Sustainable paths to a circular economy: reusing aged Li-ion FePO₄ cathodes within Na-ion cells

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Abstract

Responsible disposal and recycling are essential for the sustainability of the battery market, which has been exponentially growing in the past few years. Under such a scenario, the recycling of materials of less economic value, but environmentally much more sustainable like LiFePO₄, represents an economic challenge. In this paper an approach to recover used FePO₄ electrodes from calendar aged Lithium-ion (Li-ion) batteries and their reuse in Sodium-ion (Na-ion) cells is proposed. The electrochemical performances of the Na-ion cell are shown to be comparable with previously reported values and, since the electrode can retain the original microstructure and distribution, electrode processing can be avoided. A proof of concept of a NaFePO₄//hard carbon full cell using a very high positive electrode loading optimized for Li-ion batteries (≈14 mg cm⁻²) is shown.

1. Introduction

According to recent estimations, in 2025 there will be about 5000 000 tons of Lithium-ion batteries (LIBs) in the world [1]. This production rate will inevitably grow in the coming years, at the same time that the battery field shifts towards higher quality and innovative batteries with lower environmental impact. Under such scenario, the development of a real sustainable economy in the field of batteries is crucial, and this should comply with the triple R concept (waste reduction, reuse, recycle).

Lithium-ion (Li-ion) battery technology is mainly used in electric and plug-in hybrid electric vehicles (PHEV and EV, respectively). However, LIBs are no longer usable for traction purposes once80% of state of health is reached. At this point the battery is removed from the vehicle and can be disposed, recycled or reused in other applications, generating a circular economy scenario in which the revaluation of the waste represents an essential development, not only from an economic perspective, but above all from an environmental point of view. The application of a circular battery flow diagram to the batteries value chain should thus not only consider the final product (which should be designed to ensure competitive performance with minimal environmental impact), but also the origin of the raw materials (ethical sourcing and low toxicity) and the availability of natural resources up to the disposal, recovery and recycling of materials. The decrease in waste production and the reuse of resources in the form of raw or refurbished materials that can be reused again as base materials in the same or other applications [2] represents a relevant challenge for the next decade [3].

Indeed, sustainable approaches addressed to battery waste management that reduce the environmental impact produced once the battery has reached the end of life (EoL) are urgently needed [4]. At the same time, the environmental and economic benefits can also increase [5], since critical raw materials such as metals, graphite and plastics can be recycled, ensuring the supply of secondary raw materials while reducing
the impact due to the extraction of new raw materials [6]. Following this approach, projects like the demonstrating facility for grading and sorting EoL spent Nissan LEAF EV batteries, aiming to reduce the cost of stationary energy storage in the UK, have already been launched [7]. In this case one of the main challenges is to design an efficient battery management system able to predict the remaining useful life for a second use [8], allowing to increase the battery lifespan [9], contributing to more efficient use of primary resources [10]. Alternatively, the cells of EoL batteries can be disassembled to refurbish the cathode material to reset its lithium content using chemical processes [11].

LiFePO₄ (LFP) as well as LiFe₁₋ₓMnₓPO₄ (LFMP), are found to be an excellent cathode material for its copacetic chemical and thermal stability [12], meaning safe performance, low cost, non-toxicity, high specific energy and high cycling stability. Although nickel-rich layered oxides currently dominate the EV market cathode chemistry recent announcements have positioned the use of LFP as the first choice in the Asian EV market [13] which allows reducing the price of the final product and suppress the quantity of cobalt in the battery. This will inevitably bring to an increase of the amount of spent LFP cells in the forthcoming years, representing an economic challenge for the battery recycling sector.

Indeed, today there are processes that are able to recover high value raw materials from LIBs [14] (mainly copper, aluminum, nickel and cobalt), while only few study have been published about the recovery of graphite [15, 16]. The recycling of materials such as LFP and LFMP with less economic value (though lower toxicity and environmental risks) still require the development of suitable approaches with added value for the battery market.

Various recovery options have been proposed to process LFP based battery waste: (a) the direct regeneration of cathode material [17–19] and (b) the acid or alkaline leaching to recover the single metals present on the electrodes [20]. The first one requires a solid-state sintering process with the addition of new reactants such as LFP [17] or Li₂CO₃ [21, 22]. The first one can promote the reaction between impurities such as iron phosphate and ferric oxide so that these are suppressed. It is also reported that the addition of fresh LFP can play a role in limiting the decomposition of the polyvinylidene fluoride (PVDF) during sintering. In fact, at around 400 °C the PVDF decomposes to give HF that reacts with LFP originating LiF, consuming Li from the electroactive material resulting in poor electrochemical performances [17].

Alternatively, Li₂CO₃ is typically used as reactant for direct recycling and restore spent LFP recovered powder [18, 19, 22, 23] However, lithium volatilization at the sintering temperature is observed contributing to the poor electrochemical performances of ‘regenerated’ cathodes [22]. On the other hand, acid or alkaline leaching is used to recover the single metals present in the electrodes and it includes the use of strong acids or bases after an annealing pre-treatment [24], producing a large amount of corrosive wastes, which make the entire process economically and environmentally unattractive and therefore still far from the real application.

Rechargeable sodium-ion batteries (SIBs) represent a realistic alternative to Li-ion storage technologies [2], as offer a drop-in approach thanks to their similarities to LIBs (cell design and manufacturing production lines). SIBs also combine several attractive properties based on the lower cost of sodium, owing to its unlimited and geographically widespread resources, as well as the advantage of using aluminum as current collector in both electrodes, thus eliminating the need for heavier and more expensive copper [25–27]. The energy densities of SIBs are generally lower than LIBs, however the combination of interesting properties offered by SIBs could fill a niche that would represent an important step forward beyond lithium technologies [28]. In this context, tripilitely-NaFePO₄ (t-NFP) has been proposed as one of the cheapest and most sustainable Na-ion cathode materials [29, 30], due to its similarities to LFP, such as thermal, structural, and cycling stability together with a good chemical stability in aqueous media. Unlike t-LFP, t-NFP is not a thermodynamically stable phase [31, 32], and cannot be prepared using traditional direct synthesis routes. Instead, electroactive t-NFP phase can be obtained from LFP through electrochemical or chemical reactions [29, 33–36]. While the feasibility of this process has been demonstrated using fresh LFP, no studies have explored the possibility of using spent LFP material. With this approach the recyclability of batteries would have a two-fold interest: (a) to recover the critical raw materials of the battery such as Cu or graphite and (b) to recover the active material (LFP), refurbish it to manufacture cost-effective NFP and re-use it in SIBs. The cost of such process could even be brought further down if electrodes were directly recovered, so that not only the active material can be reused, but also the current collector, carbon additives and binder, avoiding also the electrode manufacturing process, which is costly and often uses toxic solvents.

In this paper a proof of concept for FePO₄ (FP) electrode recovery from calendar aged commercial LFP/Graphite batteries and its reuse in a Na-ion cell is shown. Accordingly, we propose an approach to recover the full cathode in the form of FP to use directly in a Na-ion cell. The electrode retains the original loading and microstructure, avoiding the need of further processing steps or the addition of extra reactants, or additives such as carbon and binder. The FP electrode is shown to offer electrochemical performances competitive with the state of the art NaFePO₄ cathodes for SIBs. Optimizing this approach towards a more
industrial strategy may pave the way for the successful development of a sustainable second life opportunity for aged or spent Li-ion batteries.

2. Experimental methods

2.1. Dismantling of the LiFePO$_4$ battery

A calendar aged 50 Ah LFP/Graphite pouch cell battery provided by Shandong RealForce Enterprises Co., Ltd (China) was stored in a safety closet at room temperature for 8 years. The battery was at first cycled in a VMP3 potentiostat (Biologic®) to check the remaining capacity at a current of C/20 (2.5 A) and then charged to obtain the complete delithiation of the cathode, until a potential of 3.65 V was reached (see supplementary figure S1 (available online at stacks.iop.org/JPMATER/4/034002/mmedia)). The battery was then taken inside a glove box (Jacomex®) in oxygen (<2 ppm) and water (<0.5 ppm) controlled environment. The casing of the pouch cell was carefully cut with a non-conductive tool avoiding any short circuit that could modify the chemistry of the different components that could lead to undesired and uncontrolled side reactions. Once opened, the pouch cell was disassembled and the different components were separated and stored individually.

2.2. Electrodes preparation

Since the positive electrode layer is coated on both sides, the electrode coating on one side of the current collector was removed for all the measurements before cutting the samples by gently rubbing N-methyl-2-pyrrolidone (NMP, Merck) using a paper cloth until reaching the current collector. To eliminate any traces of remaining salt, the electrode samples were rinsed in dimethyl carbonate (DMC, Sigma Aldrich) solvent, as is described elsewhere [37]. Disassembled electrode disks of 12 mm diameter were collected from several areas of the electrode and characterized electrochemically by galvanostatic cycling.

2.3. Electrochemical characterization of the half-cell and full cell sodium–ion batteries

Sodium–metal (Panreac) was used as a counter and reference electrode in half-cells, 16 mm diameter separators (Whatman GF/D) were included and lab-made 1 M NaPF$_6$ in 1:1 EC/DMC fresh electrolyte was added. The electrolyte was prepared by drying a solvent mixture of EC/DMC 1:1 wt% with molecular sieves during one week inside a glove box (Mbraun) in a controlled atmosphere (<0.1 O$_2$; <0.1 H$_2$O). Then, NaPF$_6$ salt was added to the solvent’s mixture, reaching the concentration of 1 M and stirred for 24 h before use. FePO$_4$ half-cells were cycled between 3.8 and 2.7 V vs Na$^+$/Na, whereas HC electrodes were tested between 0.01 and 2.0 V vs Na$^+$/Na in CR2032 type coin cell and cycled in a MACCOR battery tester potentiostat. Full cell tests were performed in a T-cell (Swagelok®) in a VMP3 potentiostat (Biologic®) between 4.0 and 1.0 V.

The entire assembly of batteries was conducted in argon atmosphere glove box, restricted to air and water exposure.

2.4. Structural and physico-chemical characterizations of FePO$_4$ and NaFePO$_4$

The XRD pattern of all samples was acquired using a Bruker D8 Discover diffractometer in Bragg-Brentano $\theta$–2$\theta$ configuration and equipped with a Copper anode x-ray source and a monochromator ($\lambda_{\text{Cu,Ka}} = 1.54056$ Å), and with a LYNXEYE XE detector. The XRD patterns were recorded in the 2$\theta$ range 10°–80°, with a step size of 0.02°, for a total time of 30 min per pattern. The identification of the crystalline phases was carried out from the XRD patterns using the program FullProf Suite and LeBail refinements [38, 39].

The morphology of the particles was observed by scanning electron microscopy (SEM) using FEI Quanta 200 field emission gun–SEM (FEG–SEM) equipment coupled with energy-dispersive x-ray spectroscopy.

Thermogravimetric analyses (TGA) and derivative thermogravimetry (DTG) were performed using a NETZSCH TG 209 F1 Libra thermo-microbalance. The samples were heated in an alumina crucible up to 700 °C (heating ramp: 10 °C min$^{-1}$) under a constant flow of synthetic air (O$_2$/N$_2$: 20/80; 60 ml min$^{-1}$).

3. Results and discussions

Figure 1 shows in detail the 50 Ah calendar aged LiFePO$_4$/graphite pouch cell battery that was first charged and then manually dismantled in a glovebox under inert atmosphere in order to recover the positive electrode.
in the form of FePO₄. The yellowish colour of the graphite anode denotes that the LiC₆ phase is formed and maintained during the opening of the battery as observed also in other reports [40, 41]. The as-recovered double coated electrode was then used for the physical and electrochemical tests. Prior to run electrochemical characterization, one side of the electrode was removed as described in the experimental section.

From the pouch cell harvested cathodes are collected electrodes of 12 mm diameter that are rinsed with DMC to get rid of the salt. The XRD patterns and the SEM images of FePO₄ recovered right after the disassembly of the pouch cell are represented in figures 2(a) and (b). Subsequently, FePO₄ electrodes are assembled in coin cell vs metallic Na with 1 M NaPF₆ in EC:DMC (1:1 wt%) electrolyte and discharged until a potential of 2.0 V vs Na⁺/Na at a current of C/20 in order to ensure the full sodiation of the cathode. Following, the cell was dismantled and the NaFePO₄ electrode recovered for XRD and SEM analysis shown
Table 1. FePO$_4$ and NaFePO$_4$ lattice parameters obtained from LeBail refinements.

| Electrodes                | $a$ (Å)  | $b$ (Å)  | $c$ (Å)  | $V$(Å$^3$) |
|---------------------------|----------|----------|----------|-------------|
| Harvested FePO$_4$        | 9.8291(5)| 5.7982(5)| 4.7816(2)| 275.51(2)  |
| NaFePO$_4$ (first sodiation) | 10.4060(4) | 6.2150(2) | 4.9375(2) | 319.31(2)  |

Figure 3. Thermogravimetric analysis curve (TGA, in black) and differential thermal analysis curve (DTG, in red) of FePO$_4$ electrode material.

in figures 2(c) and (d). Even though Na$^+$ has larger size than Li$^+$, Na$^+$ ions can be inserted in the FePO$_4$ structure and both XRD patterns show the characteristic orthorhombic $Pmn$ phase of FePO$_4$ and NaFePO$_4$, and also the presence of a limited amount of graphite and Fe$_2$P. No Fe$_2$O$_3$ was detected.

Fe$_2$P impurities can be originated during the calcination of LFP precursors in a partially reducing atmosphere. In particular it is reported that these phases enhance the electronic conductivity of the material, has although with adverse effect on Li-ion diffusion [42, 43]. The higher background appearing at low angle in figure 2(c) is mostly due to some amorphous phase coming from the glass fibre of the on the electrode separator that we were unable to completely remove and that is also evident from figure 2(d). The unit cell parameters, determined by Le Bail refinements shown in table 1, are in good agreement with those previously reported [33, 44]. As expected, the volume of the cell is higher in NFP than in the LFP phase (319.31(2) Å$^3$ vs 275.51(2) Å$^3$) due to the larger ionic radio of Na$^+$ with respect to Li$^+$ [34]. The SEM images observed in figures 2(b) and (d) show that the two samples exhibit a good homogeneity and no evidence of change in morphology and particle size after sodiation are observed.

TGA and DTG analysis of the as-recovered positive electrode was carried out to determine the quantity of active material (FePO$_4$) to be further used for the mass loading calculation (figure 3). From the DTG analysis three mass loss peaks were found at the temperature of 400 °C, 475 °C and 650 °C. These mass loss values were assigned to the loss of binder, conductive carbon and other non-identified additives respectively, representing 10% of the total weight (around 4% for binder and 6% for conductive carbon and other additives). The remaining 90% of the mass corresponds to the FePO$_4$ active material. Based on this analysis, the areal weight for an electrode of a diameter of 12 mm used for the electrochemical tests, is then calculated to be around 14 mg cm$^{-2}$. This value is quite common in commercial Li-ion batteries, although it should be noted that such high mass loadings have not been yet optimized for Na-ion technology, which is still at an early stage of development, (see table 1 in SI).

The electrochemical performance of the harvested positive electrode has been initially evaluated in half-cells versus sodium metal. Figure 4(a) shows the galvanostatic profiles of the positive electrode. The current used for this test is 0.065 mA (C/20) and gives an initial capacity relative to the first sodiation of 120 mAh g$^{-1}$ (78% of the theoretical capacity). The reversible capacity of NaFePO$_4$ stands around 100 mAh g$^{-1}$ for 15 cycles shown in figure 4(b), then the capacity decays to 80 mAh g$^{-1}$ and remains stable at least until around 45 cycles. The coulombic efficiency increases within the first 12 cycles before it stabilizes at a value of 95%. These values, even if still moderate, are very encouraging taking into account the very high loading of the electrode, whose formulation is optimized for a different chemistry. This is indeed a relevant aspect that is often disregarded, as energy-dense batteries represent a more sustainable option and, compared
Figure 4. Voltage profile (a) and charge/discharge capacity as a function of number of cycles (b) of the positive electrode assembled in half cell vs sodium metal.

Figure 5. Voltage profile of the HC/NaFePO$_4$ full-cell battery obtained by the three-electrode cell that allows monitoring the potential vs Na of cathode, anode and full cell at a current of C/30.

...higher areal weights will be required in all Na-ion positive electrodes for a given areal capacity [28].

In order to evaluate the recovered cathode in a full cell a HC anode with a mass loading of around 6 mg cm$^{-2}$ was prepared using PVDF as binder. The galvanostatic tests vs Na is depicted in figure S2. The HC anode was tested vs Na in a 0.01 V–2.00 V voltage range. A reversible capacity about 300 mAh g$^{-1}$ at a current of C/20 is obtained with a first cycle coulombic efficiency of about 76%.

After evaluating the electrochemical behaviour of the anode and of the cathode separately in half-cells, a full Na-ion cell HC/NaFePO$_4$ was assembled. The best mass balance was first determined taking advantage of a three-electrode cell. A negative over positive mass ratio of $\approx 1$ was chosen taking into account the capacity obtained in half-cell tests ($\approx 14$ mg cm$^{-2}$ for the cathode and 6 mg cm$^{-2}$ for the anode, respectively). To mitigate the negative impact of the new solid electrolyte interface (SEI) on the anode and the cathode electrolyte interface formation, an in-situ electrochemical pre-cycling of both cathode and anode was done taking advantage of a three-electrode cell by connecting alternatively positive and negative electrode versus the Na reference electrode (so that during anode and cathode precycling Na was used as counter electrode and when connected as full cell the metallic sodium was used as reference electrode). The galvanostatic cycles of the HC/NaFePO$_4$ battery were performed between 1 V and 4 V cut-off limits at a current of C/30, using 1 M NaPF$_6$ in EC:DMC (1:1 wt%) as electrolyte. Taking advantage of the three-electrode cell it was possible to track the potential of the single electrodes versus sodium in order to verify the balancing of the cell. The voltage profile of the second reversible charge–discharge cycle is shown in figure 5.

When the cell is charged at 4 V, the anode and the cathode potential reach 10 mV and 4 V respectively, Na-plating is avoided at the negative electrode. During discharge of the full cell, the anode potential reaches 1.72 V, while the cathode reaches 2.73 V.
In the following cycles a loss of active sodium was still experienced, which can occur possibly because of various reasons. Among them, non-optimized balancing, and the continuous SEI formation on the anode represent the most plausible ones and need to be further explored. An increase in the cell polarization is also observed which can be attributed to the high loading of the reused cathode.

The successful proof of concept demonstrated in this paper has shown that it is possible to use calendar aged LiFePO₄ based battery in Na-ion technology, which paves the way towards sustainable Na-ion batteries that efficiently use primary resources, use non-toxic materials, are energy dense and use of materials that are 100% conceived from ethical sourcing. The first results are optimistic considering that the high loading of the cathode used in commercial LIB is a disadvantage if is directly used in SIBs. Future research activities dedicated to increase the battery’s lifespan and roundtrip efficiency are needed to allow effective and efficient processes based on the recovery, reuse and recycling of LIBs, together with safe harvesting, storage protocols and traceability of the history and chemical components of the devices. Finally, we hope that this approach can encourage further research in the recycling topic, especially focused in design-for-recycling. From this point of view, new cell designs that consider this end-of-life pathway, might be developed in order to be implemented at an industrial large-scale level. Within this paper we have demonstrated a new way to mitigate LFP waste, giving an alternative to generate a low cost and promising material for SIBs (NaFePO₄) which otherwise is difficult to directly synthesize.

4. Summary

In this paper the possibility to recycle calendar aged Li-ion batteries and reuse its positive electrode in Na-ion batteries is discussed. A calendar aged 50 Ah LIB battery was opened in charged state with the aim to obtain a complete delithiaded phase with only FePO₄. The harvested electrodes, that present a loading of 14 mg cm⁻², were sodiated electrochemically and tested in half and full cell versus sodium and HC, respectively. The first sodiation of the cathode in half cell vs sodium metal gives an initial capacity of 120 mAh g⁻¹ despite the very high loadings typically used in commercial LIBs (around 14 mg cm⁻²). The performance in full cell versus HC was evaluated and shows an initial specific capacity of 100 mAh g⁻¹.

The combination of materials proposed in this work is expected to contribute to breaking down the costs of LFP recycling as well as to reducing environmental impact and encourage sustainability.

Data availability statement

No new data were created or analysed in this study.

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