

Oxalatos mixtos de metales de transición y capacidades no-faradaicas para electrodos negativos en baterías de ión-litio.

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In the last decade, a large number of compounds never envisaged to be possible electrode materials in lithium batteries have shown reversible reactions with lithium. Particularly, conversion electrodes involving transition metal oxides,^{1,2} and, more recently, transition metal fluorides,^{3,4} show a reduction of the metal ions to the metallic state together with the formation of lithium oxide or lithium fluoride, respectively. Recently, we were able to extend this process to submicrometric particles of manganese carbonate⁵ and iron oxalate.⁶ This study revealed that MnCO₃ and FeC₂O₄ can be used directly as a conversion electrode vs. lithium. The discharge of lithium test cells takes place by a different conversion reaction that observed for the oxide produced during the thermal decomposition of the carbonate (MnO) or oxalate (FeO). The structural and electrochemical characteristics of Fe, Co and mixed Fe-Co oxysalts as anode material are discussed on this work

The synthesis of transition metal oxalates nanoparticles was carried out by the reverse micelles method. The resulting hydrated transition metal oxalates showed reflections corresponding to an orthorhombic phase. All compounds with different Fe-Co ratio showed similar patterns. Low-temperature thermal dehydration of the as-prepared oxalates was used to obtain the anhydrous materials. Electron microscopy revealed a ribbon-like particle morphology, as well as the presence of a complex porous system after dehydration. Bulk commercial samples with micrometric particles were also investigated.

The electrochemical tests, was carried out in a two-electrode Swagelok-type cells, using 1M LiPF₆, in EC:DEC as the electrolyte. Galvanostatic charge/discharge studies were carried out at different C rates. The first discharge capacity reached a maximum value of ca. 1150 mAhg⁻¹ with an extended plateau around 1 V versus Li. By analogy with previous conversion electrode materials the first step can be associated to the formation of iron metal. An in-depth ⁵⁷Fe Mössbauer spectroscopy and XANES study have been developed to account for this interpretation. For these materials, the 2nd to 75th cycles present reversible capacities between 550 and 600 mAhg⁻¹.

An analysis of voltammetric data by the procedure described by Brezesinski et al.,⁷ showed that the first discharge is mostly faradaic and irreversible, and overpasses the theoretical capacity. The contribution of irreversible reactions with the electrolyte is demonstrated. On further cycles, the faradaic capacity gets closer to the theoretical capacity of the proposed conversion reaction, while the extra capacity comes from non-faradaic origin.

Referencias

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