New electroactive materials for lithium-ion rechargeable batteries

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NEW ELECTROACTIVE MATERIALS FOR LITHIUM-ION RECHARGEABLE BATTERIES

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Chapter 1.

Abstract

Rechargeable batteries are becoming more and more important in our life, and get increasingly present in our civilization. They supply energy to many battery-powered appliances and open new fields of everyday application (Pocket PCs, mobile phones, household appliances etc.), not to mention the electrically powered car application, which is still an attractive area. In this evolving field, Li-ion technology seems to be superior to other technologies, because of its high performances, in terms of specific charge and in terms of work temperature range.

Schematically a Li-ion accumulator is composed of:

- Anode (negative pole): constituted by special kind of graphite
- Non-aqueous electrolyte
- Cathode (positive pole): constituted by compounds (mainly oxides) which allow the reversible insertion of Li^+ within their crystal structure.

The term “Li-ion” derives from the fact that inside the system lithium is present only as ionic specie, metallic lithium is absent.

In Li-ion technology, $LiCoO_2$ is the most extensively used cathodic material with a specific charge of about 140Ah/kg. Despite this interesting performance, its cobalt content causes problems of costs and environmental pollution.

The actual research is thus devoted to eliminate, or at least to reduce, these problems. The research of this thesis was exclusively oriented to the synthesis and characterization of cathodic materials. The starting point was the previous

work of a mixed Mn-Ni based oxide, $LiMn_{0.5}Ni_{0.4}Al_{0.1}O_2$, from which performances analogues to $LiCoO_2$ have been obtained.

Several products have been synthesized and characterized with electrochemical (cyclovoltammetry, chronopotentiometry) and structural (X-ray diffraction, scansion electron microscopy and transmission electron microscopy) techniques. All products obtained belong to the crystallographic space group $R\bar{3}m$ (n.166), they have 2D layered structure (see Figure 25).

Two of the new products synthesized, $LiMn_{0.283}Ni_{0.566}Co_{0.141}Al_{0.01}O_2$ and $LiMn_{0.335}Ni_{0.495}Co_{0.160}Al_{0.01}O_2$ respectively, furnished 170Ah/kg and 160Ah/kg. This made them good candidates for a $LiCoO_2$ replacement in Li-ion batteries, because the materials are cheaper, better performers and have less environmental impact. In both products a small amount of aluminum is present (1%), because this is supposed to stabilize the structure and reduce the distortion due to the Jahn-Teller effect (which acts mainly on Mn and Ni).

A new empirical description, following the specific charge vs. cycles, has been proposed and applied to all products synthesized in this work. According to this description, a correlation between cell parameter and electrochemical performances is visible: smaller cell parameters ***a*** and ***c*** favour the electrochemical performances.

Several other products as TiO_2-(anatase) based materials were also tested; they performed very high specific charges, which is mainly due to the low Li^+ insertion potential (~1.8 Volts compared to 3.7 Volts of Mn-based oxides), and it furnished a specific energy of approximately the half, in comparison to the best Mn-based oxides.

Noticeable were the performances of $H_2V_3O_8$ nanofibers, which show a specific energy of 10-15% higher than the best Mn-based products, with a current rate 13 times higher. Unfortunately, these amazing performances last only for 50-60 cycles, after that, the product undergoes quick fading, which does not make them competitive to Mn-oxides.