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Insight into the processes controlling the electrochemical reactions of nanostructured iron oxide electrodes in Li- and Na-half cells

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Abstract

The kinetics and the processes governing the electrochemical reactions of various types of iron oxide nanostructures (i.e., nanopowders, nanowires and thin-films) have been studied via cyclic voltammetry in parallel with Li- and Na-half cells containing analogous electrolytes (Li^+/Na^+ , ClO_4^- in EC:DEC). The particular features arising from each electrode architecture are discussed and compared to shed light on the associated behaviour of the reacting nanostructured active materials. The influence of their characteristic structure, texture and electrical wiring on the overall conversion reaction upon their respective lithiation and sodiation has been analyzed carefully. The limiting factors existing for this reaction upon uptake of Li^+ and Na^+ ions are highlighted and the related issues in both systems are addressed. The results of this

investigation clearly prove that the conversion of iron oxide into metallic Fe and Na_2O is severely impeded compared to its analogous process upon lithiation, independently of the type of nanostructure involved in such reaction. The diffusion mechanisms of the different ions (i.e., Li^+ vs. Na^+) through the phases formed upon conversion, as well as the influence of various interfaces on the resulting reaction, appear to pose further constraints on an efficient use of these compounds.

1. Introduction

The renewed interest in Na-ion battery technology, as a complementary energy storage route to Li-ion batteries for stationary applications, has driven the attention of the electrochemical community towards reconsidering several elements and compounds for possible usage in this type of cells. Both Li- and Na-ion systems were initially proposed in the late 70's and through the 80's [1]. Since then, their respective developments have been totally different. Li-ion batteries today dominate the market of rechargeable power sources for portable electronics and are under intense scrutiny for massive use in plug-in (hybrid) electric vehicles, as well as in electrical grids. By contrast, Na-ion batteries have remained so far mainly matter of intriguing studies on a laboratory scale, despite the crucial point of potentially offering significant cost reductions, due to the high abundance of sodium and its easy extraction compared to lithium. Only recently, a number of commercial producers are emerging in this field. Nevertheless, electrical storage via Na-ion batteries has to face tougher challenges compared to Li-ion technology, mainly because of the difference between the ionic radii of Na^+ (1.02 Å) and Li^+ (0.76 Å), while providing a reduced energy density due to a lower red-ox potential for Na^+/Na (i.e., -2.71 V vs. SHE) compared to Li^+/Li (i.e.,

-3.04 V vs. SHE). Additionally, the pronounced reactivity of the electrode/electrolyte interface in Na⁺-based systems in presence of analogous electrode materials further complicates the electrochemical processes. A major limitation for Na⁺ is, for example, its inability to be inserted and extracted reversibly in graphitic hosts [2], thus preventing graphite to be used as a convenient negative electrode [3], although a couple of recent studies have shown the opposite effect using solvent co-intercalation phenomena in ether-based electrolytes [4, 5] or by resorting to expanded graphite [6] to fit Na⁺ via a larger interlayer spacing. So far, a limited number of materials have been proposed as possible alternatives to non-graphitic hard carbons [7-10], which still represent the most viable candidates for negative electrodes in Na-ion batteries in terms of an overall trade-off for their electrochemical performances. Different Na-alloys [11-14] and various insertion compounds, especially based on sodium titanates [15-17] have been investigated as possible replacements of hard carbons. However, such materials often suffer from mechanical stability problems [18], from interfacial instabilities [19] or both, thus leading to early capacity losses. In this respect, the role played by the solid electrolyte interphase (SEI) formed on these materials upon sodiation/de-sodiation appears crucial [19, 20] and additives have often been used to stabilize the SEI in various types of negative electrodes [21-23]. Among conversion-type compounds, which have been studied for such purpose [24-28], iron oxides are particularly attractive since they fulfil important criteria such as abundance, cost-effectiveness and environmental friendliness, which are essential for suitable materials for negative electrodes in Na-ion batteries [29]. Nanocrystalline thin films of transition metal oxides based on Fe and Ni have recently been used as anodes in full Na-ion cells with carbon coated Na₃V₂(PO₄)₃ cathodes displaying promising features [30]. Iron oxides are also easy to manufacture, and thus can be applied

conveniently to such purpose, provided that other issues arising from their conversion reactions [31, 32] are mitigated or partly solved. On the other hand, various synthesis strategies have been utilized to improve the overall electrical conductivity of iron oxides and to facilitate their production [33, 34]. The processes governing the reactions in iron oxides and the limiting factors that can arise in the respective uptake/release of Li^+ and Na^+ ions represent the key towards a better understanding of the similar and distinct aspects for these two electrochemical systems. In this context, the SEI layer formed on nanostructured Fe_2O_3 electrodes upon both lithiation and sodiation has been highlighted in a comparative systematic study, which shows the main similarities and differences existing for the associated side reactions and species distributions found on the electrode surface in presence of analogous electrolytes [35]. In particular, it has been noticed that only a limited capacity is provided by various types of iron oxide upon reaction with Na^+ ions [36-38], compared to Li^+ , and that a full conversion of these compounds into Fe^0 and Na_2O typically is not achieved [37] under normal cycling conditions.

In the present study, the kinetics and the mechanisms controlling the electrochemical reactions of different types of electrodes based on iron oxide cycled in Li- and Na-half cells with analogous electrolytes have been investigated. Three different electrode architectures have been compared in order to pinpoint the characteristic contributions of the nanostructured active materials, which have been analysed via combined Raman and XRD approach. The roles of their particular electrical wiring and their intrinsic structure are discussed in the following sections. This investigation, based on voltammetric measurements, elucidates the major limitations arising from the use of similar monovalent Li^+ and Na^+ ions upon conversion reactions, while suggesting ways of reducing the resulting issues.

2. Experimental

2.1. *Electrode preparation and materials characterization*

Nanostructured iron oxide powders were formed by pyrolysis of anhydrous iron acetate (Aldrich) in vacuum, following a procedure reported previously [36]. The electrode coatings contained a blend of nanostructured Fe_2O_3 powders, Na-carboxymethylcellulose (Aldrich – $M_w \approx 700000$, D.S. 0.90) and carbon black (Super P – Timcal Graphite & Carbon) with a weight ratio of 65:15:20 respectively for $\text{Fe}_2\text{O}_3/\text{CMC}/\text{CB}$. A water-based slurry was casted on a copper foil by a coating apparatus (KR – K Control Coater) and dried overnight in a convection oven at 80 °C. Coated disks having a radius of 5 mm were cut by a precision perforator (Hohsen). The resulting electrodes were dried for 12 h at 120 °C in a vacuum oven (Büchi) located in an Ar-filled glove box ($\text{O}_2 < 1$ ppm, $\text{H}_2\text{O} < 1$ ppm) prior to cell preparation.

Iron oxide nanowire and thin-film electrodes were directly formed on perforated discs from an iron foil (Alfa Aesar) by oxidation in air at 350 °C for 24 h and at 150 °C for 4 min, respectively. The radius of the discs was 5 mm and, after the oxidation process, they were directly used as electrodes following analogous drying procedures to those employed for the slurry-coated ones.

The surface morphology of the various electrodes was studied by scanning electron microscopy (SEM) utilizing a Zeiss Gemini 1550 microscope with a field emission (FE) source and applying an acceleration voltage of 10 kV. Secondary electrons were collected by a dedicated in-lens detector to image the surface of the specimens. Transmission electron microscopy (TEM) was performed with a JEOL

JEM-2100F microscope operated at 200 kV and equipped with a Gatan Ultrascan 1000 CCD camera. The nanostructured iron oxides were protected by epoxy for the preparation of the samples for cross-section analysis. The cross-section TEM specimens were mechanically polished to a thickness of 20 micron prior to ion-milling at 4 kV (Fischione Model 1050). X-ray diffraction (XRD) was conducted in a Bragg-Brentano configuration on a Siemens D-5000 diffractometer equipped with a Cu K α radiation source. A rotation speed of 15 rpm was applied during the analyses of the specimens. Raman spectroscopy was also employed to investigate the composition of the active materials in the various electrode systems. Raman spectra were recorded by a Renishaw inVia Raman microscope utilizing an excitation wavelength of 532 nm generated by a solid state laser diode (Renishaw) with a maximum power output of 500 mW. This wavelength was employed to trigger resonant Raman scattering in hematite to obtain an enhanced detection of this phase. Excitations wavelengths of 633 nm and 785 nm were also applied to show the influence of ‘off-resonance’ conditions in hematite on the detection of magnetite, when these two phases co-existed. The laser beam was focused on the surface of the samples via the lenses of a built-in optical microscope utilizing a 50 $\times$ magnification objective and applying a constant power fixed to 0.1% of its maximum nominal value. A preliminary calibration of the instrument before the measurements was run by having a peak from a reference Si wafer located at 520.6 cm $^{-1}$. Twenty cumulative acquisitions were collected for each spectrum with a measuring time of 20 s. Beam exposure was minimized between subsequent scans in order to avoid any possible degradation of the sample surface.

2.2. Battery assembly and electrochemical measurements

LiClO₄ and NaClO₄ salts were separately dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with a ratio EC:DEC (2:1) to obtain a 1 M electrolytic solution to be used in Li- and Na-half cells, respectively. All the electrodes were assembled in polymer-laminated aluminium pouch cells ('coffee-bags') in an Ar-filled glove box (M-Braun) with oxygen and moisture levels below 1 ppm. The three types of nanostructures, i.e., nanopowders, nanowires and thin-films, were used as working electrodes and sealed in Li-half cells having a lithium foil as combined reference and counter electrode and also in Na-half cells, where metallic sodium was used for an analogous purpose. The active mass loading was different for the various types of nanostructures and it was measured by means of a Mettler-Toledo balance (XS105 – DualRange). Slurry-coated electrodes had a typical mass loading of $\approx 0.50 \text{ mgcm}^{-2}$ of iron oxide nanopowders, whereas the Fe substrates covered with the nanowires had an approximate iron oxide content of $\approx 0.28 \text{ mgcm}^{-2}$ on each side of the oxidized discs. An accurate determination of the active mass loading for the thin-film electrodes was not possible via the balance used in this study; nevertheless values roughly comprised between 0.01-0.015 mgcm^{-2} can be expected for each side of the oxidized substrates. A thin membrane (Solupor) wetted with the respective electrolytic solutions containing Li⁺ and Na⁺ ions was utilized as separator in the associated cells.

Cyclic voltammetry (CV) was carried out at room temperature using a VMP2 equipment (Bio-Logic) applying increasing sweep rates. The latter ranged from 0.05 to 0.8 mVs⁻¹ in a voltage window comprised between 0.05 and 2.80 V vs. Li⁺/Li or vs. Na⁺/Na for the respective half cells.

3. Results and discussion

3.1. Morphological, structural and compositional analysis of the different electrodes

The characteristic morphology and structure of the different types of electrodes considered in this study are shown in the SEM micrographs of Fig.1.

Fig. 1

It is clear from Fig. 1a that the powder-based electrode possesses porosity at different levels, which also reflects the open-like structure of its nanoparticle agglomerates and crystalline aggregates. Agglomerates and aggregates have different sizes spanning approximately from 20 nm to 70 nm or higher for their respective constitutive units, as earlier reported [36]. Most of the iron oxide particles in Fig. 1a are interconnected by necks and the resulting materials are endowed with an intrinsic (meso)porosity due to the particular way in which they have been formed via pyrolysis [36]. From Fig. 1b it can be seen that the surface of the electrode relying on the iron oxide nanowires/leaves displays a distinctive morphology that clearly deviates from the previous one. Also in this case, a degree of mutual connectivity is established among the grown iron oxide structures. However, the length of the nanowires/leaves is about 1-2 μm , while their lateral dimensions largely vary from about 20 nm up to approximately 200 nm. This gives rise to the presence of several thin 'leaves' with sharp points, together with the simultaneous existence of well-defined nanowires. Contrarily to the powders in the composite electrode, their electrical connection relies on their direct contact with the underlying substrate. It is interesting to observe that under the electron beam the nanowire-based electrode charged very easily, yielding brighter features in the resulting images, while the composite electrode did not suffer

from this limitation, probably because the carbon black increased the overall electronic conductivity of the composite coating. It can be noticed that the space around these spontaneously grown structures in Fig. 1b allows an easy infiltration of the electrolyte in such electrode. However, the individual structures are expected to not possess an intrinsic mesoporosity, because they directly originate from a dense iron substrate undergoing oxidation (see Fig. S1 in Supporting Information). Similar considerations also apply to the thin-film electrode depicted in Fig. 1c, which retains to a high extent the same morphological features of the pristine Fe foil shown in Fig. 1d. A comparison between the morphology shown in Fig. 1c and Fig. 1d indicates that the formation of the thin film of iron oxide causes a slight roughening of the pristine iron surface, while the characteristic ‘tracks’ of the substrate are still visible (see also optical microscope images of the intrinsic surface morphologies of these samples in Fig. S2 in Supporting Information).

Other important features concerning the particular structure and composition of the different iron oxide nanostructures were revealed through the combination of XRD and Raman analyses, which provided complementary information on the bulk and the surface characteristics of these nanostructured electrodes.

Fig. 2 shows the results of the XRD analysis carried out for the nanopowders and the nanowires.

Fig. 2

The diffraction pattern related to the nanopowders indicates the clear presence of a well-crystallized α -Fe₂O₃ phase (JCPDF #01-1053), which displays rather sharp diffraction peaks. Additionally, the simultaneous presence of a maghemite phase with a lower degree of crystallinity, is also observed in the same diffraction pattern. A few

minor peaks matching the characteristic diffractions associated with the $\gamma\text{-Fe}_2\text{O}_3$ lattice structure (JCPDF #39-1346) are detected, thus confirming the coexistence of these two phases in the nanopowders (see also Fig. S2). The diffraction pattern associated with the nanowires in Fig. 2 exhibits various noticeable features. Most of the intense peaks in the diffractogram are ascribed to a major crystalline phase of Fe_3O_4 (JCPDF #89-0691), while the characteristic diffractions (110), (200) and (211) marked with an asterisk originate from the underlying Fe structure (JCPDF #06-0696) of the substrate. Also a crystalline $\alpha\text{-Fe}_2\text{O}_3$ phase is detected in this nanostructured electrode, as it can be noticed from the sharp feature nearly overlapping the most intense (311) diffraction of Fe_3O_4 . Indeed, the (110) peak associated to the corundum structure of hematite (i.e., marked with an acute accent symbol) demonstrates that a well-crystallized $\alpha\text{-Fe}_2\text{O}_3$ phase has been formed during the oxidation of the iron substrate. More importantly, the much higher intensity of the (110) diffraction found for the hematite, compared to the other minor peaks related to this phase, indicates that these elongated nanowires/leaves have grown preferentially along this crystallographic direction. Therefore, from these initial results, it can be seen that the outermost surface of this type of electrode is composed of highly oriented $\alpha\text{-Fe}_2\text{O}_3$ nanowires/leaves which have grown on an underlying layer of Fe_3O_4 . The latter is located between the Fe substrate and the outer coverage of nanowires/leaves, as also reported in similar earlier studies [39, 40].

The composition of the various electrodes was further investigated via Raman spectroscopy, which constitutes here a very powerful means to shed light on the overall surface properties of the corresponding structures and phases. In fact, the detection of $\alpha\text{-Fe}_2\text{O}_3$ can significantly be enhanced through resonant Raman scattering by employing a convenient excitation wavelength. Resonant Raman

scattering (RRS) in molecular systems has been described in detail in previous works [41]. The Raman spectra obtained for each type of nanostructured electrode are presented in Fig. 3 and are influenced by the resonance processes in α -Fe₂O₃ at 532 nm.

Fig. 3

The presence of hematite on the surface of each type of electrode material is noticed in the respective spectra, though this phase may have a different distribution within these particular electrode structures. The hematite signature is highlighted by the prominent feature found around 1320 cm⁻¹. The latter is assigned to a resonant two-magnon scattering in α -Fe₂O₃ [42-44], though the same peak has been ascribed also to phonon scattering [45]. All the characteristic peaks related to the corundum structure of hematite are noticed in each spectrum, thus confirming that α -Fe₂O₃ has a crystalline nature in these electrodes. The spectrum of the nanopowders also exhibits some features that are assigned to γ -Fe₂O₃, i.e., a couple of broad bands centred approximately around 700 cm⁻¹ and 1590 cm⁻¹, as well as an additional component around 1400 cm⁻¹ overlapping the main resonance peak of hematite at 1320 cm⁻¹, which results in a slight asymmetry for the baseline of the latter. The sharpest peaks detected at low wavenumbers for the hematite structure appear to be those of the nanowire electrode and this can look puzzling at first glance.

According to the previous XRD analysis, magnetite should constitute the most prominent phase in this electrode, while Fe₃O₄ is hardly detectable in the associated spectrum in Fig. 3. By contrast, a distinctive peak around 670 cm⁻¹ is noticed in the spectrum related to the thin-film electrode and proves the presence of magnetite in the oxide layer. Clearly the oxidation of the film is not complete and the outer layer of

hematite is very thin, contrarily to the elongated α -Fe₂O₃ nanowires/leaves. In this respect, it has been reported that the presence of water vapour in air favours the formation and thickening of α -Fe₂O₃ [46, 47], whereas an oxidation under dry air typically results in thicker Fe₃O₄ layers. Hematite grows as an outermost film and its thickness does not seem to vary sensibly under certain experimental conditions at both moderate and elevated temperature [48, 49]. The particular spectral characteristics in Fig. 3 can be understood considering that RRS takes place in α -Fe₂O₃, thus meaning that some Raman features of this phase are highly amplified compared to those of other iron oxide compounds which do not undergo resonant processes at 532 nm. Therefore, it is not surprising that by changing the excitation wavelength (e.g., using 633 and 785 nm), the analysis of the same nanowire electrode under ‘off-resonance’ conditions for hematite displays a progressively visible signature of magnetite, with a prominent peak at 670 cm⁻¹ (see Fig. S3 in Supporting Information) and, simultaneously, much reduced intensities for the main resonance feature at 1320 cm⁻¹. The results in Fig. S3 are particularly relevant, because they demonstrate the impact of the resonance phenomena in the analysis of these iron oxide compounds. On the one hand, these resonance processes enabled the detection of tiny amounts of hematite (e.g., in the surface of thin-film electrodes), on the other hand, they masked the presence of other iron oxide phases (e.g., Fe₃O₄), especially when the latter were not located in the immediate vicinity of the surface, as in the particular case of the nanowire electrodes.

On the basis of the previous observations, it is clear that for these nanostructured electrodes it is vital to complement the information obtained from the

Raman spectra with that acquired by the XRD patterns. This is crucial to have a clear understanding of the overall surface and bulk properties of these electrode structures, where the existence of different phases and interfaces plays certainly a role in the resulting electrochemical behaviour.

3.2. Cyclic voltammetry of Li- and Na-half cells

The initial CV cycle for each type of electrode cycled at 0.05 mVs^{-1} between 0.05 and 2.80 V vs. lithium and sodium metals with LiClO_4 and NaClO_4 electrolytes (see Fig. S4 in Supporting Information) has been object of similar earlier studies [35, 36] and therefore will not be discussed in detail here. The related electrochemical characteristics are mentioned only briefly in this context, since this investigation focuses on the main feature of reduction upon subsequent cycles obtained at different scan rates for the various types of electrodes. The drastic changes in both phase and morphology in the first cycle certainly affect the kinetics of consequent reaction for each electrode, because the active materials can also undergo a complete restructuring. This is known to occur, for example, upon full lithiation of these compounds, where both initial SEI formation and generation of a $\text{Fe/Li}_2\text{O}$ nanocomposite take place. Accordingly, the comparative analysis of these nanostructured electrodes has been centred on the cycles following the initial reduction/oxidation processes, where most of these irreversible variations have already occurred. The morphologies, textures and phases of the reacted materials are thus expected not to undergo severe changes as in their first cycle.

3.2.1. Composite electrodes based on nanopowders

The cyclic voltammograms acquired at increasing sweep rates for the composite powdered electrodes cycled in Li- and Na-half cells are presented in Fig. 4.

Fig. 4

The shapes of the voltammograms are clearly different for the corresponding cells. The uptake and release of the Li^+ ions are more favourable than those of Na^+ in these composite electrodes, as noticed from the significant higher current involved in the redox processes of the Li-half cell compared to the Na- one. The cathodic and anodic parts of the cycles associated to the Li-half cell (Fig. 4a) are more pronounced and also display more symmetric profiles with well-defined oxidation and reduction peaks, in comparison with their analogues in the Na-based battery, especially at higher sweep rates. By contrast, the cycles deriving from the Na-half cell (Fig. 4b) show a clear asymmetric shape in both the cathodic and anodic parts of the curves. No sharp feature of oxidation is noticed even at a sweep rate of 0.8 mVs^{-1} , being the anodic half cycle dominated by a broad oxidation band centred approximately around $1.45 \text{ V vs. Na}^+/\text{Na}$. Furthermore, the reduction processes exhibit their maximum current values in correspondence of the lower cut-off voltage (i.e., $0.05 \text{ vs. Na}^+/\text{Na}$), whereas only a broad peak is noticed at higher potentials (i.e., $\approx 0.60\text{-}0.30 \text{ vs. Na}^+/\text{Na}$) in the cathodic part of the curves. The comparison between the voltammograms shown in Fig. 4 suggests that both conversion and de-conversion in these composite electrodes are not favoured during Na^+ uptake and removal, when referred to the analogous processes occurring with Li^+ ions. To clarify this point, the currents and the potentials associated to the more defined reduction peaks (i.e., marked by an asterisk in the various voltammograms) corresponding to the conversion reactions of iron oxide respectively into $\text{Fe/Li}_2\text{O}$ and $\text{Fe/Na}_2\text{O}$ have been compared and analysed as a function of the scan rate, v . In both voltammograms shown in Fig. 4, the cathodic peaks due to the conversion of iron oxide shift to lower voltages with increasing sweep rate and a specular trend is noticed for the associated anodic features, which

move towards higher potentials. Such phenomenon is usually observed when the reaction process is controlled by the rate of charge transfer and/or ohmic drop [50].

The behaviours of the respective peak currents and peak potentials extracted for the half-cells from the previous voltammograms are shown in the plots of Fig. 5 as function of the sweep rates.

Fig. 5

From Fig. 5a, it can be seen that the absolute value of the peak current for the cathodic process during Li^+ uptake varies linearly with the square root of the applied scan rate. It can be deduced that such relation reflects the behaviour of a reaction occurring in a diffusion-limited regime, as a clear proportionality between the current, $|I_p|$, and $1/\sqrt{t}$ (i.e., $\sqrt{mVs^{-1}}$) exists. This type of relationship is characteristic for diffusion-controlled processes. It is worth noticing that for the same reaction the peak potential, E_p , scales linearly with the square root of the sweep rate in Fig. 5a. This feature is different from that expected in presence of a significant ohmic drop, which would influence the electrochemical system and cause E_p to scale linearly with the scan rate, as implied by Ohm's law [51].

By contrast, Fig. 5b shows that the absolute value of the peak current during Na^+ incorporation in the cathodic process follows a linear relationship with the sweep rate. This trend suggests that the Na^+ uptake behaves as a surface-controlled process and that the Na^+ incorporation occurs under thin layer electrochemical conditions [51]. Interestingly, the peak potential related to the same reaction scales neither linearly nor with the square root of the applied scan rate (see also Table S1 in Supporting Information), but it follows an exponential trend with the latter. This is confirmed by the linear relationship of E_p with the natural logarithm of the sweep rate,

indicating the existence of an activation barrier for the reaction. In any case, it should be noticed that the values of the cathodic peak currents in the processes of Na^+ and Li^+ incorporation are clearly different (i.e., the highest $|I_p|$ for the Na-half cell at 0.8 mVs^{-1} is still lower than the lowest $|I_p|$ obtained for the Li one at 0.05 mVs^{-1}). Hence, the respective processes probed here are dominated by diverse effects. It is also expected that the differences in size and mass between Li^+ and Na^+ ions can play a decisive role in this scenario.

A complementary comparison of the above results, showing the behaviour of the peak potentials as a function of the associated peak currents at the various rates for each Li- and Na-half cell can be found in Fig. S5 in Supporting Information. In Fig. S5a the trend of the peak potential is linear and matches well with the fact that both $|I_p|$ and E_p shown in Fig. 5a are proportional to the square root of the scan rate v (see also Table S1). The absolute value of slope extracted from the linear fit in Fig. S5a gives an estimated value of the overall resistance (in $\text{k}\Omega$) of the electrochemical system when the composite electrode undergoes the conversion into Fe and Li_2O (see the related value in Table S2). Similarly, Fig. S5b shows the evolution of the peak potentials as a function of the natural logarithm of the peak currents. The straight line obtained for the fit confirms the results of Fig. 5b and indicates that the Na^+ -based system does not behave as the Li^+ -based one. Clearly, an activation step is involved at this reduction stage and the overall resistive behaviour under these conditions is not constant, but increases with the scan rate.

3.2.2. Electrodes based on nanowires

Fig. 6 presents the voltammograms of the electrodes based on iron oxide nanowires cycled in the same voltage range with increasing scan rates in Li- and Na-half cells.

Fig. 6

It can be seen that the shapes of the series of cycles in Fig. 6a and 6b resemble those of the respective voltammograms related to the nanopowder-based composite electrode presented in Fig. 4. The values of the currents upon reduction and oxidation presented in Fig. 4a and Fig. 6a for these two systems differ due to the different active materials loaded in each electrode type.

The active mass loading and associated dispersing effect in each electrode structure are also expected to play an important role in the electrochemical processes. The iron oxide nanopowders, for example, possess an intrinsic porosity and are dispersed in the composite electrode coating together with the binder and carbon black (CB). The CB powders exhibit also a certain activity towards both Li^+ and Na^+ , though significantly inferior to that of iron oxide. By contrast, the iron oxide loading in the nanowire and thin-film electrodes is not ‘diluted’ with other components, directly arising from the oxidation of the underlying Fe support. The corresponding active structures are also dense, due to their formation process. The distribution of their active phases (i.e., Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$), is also not isotropic, being $\alpha\text{-Fe}_2\text{O}_3$ found as a surface thin film or extruded nanowires/leaves, while Fe_3O_4 mainly located at the growth interface with the Fe substrate. On the basis of these characteristics, different ‘electronic’ and ‘ionic’ wiring, as well as possible diffusion paths for the charge carriers, can be expected in these different electrode structures. Nonetheless, their main oxidative and reductive features match well in both Li- and Na-based cells, thereby confirming that the electrochemical signatures of the nanopowders and the nanowires are similar. This also reflects the fact that not a very large discrepancy exists in the iron oxide masses of these electrode typologies.

It is noteworthy that the cathodic and anodic currents in Fig. 4b and Fig. 6b are similar for the respective Na-half cells, thereby suggesting that the mass loading difference in these two types of electrode does not play a major role, as in the conversion upon lithiation. Accordingly, it is deduced that the electrochemical mechanisms upon sodiation and de-sodiation suffer from limitations arising during the early stage of surface reaction and incorporation of Na^+ and that not all the available active mass is directly involved into the redox processes. This agrees well with the recent findings of a study comparing the sodiation and lithiation kinetics of NiO via a series of correlated techniques [52], which show that a Na_2O reaction layer was formed at the beginning of sodiation and resulted in a blocking action for further transport of Na^+ .

The main difference between the nanopowder and nanowire electrode systems at their reduction stages can be appreciated by the shifted values of the respective peak potentials for a fixed scan rate. This is better visualized in Fig. 7, in which the trends of the peak currents and peak potentials of the nanowire-based electrodes are presented upon increasing scan rates.

Fig. 7

From Fig. 7a it is clearly noticed that $|I_p|$ follows a linear relationship with the square root of the applied sweep rate (see Table S1). This confirms that Li diffusion plays a crucial role also during the conversion of iron oxide nanowires. The latter represents a limiting factor, due to the presence of different neighbouring phases involved in the same reaction mechanism, which show different Li diffusivities [53]. Interestingly, the behaviour seen for E_p in Fig. 7a does not mimic the one shown in Fig. 5a for the nanopowders, but exhibits an exponential dependence on the applied scan rate, as

noticed from the linear fit of E_p vs. $\ln v$ (see also Table S1). This could be related to the fact that the overall resistance of the nanowires during the conversion is higher than that displayed by the composite electrode (i.e., compare SEM images in Fig. 1), since the latter contains carbon black as well. Moreover, the absence of porosity for the α -Fe₂O₃ and Fe₃O₄ phases in the nanowire electrode and the different size of the reacting materials (i.e., nanoparticles vs. elongated μ m-long structures) can account for the observed trends of E_p , as the initiation of the conversion reaction upon lithiation and its subsequent propagation could be limited in the nanowires. In this regard, the charge carriers (i.e., Li⁺ and e⁻) could not migrate immediately through the whole anisotropic structures and the newly formed phases upon ongoing conversion.

It should be mentioned here that the contact resistance of these iron oxide structures at the interface with the substrate could play a significant role, since the electrode contacts can have a greater influence than commonly thought [54]. Indeed, some previous I - V measurements of an analogous system based on α -Fe₂O₃ nanoflakes grown on Fe by thermal oxidation [39] indicate that a Schottky barrier exists at the underlying interface and that the electrical contact of these oxide structures behaves in a non-ohmic way at low applied voltages. This subtle aspect is often neglected in electrochemical studies, where the intimate contact of a metal/semiconductor interface is tacitly assumed to account for a reasonable electrical conduction, especially when the metal represent the current collector. The real situation can be different from this simplistic assumption, due to the formation of a barrier for the electrons. Under this circumstance, the behaviour of such a metal/semiconductor interface is controlled by the so-called “Fermi-level pinning”.

A comparison between Fig. 5b and Fig. 7b indicates a slight shift for the position of the peak potentials upon sodiation for these two electrode architectures, while maintaining analogous dependences for $|I_p|$ and E_p with ν and $\ln \nu$, respectively, and thus supporting the previous considerations about the formation of a barrier for Na^+ incorporation.

The characteristic trends of E_p as a function of $\ln|I_p|$ for the nanowire-based electrodes cycled in Li- and Na-half cells are separately presented in Fig. S6. The linear relationship (see r -values in Table S1) in Fig. S6a further confirms that the behaviour of the Li-half cell deviates from that seen in Fig. S5a and that its resistance varies upon iron oxide conversion. However, Fig. S6b and its inset do not provide a definite trend for E_p with either $\ln|I_p|$ or $|I_p|$. This could be correlated with the fact that the resistance of the Na-half cell system during the reduction of the iron oxide nanowires responds in a different way and that two different regimes could exist under these electrochemical conditions, depending on the values of the applied sweep rates.

3.2.3. Thin-film electrodes

Fig. 8 depicts the CV cycles obtained for the thin-film electrodes subjected to analogous cycling conditions as before, while being tested in Li- and Na-half cells.

Fig. 8

The values of the respective currents in both graphs in Fig. 8 are significantly reduced compared to those of the composite and nanowire electrodes shown respectively in Fig. 4 and Fig. 6, since the active material loading in the thin films is extremely limited. The thin-film electrode in the Na-half cell hardly gave any faradaic

contribution, as noticed from the nearly smooth lozenge-like shape of the cycles. This corroborates the idea that Na^+ has a greater difficulty in reacting with the iron oxide in absence of an adequate porosity and extended surface area. Clearly its conversion into Fe and Na_2O is hampered, although in this type of thin-film the migration lengths for both Na^+ and e^- are rather short (i.e., $\approx 20\text{-}30$ nm, see Supporting Information) and thereby should not penalize the kinetics of this reaction. The latter could stop, however, in presence of a reaction-blocking layer, as found for the sodiation of NiO [52]. A peak current and peak potential analysis was not possible for this Na-half cell. By contrast, the thin-film electrode undergoing reaction with Li^+ exhibited evident redox peaks upon both cathodic and anodic half-cycles. The overall shape of these features deviates from those earlier presented in Fig. 4a and Fig. 6a. The shift for the values of the redox potentials, as well as the appearance of shoulders or overlapping peaks in the various voltammograms, can be justified on the basis of some possible causes; namely the presence of diverse aggregates of reacting particles for the various electrodes, each one having different sizes and size distribution [55, 56] and also the occurrence of magnetite on the film surface. The influence of the particle size on the associated electrochemical redox potential has been pointed out in earlier studies [55, 57, 58]. It is not surprising to encounter this effect here, because the conversion reactions of most transition metal oxides are well known to cause electrochemical milling of their components [36, 55, 59] with the repeating formation of small metal nanoparticles embedded in a matrix of Li_2O . The enhanced electrochemical activity of such nanoparticles, combined with the extensive presence of neighbouring phase boundaries, can account for the features observed in the different voltammograms and the remarkable pseudo-capacitive behaviour shown at low voltage vs. Li^+/Li .

Fig. 9 shows the respective behaviours of $|I_p|$ and E_p as a function of $\sqrt{\nu}$ during Li^+ uptake and their mutual dependence as well.

Fig. 9

A comparison of Fig. 9a with the graphs in Fig. 5a and Fig. 7a suggests that the thin-film electrode morphology does not affect sensibly the conversion mechanism, which still appears to be limited by diffusion (i.e., $|I_p| \propto \sqrt{\nu}$), despite its reduced migration paths for the charge carriers. Nevertheless, the presence of a barrier for the peak potential, as for the nanowires, is not observed and the linear trend of E_p with $|I_p|$ in Fig. 9b ultimately confirms an ohmic-like behaviour for this cell upon varying sweep rates (see also r -values in Table S1).

A final comparison of the above results with some previous investigations showing considerable electrochemical activities for these compounds, with initial capacities not too far from those theoretically expected from a full conversion into Fe and Na_2O [60-62], should take into account the particular structures and textures employed in the corresponding electrodes. In such iron oxide materials the presence of a large surface area with accessible porosity and (nano)voids certainly played a key role, together with a convenient electrical wiring of the same active particles within the overall electrode structure [60-62]. These features are clearly relevant not only for these oxide materials, but also for conversion-type compounds more in general. The latter require an activation for their Na-ion driven conversion and their conversion efficiency is influenced by the reaction pathway and associated products [27]. Finally, different bond lengths (and strengths) for the transition metal element (e.g., Fe, Ni, Co, etc.) and the surrounding non-metallic atoms (e.g., N, P, O, F, etc.), which have distinct electronegativity in the resulting transition metal compounds, can certainly

play a role in determining to which extent a conversion reaction occurring with Li^+ will be also feasible with Na^+ , due to their difference in size and a lower reactivity for Na^+ .

4. Conclusions

The results presented in this comparative work clearly demonstrate that the conversion reaction of iron oxide into Fe and Na_2O is hampered from its early cycles and that it cannot reach its completion under the typical cycling conditions applied in Na-half cells. This not only confirms the results from previous complementary studies [37] on this compound, but also sheds light on the nature of the limiting factors existing for these reactions, while relating the latter to the structure and composition of the electrodes. These findings demonstrate that the conversion of iron oxide into Fe and Li_2O upon lithiation undergoes an intrinsic diffusion-limited mechanism, which is visible here at both low and moderate sweep rates. This crucial aspect should not be overlooked in the preparation of efficient electrodes, since this type of reaction poses *per se* other challenging issues (i.e., large voltage hysteresis upon discharge/charge), which are so far not completely solved from both theoretical and practical aspects. Moreover, the detrimental role of the contact resistance in thicker layers embedding metal/semiconductor interfaces has been briefly mentioned and clarified. This important and general aspect should be carefully assessed for both microscopic and macroscopic electrical contacts that can be present in the electrodes of these electrochemical devices.

Conversely, the incorporation of Na^+ (compared to that of Li^+ in the same materials) experiences a noticeable hindrance from its early stage of interface

reaction, as demonstrated by the significantly reduced currents obtained for the associated Na-half cells, independently of the particular morphology and exposed surface area of the respective electrodes. The existence of a barrier for the sodiation process has been demonstrated for both the nanopowders and the nanowires, whereas for the thin films it was not possible to achieve any clear Faradaic activity. The difference in active mass loading between the nanopowder and nanowire electrodes did not seem to clearly influence in the currents extracted from these two different types of structures upon sodiation, thus suggesting that the main limitations for this reaction could arise from the initial phases of surface reaction and incorporation of Na^+ and the consequent formation of reaction products. Therefore, more careful considerations are required in the design of suitable electrode structures for these materials in Na-ion cells. The limited amount of current that can reversibly be attained by cycling this compound in a voltage range suitable for operation as negative electrode in Na-ion batteries, calls for a further optimization of the whole cells. Indeed, only the most reversible and accessible processes of charge storage should be utilized, thereby posing a further constraint on the overall energy density and performances that can be achieved via these compounds in combination with Na^+ .

Nonetheless, the purpose of this study should not be limited only to these considerations and hopefully it could also promote complementary approaches to move a step forward towards the improvement of the performances of negative electrodes in Na-ion batteries, while providing a deeper understanding of conversion compounds for possible usage in these electrochemical systems more in general.

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Captions

Fig. 1. SEM micrographs showing the surface morphology of the various types of electrodes. Composite electrode based on iron oxide nanopowders mixed with CMC and CB (a). Iron oxide nanowires grown by thermal oxidation of a Fe foil (b). Thin-film of iron oxide formed by thermal oxidation of a Fe foil (c). Pristine iron foil (d). Note the different structures and textures of the active materials.

Fig. 2. XRD patterns obtained for the nanopowders formed by pyrolysis in vacuum of iron acetate at 260 °C and for the nanowires grown on iron via oxidation in air at 350 °C. Note the presence of various iron oxide phases co-existing in these electrode materials.

Fig. 3. Raman spectra obtained in correspondence of various types of iron oxide nanostructures. Note the presence of α -Fe₂O₃ on each sample surface from the common characteristic peaks and especially from the most intense feature around 1320 cm⁻¹. The detection of additional iron oxide phases is marked in the spectra by the symbols (#) for α -Fe₂O₃ and (⌘) for Fe₃O₄. The peak related to Fe₃O₄ is very weak in the nanowires spectrum.

Fig. 4. Cyclic voltammograms of coated electrodes embedding nanostructured Fe₂O₃ powders subjected to increasing scan rates ranging from 0.05 to 0.8 mVs⁻¹. The electrodes were cycled between 0.05 and 2.80 V vs. Li⁺/Li (or vs. Na⁺/Na) in Li- (a) and Na-half cells (b), respectively.

Fig. 5. Plots associated to the previous voltammograms for nanostructured Fe_2O_3 powders. The data points correspond to the cathodic peaks during uptake of Li^+ (a) and Na^+ (b) ions in the respective half cells cycled at increasing scan rates. Note the different trends for both the peak currents and the peak potentials versus the applied scan rates for these two electrochemical systems.

Fig. 6. Cyclic voltammograms for iron oxide nanowire electrodes obtained with increasing sweep rates from 0.05 to 0.8 mVs^{-1} . The electrodes were cycled between 0.05 and 2.80 V vs. Li^+/Li (or vs. Na^+/Na) in Li- (a) and Na-half cells (b), respectively.

Fig. 7. Plots related to the previous voltammograms for iron oxide nanowire electrodes. The data points correspond to the cathodic peaks during uptake of Li^+ (a) and Na^+ (b) ions in the associated half cells cycled at increasing sweep rates. Note the distinctive trends for both the peak currents and the peak potentials versus the applied sweep rates for these two electrochemical systems.

Fig. 8. Cyclic voltammograms of iron oxide thin-film electrodes obtained with increasing sweep rates from 0.05 to 0.8 mVs^{-1} . The electrodes were cycled between 0.05 and 2.80 V vs. Li^+/Li (or vs. Na^+/Na) in Li- (a) and Na-half cells (b), respectively.

Fig. 9. Trends for the cathodic peak currents and peak potentials versus the applied sweep rate related to the voltammograms of iron oxide thin-film electrodes (a). Behavior of the cathodic peak potentials as a function of the respective peak currents (b). The data sets refer to the values extracted from Fig. 8a.

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Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

Fig. 7.

Fig. 8.

Fig. 9.

Iron oxides

Nanopowders

Nanowires

Thin films

Cyclic Voltammetry