR-FTIR), X-ray diffraction (XRD), electrochemical cycling and transmission electron microscopy.

After treatment of carbon-coated $LiFePO_4$ (C-$LiFePO_4$) micropowders with NO_2, evidence of delithiation was given by $LiNO_3$ and *heterosite* $FePO_4$ as identified by ATR-FTIR and XRD (Fig. 1c and f). Specifically, the $LiNO_3$ gives rise to FTIR bands at 737, 838, 1072, 1135 cm^{-1} and a broad feature between 1300 and 1500 cm^{-1}, as well as a number of shoulders, which appear in addition to the standard *heterosite* $FePO_4$ spectrum (Fig. 1f).[15]

The completeness of the delithiation was confirmed by atomic emission spectroscopy (AES): 100 ± 3% lithium was extracted, while 2 ± 1% lithium remained in the washed $FePO_4$ sample.

As the use of aggressive oxidants to delithiate $LiFePO_4$ might lead to the formation of non-crystalline by-products or particle dissolution, high-resolution transmission electron micrographs of nano-sized carbon-free $LiFePO_4$ were recorded to assess structural integrity of the reaction product. From Fig. 2, it is clear that the overall shape, size and appearance of the particles remain unaltered. Furthermore, $FePO_4$ particles remain crystalline while a salt layer forms non-uniformly on the surface, accumulating in gaps and contact points. X-Ray photoelectron spectroscopy reveals a nitrogen containing compound on the material surface. Fig. 3 shows the N 1s peak at 406.7 eV, lying in between the values reported for $AgNO_3$[16] and NH_4NO_3,[17] thus suggesting the presence of $LiNO_3$ on the surface. The same references report O 1s peaks at 532.3 and 532.5 eV, which compares well to the observed component at 532.4 eV.

The electrochemical activity of oxidized C-$LiFePO_4$ was assessed in research coin cell batteries, assembled with great care to avoid any accidental short-circuit. Electrochemical testing was initiated in discharge mode, without prior charging. This first discharge (Fig. 4a) indicates a stable potential plateau

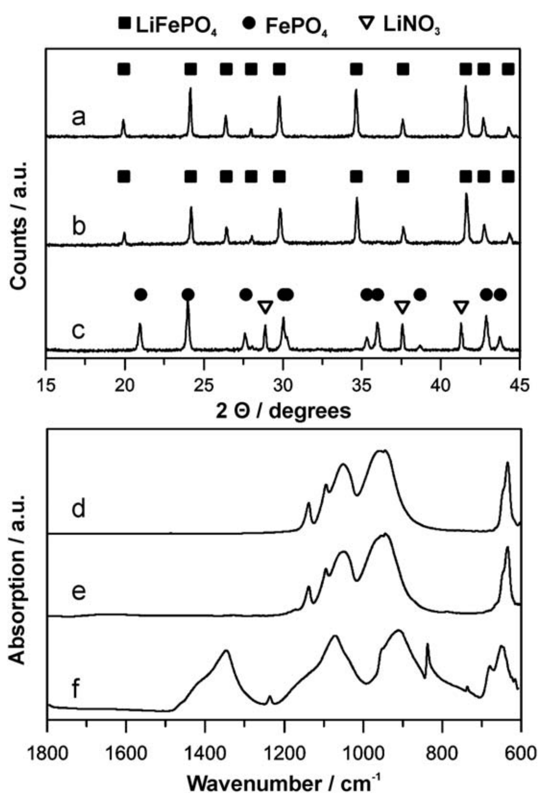

Fig. 1 Crystallographic and chemical analysis of the reaction product of C-$LiFePO_4$ with O_3 and NO_2. X-Ray diffractograms (a–c) and ATR FTIR spectra (d–f) of pristine C-$LiFePO_4$ (a and d), O_3 exposed C-$LiFePO_4$ (b and e) and NO_2 oxidized C-$LiFePO_4$ (c and f). The symbols mark the location of strong reflections according to literature crystallographic data.[12–14]

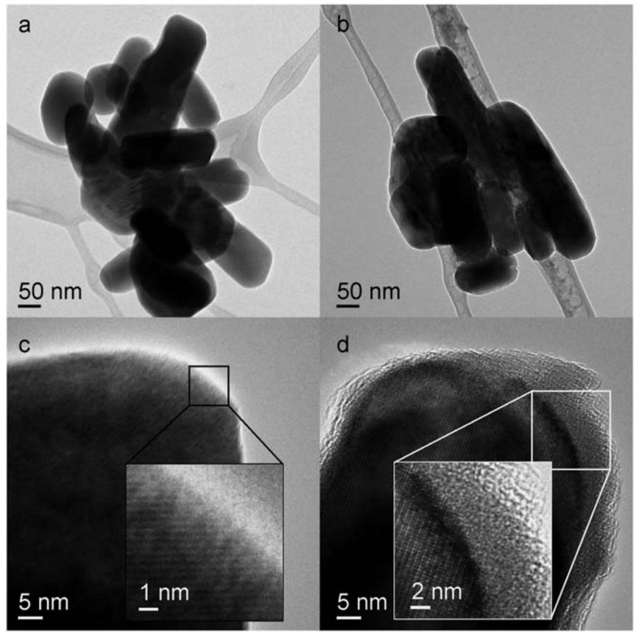

Fig. 2 TEM images of $LiFePO_4$ before oxidation (a and c) and after oxidation with nitrogen dioxide (b and d). HRTEM images show crystallinity of particles up to the surface before oxidation (c) and an amorphous surface layer after oxidation (d).

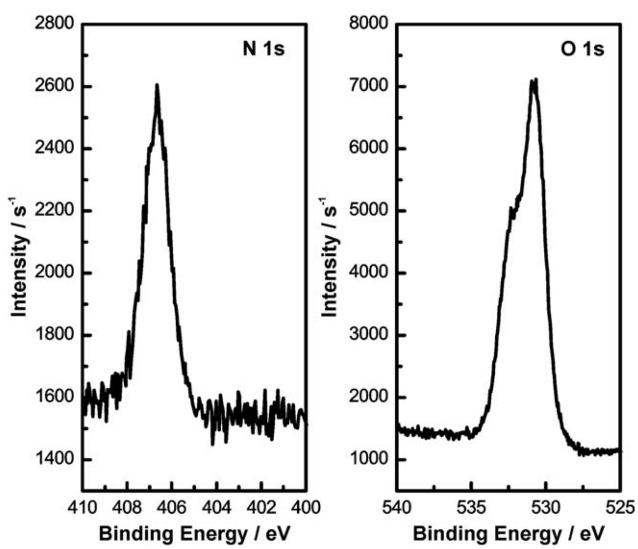

Fig. 3 XPS analysis of the nitrogen and oxygen 1s peaks of the oxidized sample confirms the presence of $LiNO_3$ at the surface.

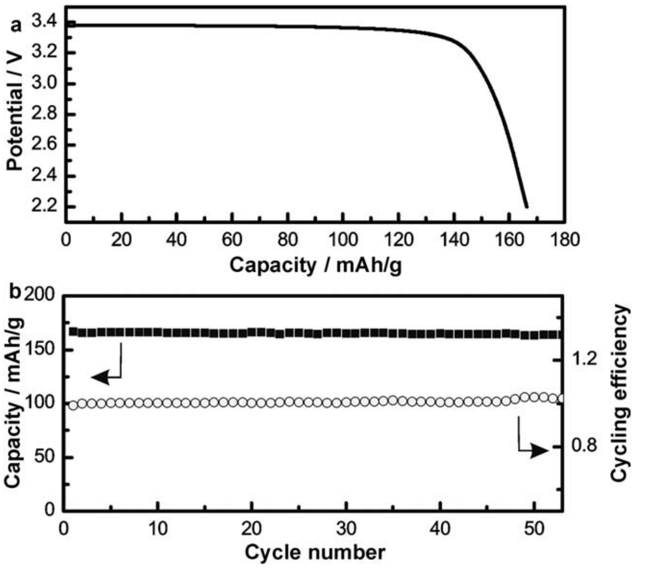

Fig. 4 (a) First-cycle discharge curve (rate C/10) and (b) cycling performance (rate C/2) of oxidized, washed and dried C-$LiFePO_4$ confirm complete oxidation and retention of electrochemical activity of the oxidized material.

around 3.4 V *vs.* Li/Li^+ and practical capacity of 165 mA h g^{-1} (theoretical capacity: 170 mA h g^{-1}). Combined with the cycling stability over 50 cycles (Fig. 4b), this indicates that the material retains its electrochemical properties and is not damaged by the aggressive delithiation.

As mentioned above, $LiFePO_4$ was also exposed to ozone. This gas did not lead to a significant alteration of the starting material, *i.e.* the bulk *olivine* structure remains intact, as observed in XRD, and further confirmed by only very minor changes to the ATR-FTIR spectrum (Fig. 1b and e).

Thermodynamics of $LiFePO_4$ delithiations with gases

It is clear, that the key to the observed differentiated reaction behaviours lies within the nature of the oxidant. Table 1 summarizes some reaction Gibbs free energies for delithiation reactions of $LiFePO_4$ with different oxidizing gases using actual reaction conditions for NO_2, Cl_2 and O_3 oxidations, and ambient conditions for O_2. The thermodynamic discussion of oxidation pathways of $LiFePO_4$ with gases may further be extended to the extraction of iron ions from, or introduction of oxygen into the $LiFePO_4$ structure. However, molecular modelling shows, that those ions are strongly bound to their lattice site in the $LiFePO_4$ structure, compared to a more mobile lithium.[18] Bulk diffusion kinetics should hence favour delithiation reactions. Delithiation of $LiFePO_4$ with O_3 and O_2 in the presence of CO_2 is thermodynamically possible with free energies down to −60 kJ mol^{-1} at standard conditions depending on the pathway.[19] This delithiation is *not* observed, suggesting surface kinetics are responsible for its inhibition *e.g.* surface localized species may block the reaction. Given that ozone is a strongly oxidizing allotrope of oxygen, the reaction products of $O_2/LiFePO_4$ and $O_3/LiFePO_4$ may be quite similar, thus potentially yielding new information on the dry air aging mechanism of $LiFePO_4$.

Table 1 Gibbs free energies of delithiation reactions under reaction/ambient conditions[a,18,19]

Reaction	$\Delta_R G$/kJ mol^{-1}
$LiFePO_4 + ½Cl_2 \rightarrow LiCl + FePO_4$	−53
$LiFePO_4 + 2NO_2 \rightarrow LiNO_3 + FePO_4 + NO$	−65
$LiFePO_4 + ½O_3 \rightarrow ½Li_2O + FePO_4 + ½O_2$	−19
$LiFePO_4 + ½O_3 + ½H_2O \rightarrow LiOH + FePO_4 + ½O_2$	−60
$LiFePO_4 + ¼O_2 \rightarrow ½Li_2O + FePO_4$	+51
$LiFePO_4 + ¼O_2 + ½H_2O \rightarrow LiOH + FePO_4$	+11
$LiFePO_4 + ¼O_2 + ½CO_2 \rightarrow ½Li_2CO_3 + FePO_4$	−38

[a] 20 °C, 20.9% O_2, 0.035% of CO_2, and 70% rel. humidity were assumed ambient conditions.

Kinetics

In an attempt to quantify the exceptionally high reaction rate, *in situ* time-resolved XRD was performed. Fig. 5 shows evidence of

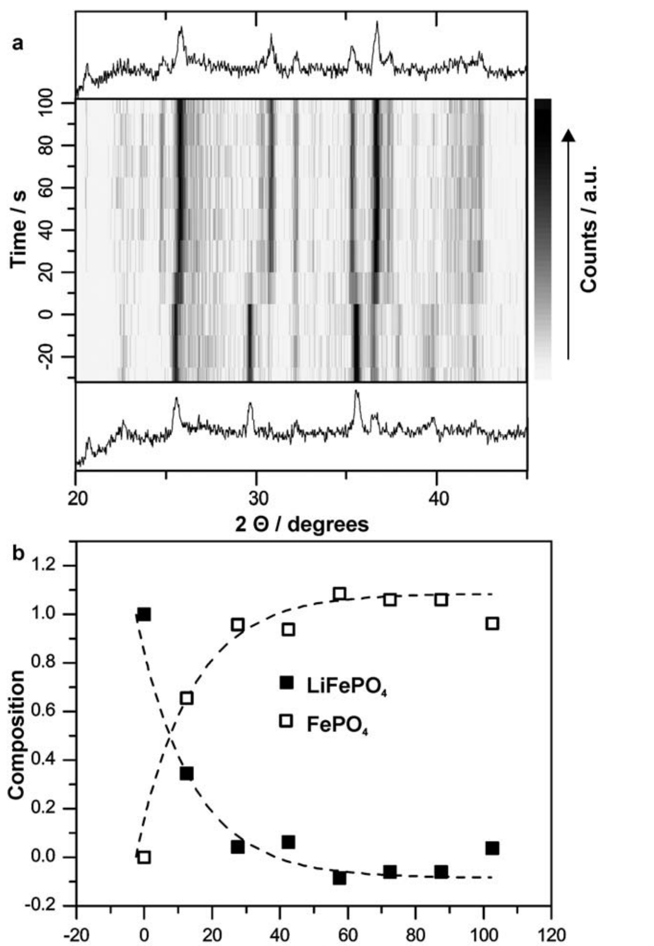

Fig. 5 (a) Time-resolved XRD during delithiation of C-$LiFePO_4$ by NO_2 gas as a greyscale map. The initial and final diffractograms are displayed at the top and bottom, respectively; $t = 0$ marks the time of gas injection. (b) Composition of the mixture $LiFePO_4/FePO_4$. The composition was determined from time-resolved XRD by integration and normalization to the corresponding theoretical intensity of the $LiFePO_4$ reflection at 30° 2θ and the $FePO_4$ reflection at 31° 2θ (based on a Cu-Kα anode X-ray source).

complete delithiation of C-$LiFePO_4$ particles of 590 nm average diameter within significantly less time than one minute. The rate of delithiation was also confirmed by AES with 61 ± 14% delithiation at 30 s and 94 ± 4% delithiation at 60 s. This translates into a $LiFePO_4$ charge to 160 mA h g^{-1} within one minute. Importantly, the reaction temperature peaked at 29.7 °C ± 1.1 °C, thus excluding any major thermal increase of the kinetics resulting from the exothermic nature of the reaction. Moreover, preliminary tests using C-$LiFePO_4$ and Cl_2 have shown similar kinetics. $LiFePO_4$ nanopowder samples of approximately 200 nm average particle diameter with and without carbon coating have been studied as well. Regardless of the presence or absence of coating, these showed reaction rates that were too fast to be captured within the 15 seconds time resolution of this conventional X-ray diffraction set-up.

For comparative purposes, our data provides a *lower limit* on the apparent diffusion coefficient of about 3.1×10^{-11} cm^2 s^{-1}, using a one-dimensional pure diffusion model, as has been done in previous electrochemical studies.[20] As such, this study shows that the rates provided by Ceder *et al.*[7] and Munakata *et al.*[8] are entirely feasible *provided* that the removal of electrons from the particle surface is sufficiently fast.

Conclusion

Unique to the gas reaction discovered here, is the delithiation of $LiFePO_4$ at high speed *without* the presence of a liquid. *In situ* X-ray diffraction corroborated by elemental analysis provides proof that $LiFePO_4$ bulk kinetics supports a charge to 160 mA h g^{-1} in less than 60 seconds under ambient conditions. This finding has been confirmed with two $LiFePO_4$ materials resulting from different synthesis routes regardless of the presence or absence of carbon coating. The reaction is comparable to the electrochemical process in so far as the resulting $FePO_4$ is indistinguishable from electrochemically delithiated Li_0FePO_4 and the thermodynamic driving force corresponds to a charge to 4.1 V *vs.* Li/Li^+. It provides thus new possibilities to study the delithiation mechanism of $LiFePO_4$ *in situ* and *ex situ*. As such, XRD and TEM studies are currently underway. The findings further disprove the paradigm of slow lithium bulk diffusion in $LiFePO_4$.

In conclusion, the presented data suggest that developing $LiFePO_4$ materials with improved bulk lithium diffusivity will not improve rate capabilities of the derived lithium-ion batteries. Instead, electrode design, electronic conductivity and surface kinetics should be the focus of continued research.

Experimental

Micro-sized carbon coated $LiFePO_4$ (C-$LiFePO_4$, *US Pat.*, 7,457,018) and carbon-free nano-$LiFePO_4$ (*US Pat.*, 7,807,121 B2) were donated by Clariant (Canada) Inc. (former Phostech Lithium Inc).

C-$LiFePO_4$ (chemical and crystallographic analysis) and carbon-free nano-$LiFePO_4$ (used for XPS) samples were exposed to nitrogen dioxide and ozone gas, respectively, for at least 30 minutes. For chemical quantification of the oxidation, oxidized samples were washed in water and filtered. $FePO_4$ was subsequently dissolved in conc. HNO_3. Wash water and dissolved $FePO_4$ were analysed by AES. To achieve time resolution, the oxidation was stopped after different exposure times by replacing NO_2 gas with a stream of dry air. TEM samples were prepared by depositing carbon-free nano-$LiFePO_4$ onto lacey carbon nickel grids from a suspension in acetonitrile. Selected sample covered grids were exposed to NO_2 gas before analysis in the TEM. Carbon-coated nano-$LiFePO_4$ shows the same characteristics.

The electrodes for battery testing were produced by coating 85 wt% washed, completely oxidized $LiFePO_4$, 6 wt% PVDF binder and 9 wt% carbon additive on to a carbon-coated aluminium foil. The battery contained a metallic lithium negative electrode and $LiPF_6$ in 1 : 1 ethylene carbonate and dimethyl carbonate mixture electrolyte.

Time-resolved X-ray diffraction was performed using a flow of NO_2 gas below a filter paper on which $LiFePO_4$ was fixed. X-ray access to the XRD cell was enabled through a Kapton window. In similar experiments, the peak temperature of $LiFePO_4$ during NO_2 oxidation was recorded, using an infrared thermometer and confirmed in independent experiments with a thermocouple.

For more experimental details, suppliers and instruments, please see the ESI.†

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