

NOVEL NANO-SIZED IRON OXYHYDROXIDE AND IRON OXIDE COMPOUNDS AS LITHIUM INTERCALATION CATHODES

Jun John Xu, Gaurav Jain and Jingsi Yang

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

Iron based compounds constitute a most attractive class of lithium intercalation host materials from environmental and cost standpoints. A large number of iron compounds, from oxides to sulfides to phosphates, have been investigated as intercalation cathodes for rechargeable lithium batteries. Achieving good electrochemical performance, however, remains a challenge for most of these compounds. For instance, layer-structured LiFeO_2 [1-3] compounds, which have received much attention, show a low intercalation capacity of typically 100 mAh/g and exhibit poor cyclability, partly due to the inherent instability associated with the Fe^{4+} cation. Compounds such as $\alpha\text{-Fe}_2\text{O}_3$ [4-7], spinel-based LiFe_5O_8 and $\gamma\text{-Fe}_2\text{O}_3$ [8-9] also show very low intercalation capacities in the voltage range suitable for cathodes and poor reversibility for deep discharge.

We report here novel nano-sized iron oxyhydroxide and iron oxide compounds, synthesized via a low temperature aqueous solution route, that exhibit excellent electrochemical characteristics. An aqueous Fe^{2+} precursor is reacted with NaOCl in an alkaline medium, leading to instantaneous precipitation. By careful optimization of the synthesis parameters, nanosized powders of nearly amorphous iron oxyhydroxide are obtained. Upon charge/discharge cycling at a C/10 rate, between 1.5 V to 4.3 V versus Li/Li^+ , the material delivers a specific capacity of 215 mAh/g with nearly perfect capacity retention over 30 cycles. At a C/100 rate, the material delivers an intercalation capacity of 0.9 Li/Fe, or 260 mAh/g, with nearly perfect reversibility. The nano-sized amorphous structure of the compound appears to be rather stable, allowing reversible lithium intercalation and nearly perfect capacity retention upon cycling at close to the theoretical intercalation capacity corresponding to the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.

Dehydration of the as-prepared oxyhydroxide material at 250°C in air for 24 hours yields a nanocrystalline $\alpha\text{-Fe}_2\text{O}_3$, as indicated by X-ray and electron diffraction. This nanocrystalline ferric oxide delivers intercalation of ca. 1.37 Li/ Fe_2O_3 , or 220 mAh/g, between open circuit voltage and 1.5 V versus Li/Li^+ , at a C/5 rate. Conventional, microcrystalline $\alpha\text{-Fe}_2\text{O}_3$ typically yields intercalation of merely 0.1 Li/ Fe_2O_3 , an order of magnitude lower, at similar discharge rates and in the same voltage range. The dramatic advantage of the nanocrystalline ferric oxide is clearly evident from these results. Upon cycling of the nanocrystalline ferric oxide between 1.5 V and 4.3 V versus Li/Li^+ , the capacity fades in the first 4-5 cycles and stabilizes at 195 mAh/g, with virtually no fading over the next 40 cycles. At a C/50 rate, the material allows intercalation of 1.48 Li/ Fe_2O_3 , or 249 mAh/g, with nearly perfect reversibility. This intercalation capacity is even higher than that reported by Thackeray et al [4] for microcrystalline $\alpha\text{-Fe}_2\text{O}_3$ under open circuit or equilibrium conditions, suggesting some unique thermodynamic effect of the nano-sized material.

In this contribution, the synthesis, processing, structural and electrochemical characterization of these materials will be reported. The effect of their novel structures and morphologies, and the presence of structural water in the oxyhydroxide material, on intercalation properties will be discussed.

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