Towards Safe, Low Cost and Sustainable Lithium Ion Polymer Batteries

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In the present lithium ion technology large interest is focused on the development of battery systems characterized by a high degree of reliability and safety, especially in view of their prospected use in the hybrid vehicle market. In this respect, it appears mandatory to select electrodes having operating voltage evolving within the stability window of the electrolyte. In addition, high capacity, high rate, long cycle stability, low cost and environmental compatibility are also highly welcome characteristics. Finally, an extra step towards reliability and cell design modularity may be achieved by moving from the standard liquid-like electrolyte to a polymer electrolyte configurations.

In this work, we have chosen suitable electronic materials and combined them with a PVdF based gel electrolyte [1] in order to realize a safe, low cost and sustainable lithium ion polymer battery.

As positive electrodes, lithium iron phosphate and lithium manganese spinel appear at the present as the most suitable choices. Lithium iron phosphate LiFePO₄ [2] has an olivine structure that, upon electrochemical lithium extraction, evolves reversibly into triphylite, FePO₄:\n
\[
\text{LiFePO}_4 \rightleftharpoons \text{FePO}_4 + \text{Li}^+ + e^- \]

this being accompanied by a very flat voltage evolving around 3.45 V vs. Li/Li⁺ at 25 °C. LiₓM₃Mn₄₋ₓO₁₂ having a spinel structure from which lithium can be reversibly extracted at an high average potential than in the case of the olivine: 4.0-4.5 V according to the nature and the amount of the M substituent.

Among negative electrodes, cycle stability is still an unresolved problem. Graphites and the more recent lithium alloys suffer of an irreversibility in the first cycles. An interesting alternative is lithium titanium oxide, LiₓTi₁₋ₓOₓ which has a spinel-type structure where the electrochemical process involves the reversible rearrangement of the tetrahedral lithium ions in the spinel framework with a process occurring at a stable voltage of −1.55 V vs. Li/Li⁺ at 25 °C and with almost zero structural strain and irreversibility [3]:

\[
\text{Li}[(\text{Li}_{0.5}\text{Mn}_{1.5})\text{O}_4 + \text{Li}^+ + e^- \rightleftharpoons \text{Li}[(\text{Li}_{0.5}\text{Mn}_{1.5})\text{O}_4] \]

The proposed Li-ion cells operate according to the following charge-discharge process: LiFePO₄ + LiₓTi₁₋ₓOₓ ⇌ FePO₄ + LiₓTi₁₋ₓOₓ

\[
\text{LiM}_{y}\text{Mn}_{1-y}\text{O}_4 + x\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4 \rightleftharpoons \text{Li}_{1.33}\text{M}_{y}\text{Mn}_{1-y}\text{O}_4 + x\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4
\]

In Figure 1 is reported a typical cycle at room temperature of the Li₁.₃₃Ti₁.₆₇O₄/ LiFePO₄ plastic battery [4]. The cell exhibits stable voltage and safely operates within the stability window of the electrolyte. Thus this new type of lithium ion batteries may be considered as a suitable power sources for electric and hybrid vehicles.

References.