

Reversible Lithium Reaction with Nanostructured, Short-Range-Order Ferric Oxides

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In the search for cost-effective and environmentally favorable alternatives to the LiCoO_2 cathode material for rechargeable lithium batteries, oxides of iron have attracted considerable attention. Hematite or $\alpha\text{-Fe}_2\text{O}_3$ is one of the most naturally abundant and stable iron oxides and has been studied in the past for its electrochemical properties. Hematite possesses a rhombohedral structure with R-3C space group. The structure consists of a hexagonal packing of oxygen ions with $2/3^{\text{rd}}$ of the octahedral sites occupied by Fe. The Fe distribution is such that the structure possesses pairs of face-sharing $[\text{Fe-O}_6]$ octahedra in the crystallographic c direction, with one vacant octahedron on either side of these pairs. The face sharing of these octahedra causes the Fe to sit slightly off-center at the octahedral site and also makes occupation of the vacant octahedra by another cation, such as Li^+ , energetically unfavorable.

Thackeray et al. investigated the characteristics of hematite upon discharge versus lithium¹. They reported that the hexagonal lattice undergoes a transformation to cubic upon intercalation of a very small amount of Li (ca. 0.1 $\text{Li/Fe}_2\text{O}_3$). Such a transformation likely helps to reduce the electrostatic repulsion by resulting in larger inter-cation distances. Recently, Larcher et al.²⁻³ contrasted the behavior of a micro-metric $\alpha\text{-Fe}_2\text{O}_3$ versus a nano-metric $\alpha\text{-Fe}_2\text{O}_3$. They reported that the hexagonal to cubic phase transformation is much delayed in the nano-metric sample, which showed superior electrochemical performance.

We have recently reported⁴ a nanocrystalline Fe_2O_3 synthesized via a low-temperature aqueous synthesis route, which exhibits excellent electrochemical properties. At C/50 the material delivers a discharge capacity of 249 mAh/g, corresponding to reaction with 1.48 Li per formula, with > 99% reversibility. At C/5, the material yields a capacity of 195 mAh/g with nearly perfect capacity retention upon repeated cycling. The specific energy of the material is between 400-450 mWh/g, close to the 500 mWh/g of the commercially used LiCoO_2 .

A detailed study of this material and related materials reveals that in addition to particle size, the degree of crystallinity or amorphicity, defects and vacancies in the crystal structure are also important factors determining the electrochemical properties. In this report, the electrochemical properties of $\alpha\text{-Fe}_2\text{O}_3$ as a function of crystallinity and grain size will be presented and the interesting trend observed of the electrochemical performance from long-range-order to short-range-order compounds will be discussed. The results illustrate the advantages of short-range-order structures in yielding large single-phase, reversible intercalation capacities, superior reversibility and improved kinetics as rechargeable lithium battery cathodes. Associated mechanistic questions will be addressed.

References:

1. M. M. Thackeray, W. I. F. David and J. B. Goodenough, *Mat. Res. Bull.* **17**, 785 (1982).
2. D. Larcher, C. Masquelier, D. Bonnin, Y. Chabre, V. Masson, J.-B. Leriche and J.-M. Tarascon, *J. Electrochem. Soc.*, **150**, A133 (2003).
3. D. Larcher, D. Bonnin, R. Cortes, I. Rivals, L. Personnaz and J.-M. Tarascon, *J. Electrochem. Soc.*, **150**, A1643 (2003).
4. J. J. Xu and G. Jain, *Electrochem. & Solid State Lett.*, **6**, A190 (2003).