

Iron Oxyhydroxides as Rechargeable Lithium Battery Cathodes: Crystallinity and Particle Size Effects

Gaurav Jain and Jun John Xu

Department of Ceramic and Materials Engineering
Rutgers, The State University of New Jersey
Piscataway, NJ 08854

Iron oxides and oxyhydroxides constitute a rich class of compounds which occur naturally in many different crystal structures and phases and have been extensively studied. Synthetic methods for preparation of these compounds have also been extensively investigated¹. The abundance, low costs and environmental benignity of these compounds make them particularly attractive as electrode candidates for lithium batteries, and their rich solid-state chemistry would suggest possibilities for desired electrochemical properties. These factors have inspired a number of investigations²⁻⁵.

In the present work, goethite or α -FeOOH compounds have been studied for lithium intercalation and the effects of crystallinity and particle size on their electrochemical characteristics investigated. A nanostructured, largely amorphous goethite (a-FeOOH)⁶, a nanocrystalline goethite (n-FeOOH) and a microcrystalline goethite (m-FeOOH) sample with marked distinctions in crystallinity and particle sizes have been synthesized (Fig. 1). Differences are seen in the phase transformation behavior of these samples upon reaction with lithium. At the same time, interesting trends in their electrochemical properties are observed. The microcrystalline α -FeOOH sample readily undergoes a phase transformation upon reaction with lithium during discharge. Upon charging, the sample displays large hysteresis and poor reversibility. In contrast, the nanostructured samples, n-FeOOH and a-FeOOH, appear to exhibit a much reduced tendency to undergo phase transformations and show improved reversibility, with lower hysteresis on charging. The nanostructured amorphous a-FeOOH sample, in particular, shows nearly perfect reversibility over repeated cycling, excellent rate capability and superior overall electrochemical properties than the microcrystalline and nanocrystalline samples.

The nanostructured amorphous sample yields a capacity of 214 mAh/g at a C/10 rate, with nearly perfect reversibility and capacity retention over repeated cycling. At the same rate, the n-FeOOH sample yields a reversible capacity of 170 mAh/g and the m-FeOOH sample a capacity of < 100 mAh/g, after a large drop in capacity in the first cycle, as shown in Fig. 2. The high rate properties of the a-FeOOH sample are also very interesting; the sample yields a capacity of 170 mAh/g at C/1 rate or 5 mA/cm², with perfect charge/discharge reversibility and capacity retention over extended cycling.

Goethite or α -FeOOH possesses a 2x1 tunnel structure similar to that of diasporite (α -AlOOH) or ramsdellite (MnO₂). A phase transformation in this compound upon reaction with lithium, as observed in the case of the microcrystalline m-FeOOH, appears likely since the tunnels in this compound have H⁺ ions residing in them and would not be able to accommodate Li⁺ intercalation. In this respect, the apparent large single-phase intercalation capacities of the n-FeOOH and a-FeOOH samples are indeed intriguing. Lack of long-range-order in these compounds and the nanostructured morphology

appear to suppress the tendency for global structural changes and allow accommodation of lithium ions even though such intercalation in long-range-order counterparts would entail build-up of electrostatic repulsion forces at the atomic scale and strain in the microscopic scale leading to phase transformations. In addition, defects in the structure of the n-FeOOH and a-FeOOH samples, seen in the form of Fe vacancies, also appear to play a role in allowing lithium intercalation without inducing phase transformations.

In this contribution, synthesis and electrochemical properties of these compounds will be presented. Results of x-ray diffraction analysis of the compounds conducted at the end of first discharge and charge steps as well as after repeated cycling will be shown to illustrate their phase behaviors. Detailed discussions on structural aspects, comparing long-range-order versus short-range-order structures, as well as effects of particle size on electrochemical properties, will be presented.

References

1. U. Schwertmann and R. M. Cornell, *Iron Oxides in the Laboratory*, pp. 61, VCH, Germany (1991).
2. M. M. Thackeray, W. I. F. David and J. B. Goodenough, *Mat. Res. Bull.* **17**, 785 (1982).
3. K.M. Abraham, D.M. Pasquariello and E.B. Willstaedt, *J. Electrochem. Soc.*, **137**, 3, 743 (1990).
4. S. Morzilli, B. Scrosati and F. Sgarlata, *Electrochim. Acta*, **30**, 10, 1271 (1985).
5. R. Kanno, T. Shirane, Y. Kawamoto, Y. Takeda, M. Takano, M. Ohashi and Y. Yamaguchi, *J. Electrochem. Soc.*, **143**, 8, 2435 (1996).
6. G. Jain, C. J. Capozzi and J. J. Xu, *J. Electrochem. Soc.*, **150**, A806 (2003).

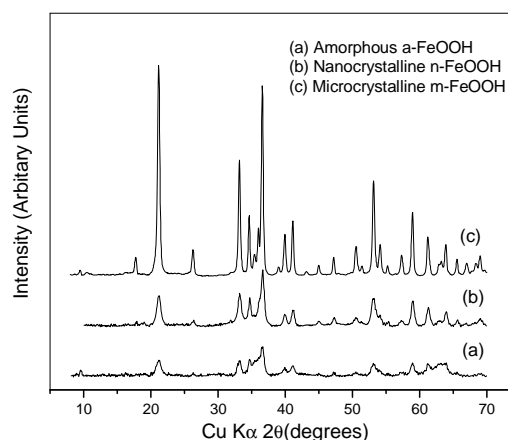


Figure 1. XRD pattern of the FeOOH samples.

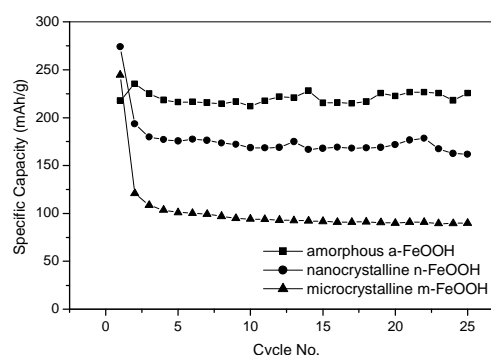


Figure 2. Cycling performance of the FeOOH samples at C/10.