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## Demonstrating the steady performance of iron oxide composites over 2000 cycles at fast charge-rates for Li-ion batteries†

Z. Sun,<sup>\*ab</sup> E. Madej,<sup>a</sup> A. Genç,<sup>cd</sup> M. Muhler,<sup>e</sup> J. Arbiol,<sup>cf</sup> W. Schuhmann<sup>a</sup> and E. Ventosa<sup>\*a</sup>

**The feasibility of using iron oxides as negative electrode materials for safe high-power Li-ion batteries is demonstrated by the carbon-coated FeO<sub>x</sub>/CNT composite synthesized by controlled pyrolysis of ferrocene, which delivered a specific capacity retention of 84% (445 mA h g<sup>-1</sup>) after 2000 cycles at 2000 mA g<sup>-1</sup> (4C).**

The energy density of the state-of-the-art Li-ion batteries (LIBs) is sufficient to fulfill the requirements for hybrid electric vehicles (HEVs); nevertheless, it is still below the needs for full electric vehicles (EVs).<sup>1</sup> Consequently, great effort is being devoted to the development of high-energy-density materials, which is essential for the consolidation of EVs. When tackling this major challenge, other important parameters that determine the overall performance of a battery material, namely energy density, power density, cost, lifetime, and safety,<sup>2,3</sup> may sometimes be overseen.

Graphite is a well-performing, cheap and high-energy-density material; however, safety issues arise at high charge rates (C-rates) due to the small voltage gap (<0.1 V) between lithiation of graphite and electrodeposition of lithium. Iron oxides are considered to be alternative negative electrode materials owing to their high specific charge capacity (1000 mA h g<sup>-1</sup>) and low cost.<sup>4–6</sup> Compared to graphite, they operate at more anodic potentials and thus offer higher safety. Nevertheless, the lifetime and power density of iron oxides do not meet the requirements for implementation in commercial LIBs. To compete with graphite, iron oxides must

improve their performance, namely the retention of storage capacity at fast C-rates. Therefore, iron oxide must retain its reversible specific charge capacity upon many cycles (>1000) under demanding electrochemical conditions, which is very difficult to achieve due to the charge storage mechanism in iron oxides.<sup>6</sup> Metallic iron and lithium oxide are formed during the reduction of iron oxide. On the one hand, the formation of the ionic and electric insulating lithium oxide hinders the reversibility of the electrochemical process. On the other hand, the volume changes accompanying the reversible process lead to the pulverization of the electrode material. The detrimental impacts of these factors are magnified when operating at high C-rates due to the mechanical stress induced by the fast volume changes as well as the large overpotentials caused by the high current intensities. Herein, we present a facile synthesis strategy for carbon@FeO<sub>x</sub> composite materials with improved cycle stability at high C-rates. By controlled pyrolysis of ferrocene, a precursor that supplies both iron and carbon, at 550 and 650 °C in an autoclave, carbon-coated FeO<sub>x</sub>/carbon nanotube (CNT) composites were synthesized (Fig. S1, ESI†). The composites delivered an outstanding specific charge retention of up to 84% (445 mA h g<sup>-1</sup>) after 2000 cycles under fast cycling conditions (2000 mA g<sup>-1</sup> and 4C).

Barreiro *et al.* showed that single-walled CNTs can be obtained by the decomposition of ferrocene at 900 °C,<sup>7</sup> whereas Brandt and Balducci employed ferrocene as a precursor for the synthesis of the carbon@Fe<sub>2</sub>O<sub>3</sub> composite at 1050 °C which delivered good electrochemical performance as an active material for LIBs demonstrating that ferrocene is a suitable precursor for battery materials.<sup>8</sup> To achieve long-term stability at high C-rates, iron oxide based electrodes would benefit from (i) small FeO<sub>x</sub> particle sizes that can facilitate the electrochemical reaction and lower the mechanical stress,<sup>9–11</sup> (ii) graphitic carbon coating of FeO<sub>x</sub> for mechanical stability,<sup>12–14</sup> and (iii) interconnected CNTs enhancing the inter-particle electrical conductivity at high C-rates.<sup>15–17</sup> Since the role of the carbon coating (electrical conductivity and mechanical stability) is more important than that of CNTs, the pyrolysis of ferrocene was carried out at lower temperatures (550 and 650 °C) in the absence of precursor flow

<sup>a</sup> Analytical Chemistry – Center for Electrochemical Sciences (CES), Ruhr-Universität Bochum, D-44780 Bochum, Germany. E-mail: edgar.ventosa@rub.de

<sup>b</sup> State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: sunzy@mail.buct.edu.cn

<sup>c</sup> Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and The Barcelona Institute of Science and Technology, Campus UAB, Bellaterra, 08193 Barcelona, Catalonia, Spain

<sup>d</sup> Metallurgy and Materials Engineering Department, Faculty of Engineering, Bartın University, 74100, Bartın, Turkey

<sup>e</sup> Laboratory of Industrial Chemistry, Ruhr-Universität Bochum, D-44780 Bochum, Germany

<sup>f</sup> Institució Catalana de Recerca i Estudis Avançats, ICREA, 08010 Barcelona, Spain

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reflections of  $\text{Fe}^0$  became significantly weakened upon calcining as seen in traces B (Fig. 3a). The carbon content of  $\text{FeO}_x(650)/\text{C}$  and  $\text{FeO}_x(650)/\text{C}_{\text{ox}}$  was determined by elemental analysis to be 43 wt% and 30 wt%, respectively. Utilizing the Scherrer equation for relating the coherently scattering domains to Bragg peak widths:  $L = k\lambda/B \cos(\theta)$ , in which  $k = 0.89$  for spherical particles and  $B$  is the full angular width at half-maximum of the peak in radians, the average crystallite sizes in  $\text{FeO}_x(650)/\text{C}$  was determined to be around 20 nm using the (311) reflection. Based on this estimation, no change in the particle size was observed during the thermal post-processing. The mean particle diameter was estimated to be  $20 \pm 14$  nm based on TEM imaging of 100 different particles (Fig. S10, ESI<sup>†</sup>), which is in good agreement with the XRD results. Nitrogen adsorption/desorption measurements of  $\text{FeO}_x(650)/\text{C}$  (Fig. S11, ESI<sup>†</sup>) indicate a mesoporous character of the sample as well as a high specific surface area ( $66 \text{ m}^2 \text{ g}^{-1}$ ), which is beneficial for electrolyte accessibility and rapid Li-ion diffusivity.<sup>21–25</sup> The presence of maghemite, magnetite and hematite in the sample prior to and after calcining was also verified using two vibrational spectroscopy techniques (FTIR and Raman) (Fig. S12 and S13, ESI<sup>†</sup>).

To provide insight into the surface composition of  $\text{FeO}_x(650)/\text{C}$ , X-ray photoelectron spectroscopy (XPS) was employed. There are three elements detected in the samples, *i.e.*, Fe, O and C (Fig. S14a, ESI<sup>†</sup>). The C 1s region (Fig. S14b, ESI<sup>†</sup>) shows a dominant peak at around 284.6 eV regardless of calcining, corresponding to graphitic carbon. Deconvolution of the spectra manifests three additional small peaks at  $\sim 285.4$  and  $286.7$  and  $288.9$  eV, which are assigned to carbon singly bound to oxygen in phenols and ethers (*i.e.* C–O), carbon doubly bound to oxygen in ketones and quinones (*i.e.* C=O), carbon bound to two oxygen atoms in carboxyls, carboxylic anhydrides and esters (*i.e.* –COO), respectively. The main graphitic C peak comprises  $\sim 75\%$  of the spectrum for the sample prior to calcining. Upon calcination, the graphitic C content decreased to

$\sim 67\%$  due to the mild oxidation of the C structure. Despite this, the value is still much higher than the one reported for graphene oxide (31% graphitic C).<sup>26</sup> The Fe 2p<sub>3/2</sub> region (Fig. S14c, ESI<sup>†</sup>) consists of a peak centred at  $\sim 711.1$  eV typical of  $\text{Fe}^{3+}$ . A lower binding energy Fe 2p shoulder is also observed, indicating the  $\text{Fe}^{2+}$  species. The broad satellites centred at  $\sim 714.5$  and  $\sim 719.1$  eV are characteristic of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  species, respectively. The O 1s spectrum (Fig. 3b) was deconvoluted into three peaks at around 529.8, 532.0 and 533.4 eV. The peak at 529.8 eV originates from the lattice oxygen of iron oxides, the intensity of which was enhanced upon calcination. The peaks at higher binding energies may correspond to O doubly ( $\sim 532.0$  eV) and singly ( $\sim 533.4$  eV) bound to carbon, consistent with the results derived from the C 1s spectra.

The performance of the composites was evaluated as active materials for LIBs in three-electrode half-cell configuration to ensure that the counter-electrode did not limit the electrochemical performance. Note that the carbon content was adjusted to be the same in all samples with addition of carbon black. Fig. 4a shows the potential profiles of commercial  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}_x(650)/\text{C}$  and  $\text{FeO}_x(650)/\text{C}_{\text{ox}}$  in the first electrochemical cycle between 3.0 and 0.1 V vs. Li/Li<sup>+</sup>. The lower cut-off potential was intentionally set to 0.1 V to increase the safety at high C-rates. All four samples displayed the characteristic behavior of Li-ion storage in iron oxides.<sup>4–6,8–17,21–25</sup> The lower initial reversible capacity of both composites suggests the presence of metallic iron, which, together with the larger surface area, led to lower coulombic efficiency in the first cycle (Fig. S15, ESI<sup>†</sup>). Electrolyte additives, prelithiation or preactivation may be used to mitigate low coulombic efficiency in the first cycle.<sup>27–30</sup> However, this issue is beyond the purpose of this work, which focuses on demonstrating the long cycle life achieved using the synthesized composites at high C-rates. At  $1000 \text{ mA g}^{-1}$ , commercial iron oxide electrodes were unable to retain the reversible capacity (Fig. 4b), which was dropping below 50% after only 10 cycles.

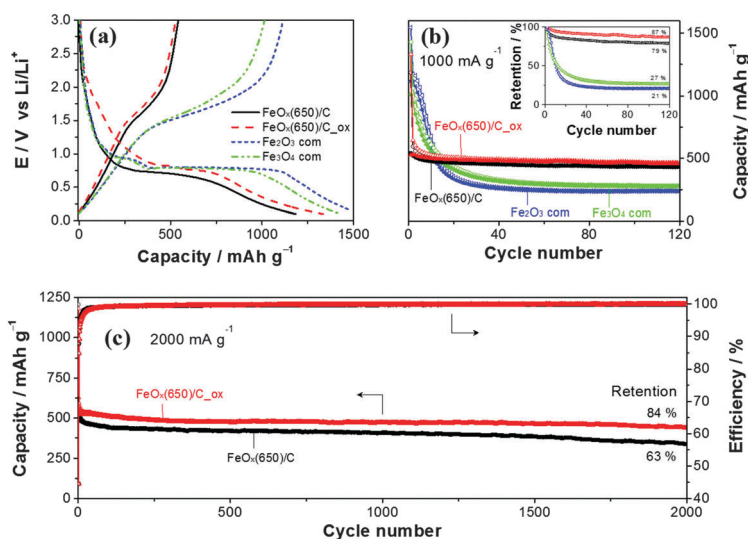


Fig. 4 (a) Electrochemical characterization of  $\text{FeO}_x(650)/\text{C}$ ,  $\text{FeO}_x(650)/\text{C}_{\text{ox}}$  and commercial  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ . (a) Potential profiles of the first cycle. (b) Capacity versus cycle number at  $1000 \text{ mA g}^{-1}$  (ca. 2C) and the corresponding capacity retention in the inset. (c) Capacity versus cycle number at  $2000 \text{ mA g}^{-1}$  (ca. 4C).



Indeed, the main limitation of iron oxides, even for the nanostructured ones (BET surface area of *ca.* 40 m<sup>2</sup> g<sup>-1</sup> for the commercial Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>), is its short cycle life, especially at high C-rates. In contrast, both composites show excellent cycle life retaining 87% of the initial reversible capacity after 120 cycles. In addition, the coulombic efficiency of the composites after the first cycle outweighed those of the commercial ones indicating higher Li-ion storage reversibility of the composites. Even at 2000 mA g<sup>-1</sup> (4C), both composites delivered remarkable electrochemical performance, *e.g.* FeO<sub>x</sub>(650)/C<sub>ox</sub> (Fig. 4c) storage 445 mA h g<sup>-1</sup> (84% retention) after 2000 cycles. The slightly higher capacity of the oxidized composite may be attributed to the lower metallic iron content, while the higher capacity retention after 2000 cycles (84% *vs.* 63%) could have resulted due to the removal of the low conducting amorphous carbon. To the best of our knowledge, FeO<sub>x</sub>(650)/C<sub>ox</sub> delivers the best long term cyclability observed for iron oxide based electrodes at high C-rates comparable to the remarkable cycle life recently reported for FeOOH at 2.5C.<sup>31</sup> Electrochemical impedance spectroscopy (EIS) revealed easy charge transfer for FeO<sub>x</sub>(650)/C<sub>ox</sub> (Fig. S16, ESI<sup>†</sup>). In contrast to commercial iron oxides, the EIS spectra of FeO<sub>x</sub>(650)/C<sub>ox</sub> did not evolve significantly upon cycling which was in good agreement with its excellent cyclability (more details in the ESI<sup>†</sup>). For comparison, commercial CNTs before and after oxidation (air-annealed at 300 °C) were tested (Fig. S17, ESI<sup>†</sup>). At 2000 mA g<sup>-1</sup>, both samples stored reversibly only *ca.* 130 mA h g<sup>-1</sup> between 3.0 and 0.1 V. The electrochemical performances of composites prepared at 550 °C are also presented in the ESI<sup>†</sup> (Fig. S18 and S19). Here, the capacity retention of the oxidized samples decreased to 63% after 2000 cycles at 2000 mA g<sup>-1</sup> (4C). The relatively lower graphitic character of the carbon coating obtained at 550 °C is likely responsible for the poorer electrochemical performance. The specific charge of FeO<sub>x</sub>(650)/C<sub>ox</sub> was also evaluated at lower C-rates after prolonged cycling (Fig. S20, ESI<sup>†</sup>) revealing an excellent C-rate retention. The specific charge at 0.5C also shows that the average state of oxidation of Fe in FeO<sub>x</sub> is not +3, but lower. A value of *X* = 0.63 (+1.25) was electrochemically estimated (ESI<sup>†</sup>).

In conclusion, we showed that iron oxide based electrodes can operate at high C-rates and with long cycle life demonstrating the feasibility of using iron oxides as negative electrode materials for safer high-power Li-ion batteries. We synthesized carbon-coated FeO<sub>x</sub>/CNTs composites by controlled pyrolysis of ferrocene, which delivered a specific capacity retention of 84% (445 mA h g<sup>-1</sup>) after 2000 cycles at 2000 mA g<sup>-1</sup> (4C).

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