Iron-Based Electrodes Meet Water-Based Preparation, Fluorine-Free Electrolyte and Binder: A Chance for More Sustainable Lithium-Ion Batteries?

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Introduction

Rechargeable Li-ion batteries (LIBs) represent an energy-storage technology that has undergone tremendous development in recent decades with significant progress in terms of energy and power densities. This has enabled these batteries to conquer the portable-electronics market and expand into those of power tools and electric vehicles. Nevertheless, an increasing concern is connected to a parallel and necessary development of more sustainable LIBs, as their components and manufacturing are expensive, account for obnoxious gas emissions and rely on toxic and hazardous materials, which ultimately represent a threat to the environment.

Fluorine-rich compounds, such as polyvinylidene fluoride (PVdF) binders and LiPF₆ electrolyte salt, are classical examples of toxic and hazardous components that are found ubiquitously in LIBs and also require a high energy expense for their synthesis and processing in battery manufacture.[1] Attempts to substitute PVdF with cheaper renewable water-soluble binders such as carboxymethyl cellulose (CMC)[2] or alginic acid[3] have been successful and have improved not only the sustainability of such electrode preparations (see Table 1) but also their overall electrochemical performances. This is the case for most active materials for negative electrodes[4–6] and also for a few positive ones[7–11] that are not extremely sensitive to moisture (e.g., LiFePO₄).[12] Conversely, the replacement of LiPF₆ with a fluorine-free salt has not experienced the same degree of success, as LiPF₆ still provides the most desirable combination of properties for applications in LIBs (see Table 2), for example, high ionic conductivity, electrochemical stability over a broad voltage window, stable solid–electrolyte interface (SEI) formation, Al passivation and a wide range of operation temperatures.[13,14] Nonetheless, lithium bis(oxalato)borate (LiBOB) has been investigated in several studies[15] and is a viable candidate for the replacement of LiPF₆ in high-temperature applications (e.g., 60 °C) despite its moderate solubility and ionic conductivity, thicker SEI and narrower voltage-window stability, as it has enhanced thermal stability[16–18] and can passivate Al.[19] This should avoid the presence of highly corrosive substances generated from LiPF₆ decomposition (i.e., HF and POF₆), which is typically exacerbated at temperatures above 40 °C[16,20] and, thus, improve cell safety.
during operation.\textsuperscript{[21]} LiBOB is also superior to LiPF\textsubscript{6} in terms of cycling stability in full cells containing LiFePO\textsubscript{4} and graphite.\textsuperscript{[22]}

Other crucial steps are still necessary to advance the overall sustainability of the next generation of LIBs, especially in terms of material choice and associated chemistry. According to recent directives of the European Union on the development of energy technologies for a transition to a low-carbon economy,\textsuperscript{[23, 24]} cobalt and graphite are much more critical than lithium from an economic perspective (see Table 3). Cobalt ores are not abundant, and Co is a toxic and expensive material, the role of which is nowadays considered strategic for a series of applications. Clearly, the early quest for Co-

| Table 1. Comparative table of the main features of some polymer binders used in LIBs. |
|---|
| Polymer binder | Cost [\$/kg]\textsuperscript{[a]} | \(\rho_{25}\) [g/cm\textsuperscript{3}] | Source type | Solvent type | Substrate adhesion | \(T_m\) [°C] | Swelling in electrolyte |
| PVdF | 8–10 | 1.76 | synthetic | NMP\textsuperscript{[b]} | moderate | 170 | large |
| CMC | 3–5 | 1.55 | natural | water | very good | 270 | minor |
| alginate | 3–8 | 1.59 | natural | water | excellent | > 300 | negligible |
| polyacrylic acid (PAA) | 2–3 | 1.41 | synthetic | water, EtOH | excellent | 106 | negligible |
| styrene-butadiene rubber (SBR) | 2–3 | 0.94 | synthetic | water | good | 120\textsuperscript{[c]} | moderate |

\textsuperscript{[a]} Typical range of prices for medium/large quantities on Alibaba.com. \textsuperscript{[b]} NMP = N-methylpyrrolidone. Copolymers are soluble also in acetone and water. \textsuperscript{[c]} Maximum service temperature; \(-63°C \leq T_s \leq -58°C\). |

| Table 2. Comparative table of some properties of the most relevant electrolyte salts in LIBs. |
|---|
| Electrolyte salt | Molar mass [g mol\textsuperscript{-1}] | \(\rho_{25}\) [g/cm\textsuperscript{3}] | Cost [\$/kg]\textsuperscript{[a]} | \(T_m\) [°C] | \(T_{dec}\) [°C] | \(\sigma_{\text{ion}}\) [mS cm\textsuperscript{-1}]\textsuperscript{[b]} | Al passivation | Hazards and toxicity\textsuperscript{[c]} |
| LiPF\textsubscript{6} | 151.9 | 2.83 | 500 | 200 | 176 | > 10 | excellent | 
| LiBOB | 193.8 | 0.8–1.2 | 650 | 302 | 275 | \(\approx 8–9\) | good |
| LiTFSI\textsuperscript{[d]} | 287.1 | 1.33 | 650 | 234 | 360 | \(\approx 9\) | insufficient |

\textsuperscript{[a]} Average prices taken from Ref. [14]. \textsuperscript{[b]} Ionic conductivity at 25°C in relevant non-aqueous solvents. \textsuperscript{[c]} Pictograms and labelling according to regulation (EC) No. 1272/2008. \textsuperscript{[d]} Lithium bis(trifluoromethanesulfonyl)imide. |

| Table 3. Synoptic table of the most common elements found in Li-ion battery manufacture. The costs refer mainly to their ores. |
|---|
| Element | Earth abundance by weight [ppm]\textsuperscript{[a]} | Cost [\$/ton]\textsuperscript{[a]} | \(\rho_{25}\) [g/cm\textsuperscript{3}] | Criticality (EU rating)\textsuperscript{[b]} | Recycling (US trend) |
| Al | 83 000 | 1.65\textsuperscript{[a]} | 2.699 | none | high |
| Cu | 68 | 4.70\textsuperscript{[a]} | 8.960 | low | medium-high |
| Ni | 99 | 8.90\textsuperscript{[a]} | 8.908 | low | high |
| Li | 18 | 6.40\textsuperscript{[a]} | 0.534 | medium-low | low\textsuperscript{[a]} |
| Na | 22 700 | 0.14\textsuperscript{[e]} | 0.571 | none | insignificant |
| Fe | 62 000 | 0.084\textsuperscript{[e]} | 7.874 | none | high |
| Co | 29 | 23.75\textsuperscript{[a]} | 8.900 | medium | medium-high |
| Mn | 1060 | 3.8\textsuperscript{[a]} | 7.430 | none | negligible |
| Ti | 6320 | 0.75\textsuperscript{[a]} | 4.540 | none | none |
| V | 136 | 1.99\textsuperscript{[a]} | 6.110 | medium | medium |
| C | 180 | 1.24\textsuperscript{[a]} | 2.266\textsuperscript{[f]} | high-medium\textsuperscript{[f]} | medium-low\textsuperscript{[f]} |
| Sn | 2 | 17.20\textsuperscript{[a]} | 7.256 | medium | medium-high |
| Zn | 76 | 1.85\textsuperscript{[a]} | 7.133 | none | high |
| P | 1120 | 0.08\textsuperscript{[a]} | 1.820 | low | none |
| Si | 272 000 | 0.06\textsuperscript{[a]} | 2.336 | low | insignificant |
| O | 455 000 | – | gas | none | none |
| F | 544 | 0.33\textsuperscript{[a]} | gas | none | low |
| S | 340 | 0.1\textsuperscript{[a]} | 2.070 | none | medium |
| N | 19 | 0.47\textsuperscript{[a]} | gas | none | none |
| B | 9 | 0.4\textsuperscript{[a]} | 2.350 | medium-low | insignificant |

\textsuperscript{[a]} Chemistry of the Elements by Greenwood & Earnshaw, Second Edition, Butterworth-Heinemann (1997). \textsuperscript{[b]} https://setis.ec.europa.eu/publications/setis-magazine/materials-energy/critical-materials-energy-technologies COM(2014) 297 final. \textsuperscript{[c]} http://www.lme.com/en-gb/metals/. \textsuperscript{[d]} http://minerals.usgs.gov/minerals/pubs/commodity/. \textsuperscript{[e]} Currently increasing. \textsuperscript{[f]} Graphite. \textsuperscript{[g]} Nitrogen fixed in NH\textsubscript{3}. |
free cathodes containing safer and more abundant elements was one of the main driving forces that led to the successful development of lithium iron phosphate (LFP),\textsuperscript{[24–27]} lithium manganese spinel (LMS)\textsuperscript{[38–39]} and, more recently, Ni-rich layered materials with low Co contents.\textsuperscript{[36,37]} The unexpected criticality of graphite is attributed mainly to its uneven distribution, the ever-increasing demand for its natural form for industrial applications (e.g., steelmaking and lubricants) and the possible realization of cheaper LiB anodes.\textsuperscript{[32]} These circumstances have led the experts to flag this material in Europe, despite its key role in LiBs. Owing to the exceptional properties of graphite, the search for a suitable and cost-effective substitute for anodes is perhaps one of the toughest challenges in this field, especially if abundant and non-toxic materials should be employed. Currently, the most viable candidates are Si\textsuperscript{[33–36]} or perhaps Al\textsuperscript{[37]} which both form Li alloys, and conversion compounds based on Fe\textsuperscript{[38–40]} and Mn\textsuperscript{[41]} have also been proposed.\textsuperscript{[42,43]} However, the cycling-induced structural changes of these materials still represent a weak point that often causes an early deterioration of their electrochemical performance.\textsuperscript{[42,44]} This becomes particularly severe if huge volume variations occur and cause extensive damage to the interface and electrical wiring of the active materials, although the presence of inactive semiconductor or metallic phases in Li-alloy-type compounds often alleviates this issue (e.g., Fe\textsubscript{Si}Si/Li@C\textsuperscript{[45]} and TiSnSb\textsuperscript{[46]}).

Another crucial point is the simultaneous provision of high power levels without the need for elaborate material engineering. LiFePO\textsubscript{4}/Li\textsubscript{T}iO\textsubscript{2}\textsubscript{2} full cells\textsuperscript{[47]} represent an outstanding example of high-power and long-lasting batteries but suffer from unavoidable drawbacks of substantially lower energy density and higher synthesis costs compared with those of graphite-based LiBs. Nonetheless, Li\textsubscript{T}iO\textsubscript{2} eliminates fully the main problem of graphite anodes, that is, the risk of failure through a lithium-plating mechanism during high-power charging or upon charge under a low-temperature operation regime.

Some initial progress towards a graphite substitute was achieved along the possible route of conversion-type materials. Recently, high-power LiBs based on carbon-coated ZnFe\textsubscript{2}O\textsubscript{4}\textsuperscript{[48,49]} and CNT–LiFePO\textsubscript{4} (CNT = carbon nanotube) active materials assembled with sodium carboxymethyl cellulose (NaCMC) and a 1 M LiPF\textsubscript{6} electrolyte showed exceptional electrochemical performance\textsuperscript{[50]} and, in principle, met most of the requirements for a potential alternative to conventional graphite-based cells. This interesting type of battery system has motivated us to go a step further, namely, to explore the direct utilization of Zn-free nanostructured iron oxide from straightforward syntheses at low temperatures and to fully exploit for the first time the pseudo-capacitive behaviour\textsuperscript{[51]} of its reacted form (i.e., Fe/Li\textsubscript{2}O) in completely fluorine-free Li-ion cells containing an additive-free 0.8 M LiBO\textsubscript{2} electrolyte, sodium alginate binder and commercial LiFePO\textsubscript{4} powder as a cathode.

This study clearly shows that, even without any particular engineering of the iron oxide anode (e.g., C-coating,\textsuperscript{[52,53]} hollow nanoparticles,\textsuperscript{[54]} micro-boxes,\textsuperscript{[55]} or yolk–shell structures),\textsuperscript{[56,57]} it is possible to cycle the corresponding full cells with LFP at room temperature at high rates with good performances and stability for more than 1000 cycles with good Coulombic efficiencies and a remarkable improvement of round-trip efficiencies. The energy efficiencies for the corresponding full cells are not limited by the large voltage hysteresis caused by the typical conversion/de-convolution of iron oxide, as its pseudo-capacitance at low voltages versus Li\textsuperscript{+}/Li (i.e., in its deep-lithiated Fe/Li\textsubscript{2}O nanocomposite form) is utilized here. This approach, in which the negative electrode is pre-loaded with Li before its assembly with the other cell components, leads to an increase of the output voltage and the corresponding batteries. The crucial step of iron oxide pre-lithiation is discussed, and direct reactive contact with Li metal enables a wide range of operation voltages for the associated cells with LFP and represents a possible (e.g., quicker) alternative to electrochemical pre-cycling of the same material. This route grants access to average cell operation voltages in the range 2.6–3.1 V with excellent stability for the electrochemical reactions even in presence of a cycling window as large as 3 V. To the best of our knowledge, this cell potential is the highest obtained to date with this particular combination of active materials. An enhanced electrochemical activity owing to the formation of small Fe nanoparticles and the associated wide distribution of potentials\textsuperscript{[58]} for extensive charge storage at the phase boundaries with Li\textsubscript{2}O\textsubscript{5} results in voltages very close to that of the Li\textsuperscript{+}/Li couple. No sign of degradation, such as lithium plat- ing on graphite, has been observed here even during fast charge and discharge. A sloping plateau, beneficial to many applications, was obtained in the voltage profiles of these cells, and the features of LiBs and those of supercapacitors are bridged in this way.

Through the present approach, a series of crucial aspects are addressed in these cells: 1) effective Li storage at the phase boundaries\textsuperscript{[60,61]} and double-layer charging are enhanced, 2) the range of operation potentials can be tuned to limit volume variations and structural rearrangements in the reacted iron oxide or to access a “built-in Li reservoir”, 3) the energy efficiencies are improved dramatically compared with those of Li half-cells based on iron oxide, 4) no HF can be formed and released in the electrochemical processes; therefore, the safety of the cells and their stability over long-term cycling are improved, 5) high charge/discharge rates are accessible without the risk of dendrite formation (e.g., as in graphite anodes) thanks to the wider electroactive potential window provided by Fe/Li\textsubscript{2}O upon reaction at low voltages versus Li\textsuperscript{+}/Li and its tendency towards surface passivation,\textsuperscript{[62]} 6) the hazards during the entire electrode fabrication, cell assembly and operation as well as the possible recycling of the various components after battery disposal are reduced. A preliminary investigation of the effects brought about by direct pre-lithiation and electrochemical pre-cycling of the anodes in these LiBO\textsubscript{2}-based cells has also been performed.
Results and Discussion

Morphological, structural, and compositional analyses of the iron oxide electrodes

The characteristic morphologies of the iron oxide materials are shown in the SEM images in Figure 1 together with that of the LFP electrode, which is considered for comparison here.

The composite negative and positive electrodes (Figure 1c and d) both display agglomerates of active nanoparticles surrounded by carbon black. The LFP particles in Figure 1d have shapes similar to platelets or elongated disks with typical dimensions spanning from 50 nm to approximately 0.5 μm. Conversely, the iron oxide powders in Figure 1a and c consist of small nanoparticles (i.e., < 50 nm), which form fluffy agglomerates with typical sizes below 1 μm, as well as larger and more compact aggregates with micron-sized dimensions. The morphology of the iron oxide nanowires/leaves (Figure 1b) is also distinctive, and they have lengths of approximately 1–2 μm and reduced thicknesses of a few nm.

The formation of the nanostructured iron oxide powder and the nanowires/leaves was studied by XRD. The diffraction patterns before and after the pyrolysis of iron acetate as well as those for iron oxidation are presented in Figure 2. The diffraction pattern of the pristine iron acetate powder suggests a rather limited crystallinity of this precursor salt, which also possesses a complex crystal structure. The pattern obtained after the pyrolysis process displays broad peaks and bands that correspond to the formation of small nanoparticles of Fe₃O₄, γ-Fe₂O₃ or both, as indicated by the Miller indexes associated with these spinel structures. At this stage, it is very difficult—if not impossible—to distinguish between these two oxide phases, because they share the same crystal structure and the diffraction peaks in Figure 2 are very broad and do not enable the extraction of more detailed information.

In any case, the magnetic nature of the pyrolyzed powder is evident if it is subjected to the field of a small permanent magnet (see Figure S1 in the Supporting Information). It should be noted that the existence of Fe₃O₄ is related to that of γ-Fe₂O₃ in many cases (i.e., Fe₃₋ₓOₓ with ordered vacancies) and that these oxides can also undergo further transformations into α-Fe₂O₃ (e.g., “martitization”). Especially if small crystals are exposed to air, the diffraction diagrams of the iron substrate before and after oxidation exhibit sharp peaks owing to the presence of highly crystalline phases. After oxidation, three main crystalline components are detected clearly, namely, Fe, Fe₃O₄ and α-Fe₂O₃. The latter possesses a pronounced crystal orientation along (110), as can be seen from the associated diffraction signal, which almost overlaps the most intense (311) diffraction peak of the main magnetite phase.

Raman micro-spectroscopy was performed to investigate the structure and composition of the formed oxide phases in more depth and to probe separately the LFP surface (see Figure S2). The spectra of the iron oxide materials formed through
peaks at $\nu \approx 1390$ and $1580 \text{ cm}^{-1}$ have been reported as distinctive signatures of $\gamma$-$\text{Fe}_3\text{O}_4$.[66] The weak and broad bands below $\nu = 600 \text{ cm}^{-1}$ can be attributed to both Fe$_3$O$_4$ and $\gamma$-$\text{Fe}_3\text{O}_4$.[66,67] A faint feature in the same spectrum at $\nu \approx 2932 \text{ cm}^{-1}$ corresponds to the sharpest peak observed for the acetate precursor.[66] The presence of species very similar to iron acetate on the surface of the pyrolyzed powder was confirmed by FTIR spectroscopy of the respective samples before and after pyrolysis (see Figure S3 in the Supporting Information). The eventual formation of traces of $\alpha$-$\text{Fe}_2\text{O}_3$ in the pyrolyzed powder, owing to exposure to air and the possible additional oxidation of Fe$_2$O$_3$/$\gamma$-$\text{Fe}_3\text{O}_4$, can be excluded here, as no resonance peak is detected at $\nu \approx 1320 \text{ cm}^{-1}$. The latter represents a very sharp feature that is observed for $\alpha$-$\text{Fe}_2\text{O}_3$ owing to a resonant two-magnon scattering,[65,66,69] though the same peak has also been associated with phonon scattering.[70] This resonance peak is very pronounced in Figure 3 for the nanowires/leaves upon excitation at $\lambda = 532 \text{ nm}$. Although this mechanism is ideal for the detection of $\alpha$-$\text{Fe}_2\text{O}_3$ even in tiny amounts here, it also hinders the simultaneous detection of Fe$_3$O$_4$, which does not undergo resonance. This minor issue can be solved by using a different excitation wavelength and, thus, moving to “off-resonance” conditions, which clearly suppress the feature at $\nu = 1320 \text{ cm}^{-1}$ and highlight better the characteristic peak of Fe$_3$O$_4$ at $\nu \approx 667 \text{ cm}^{-1}$.

TEM, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and selected-area electron diffraction (SAED) were also conducted to gain further insights into the local structures and textures of these iron oxide nanostructures. The results of these analyses are presented in Figure 4.

The nanostructured powders show a characteristic structure composed of agglomerated nanoparticles. The typical size of the primary particles is approximately 10–15 nm, and the latter seem to have a rather homogeneous size distribution in the related micrographs of Figure 4. A cross-section TEM image of the iron oxide nanowires/leaves is shown in Figure 4f. The general morphology of the nanowires/leaves exhibits its sharp tips and edges with some degree of bending. The maximum width of the base of the “leaves” is almost 0.5 $\mu$m whereas their lengths cover different extents from approximately 0.5 $\mu$m up to a couple of microns for the longest ones (see inset in Figure 4f). The presence of extended defects in these elongated structures is also visible in Figure 4f. A high crystallinity was clearly shown for the nanowires/leaves by the previous XRD and Raman analyses whereas the crystalline properties of the nanoparticles constituting the pyrolyzed powders are confirmed here by the SAED pattern (see inset of Figure 4a). A series of spotty rings corresponding to the major diffractions associated with the lattice structure of Fe$_3$O$_4$ and $\gamma$-$\text{Fe}_3\text{O}_4$ can be observed. Moreover, various lattice fringes are
powders determined by BET analysis are very close to 10 g, which has also been ascribed to the reversible formation of large voltage windows. 3) the SEI layer generated on the iron oxide electrode in the pre-lithiation process results in dissolution of veil-like organic surface layers. At the same time, the pre-lithiated anode can undergo additional Li\textsuperscript+ uptake by enhanced interfacial storage at the Fe/Li\textsubscript{2}O phase boundaries through a pseudo-capacitive mechanism which has also been ascribed to the reversible formation and dissolution of veil-like organic surface layers. The broad shape and significant asymmetry of the first anodic peak can be understood on the basis that 1) the pre-lithiated iron oxide powders create a distribution of potentials owing to the different sizes of the reacted particles; 2) the SEI layer generated on the iron oxide electrode in the pre-lithiation process could be not entirely stabilized or fully formed in the inner-

visible in the images shown in Figure 4c and e, which confirm the polycrystalline nature of these powders. The HAADF-STEM images presented in Figure 4b and d provide additional information regarding two other important features of these powders, namely, the existence of a continuous "surface layer" (most likely composed of remnant species with features similar to those of the acetate precursor) of approximately 10–20 nm around the particle agglomerates (see arrows in Figure 4d) and the ubiquitous presence of a prominent micro-porosity throughout the pyrolyzed material. These particular characteristics are not surprising and are perfectly in line with the previous FTIR and Raman spectroscopy results (see Figures S3 and 3) for the surface composition of the powders as well as with the particular pyrolytic process through which the material was formed. The presence of a large surface area caused by the presence of micropores is also suggested by the findings of the gas adsorption–desorption measurements (see Figure S4 and Table S1). Although the specific surface area of the Fe\textsubscript{2}O\textsubscript{3} powders determined by BET analysis is very close to 50 m\textsuperscript{2}g\textsuperscript{-1}, both the results shown in Figure S4b and the value of the t-plot external surface area (≈ 54 m\textsuperscript{2}g\textsuperscript{-1}) in Table S1 indicate that the contribution of the micropores (i.e., < 2 nm) in this material is not negligible. The impact of the micropores on the overall surface area could be larger than that estimated by these measurements, as their accessibility might have been limited by the surrounding layer observed in Figure 4d. In any case, from the HAADF-STEM and N\textsubscript{2} adsorption–desorption results, it can be concluded that the (micro)porous nature of the pyrolyzed powders could play an important role in the resulting properties and associated electrochemical behaviour, as it could ease the transport of the charge carriers (Li\textsuperscript{+}, e\textsuperscript{-}) through such an extended interface.

**Electrochemical performances of full cells**

The electrochemical behaviour of the full cells based on coated electrodes containing commercial LFP powders and deeply lithiated nanostructured iron oxide is the main focus of the discussion here, and the individual properties of the positive and negative electrodes, studied in Li half-cells, are presented separately in the Supporting Information. Only some results of such electrochemical analyses will be recalled in the following, as the main goal of this investigation was to assess the feasibility of Li-ion cells relying entirely on iron-based cathodes and anodes in combination with 100%-fluorine-free components.

**Cyclic voltammetry of full cells**

A series of 50 cyclic voltammograms is presented in Figure 5a for a full cell cycled at scan rate of 1.0 mV s\textsuperscript{-1} in a large voltage window between 1.2 and 4.2 V. The cell contains 0.8 M LiBOB electrolyte, an LFP cathode and a pre-lithiated nanostructured iron oxide anode obtained through direct-contact activation. The utilization of a wide voltage range here was intended to probe most of the electrochemical reactions that can occur with this combination of materials and to establish whether such processes are favourable or detrimental for the ultimate cell performance, especially when these batteries are operated under unconventional conditions.

In Figure 5a, it can be seen that the initial cycle shows a broad and highly asymmetric anodic peak, and the maximum oxidative current is observed at approximately 3.65 V. This reaction corresponds to the change in oxidation state from Fe\textsuperscript{III} to Fe\textsuperscript{IV} in LFP and the concomitant extraction of a Li\textsuperscript{+} ion from its olivine structure according to Equation (1):

\[
\text{Li}_{x}\text{FePO}_4 \rightarrow x\text{Li}^+ + x\text{e}^- + \text{FePO}_4
\]

At the same time, the pre-lithiated anode can undergo additional Li\textsuperscript{+} uptake by enhanced interfacial storage at the Fe/Li\textsubscript{2}O phase boundaries through a pseudo-capacitive mechanism which has also been ascribed to the reversible formation and dissolution of veil-like organic surface layers. The broad shape and significant asymmetry of the first anodic peak can be understood on the basis that 1) the pre-lithiated iron oxide powders create a distribution of potentials owing to the different sizes of the reacted particles; 2) the SEI layer generated on the iron oxide electrode in the pre-lithiation process could be not entirely stabilized or fully formed in the inner-

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**Figure 3.** Raman spectrum of the nanostructured iron oxide powder obtained by pyrolysis of iron acetate and comparative spectra obtained at different excitation wavelengths of the iron oxide nanowires/leaves grown on an oxidized iron foil. Note that all of the materials were analysed at λ = 532 nm, which causes resonant Raman scattering in α-Fe\textsubscript{2}O\textsubscript{3} as demonstrated by the prominent peak seen at \(\nu = 1320\) cm\textsuperscript{-1} for the nanowires. The presence of magnetite in the nanowires is revealed through excitation with a λ = 785 nm laser source, which yields an almost complete suppression of the resonance peak at \(\nu = 1320\) cm\textsuperscript{-1}.
most part of the porous Fe₃O₄/γ-Fe₂O₃ particles (see Figure 4d), 3) the initial surface interaction of the composite Na-alginate/LFP electrode with the LiBOB electrolyte could also contribute to further broadening and asymmetry of this peak (see, for example, Figure S5) and 4) the carbonaceous additives in the negative electrode could also participate in partial Li⁺ ion uptake in this range of potentials. The subsequent peak in the first cathodic scan displays a sharper profile with its maximum reductive current centred at approximately 3.30 V. This feature is due to the reduction of Fe³⁺ to Fe²⁺ [Eq. (1)] and the reinsertion of Li⁺ ions into the olivine structure and crucially suggests that the pre-lithiated iron oxide operates simultaneously in a range of potentials close to that of the Li⁺/Li couple. The possibility of Li plating on the Fe/Li₂O anode through

Figure 4. TEM images of the iron oxide nanostructures utilized as negative electrodes. (a) Low-magnification image of nanostructured iron oxide powder obtained by pyrolysis of iron acetate and related SAED pattern (inset). (b) HAADF-STEM image of the nanostructured iron oxide powder. (c) Magnified detail of the nanostructured iron oxide powder. (d) HAADF-STEM image at higher magnification showing the presence of a surface layer around the agglomerated nanoparticles (see arrows) and a prominent micro-porosity. (e) HR-TEM image displaying the crystalline features of the nanoparticles and their lattice fringes. (f) Cross-section micrograph of the iron oxide nanowires/leaves grown on an oxidized Fe foil. The inset in (f) is a low-magnification image of these elongated structures and their full lengths.
under-potential deposition (UPD) in the first cathodic half-cycle cannot be excluded here. A tail extending to approximately 1.75 V is also observed together with a slight bump at approximately 2.3 V. A distinctive peak is noticed in the same cathodic scan at approximately 1.5 V (marked with ‘*’ in Figure 5a) and this can be attributed to the partial de-conversion of deeply lithiated iron oxide (i.e., marked with ‘#’ in Figure 5a) is shifted clearly to a lower potential ($\approx 1.33$ V), and its maximum intensity is reduced compared with that for the first cycle but is almost constant in the following ones.

From the third cycle on, a continuous shift towards lower potentials is observed in Figure 5a for both the cathodic and the anodic peaks, together with a more symmetric profile for the anodic reaction compared with those for the first two cycles. The widths of the main cathodic and anodic peaks increase with cycling, whereas their maximum currents decrease slightly. The cathodic feature due to the partial de-conversion at low voltage disappears after 15 cycles and shifts progressively towards lower potentials. The evolution of the subsequent redox peaks is presented in Figure 5b, in which the cyclic voltammograms for the remaining 35 cycles are depicted. A gradual shift towards lower potentials for the redox peaks can be seen clearly, together with a simultaneous enlargement of their bases and a concomitant fading of their maximum cathodic and anodic currents (see also the multimedia materials in the Supporting Information). From this preliminary qualitative analysis, it can be inferred that the electrochemical behaviour of these full cells is dynamic (see Figure S7a and b in the Supporting Information) and that the system does not respond in exactly the same way in each cycle, although a progressive stabilization of its charge retention is also observed after the first cycles (Figure S7c).

Nevertheless, this dynamic aspect is not surprising here, as conversion compounds such as iron oxide are known to undergo progressive “electrochemical milling” during repeated conversion and de-conversion, which typically occurs over a broad range of potentials (e.g., 0.05–2.80 V vs. Li$^+$/Li). This process, in combination with the formation of a surface passivating layer, which typically occurs at approximately 1.7–1.8 V versus Li$^+$/Li for this electrolytic salt, although lower voltages of approximately 0.5 V versus Li$^+$/Li have also been found for graphite cycled in various LiBOB-based electrolytes. The relatively broad shape of the peak at approximately 1.5 V is likely caused by the superposition of these two electrochemical processes as well as the size distribution of the reacting particles on both electrodes. The de-conversion feature can play an important role depending on the voltage window under which this type of cell is operated. Indeed, by utilizing voltages below 1.75 V, it is possible to access a “built-in Li reservoir” in the pre-lithiated anode and to compensate for Coulombic losses during the first half-cycle (i.e., the first charge).

The anodic peak in the second cycle (Figure 5a) broadens by approximately 0.2 V towards lower voltages and retains an asymmetric shape. This behaviour can be justified by the above considerations and the additional contribution of some extra Li$^+$ ions involved in the processes occurring in the first cathodic half-cycle. The reduction peak in the subsequent cathodic scan does not shift, and its current at 3.3 V is slightly higher than that observed in the first cycle; this result demonstrates a full functionality for LFP, as it is the only compound that can incorporate Li$^+$ ions at this potential. The feature attributed to the partial de-conversion of deeply lithiated iron oxide (i.e., marked with ‘*’ in Figure 5a) is shifted clearly to a lower potential ($\approx 1.33$ V), and its maximum intensity is reduced compared with that for the first cycle but is almost constant in the following ones.
although real de-conversion for Fe/Li$_2$O clearly does not occur in this case. The changes caused by the partial rearrangement of these reactive interfaces upon cyclic voltammetry (CV) cycling are most likely responsible for the progressive shift of the redox potentials. Negative shifts of the electro-chemical potential for the reaction of small clusters of metal atoms have been observed for many metallic nanoparticle systems.

However, such a phenomenon and the presence of extensive phase boundaries at the Fe nanoparticle interfaces are not necessarily detrimental, as it will be shown later that they contribute to fast charging and discharging of the same cell subjected to a series of currents spanning over two orders of magnitude.

**Galvanostatic tests of full cells**

After this preliminary CV analysis, more detailed measurements were performed with three-electrode cells under galvanostatic conditions to monitor the potentials of both the cathode and the anode simultaneously and reference the latter to the Li$^+/\text{Li}$ couple. The results of these tests are presented in Figure 6.

The cell voltage ($E_{\text{cell}}-E_{\text{ref}}$), the potential of the LFP working electrode ($E_{\text{LFP}}$ vs. Li$^+/\text{Li}$) and that of the pre-lithiated iron oxide counter electrode ($E_{\text{Fe/Li}}$ vs. Li$^+/\text{Li}$) are shown in Figure 6a, and the plots are stacked to allow their simultaneous evolution to be followed easily. The system was operated with three different lower-voltage cutoffs of 1.8, 1.5 and 1.2 V for increasing current densities of 0.1, 0.2 and 0.3 mA cm$^{-2}$, respectively. The potentials of both LFP and pre-lithiated iron oxide shifted continuously; thus, the results confirm the previous voltammetric measurements. This shift is more pronounced in the initial cycles (see also magnified portions of the graph in Figure S8), which proceeded at an approximate rate of 1.5 C (i.e., $\approx$ 40 min for a full charge or discharge) upon the application of 0.1 mA cm$^{-2}$. As is demonstrated clearly in Figures 6a and S8, no lithium plating occurs with progressive cycling, as the $E_{\text{Fe/Li}}$ potential of the pre-lithiated iron oxide is sensibly above 0 V versus Li$^+/\text{Li}$ after the first couple of cycles and the whole cell approaches the upper cutoff voltage of 4.2 V during charge.

The minimum and maximum values of $E_{\text{Fe/Li}}$ shifted, especially the upper extreme during the initial cycles. The corresponding voltage profiles for the LFP electrode are influenced in a peculiar manner by this phenomenon, as $E_{\text{LFP}}$ varies more significantly in the proximity of its lower extreme during cell discharge whereas the maximum values of $E_{\text{LFP}}$ during charge remain almost unchanged and very close to the upper cutoff of the whole cell. After approximately 150 h of cycling (see Figure S8a), the highest value for $E_{\text{LFP}}$ is approximately 4.3 V versus Li$^+/\text{Li}$, and a clear stabilization of both its upper and lower extremes can be noticed.

A comparison of the voltage profiles of $E_{\text{Fe/Li}}$ and $E_{\text{Fe/Li}}$ reveals characteristic charge/discharge plateaus at approximately 3.45 V versus Li$^+/\text{Li}$ for LFP whereas a slope-like feature is observed for the pre-lithiated iron oxide, which then reacts in its nanocomposite Fe/Li$_2$O form without showing evident signs of de-conversion. It is important to realize that the potential shift is generated by the deeply lithiated iron oxide: for constant upper (4.2 V) and lower (1.8 V) cutoff voltages for the whole cell, the features of the voltage profiles of $E_{\text{Fe/Li}}$ have a clear influence on those observed for the LFP counterpart (i.e., compare the variations of $E_{\text{Fe/Li}}$ in proximity to its lower cutoff with those of $E_{\text{LFP}}$ near its upper limit). The range of potentials spanned by $E_{\text{Fe/Li}}$ is not only a shifted but also widens (e.g., compare the $E_{\text{Fe/Li}}$ profiles after 10 and 100 h in Figure S8), confirming again the results of the CV analysis. This remarkable potential shift for Fe/Li$_2$O and the simultaneous increase of its electroactive voltage range upon cell discharge (e.g., the removal of Li$^+$ ions from the Fe/Li$_2$O interface and reinsertion into the LFP structure) are in line with earlier results on the electrochemical properties of small metal nanoparticles, especially considering that the metallic particles formed in conversion reactions are very small with typical sizes of 1–5 nm. Additional galvanostatic tests of full cells containing pre-lithiated iron oxide nanowires/leaves with the same LiBOB electrolyte and LFP cathode (see Figure S9 in the Supporting Information) confirmed that the Fe nanoparticles in the resulting Fe/Li$_2$O nanocomposite play a major role in the sloping voltage profiles and their shifts and generate a large electroactive window that extends over 3 V. This test rules out any possible influence of the carbonaceous additives and alginate binder on the observed shapes and shifts of the charge/discharge curves. The range of potentials spanned by the full cell also appears to be broader in Figure S9, likely because of the large size distribution of the as-grown iron oxide nanowires/leaves (see Figures 1b and 4f) before their contact pre-lithiation. This aspect was verified by complementary CV analyses of the pristine iron oxide nanowires/leaves in Li half-cells (see Figure S10 in the Supporting Information), which showed a wide distribution of potentials. Hence, this phenomenon can also be expected in the respective full cells.

It can also be seen in Figure 6a that the minimal $E_{\text{Fe/Li}}$ values are still well above that of lithium metal even at higher currents (e.g., $\approx$ 0.1 V vs. Li$^+/\text{Li}$ at 0.3 mA cm$^{-2}$ after 260 h) and, thus, inherently safe from the dangerous formation of lithium dendrites. The simultaneous evolution of the average voltage per cycle for ($E_{\text{Fe/Li}}-E_{\text{Fe/Li}}$), $E_{\text{Fe/Li}}$ and $E_{\text{Fe/Li}}$ is presented in Figure 6b and shows that a mean operative voltage, approximately in the range of 3.0–2.6 V, can be obtained from this type of cell under different cycling conditions. The evolution of the charge/discharge capacities (Figure 6c) demonstrates not only a stable behaviour for this cell but also a compensating effect of the lower cutoff values (i.e., 1.8–1.5–1.2 V) on the overall capacity retention upon the application of higher current densities. The cell capacity (relative to the active mass of the LFP cathode) remains stable at approximately 120 mAh g$^{-1}$ after more than 300 cycles in correspondence to a practical C rate approaching 5 C at 0.3 mA cm$^{-2}$ in the last 100 cycles. Importantly, an average Coulombic efficiency of (99.7 ± 1.2)% was obtained over 320 cycles together with an average energy efficiency of (90.7 ± 1.9)%. The latter represents a step improvement for a conversion compound utilized in an unoptimized
full cell (i.e., with no specific additives, electrode engineering, etc.). Nonetheless, high-precision coulometry would be better suited to follow more accurately the evolution of the reactions upon progressive charge/discharge and the eventual stabilization of their capacities.

The electrochemical behaviour of these cells with contact-pre-lithiated iron oxide and LiBOB was also compared with 1) an analogous system containing a standard LiPF$_6$ electrolyte and 2) LiBOB-based cells with electrochemically lithiated (i.e., “pre-cycled”) iron oxide anodes (see Figure S11 in the Supporting Information). The results for these comparative experiments are presented in Figures 7 and 8, for which the full cells were cycled at 0.1 mA cm$^{-2}$ between 1.8 and 4.2 V for 100 cycles.

A progressive decrease of the cell voltage is noticed in all of the batteries during the initial cycles, as shown in Figure 7. A shift in the incremental capacity is observed together with a charge/discharge end-point slippage mostly for the pre-lithiated anode in the LiPF$_6$ cell whereas, to a minimal extent, for the pre-cycled anode in the LiBOB battery (Figure 7a, c and e). The separation in voltage (i.e., “polarization”) between the charge and discharge curves (e.g., taken at their half-capacity
point in Figure 7a, c and e) after 50 cycles seems rather similar for all of the cells (≈ 0.17–0.21 V). To address this point systematically, the mean charge/discharge voltages in each half cycle were also calculated. These data, together with the average values and the differences taken between the mean potentials obtained for each charge/discharge half-cycle (i.e., “gap”), are shown in Figure 7b, d and f. A comparison of the data points in Figure 7b, d and f suggests a similar electrochemical behaviour for all cells with a clear stabilization of their average operation potentials at approximately 2.95 V after 100 cycles and comparable values for their respective “voltage gaps”. The latter remains below approximately 0.3 V for all of them after 100 cycles; therefore, the combination of LiBOB and pre-lithiated iron oxide performs as reliably as that of LiBOB and electrochemically pre-cycled iron oxide. It only takes more time or cycles for the voltage profile to stabilize. The differences in the voltage profiles shown in Figure 7 can be understood on the basis that the pre-cycled anode had undergone a preliminary series of full charges/discharges in a Li half-cell (Figure S11 in the Supporting Information) and had been exposed in this way to different electrochemical and mechanical conditions compared to those for the direct-contact activation.

The capacity retention and efficiencies of these batteries are depicted in Figure 8. The capacities of the cells are stable at approximately 130 mAh g⁻¹, irrespectively of the differences in their electro-
lyte and anode activation. The slightly undulating features in the various graphs are due to temperature fluctuations (e.g., day/night) throughout the cycling, as the cells were tested under ambient conditions without any thermostating. Some differences in their performances can still be noted in Figure 8, as the LiBOB/pre-cycled iron oxide battery was the most stable in terms of capacity retention and energy efficiency after 100 cycles (i.e., ≈ 91.2%). The small differences noticed for the pre-lithiated and pre-cycled iron oxide electrodes do not seem to have an immediate effect on the overall behaviour of the respective cells, though this could manifest after a prolonged cycling period. Conversely, it can be noticed in Figure 8 that the cell with LiPF$_6$ did not perform as well as the other ones with LiBOB, as its energy efficiency exhibited a more pronounced tendency towards fading with a value of approximately 89.2% after 100 cycles. A comparative overview of the average features of these cells during cycling can be found in Table 4.

The long-term cycling (i.e., 1200 cumulative cycles over 1–2.2 months) of the cells was performed at various current densities and cutoff voltages to probe their overall responses and to highlight possible weak points, which are often not apparent in brief tests involving only a few hundred cycles. The results of these galvanostatic tests are presented in Figure 9 for the cells with pre-lithiated iron oxide coupled to LiBOB and LiPF$_6$ whereas those obtained for the other battery with LiBOB...
and pre-cycled iron oxide are shown in Figure S12 in the Supporting Information.

The superior performances of the cells with LiBOB compared with that of the battery containing LiPF$_6$ is the most evident feature here, and, although the early mechanism of failure of the latter (after roughly 300 cycles) asks for a separate in-depth study, some important aspects can nevertheless be highlighted. Indeed, a whole water-based electrode processing may inherently lead to higher residual water content in the cells. This could promote the hydrolytic degradation of LiPF$_6$ and the production of HF in amounts that could trigger a loop of side-reactions, which would eventually lead to a progressive deterioration of the cell.$^{[90,91]}$ Considering the high surface area of the Fe/Li$_2$O nanocomposite, such an outcome would not be
surprising. Furthermore, the direct contact of the highly reactive Fe/Li₂O nanocomposite with the fluorinated electrolyte can only exacerbate the detrimental action of possible HF traces. Accordingly, the combination of water-based electrode coatings with high-surface-area materials requires extra precautions with the use of electrolytes relying on LiPF₆. On the other hand, both LiBOB-based cells displayed a moderate fading of their performances through this long-term cycling test and still retained approximately 80% of their initial discharge capacities, and a slightly better stabilization of the value was observed for the battery with the pre-lithiated anode (compare Figures 9a and S12a). This clearly demonstrates that a well calibrated combination of Fe/Li₂O nanocomposite anodes with "medium-voltage" cathodes (i.e. < 3.6 V vs. Li⁺/Li) enables a convenient use of LiPF₆-free electrolytes for full-cell safety and cost advantages.

A rate capability test performed with a fixed voltage range between 1.2 and 4.2 V is finally presented in Figure 10 for a LiBOB cell with a pre-lithiated iron oxide anode after its stabilization over fifty preliminary CV cycles (see Figure S5) and for an analogous galvanostatically cycled LiBOB battery containing a pre-cycled iron oxide anode.

The responses of both cells upon the application of increasing current densities spanning two orders of magnitude appear to be satisfactory as they can withstand cycling rates as high as 30C with almost complete recovery of the capacity at subsequent low-C-rate cycles. The performances of the galvanostatically cycled full cell containing pre-cycled iron oxide appeared to be slightly better than those offered by the CV-cycled one with a pre-lithiated iron oxide anode. In particular, both cells delivered half (≈88 mAh g⁻¹) or slightly more than half (≈95 mAh g⁻¹) of their initial capacities upon fast discharge/charge at a rate of 6C (Figure 10a and c). It is worth mentioning that charging at rates beyond approximately 3C over a 50% state-of-charge window remains a crucial challenge for graphite anodes, especially for their use in electric vehicles. Nevertheless, these excellent rate performances and cyclabilities have been achieved here for a low active mass loading and without electrode calendaring. Commercial LIBs rely on much more heavily loaded and calendared electrodes than those presented in this study to achieve suitable energy densities for the various applications they are made for. Adapting the manufacture of Fe/Li₂O nanocomposites to that of commercial graphite electrodes clearly poses further challenges. In this respect, it is also most likely that this Fe/Li₂O nanocomposite falls short in terms of volumetric capacity compared with that of lithiated graphite, though the conversion mechanism per se yields rather closely spaced Fe/Li₂O boundaries in

Figure 10. Rate-capability tests performed on (a, b) a CV-cycled full cell containing a pre-lithiated iron oxide anode in combination with LiBOB and (c, d) an analogous galvanostatically cycled full cell with a pre-cycled iron oxide anode. (a, c) Series of cycles obtained by applying increasing current densities leading to progressively higher C rates. (b, d) Evolutions of the typical charge/discharge capacities obtained in each cycling step of the tests as a function of the corresponding applied current density. Note that the cell voltage window was fixed between 1.2 and 4.2 V throughout the tests of both batteries.
reacted micron-sized iron oxide particles. These extensive reactive interfaces ultimately account for the enhanced pseudo-capacitive charge storage utilized here.

In any case, the above results represent a significant improvement of the overall performances initially reported for “lithium–iron” cells\textsuperscript{[29]} with pre-lithiated $\alpha$-Fe$_2$O$_3$, LiFePO$_4$, PVdF and 1 M LiPF$_6$. Such a system was limited by a 50% loss of its capacity in 190 cycles at rates of less than 1C, unspecified round-trip inefficiencies and an average output voltage of only approximately 2.2 V. Nonetheless, previous systematic studies of the chemical and electrochemical lithiation of iron oxide\textsuperscript{[30]} have also contributed to the development of Fe$_2$O$_3$/Li$_x$[Ni$_{50}$Co$_{20}$Mn$_{30}$]O$_4$ batteries with a higher operation voltage and a longer cycle life.

Overall, our Li-rich electrodes based on Fe nanoparticles embedded in Li$_2$O demonstrate an alternative concept to overcome effectively the main drawbacks of iron oxide utilization in LIBs. Most likely, this could also be applied to similar conversion-type anode materials through the general approach devised here. High charge-rates, low polarization and stable cycling over a long time or for many cycles should now also be viable for these systems.

**Conclusions**

Safer and more environmentally friendly batteries, which could represent an alternative to conventional LiFePO$_4$–graphite cells, have been demonstrated here. This electrochemical system relies on a new approach with nanostructured iron oxide in a deeply lithiated Fe/Li$_2$O state as an anode in combination with an entirely fluorine-free binder (sodium alginate) and electrolyte salt [lithium bis(oxalato)borate (LiBOB)] coupled to a LiFePO$_4$ cathode.

The results of this study clearly suggest that: First and foremost, an average output voltage as high as approximately 3 V can be obtained, and the hysteresis losses arising from the conventional use of conversion materials can be overcome. Very good electrochemical performances have been displayed at various C rates in combination with long-term cycling (1–2.2 months) for 1200 cycles with overall capacity retention of approximately 80% of the initial discharge values, despite the complete lack of any carbon coating on the iron oxide and dedicated electrode structure engineering.

The above points have led to a remarkable improvement in energy efficiency. Energy efficiencies as high as approximately 92% were attained at practical C rates of approximately 1.5 C in combination with average Coulombic efficiencies of approximately 99.6%, despite the non-optimized nature of the materials and the total absence of any electrolyte additive.

An enhanced pseudo-capacitive behaviour of the nanocomposite anode can be utilized to enable relatively high rates ($\approx$ 1–5 C) with no apparent capacity losses and, most importantly, with no Li plating, which is often a critical issue for graphite electrodes operated under similar conditions. This is especially evident if this electrochemical system is operated over larger voltage windows.

This approach also shows the influence of the size effects generated by the Fe nanoparticles embedded in Li$_2$O and harnesses their related potential shifts to promote the safer operation of these cells at high current densities. This phenomenon represents an interesting bridge between battery and supercapacitor properties without requiring major trade-offs in terms of performance, independently of the way in which this type of system is operated.

Finally, such a moderate output voltage for these cells provides an excellent opportunity for the complete replacement of fluorine with less harmful species in both the electrolyte and the polymer binder. In turn, this improves the overall cell safety by eliminating any risk for accidental HF formation and simultaneously reduces those hazards associated with the production of the raw materials, the electrode fabrication, subsequent cell assembly and operation as well as the ultimate recycling of the components after disposal.

**Experimental Section**

Materials synthesis and electrode preparation

Nanostructured iron oxide powders were synthesized by the pyrolysis of anhydrous iron acetate (Aldrich) under vacuum by a procedure similar to that reported previously\textsuperscript{[31]} Here, the pyrolysis temperature was increased slightly to 270 °C to form and stabilize nanostructured Fe$_2$O$_3$/γ-Fe$_2$O$_3$ as an anodic material. Commercial lithium iron phosphate (LFP-P2, SüdChemie) powder was utilized directly as the active cathode material without any further processing. The electrode coatings for the cathodic and anodic materials were algicin acid sodium salt from brown algae (Na-Alg, Aldrich, $M_w$ $\approx$ 80 000–100 000) as a renewable water-soluble polymer binder. The negative electrode coatings consisted of a mixture of nanostructured Fe$_2$O$_3$/γ-Fe$_2$O$_3$, Na-alginate, carbon black (CB-C-65, C-Energy) and carbon nanofibers (CNF, Aldrich, 100 nm x 20–200 μm) with a Fe$_2$O$_3$/Na-Alg/CB/CNF weight ratio of 75:12.5:10:2.5. The positive electrode coatings included a blend of LFP, Na-alginate and CB in a weight ratio of 75:10:15. The slurries were cast by means of a coating apparatus (K-F-K Control Coater) on a one-sided roughened copper sheet (Swedecal) for the negative electrodes and on carbon-coated aluminium foil (Leclanché, EB012 + Al 20 μm) for their positive counterparts. All of the coatings were dried overnight in a convection oven at 80 °C. Coated disks with a radius of 10 mm for the anode and cathode materials were cut by a precision perforator (Hohsen). Extra disks of coated cathodes with 5 mm radius were also punched for additional tests. The positive and negative electrode coatings were subsequently dried for 12 h at 120 °C in a vacuum oven (Büchi) located in an Ar-filled glove box ($O_2$ < 1 ppm, $H_2O$ < 1 ppm) before further manipulation or cell preparation.

A second type of iron oxide anode (i.e., nanowires/leaves) was prepared through a direct-growth method by the oxidation in air of perforated 0.025 mm thick iron foil (Alfa Aesar, 99.5 metals basis) disks heated at 350 °C for 24 h.\textsuperscript{[32]} The Fe disks had a radius of 5 mm (i.e., 10 mm holes in the punched foil) and, after oxidation, were subjected to vacuum drying, analogously to the coated electrodes. This approach provided an electrode preparation free from wet processing as well as from binders and carbon additives and, thus, combined metallurgy directly with electrochemistry.\textsuperscript{[33]} This type of electrode was sandwiched between two LFP-coated elec-
trodes with one separator on each side and the electrolyte solution soaking both of them.

Structural and compositional characterization

The surface morphologies of the various electrodes were probed by SEM with a Zeiss Gemini 1550 microscope equipped with a field-emission gun (FEG). A dedicated in-lens detector was utilized to collect the secondary electrons emitted from the surfaces of the specimens. The XRD was conducted in a Bragg–Brentano configuration with a Siemens D-5000 diffractometer with a CuKα radiation source. A rotation speed of 15 rpm was applied during the analyses of the samples. Raman spectroscopy was also performed to investigate the compositions of the active materials used in the various electrodes. All of the spectra were obtained with a Renishaw inVia Raman microscope at two excitation wavelengths (i.e., 532, 785 nm) provided by two separate laser diodes (Renishaw) with a maximum output power of 500 mW. The laser beam was focused on the sample surface through a 50× magnification objective, and a constant laser power, fixed to 0.1% of its maximum nominal value, was applied during the analyses. A preliminary calibration of the spectrometer was performed with a Si wafer to obtain a characteristic reference peak located at $\rho = 520.6$ cm$^{-1}$. Twenty cumulative acquisitions were run for each spectrum with a measuring time of 20 s. A minimization of the beam exposure between subsequent scans was also applied to avoid possible degradation of the sample surface. The FTIR spectroscopy was performed in the wavenumber range between 600 and 4000 cm$^{-1}$ using a PerkinElmer (Spectrum One) spectrometer in an attenuated total reflectance (ATR) mode. The IR spectra were recorded for 20 cumulative acquisitions to improve the signal-to-noise ratios of the spectral features. The HR-TEM and SAED were performed with a JEOL JEM-2100F microscope operated at 200 kV and equipped with a Gatan Ultrascan 1000 CCD camera and a dedicated energy filter (GIF Tridiem). HAADF-STEM was also performed on the powder sample to obtain additional information about its outermost surface and to obtain deeper insights into its local microstructure and porosity. The powder was ground in a mortar and subsequently loaded onto a TEM copper grid with a holey carbon film. The samples containing iron oxide nanowires/leaves were protected by epoxy for their preparation for cross-section analysis. The cross-section TEM specimens were polished mechanically to a thickness of approximately 20 μm before ion milling at 4 kV using a dedicated Ar-sputtering equipment (Fischione Model 1050).

The gas adsorption measurements were performed through nitrogen physisorption at 77 K with a Micromeritics (ASAP 2020) instrument with the ASAP 2020 V3.04 E software. The powders were heated overnight at 120 °C to remove possible traces of moisture before the analyses. The BET methodology was applied to evaluate the specific surface area of the powder, and DFT calculations were performed to estimate the pore size distribution.

Battery assembly and electrochemical characterization

LiBOB (Chemetall) was dried at 120 °C for 12 h in a vacuum oven placed in an Ar-filled glovebox (M-Braun) and subsequently dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in an EC/DEC ratio of 1:1 to prepare a 0.8 M electrolyte for the assembly of both Li half-cells and full Li-ion batteries. An analogous 0.8 M LiPF$_6$ electrolyte with EC/DEC 1:1 v/v was also prepared at the same time and utilized as a standard reference in a parallel test for the comparison of the performances of the full cells. All of the electrodes were vacuum-sealed in polymer-laminated aluminium pouch (i.e., “coffee-bag”) cells in an Ar-filled glovebox (M-Braun) with oxygen and moisture levels below 1 ppm. The electrode coatings contained a typical active mass loading of approximately 1 mg·cm$^{-2}$ of Fe$_3$O$_4$/γ-Fe$_2$O$_3$ and approximately 0.8 mg·cm$^{-2}$ of LFP, though some deviations could be expected owing to the slight unevenness of their respective metal current collectors, possible local coating inhomogeneity or both. This ratio of the active masses was suitable for the sustained operation of the anode within a deeply lithiated regime. The LFP-based cathodes had a typical thickness of approximately 8–10 μm, and analogous values were also found for the Fe$_3$O$_4$/γ-Fe$_2$O$_3$ anode coating, both measured with a digital calliper (Mitutoyo). The use of thin electrode coatings ensures that the focus is on the effective performance of the active materials rather than on possible kinetics effects caused by the electrode thickness.

Different types of cells were prepared with these composite electrode coatings and with the iron oxide nanowires/leaves, namely, 1) Li half-cells with lithium foil as a combined reference and counter electrode, 2) full Li-ion cells (two-electrode cells) with deeply lithiated iron oxide as the anode and LFP as the cathode and 3) full cells with an additional lithium reference electrode (three-electrode cells) to monitor simultaneously the voltage evolution on the cathode and anode sides with respect to the Li$^+$/Li reference potential. A thin membrane (Solupor) wetted with the corresponding electrolytes was used as the electrode separator in all the cells.

Pre-lithiation, preliminary SEI formation and the initial conversion of such iron oxide based anodes were performed for all of the electrodes employed in full Li-ion cells. Such a procedure consisted of soaking the electrodes with the LiBOB (or LiPF$_6$) electrolyte and subjecting them to a face-to-face contact with the surface of a metallic lithium strip. This reactive interface contact was maintained for 2 h using an enveloping polymer-coated aluminium pouch while applying a constant pressure through a couple of rigid supports and a pair of clamps. After this pre-lithiation step, the lithium strip was carefully removed and the Li-loaded (i.e., converted Li$_2$O/Fe) electrode was directly utilized for the assembly of a Li-ion battery by applying a separator, one drop of LiBOB (or LiPF$_6$) electrolyte and a LFP cathode in sequence. The entire electrode stack was transferred to a pouch cell having two metal tabs made of Cu and Al for the respective anode and cathode contacts and finally vacuum-sealed. For comparison, the electrodes based on nano-structured Fe$_3$O$_4$/γ-Fe$_2$O$_3$ were also loaded with Li through an electrochemical lithiation procedure by pre-cycling in Li half-cells at a low current density to obtain a corresponding deeply lithiated Li$_x$O/Fe state (i.e., a cell stopped during discharge at 0.01 V vs. Li$^+$/Li) after a few galvanostatic cycles. Their subsequent assembly in full cells was performed as described above.

Cyclic voltammetry (CV) analyses were performed at room temperature using a VMP2 instrument (Bio-Logic) at increasing scan rates. The sweep rates typically spanned from 0.1 to 1.6 mV·s$^{-1}$ in a voltage range between 0.01 and 3.00 V versus Li$^+$/Li for Li half-cells containing iron oxide based electrodes whereas higher rates of up to 3.2 mV·s$^{-1}$ were applied to LFP electrodes tested in analogous half-cells cycled between 2.2 and 4.2 V versus Li$^+$/Li. The full cells were also subjected to several CV scans at 1.0 mV·s$^{-1}$ in a wide range of operation potentials between 1.2 and 4.2 V.

Galvanostatic tests were performed with VMP2 (Bio-Logic) and Digi-heat BTS 600 cycling instruments at various current densities and voltage ranges. The long-term stability tests of the full cells...
were conducted mainly at a current density of 0.1 mA cm\(^{-2}\) with a couple of intermediate cycling steps at 0.2 and 0.3 mA cm\(^{-2}\) with a larger range for their related cutoff voltages.

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Conflict of interest

The authors declare no conflict of interest.

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[1] D. L. Wood, J. L. Li, C. Daniel, J. Power Sources 2015, 275, 234.
[2] J. Li, R. B. Lewis, J. R. Dahn, Electrochem. Solid-State Lett. 2007, 10, A17.
[3] I. Kovalenko, B. Zdyrko, A. Magasinski, B. Hertzberg, Z. Milicev, R. Burto-vyy, I. Luzinov, G. Yushin, Science 2011, 334, 75.
[4] J. Li, H. M. Dahn, L. J. Krause, D. B. Le, J. R. Dahn, J. Electrochem. Soc. 2008, 155, A812.
[5] B. Lestriez, S. Bahri, I. Sandu, L. Roué, D. Guyomard, Electrochim. Commun. 2007, 9, 2801.
[6] S. F. Lux, F. Schappacher, A. Balducci, S. Passerini, M. Winter, J. Electrochem. Soc. 2010, 157, A320.
[7] S. Mitra, P. S. Veluri, A. Chakraborty, R. K. Petla, ChemElectroChem 2014, 1, 1068.
[8] A. Darwiche, C. Marino, M. T. Sougrati, B. Fraisse, L. Stievano, L. Monconduit, J. Am. Chem. Soc. 2012, 134, 20805.
[9] S. F. Lux, A. Balducci, F. M. Schappacher, S. Passerini, M. Winter, ECS Trans. 2010, 25, 265.
[10] J. Li, R. Köpisch, S. Nowak, M. Kunze, M. Winter, S. Passerini, J. Power Sources 2011, 196, 7687.
[11] M. H. Ryoo, S. Hong, M. Winter, H. Lee, J. W. Choi, J. Mater. Chem. A 2013, 1, 15224.
[12] W. Porcher, B. Lestriez, S. Jouanneau, D. Guyomard, J. Electrochem. Soc. 2009, 156, A133.
[13] J. Scheers, D. H. Lim, J. K. Kim, E. Paillard, W. A. Henderson, P. Johansson, J. H. Ahn, P. Jacobsson, J. Power Sources 2014, 251, 451.
[14] B. Younesi, G. M. Veith, P. Johansson, K. Edström, T. Vegge, Energy Envi-ron. Sci. 2015, 8, 1905.
[15] W. Xu, C. A. Angell, Electrochem. Solid-State Lett. 2001, 4, E1.
[16] K. Xu, S. S. Zhang, T. R. Jow, W. Xu, C. A. Angell, Electrochem. Solid-State Lett. 2002, 5, A26.
[17] J. Jiang, J. R. Dahn, Electrochem. Commun. 2004, 6, 724.
[18] J. Jiang, J. R. Dahn, Electrochem. Commun. 2004, 6, 39.
[19] X. Y. Zhang, T. M. Devine, J. Electrochem. Soc. 2006, 153, B365.
[20] S. E. Sloop, J. K. Pugh, S. Wang, J. B. Kerr, K. Kinoshita, Electrochem. Solid-State Lett. 2001, 4, A42.
[21] V. Aravindan, J. Gnanaraj, S. Madhavi, H. K. Liu, Chem. Eur. J. 2011, 17, 14326.
