Nanometric mixed iron-titanium oxides were prepared by mechanical milling with a view to determining their ability to act as anodic materials in lithium cells. At a TiO₂/Fe₂O₃ molar ratio of 0.4, a solid-state reaction occurs that leads to the formation of Fe₃TiO₆, which possesses a spinel-like structure; at lower ratios, however, the structure retains the hematite framework. Li/Fe₂O₃ cells exhibit poor electrochemical reversibility; by contrast, Ti-containing electrodes possess improved cycling properties. Changes in the electrodes upon cycling were examined by X-ray photoelectron spectroscopy (XPS). XPS data confirm the participation of electrolyte in the electrochemical reaction and the different type of electrochemical reversibility exhibited by samples. Both processes were influenced by the presence of titanium. Titanium dioxide, in the presence of iron oxides, seems to be inactive to the electrochemical process. Based on the step potential electrochemical spectroscopy (SPES) curves and photoelectron spectra obtained, the presence of Ti increases the reversibility of the redox reactions undergone by the electrolyte during discharge/charge processes. The increased active-material/electrolyte/inactive-material interaction which is reported here offers new perspectives for the use of well-known transition oxides as anode materials in Li-ion batteries.

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spectrometer manufacturer (Physical Electronics, Eden Prairie, MN). In order to avoid reduction of higher metallic oxidation states by X-rays, spectra were collected with short acquisition times. Ex situ XPS measurements were performed on the acetonitrile-washed pellet from the dismantled cell. All manipulations were done under an argon atmosphere; also, a special glove box connected to the spectrometer antechamber allowed samples to be transferred to the spectrometer without direct contact with air.

Electrochemical measurements were performed in two electrode cells, using lithium as a counter electrode. The electrolyte was Merck battery electrolyte LP 40 (EC:DEC = 1:1 w/w, 1 M LiPF₆). Electrode pellets were prepared by pressing, in an stainless-steel grid, ca. 4 mg of active material with polytetrafluoroethylene (PTFE) (5 wt %), and acetylene black (10 wt %) at 4 ton. Galvanostatic tests were conducted under various galvanostatic regimes from C to C/6 (C being defined as 1 Li⁺ exchanged in 1 h). Step potential curves were recorded at 2.5 mV/0.22 h per step. All electrochemical measurements were controlled via a MacPile II potentiostat.

Results and Discussion

Figures 1 and 2 show the X-ray powder diffraction patterns for α-Fe₂O₃ and the iron-titanium oxides. Milling of α-Fe₂O₃, hereafter referred to as g-Fe₂O₃, decreased particle crystallinity as reflected in the smaller, broader peaks obtained with both structural and ionic radius size considerations, is unlikely as Ti⁴⁺ can hardy have been reduced to Ti³⁺ under the experimental conditions of the grinding process. The other noteworthy difference is that the intensity of the peaks with an l index of zero [reflections (110) and (300)] increased with increasing grinding (the calculated I₁₁₀/I₃₀₀ values were 0.7, 0.85, and 0.98 for standard α-Fe₂O₃, g-Fe₂O₃ and sample A, respectively). A similar trend was observed for the I₃₀₀/I₄₄₀ ratio. This was particularly so in the titanium-containing sample. This phenomenon has previously been observed²³ and suggests a pronounced preferred orientation in the samples typical of an acicular habit, with elongation along [001] that boosts hkl reflections. The phase composition of sample A was calculated by subjecting the XRD data to Rietveld refinement²⁴ using the GSAS software suite. Based on the results, the materials contain ca. 96% α-Fe₂O₃ and 4% rutile TiO₂. Therefore, a significant fraction of TiO₂ goes undetected by X-radiation, either because the milling process renders it amorphous or because it is occluded by hematite particles.

Calcination of samples A and B at 700°C for 24 h shed some light on the structural changes caused by grinding. Thus, the ulvospinel phase found in sample B decomposed into hematite and pseudobrookite, Fe₅TiO₈, under these conditions (see the inset in Fig. 2d), the former being the major component. No reflections corresponding to the rutile phase were observed. By contrast, the XRD pattern for calcined sample A exhibited reflections typical of α-Fe₂O₃, rutile TiO₂, and Fe₅TiO₈ (Fig 2c). The presence of rutile, which was a minor component in the pristine sample, suggests that this phase does not react with α-Fe₂O₃ at this temperature level.

Table I. Unit cell parameters and crystallite size (nm) for ground iron and iron-titanium oxides.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a, b(Å)</th>
<th>c(Å)</th>
<th>V(Å³)</th>
<th>L₁₁₀</th>
<th>L₃₀₀</th>
<th>L₄₄₀</th>
<th>L₄₄₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-Fe₂O₃</td>
<td>5.036(1)</td>
<td>13.754(1)</td>
<td>261.6</td>
<td>25</td>
<td>21</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A (0.8Fe₂O₃·0.2TiO₂)</td>
<td>5.039(1)</td>
<td>13.810(4)</td>
<td>262.9</td>
<td>15</td>
<td>13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>B (Fe₅TiO₈)</td>
<td>8.46(1)</td>
<td>8.46(1)</td>
<td>605.4</td>
<td>-</td>
<td>11</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>
Therefore, the pseudobrookite phase may form as an amorphous compound during grinding or by reaction of amorphous or occluded TiO₂ particles with hematite particles during heating.

Figure 3 shows selected transmission electron micrographs for the iron-titanium oxides A and B. The micrographs for A are similar to those for \( \alpha\)-Fe₂O₃ and show agglomerates of nanoparticles ca. 20 nm in size. Sample B, with a different structure, also possesses a different morphology. Its particles are largely semipolyhedral in shape and 100-300 nm in size. Crystallite size was calculated from the broadening of two X-ray peaks using the Scherrer equation. The values thus obtained are listed in Table I. The crystallite sizes for g-Fe₂O₃ and sample A are similar to those calculated from the TEM images, which suggests that the particles are formed as single coherent diffracting domains. Sample B behaved differently, and its crystallite size was much smaller than its particle size.

Figure 4a shows the initial discharge-charge curves for g-Fe₂O₃ as recorded at C/6 rate. The first discharge curve exhibits a high lithium uptake up to a 0.0 V cutoff potential (8.8 Li per Fe₂O₃ mole, equivalent to 1476 mAh/g). The shape profile is similar to one reported elsewhere. The potential steeply drops on approaching 1.7 V and is followed by a small pseudoplateau at 1.6 V and a smooth drop to a wide plateau in the 0.8-0.5 V range and, finally a sustained decrease to 0.0 V. One salient feature of this curve is the presence of the 1.6 V step, which has only been reported for nanometric hematites and ascribed to Li insertion into the Fe₂O₃ structure. The plateau is thus consistent with the nanometric nature of the milled hematite. Based on complete reduction of \( \text{Fe}^{3+} \rightarrow \text{Fe}^{0} \), one would expect a maximum uptake of 6 Li/Fe₂O₃. The excess capacity appears to derive from electrolyte decomposition in the low-potential region, and the subsequent formation of an organic layer on the surface of the particles. The electrolyte seemingly plays a major role in the overall electrochemical process for these \( \text{M}_x\text{O}_y \) electrodes, where the formation of a solid electrolyte interface (SEI) upon discharge at low potentials has been suggested.

The charge curve exhibits a strong polarization near 1.4 V, which is followed by a plateau centered at ca. 1.8 V. The amount of lithium removed is about 5.5 Li per unit formula, which is somewhat smaller than the 6 lithium atoms at a cutoff voltage of 3.0 V predicted from stoichiometric calculations based on Reaction 1. The amounts of inserted and extracted lithium tend to decrease on cycling. A continuous loss of the specific capacity delivered by the cell on cycling is thus observed, whatever the charge/discharge rate (Fig. 4b). Such poor electrochemical behavior can be ascribed to various factors, namely, the excess capacity spent in the SEI film formation, which is greater for iron oxide particles than for other oxides with better cell performance such as CuO² and Co₃O₄, and to the loss of physical integrity of the electrode on successive cycling.

Figure 3. TEM images of (a) g-Fe₂O₃; (b) sample A, and (c) sample B.

Figure 4. (a) First galvanostatic curves and (b) specific discharge capacity recorded at different discharge rates for Li/g-Fe₂O₃ cells.
Figure 5 shows the galvanostatic curves at C/16 regime samples A and B. The faradaic yield was calculated by using a molecular weight defined from the compositions shown in Table I. The electrode from sample A exhibits curve profiles similar to those for g-Fe₂O₃ (Fig. 5a). The lithium uptake is lower, consistent with the smaller amount of iron in this sample. This suggests some electrochemical inactivity in the titanium atoms. The discharge/charge curves for sample B are slightly different from those for sample A (Fig. 5b) and exhibit a similar Li/Fe ratio (4.4 and 4.2 for the first discharge of samples A and B, respectively). The most salient difference is the absence of the small plateau at 1.6 V in the former, consistent with a different structure as noted earlier.

The addition of TiO₂ to α-Fe₂O₃, followed by grinding, improves the reversibility of the electrochemical reaction of hematite (Fig. 5a). The capacity retention values, R₁₅, defined as the ratio between the discharge capacity of the 15th and second cycle, varied from 0.34 for g-Fe₂O₃ to 0.62-0.67 for the titanium-containing oxides. This improvement can be observed more easily by plotting the charge recovery, a term that defines the specific capacity stored by the cell in the charge process in relation to that delivered in the discharge process. The charge recovery on cycling of Li/g-Fe₂O₃, Li/sample A, and Li/sample B cells, which is somewhat more positive than that for graphite-based materials and make transition metal oxide-based compounds attractive as anodic materials in terms of energy.

In order to shed some light on these electrochemical processes, additional data were obtained by combining the step potential electrochemical spectroscopy (SPES) technique with ex situ XRD and XPS measurements. Figure 7 shows the SPES curves for g-Fe₂O₃ and samples A and B. The first cathodic curves for hematite and sample A are very similar, with two well-defined peaks at 1.6 and 0.6 V. The former peak is absent in the corresponding curve for sample B, and the strong peak at 0.6 V is accompanied by a shoulder at the right side of the peak. The first anodic curves for the three samples are similar and include two overlapping broad peaks at ca. 1.5 and 1.9 V. A low, broad signal at ca. 0.7 V was also observed, the intensity of which increased with increasing titanium content. The second and subsequent discharge curves were increasingly similar. The peaks at 1.6 V for g-Fe₂O₃ and sample A, and the shoulder for sample B disappeared. Also, the strong peak shifted to high voltage values. The main changes in the second and subsequent charge curves reflected in a decrease in peak intensity.

The peak at 1.6 V in the cathodic curve can be assigned to lithium insertion into α-Fe₂O₃ and the strong peak at ca. 0.6 V to Fe³⁺ → Fe⁰ reduction. This latter assignation is based on theoretical and experimental electromotive force values for Reaction 1 and related systems such as ZnFe₂O₄ and Ca₂Fe₂O₅. Below this peak, one should observe the electrolyte reduction. The presence of titanium seems to facilitate this process; also, its effect on the SPES profile is more pronounced in sample B as a result of its increased titanium content or of a different structure. The disappearance of the peak at 1.6 V in the second discharge indicates that the lithium insertion reaction is irreversible. The double peak observed on charging the cell can be assigned to a change in iron oxidation state in two steps (viz., Fe⁰ → Fe⁺ at ca. 1.6 V and Fe⁺ → Fe⁺⁺ at ca. 1.9 V). These cycling curves reflect the favorable effect of titanium on the reversibility of the electrochemical reaction. The decrease in the peak intensity on cycling for samples A and B (Fig. 7b and c) was much smaller than that for pure hematite (Fig. 7a). Based on reported data, the broad peak at ca. 0.7 V in the anodic scans can be assigned to partial oxidation of the SEL. Interestingly, this peak, which is observed in the titanium-containing oxides, is virtually absent for g-Fe₂O₃. This suggests that the presence of titanium...
may increase the reversibility of the electrochemical reaction undergone by the electrolyte.

The role of titanium in the electrochemical process is controversial. TiO₂ has been proposed as an anode for lithium batteries. The discharge curve exhibited an extended plateau at ca. 1.8 V, which is close to the potential for the small peak in the first cathodic scan of Fig. 7a and b. However, the voltage window used was 2.6-1.2 V and only the first cycle was reported. This prompted us to revisit the Li/TiO₂ system. To this end, we used TiO₂ morphologically similar to the iron-titanium oxides and the same conditions in the electrochemical study. The discharge curve, Fig. 8, exhibits a well-defined potential plateau at 1.75 V followed by a voltage decrease with two subtle slope changes at 1.4 and 0.8 V. The lithium uptake at a 0.0 V potential plateau at 1.75 V followed by a voltage decrease with two components. Thus, the titanium-containing sample has a higher content of Ti³⁺, with a low atomic concentration (ca. 5.9%). The major component, which appears at higher binding energy (BE), was assigned to Ti⁴⁺. These data confirm the limited participation of Ti⁴⁺ in the electrochemical process as most titanium atoms remain in the tetrahedral state; however, a potential role of the sputtering process cannot be excluded. The Fe 2p XPS spectra, Fig. 9b, exhibits multiple components that can be assigned to various oxidation states (Fe³⁺, Fe²⁺, and Fe⁰). Also, the shake-up satellite structure provides independent, qualitative/quantitative estimation of the relative concentrations of Fe³⁺ and Fe²⁺. Table II shows the BE and the relative areas of the different components obtained by peak deconvolution using a Gaussian-Lorentzian mixed function. Peaks were assigned according to reported values. The Fe 2p photoemission spectra for the electrodes charged up to 3 V corresponding to g-Fe₂O₃ and sample A following sputtering with Ar⁺ for 2 min to improve the signal-to-noise ratio. No signals were detected for the discharged electrodes, even after sputtering with Ar for long periods of time; this suggests that the particles are coated with a thick organic layer originating from the electrolyte decomposition. The Ti 2p profile was fitted to two components (Fig. 9a). The smaller component was assigned to Ti⁵⁺, with a low atomic concentration (ca. 5.9%). The major component, which appears at higher binding energy (BE), was assigned to Ti⁴⁺. These data confirm the limited participation of Ti⁴⁺ in the electrochemical process as most titanium atoms remain in the tetrahedral state; however, a potential role of the sputtering process cannot be excluded. The Fe 2p XPS spectra, Fig. 9b, exhibits multiple components that can be assigned to various oxidation states (Fe³⁺, Fe²⁺, and Fe⁰). Also, the shake-up satellite structure provides independent, qualitative/quantitative estimation of the relative concentrations of Fe³⁺ and Fe²⁺. Table II shows the BE and the relative areas of the different components obtained by peak deconvolution using a Gaussian-Lorentzian mixed function. Peaks were assigned according to reported values. The main conclusion from these data is the presence of the three oxidation states in both ground hematite and sample A in the charged state, albeit in different proportions. Thus, the titanium-containing sample has a higher content in Fe³⁺ and hence lower contents in Fe²⁺ and Fe⁰ (see Table III). Based on these composition data, and on the assumption that iron is completely reduced in the previous reduction process, the overall electrochemical reactions in the first cycle are

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + 6\text{Li}^+ & \rightarrow 2\text{Fe}^+ + 3\text{Li}_2\text{O} & \text{Discharge up to 0.0 V} \\
-0.11\text{Fe}^+ + 1.29\text{FeO} + 0.30\text{Fe}_2\text{O}_3 + 4.38\text{Li}^+ + 0.81\text{Li}_2\text{O} & \text{Charge up to 3.0 V} \\
0.8\text{Fe}_2\text{O}_3 + 0.2\text{TiO}_2 + 4.8\text{Li}^+ & \rightarrow 1.6\text{Fe}^+ + 2.4\text{Li}_2\text{O} + 0.2\text{TiO}_2 \\
\text{Discharge up to 0.0 V} & -0.05\text{Fe}^+ + 0.87\text{FeO} + 0.34\text{Fe}_2\text{O}_3 + 0.2\text{TiO}_2 + 3.78\text{Li}^+ + 0.51\text{Li}_2\text{O} \\
\text{Charge up to 3.0 V} & -0.11\text{Fe}^+ + 1.29\text{FeO} + 0.30\text{Fe}_2\text{O}_3 + 4.38\text{Li}^+ + 0.81\text{Li}_2\text{O}
\end{align*}
\]

These stoichiometries are consistent with the corresponding charge profiles for the electrodes (insets in Fig. 9d and e). The amount of lithium calculated from these data in the potential window better comparison with the SPES curves of Fig. 7. The shapes of these two plots are different, consistent with a minor influence of titanium on the electrochemical properties of our samples.

The FEI X-ray photoelectron spectrometer XPS was used to study the Fe 2p and Ti 2p core levels of the charged electrodes at 3.0 V. The BEs and satellite structures were found for both Fe 2p and Ti 2p core levels. The FEI X-ray photoelectron spectrometer XPS was used to study the Fe 2p and Ti 2p core levels of the charged electrodes at 3.0 V. The BEs and satellite structures were found for both Fe 2p and Ti 2p core levels.

Table III. Binding energies for Fe 2p components. XPS spectra were recorded from the charged electrodes at 3.0 V.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe³⁺</th>
<th>Fe²⁺</th>
<th>Fe⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>⁳p/2</td>
<td>⁴p/2</td>
<td>⁵p/2</td>
</tr>
<tr>
<td>g-Fe₂O₃</td>
<td>711.1</td>
<td>724.2</td>
<td>718.0</td>
</tr>
<tr>
<td>A</td>
<td>711.1</td>
<td>724.2</td>
<td>717.3</td>
</tr>
</tbody>
</table>

Table II. Percent atomic composition of the charged electrodes as calculated from the Fe 2p photoemission peak.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe (III)</th>
<th>Fe (II)</th>
<th>Fe (0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-Fe₂O₃</td>
<td>30.5</td>
<td>64.3</td>
<td>5.2</td>
</tr>
<tr>
<td>A</td>
<td>42.6</td>
<td>54.5</td>
<td>2.9</td>
</tr>
</tbody>
</table>
1.2–3.0 V, where the Fe$^0 \rightarrow$ Fe$^{n+}$ oxidation process occurs, is 4.4 and 3.8 Li$^+$ ions for g-Fe$_2$O$_3$ and sample A, respectively. Such good agreement between the XPS and electrochemical data is consistent with the inactivity of TiO$_2$ during the electrochemical process and the preservation of the identity of the iron species during the XPS experiment. In addition, the increased Fe$^{3+}$ content calculated for the titanium-containing charged electrode confirms the favorable effect of this element on cell performance.

The C 1s spectra for the charged electrodes provide additional support for the role played by titanium in the redox reaction of the electrolyte. The two spectra were fitted to four components with identical binding energies. The peaks were assigned on the basis of literature reports describing the discharge products of CoO up to 0.0 V in lithium cells. The authors assumed the formation of some species proposed by Aurbach et al. and proposed others such as RCO$_2$Li, Li$_2$CO$_3$, and CH$_2$-CH$_2$O$_n$. In fact, this latter polymer, the binding energy of which is at 286 eV, disappears on charging. Thus, O bound to C species are formed during the reduction process, probably below 0.5 V. The BE and atomic composition values are listed in Table IV. These results contradict those reported by Dedryvère et al., as the peak at 286.1 eV assigned to the CH$_2$-CH$_2$O$_n$ polymer disappeared during the charge process. The main difference between the two samples is the lower content in O bound to carbon species in the titanium-containing sample, particularly in O-C=O form. Thus, the Ti could either increase the oxidation rate of the reduced species coming from the electrolyte, as reflected in the SPES curves of Fig. 7b and c, or decrease the reduction rate of the electrolyte. Both models would lead to reduction of the SEI layer thickness and result in improved battery performance.

**Conclusions**

The influence of titanium on the electrochemical behavior of hematite as an anode material in lithium cells was examined. Titanium-containing samples were prepared by following a mechanical milling procedure that provides nanometric particles. At a TiO$_2$/Fe$_2$O$_3$ mole ratio of 0.4, a solid-state reaction occurs that leads to the formation of Fe$_5$TiO$_8$, which possesses a spinel-like structure. The electrochemical reaction with lithium was studied in the potential window 3.0–0.0 V. Under these conditions, the discharge capacities values exceeded those delivered in the total reduction of iron. Therefore, some electrolyte molecules also undergo a reduction process that leads to the formation of an organic layer on the surface of the metal particles. All reduction products are amorphous and fail to regain crystallinity on charging at 3.0 V. The Li/Fe$_2$O$_3$ cell exhibits poor electrochemical reversibility, probably because of the large ca-

---

**Table IV. Binding energies for C 1s components.** XPS spectra were recorded from the charged electrodes at 3.0 V. The values in parentheses correspond to the atomic concentrations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C-C (eV)</th>
<th>C-O (eV)</th>
<th>O-C=O (eV)</th>
<th>CO$_3^{2-}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>g-Fe$_2$O$_3</td>
<td>284.8 (55.9)</td>
<td>286.1</td>
<td>287.6</td>
<td>289.8 (9.9)</td>
</tr>
<tr>
<td>A</td>
<td>284.8 (60.8)</td>
<td>286.1 (15.8)</td>
<td>287.6 (13.9)</td>
<td>289.8 (9.5)</td>
</tr>
</tbody>
</table>

---

**Figure 8.** First galvanostatic curves for the Li/TiO$_2$ cell. The inset shows the corresponding differential capacity plot.

**Figure 9.** (a) XPS Ti 2p and (b) Fe 2p core level spectra for the electrode from sample A. (c) Fe 2p core level spectra for the g-Fe$_2$O$_3$ electrode. Both spectra were obtained after the first charge up to 3.0 V. Inset: charge curve after complete reduction up to 0.0 V for (d) sample A and (e) g-Fe$_2$O$_3$ electrodes.
Fe\textsuperscript{3+}, Fe\textsuperscript{2+}, and Fe\textsuperscript{0}, the last being the minor species. The atomic trum for the charged electrodes is consistent with the presence of which contradicts the electrochemical calculations. The Fe 2p spectra were recorded after the first charge up to 3.0 V.

during the discharge/charge process as reflected in both the SPES curves and the C 1s spectra for the charged electrodes. Finally, the reversibility of the redox reactions undergone by the electrolyte containing electrodes exhibit better cycling properties. The XPS data capacity excess used in the electrolyte decomposition. The Ti- transition metal oxides as anode materials, via an enhancing of the electrolyte redox process.

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Universidad de Córdoba assisted in meeting the publication costs of this article.

References


Figure 10. XPS C 1s core level spectra for (a) g-Fe\textsubscript{2}O\textsubscript{3} and (b) sample A electrodes. The spectra were recorded after the first charge up to 3.0 V.