Optimization and Characterization of the Thermal Synthesis of Lithiated Manganese Dioxide, $Li_{0.33}MnO_2$, for Li-ion Batteries

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Preparation of the majority of positive electroactive materials for Li-ion batteries involves a thermal processing step as the last step in their synthesis. The experimental conditions (e.g., heating temperature, duration, atmosphere) under which this takes place are significant in determining the properties of the final material, which, in turn, affect the electrochemical performance. Optimizing this process is therefore of primary importance to enhance the specific capacity and cycling performance of these materials.

It has been shown that Li_xMnO_2 phases (where $x \leq 0.33$) show good capacity retention upon cycling in Li-ion cells [1, 2]. The low cost of these MnO_2-based materials (estimated at ~1% of the cost of Co raw materials) and their increased safety margin to over-charge conditions, makes them an attractive Li-ion cathode candidate [3, 4].

In this work we demonstrate a method for identifying the optimum thermal synthesis temperature and time for the preparation of $Li_{0.33}MnO_2$, from γ-MnO_2 and $LiNO_3$ using a melt-impregnate method [2]. Kinetic analysis of the thermal processes occurring during $Li_{0.33}MnO_2$ formation was performed using iso-conversional methods [5]. The modeling and analysis arising from monitoring the differential thermal analysis (DTA) signal during material formation gave rise to the pre-exponential factor and, most importantly, the activation energy for the transition. The activation energy was found to increase with increasing extent of conversion, in the range 250-500 kJ/mol.

This kinetic analysis technique was then used to determine the isothermal heating time at various temperatures to theoretically completely convert the material from the precursors to single-phase $Li_{0.33}MnO_2$. The effect of these heat treatment regimes on material structure, morphology and composition is investigated using various physical techniques, including X-ray diffraction, gas adsorption and ICP-OES. Further, the electrochemical characteristics of these materials are examined at two discharge rates, 5 and 30 mAh/g.

References

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