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The Critical Role of Carbon in the Chemical Delithiation Kinetics of LiFePO₄
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The chemical delithiation of LiFePO₄ has been carefully studied using two different types of LiFePO₄: (1) carbon coated LiFePO₄ and (2) non-carbon coated LiFePO₄. We have observed that only carbon coated LiFePO₄ can be successfully delithiated at room temperature using Na₂S₂O₈ as oxidizing agent. In order to unravel the role of carbon in the chemical delithiation process of non-carbon coated LiFePO₄ we have performed a systematic study using different carbon sources as well as different amount of extraneous carbon in the solution. The results obtained demonstrate that the addition of carbon is fundamental for the effective removal of lithium at room temperature, and only a very small amount of carbon of any nature is enough to achieve the successful chemical delithiation of non-carbon coated LiFePO₄.

A more eco-friendly option is the use of K₂S₂O₈ or Na₂S₂O₈ in aqueous solution (LiFePO₄ is stable in water), using a cost-competitive process that additionally

The phospho-olivine LiFePO₄ (triphylite) represents the first commercial polyanionic Li-ion cathode, able to deliver 3.5 V vs Li⁰/Li with a theoretical capacity of 170 mAh·g⁻¹. It was first proposed as alternative to LiCoO₂ by the Nobel prize J.B. Goodenough in 1997,¹ motivated by the low natural abundance, high cost, and toxicity of cobalt derivatives used as cathode materials. However, it took almost three years to capture the battery community because of its poor electronic conductivity. To overcome the electrode kinetic issues linked to such low intrinsic conductivity, Armand and co-workers proposed to nano-paint the LiFePO₄ particles with a thin carbon layer,²,³ which represented an innovative approach and a breakthrough towards its practical implementation. And we think that in the near future, LiMn₁–xFexPO₄ will also be implemented and will find its way to commercialization. This carbon coating can effectively match with both types of systems. A number of works have shown its potential as cathode material for Na-ion batteries, and still stands as a commercial success, reaching 34% of the cathode materials market share in 2018, driven mainly by the Chinese e-mobility sector and stationary applications, for which cost and life time are the prevailing criteria.⁵ The total production of carbon coated LiFePO₄ has been in excess of 1.3 · 10⁶ tons in 2018. A number of disruptive battery technologies are now pushing to take a share of lithium-ion’s market. By leveraging the knowledge created during 30 years of development, scientists are turning their interest toward systems based on other ions, the most prominent being Na⁺; or revisiting lithium metal-based chemistries in hopes of enabling the desired increases in energy density.⁶ The case for Na-based chemistries is driven by the much higher abundance and lower price of the ores containing this alkali metal compared to Li and the ability to use less expensive current collectors such as Al in both electrodes, enabling safe transportation of discharged cells.⁸

In turn, the use of Li⁺ as the anode represents a significant increase in energy density and creates the opportunity of employing positive electrodes that are Li-free.⁹ The latter offer several additional benefits as the possibility to economize lithium resources, increased gravimetric energy density and, more importantly, allow electrochemically cleaning the surface of the metal Li anode in the first discharge. The peeling off of the initial oxide film found in all forms of metallic Li is an effective way to form a stable Solid Electrolyte Interphase (SEI) and ensure durable cycling.¹¹

Heterosite FePO₄ (space Group Pnma), the delithiated counterpart of triphylite LiFePO₄, represents an excellent cathode to be effectively matched with both types of systems. A number of works have shown its potential as cathode material for Na-ion batteries, either in its sodiated form NaFePO₄ or desodiated FePO₄. In both cases, it is typically prepared from triphylite LiFePO₄ by chemical or electrochemical delithiation.¹²–¹⁸

Several oxidizing agents such as NOPF₆ or NO₂BF₄ in acetonitrile under inert atmosphere¹⁹–²⁰ and Br₂²¹ are typically employed to delithiate LiFePO₄. A more eco-friendly option is the use of K₂S₂O₇ or Na₂S₂O₈ in aqueous solution (LiFePO₄ is stable in water),²²,²³ using a cost-competitive process that additionally

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enables the recovery an subsequent reuse of lithium.\textsuperscript{24} Using all these options, heterosite FePO\textsubscript{4} can be effectively prepared, but the role of the carbon coating of battery-grade LiFePO\textsubscript{4} has not been explored to date.

In this work the critical role of carbon in the delithiation process of tryphilitic LiFePO\textsubscript{4} using Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} is unveiled from the comparison of the delithiation products obtained from carbon-coated LiFePO\textsubscript{4} (cc-LFP) and non-coated LiFePO\textsubscript{4} (ncc-LFP). To complete the study different forms of carbon were also added in different amount to the ncc-LFP suspensions. Our results show that carbon plays an active part in the delithiation process of LFP and is essential for the effective removal of lithium at room temperature.\textsuperscript{25}

**Experimental**

Non-carbon coated and carbon coated LiFePO\textsubscript{4}, hereinafter referred to ncc-LFP and cc-LFP respectively, were supplied by Hydro-Québec. The chemical delithiation of both cc-LFP and ncc-LFP was done according to the following reaction:\textsuperscript{26}

\[ 2\text{LiFePO}_4 + \text{Na}_2\text{S}_2\text{O}_8 \rightarrow 2\text{FePO}_4 + \text{Na}_2\text{SO}_4 + \text{Li}_2\text{SO}_4 \] \[ [1] \]

LFP and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} (Sigma-Aldrich, 98\%) were mixed with deionized water and the solution was kept under stirring at room temperature for 24 h. After filtration, the solids were washed and dried overnight at 60 °C–75 °C.

Bruker D8 Discover diffractometer with a Cu-K\textalpha\ (\(\lambda = 1.5418 \, \text{Å}\)) radiation was used to perform X-ray diffraction (XRD) measurements within the 2\theta range 10°–80°. Le Bail refinements of the XRD patterns were carried out using the FullProf software\textsuperscript{27} to monitor the delithiation process as well as to compare the structural parameters of the materials obtained after delithiation. The morphology and homogeneity of samples were examined by means of scanning electron microscopy (SEM, FEI—QUANTA 200FEG) using a current accelerating voltage of 30 kV and equipped with energy-dispersive X-ray spectroscopy (EDX).

**Results and Discussion**

**Effect of carbon coating on the delithiation of LiFePO\textsubscript{4}**—The XRD patterns of the products obtained after delithiation of cc-LFP and ncc-LFP are shown in Fig. 1 compared to simulated patterns of ideal LFP and FP materials calculated from the Inorganic Crystal Structure Database (ICSD-56291 and ICSD-92199, profiles calculated using the pseudo-Voigt profile function of Thompson, Cox and Hastings with \(U = 0.00413, V = -0.00762, W = 0.00625, X = 0.019\)).\textsuperscript{28} The XRD patterns of both pristine cc-LFP and ncc-LFP are shown in Fig. S1, is (available online at stacks.iop.org/JES/167/070538/medMedia) together with SEM images of both samples. Both LFP compounds crystallize in the same space group \(Pnma\) with the same unit cell parameters (Table S1). Figure 1 shows that successful delithiation of LiFePO\textsubscript{4} could only be achieved with cc-LFP, thereby resulting in carbon coated FePO\textsubscript{4} (cc-FP). Strikingly, the non-carbon coated sample still shows the characteristic diffraction peaks of LFP, and total absence of FP, and is therefore labelled as “ncc-LFP after delithiation.” This was further confirmed from the refined unit cell parameters determined by Le Bail refinements shown in Fig. S2 and given in Table S1. The homogeneity degree and the particle size of the compounds obtained after the delithiation process are shown in Fig. S2, no changes in the particle size and morphology after delithiation are observed compared to the corresponding images in Fig. S1. From the results obtained it can be concluded that carbon coating plays a pivotal role in achieving successful delithiation of LFP.

**Effect of the amount of carbon added into the solution.**—In order to further explore the crucial role of carbon in the delithiation process, Ketjen Black\textsuperscript{®} was added to the solution during the delithiation process of ncc-LFP in different carbon:LFP weight ratios (5\%, 2.5\%, 1\%, 0.5\% and 0.01\%). Independently of the carbon amount, all the samples obtained after the delithiation process are pure materials as determined from X-ray diffraction data (Fig. 2), and exhibit the characteristic diffraction peaks of FP (as confirmed by the refined unit cell parameters determined by Le Bail refinements (Fig. S3), summarized in Table SII). The obtained results clearly indicate that a very small amount of carbon into the suspension is needed to achieve the successful delithiation of ncc-LFP.

**Effect of the different carbon source/nature added into the solution.**—Different types of carbon have been tested in order to explore if the nature of the carbon has a direct impact in the delithiation process. In this case 5\% of Ketjen black\textsuperscript{®} (Kb), Denka\textsuperscript{™} black (Dk), Super P\textsuperscript{TM} (SP), vapor grown carbon fiber (VGCF), graphene (Grphn), graphite (Grph) and mixtures of some of them such as graphene-VGCF (Grphn-VGCF), graphite-Ketjen black\textsuperscript{®} (Grph-Kb), graphite- Denka\textsuperscript{™} black (Grph-Dk) and graphite-Super P\textsuperscript{TM} (Grph-cSP) were tested. Figure 3 shows the XRD patterns of the compounds obtained after delithiation reaction and Le Bail refinements (Fig. S4) revealed that every recovered compound corresponds to FP (see refined unit cell parameters listed in Table SIII).
The technological push toward the design of batteries that overcome current systems is driving research interests in several exciting directions, with Na-ion batteries and Li metal batteries on the horizon. In both cases, heterosite FePO₄ obtained from the delithiation of triphylite LiFePO₄ can be successfully employed as positive electrode (following chemical sodiation in the first case). This process can be performed using Na₂S₂O₈ as an oxidizing agent in aqueous solution, however, we have observed that only carbon coated LiFePO₄ can be successfully chemically delithiated at room temperature. In the case of non-coated LiFePO₄ delithiation can also be achieved if carbon is added separately, regardless the amount and form, or at higher temperature if carbon is avoided. These results are the first proof of the catalytic role of carbon in such reaction and are relevant for the use of heterosite FePO₄, a key material for batteries employing lithium metal and the source of NaFePO₄, as positive electrode in the next generation of batteries.

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Figure 3. XRD patterns of compounds obtained after delithiation of ncc-LFP using 5% of different types of carbon sources into the solution. Calculated XRD patterns of LFP and FP from ICSD database structures (ICSD-56291 and ICSD-92199) are shown for comparison.

Discussion.—The successful chemical delithiation of LFP at room temperature using Na₂S₂O₈ as oxidizing agent has been shown to require carbon in the reaction medium, either as a coating layer, or as additive. It has been shown that a minuscule amount of carbon in the solution is sufficient to successfully delithiate LFP using Ketjen Black® as source of carbon, and, at a fixed carbon amount of 5% (carbon:LFP weight ratio), we have shown that the nature of the carbon source has no impact in the obtained product, resulting in all cases in successful delithiation. In view of these results, it can be concluded that carbon acts as a catalyst of the delithiation reaction of LFP. This is further confirmed by the fact that increasing the temperature of the chemical delithiation of ncc-LFP without carbon source in the solution up to 60 °C, the reaction also takes place. It can thus be considered that carbon allows lowering the activation energy of the chemical delithiation of LiFePO₄ as speeds up the chemical reaction without being consumed by the reaction, and therefore the reaction rate increases by lowering the activation energy.

This phenomenon of catalysis by carbon, either as a coating or extraneous, in suspension, is very intriguing. It is unlikely that the very short time of contact when the different particles are stirred together can provide a galvanic effect, from the surface initially, to the bulk of the LFP. This is especially true at the lowest carbon concentrations that were tried. If this were the case, other conductive materials would achieve the same result. In order to be inert to S₂O₈²⁻, the particles would have to be of a noble metal, like platinum, losing the advantage of easy industrial scale-up. Tentatively, we assign the effect to the catalytic role of carbon-oxygen compounds at the surface of the grains/sheets, likely quinone groups (>C=O), to mediate the reaction S₂O₈²⁻ → 2SO₄²⁻ followed by LiFePO₄ + SO₄²⁻ → FePO₄ + Li⁺ + SO₄²-. On the other hand, temperature increases the number of reactant particles that have more energy than the activation energy, also resulting in increased reaction rate, and therefore, at high temperature, the self-dissociation of the peroxodisulfate is sufficiently fast.