

**HIGH CAPACITY, HIGH PERFORMANCE
AMORPHOUS MANGANESE-BASED CATHODES
PREPARED
BY AN AQUEOUS OXIDATION ROUTE**

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Manganese-based compounds are most attractive as lithium battery cathodes owing to their low cost, environmental friendliness and the battery community's familiarity with them. The most studied forms of manganese oxides, namely, the spinel and layered lithium manganese oxides, typically synthesized by high-temperature solid state reactions, have however been plagued by relatively low capacities and poor cycling performance. In recent years, various low temperature solution synthesis procedures have been emerging as novel routes to new metastable phases of manganese-based intercalation compounds with unique structures and morphologies. Some recent reports [1-6] have shown that completely x-ray amorphous manganese oxides possess dramatically higher lithium intercalation capacities, approximately 2-3 times that of the crystalline phases. An aqueous reduction synthesis route to amorphous manganese oxides has been reported by Xu et al [1] exhibiting a remarkably high capacity of 435 mAh/g. Leroux et al [2] and Palos et al [3] also reported aqueous reduction synthesis of amorphous manganese oxides that showed specific charge capacities in the range of 160-220 mAh/g, higher than the capacity of most manganese based crystalline cathodes (120 mAh/g). Capacity retention with cycling however remains a challenge with most of these high capacity amorphous oxides synthesized following a similar aqueous-reduction strategy. Kim et al [4] reported amorphous manganese oxyiodides with a high capacity of 275 mAh/g at high discharge rates and superior cycling performance for materials synthesized in a non-aqueous medium. The manganese oxyiodides synthesized in the aqueous medium [5] however showed a lower intercalation capacity of 200 mAh/g.

We have developed an aqueous oxidation synthesis process for amorphous manganese oxides that yields a number of advantages over the reduction process followed for amorphous manganese oxides hitherto. This oxidation strategy yields good control over the oxidation state of the manganese in the resultant oxide and allows easier manipulation of the chemistry of the oxide to attain desirable electrochemical properties. We synthesized powders as pure (undoped) amorphous manganese oxides with very fine particle sizes and high surface areas (150-300 m²/g) that exhibit capacities close to 350 mAh/g for slow discharge rates of C/100 or 30 – 35 μ A/cm², a value of 1.51 Lithium per manganese. For discharge at high rates of C/5 or 0.6-0.7 mA/cm², these materials yield capacities close to 250 mAh/g. The high capacity metastable structure of these un-doped amorphous manganese oxides however, shows a tendency to undergo gradual structural relaxations, stimulated by the movement of lithium ions during repeated cycling, leading to a capacity fading of 0.5-1% per cycle. Utilizing the ease of cationic doping with the oxidation process, we have developed amorphous manganese oxides doped with varying contents of other 3d transition metals. These

doped amorphous manganese oxides have yielded a significant enhancement in the capacity retention with cycling, showing capacity fading of less than 0.3% per cycle. Moreover, the doped samples indicate a considerable improvement in the rate performance leading to an intercalation capacity much higher than the undoped amorphous manganese oxides at high rates.

In this contribution the novel oxidation synthesis route to amorphous manganese oxides will be discussed. Strategies involving controlled doping of the amorphous oxides will be presented. Electrochemical data of the undoped manganese oxides indicating the association of capacity fading with structural relaxation and electrochemical results for the doped manganese oxides elucidating the enhancement of cycling performance as well as rate capabilities with optimum levels of cationic doping will be presented and discussed.

References:

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