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A study on the usage of cathode materials for lithium batteries

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Abstract
After an introduction to lithium insertion compounds and the principles of Li-ion cells, we present a comparative study of the physical and electrochemical properties of positive electrodes used in lithium-ion batteries (LIBs). Electrode materials include three different classes of lattices according to the dimensionality of the Li^+ ion motion in them: olivine, layered transition-metal oxides and spinel frameworks. Their advantages and disadvantages are compared with emphasis on synthesis difficulties, electrochemical stability, faradaic performance and security issues.

Keywords: lithium-insertion compounds; Li-ion batteries; phase diagram; safety

Introduction

Since three decades, lithium-ion batteries (LIBs) have been amongst the most promising chemical-electrical energy converter (rechargeable or secondary sources) for power electronic devices such as cellular phones, laptop computers, camera, *etc.* In 2002, the commercial success of LIBs based on carbon, a non-aqueous electrolyte, and lithium cobaltate ($LiCoO_2$) offered great promise as being the first rechargeable battery technology for personal electronics in the near future.

Today, this technology is applied to green transportation systems such as electric vehicles (EVs) or hybrid EVs (HEVs). The increase in the demand of highly functionalized applications always includes higher power density, higher energy density, excellent charge-discharge cycling performance, and more safety.

A key element that limits the performance of the batteries is the active element of the positive electrode, and it is also the most expensive part. From 2000 to present, continuous efforts have been devoted by Good enough to propose and study oxides compounds based on transition-metal (TM) element with focus to those compounds that crystallize in structures that favour large mobility of the Li^+ ions in order to transfer energy during the redox reaction. Milestones were made in 2000 for the $LiCoO_2$ layered structure, 2006 for $LiMn_2O_4$ spinels and 2007 for the Li*M*PO_4 (*M* = Fe, Mn, *etc.*) olivine family.

Rapidly, all these substances have been widely studied and effectively applied to the construction of commercial Li-ion batteries. Layered materials are used as cathodes for high-energy systems, while spinel oxides and olivines are considered in the case of high-power Li-ion batteries because low cost and long-life requirements, respectively. However, these lithium-insertion compounds must fulfill specific properties such as chemical stability, capacity, rate capability, toxicity, cost and safety. All of them, however, achieve theoretical specific capacity >140 mAh g−1 at a potential >3.4 V *vs.* Li0/Li^+.

This paper deals with the advantages and disadvantages of the positive electrodes materials used in Li-ion batteries: layered $LiCoO_2$ (LCO), LiNi*y*Mn*y*Co1^{-2}*y*O_2 (NMC), spinel $LiMn_2O_4$ (LMO), $LiMn1.5Ni0.5O_4$ (LMN) and olivine $LiFePO_4$ (LFP) materials. Despite thousands of published papers considering the development of such materials, comparative studies of their properties as active electrochemical elements are rather scarce. It is our purpose to report difficulties of synthesis, electrochemical stability and performance, and security issues of these three classes of lattices from the point of view of Li^+ ion motion in them.

As effective lithium-insertion compounds, special attention is given to the olivine Li(Fe, Mn)PO_4 that is considered as the most promising candidate for the next-generation of large-scale Li-ion batteries, not only for use in EVs or HEVs, but also to solve intermittence on smart grids and energy storage for high-power applications.

Research study

The crystal structures of the three classes of Li-insertion compounds are shown in Figure. Their classification corresponds to the ion diffusion pathways and activation energy that govern Li-ion transport within the electrode materials. Archetypes are the two-dimensional Li [*M*] O_2 with *M* = Co, Ni, (Ni*x*Co1−*x*) or (Ni*x* Mn*y* Co*z*), the three-dimensional Li[*X*] 2O4 with *X* = Mn, (Mn1−*y*/2Li*y*/2) or (Mn3/4Ni1/4) and uni-dimensional Li [*M*'] PO4 with *M*' = Fe, Mn, Ni, Co or (Fe*y*Mn^{1-y}).

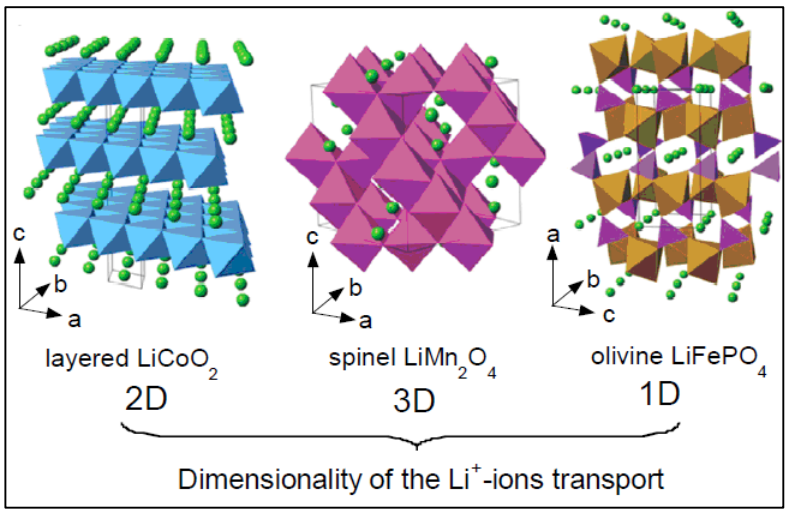

Fig 1: Crystal structure of the three lithium-insertion compounds in which the Li+ ions are mobile through the 2-D (layered), 3-D (spinel) and 1-D (olivine) frameworks.

Li[*M*]O_2 (*M* = Co, Ni) oxides are isostructural to the layered α-$NaFeO_2$ (space group *R*3*m*, No. 166) with the oxygen ions close-packed in a cubic arrangement and the TM and Li ions occupying the octahedral sites of alternating layers with an ABCABC… stacking sequence called "O3-type" structure.

In $LiCoO_2$, the cobalt is trivalent in the electronic configuration (*t*2*g*)6(*eg*)0, *i.e.*, in the low-spin state (*S* = 0). However, LCO adopts the rhombohedral symmetry in the high temperature form, with Li in 3*a*, Ni in 3*b* and O in 6*c* sites. The unit-cell of the hexagonal setting contains three formula units. During the cycling of a lithium cell, the Li^+ ions are reversibly removed from and incorporated into this framework creating or annihilating vacancies within the lithium planes.

The $LiFePO_4$ structure consists in three non-equivalent O sites. Most of the atoms of the olivine structure occupy the 4*c* Wyckoff position except O(3) which lies in the general 8*d* position and Li^+ ions occupying only the 4*a* Wyckoff position (*M1* site on an inversion center). The Fe magnetic ions are in the divalent Fe^{2+} state and occupy only the 4*c* Wyckoff position (*M2* site in a mirror plane), *i.e.*, the center of the FeO_6 units. As a consequence, Fe is distributed so as to form FeO_6 octahedra isolated from each other in $TeOc_2$ layers perpendicular to the (001)-hexagonal direction.

In addition, the lattice has a strong two-dimensional character, since above a $TeOc_2$ layer comes another one vertical to the previous one, to build (100) layers of FeO_6 octahedra sharing corners, and mixed layers of LiO_6 octahedra and PO4 octahedra. The lithium iron phosphate material differs from the primary mineral triphylite Li (Mn, Fe) PO_4 by the fact that triphylite is only rich in iron, with some manganese ions also in the *M2* site. However, while the triphylite is a naturally occurring mineral, $LiFePO_4$ is an artificial product.

Also, the cell voltage *Voc* determined by the energies involved in both the electron transfer and the Li^+ transfer highlights the concept of rechargeable lithium batteries. While the energy involved in electron transfer is related to the work functions of the cathode and anode, the energy involved in Li^+ transfer is determined by the crystal structure and the coordination geometry of the site into/from which Li^+ ions are inserted/extracted.

Significance of the study

The stabilization of the higher oxidation state is essential to maximize the cell voltage and the energy density. The location of O:2*p* energy and a larger raising of the *Mn+*:*d* energies due to a larger Madelung energy make the higher valent states accessible in oxides.

That is why transition-metal oxide hosts were pursued as positive electrode candidates for Li-ion secondary batteries.

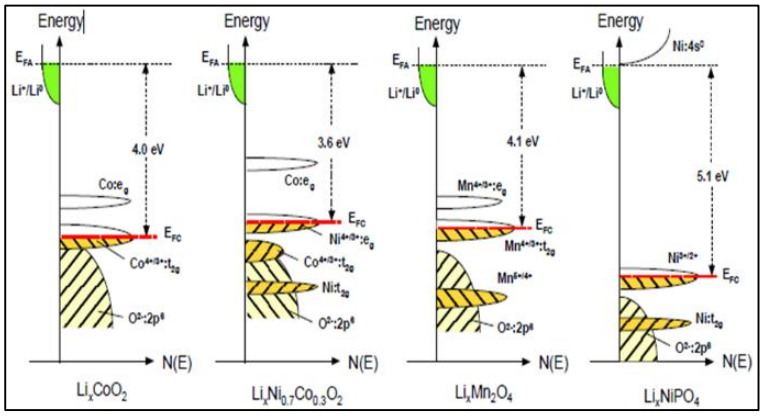

Fig 2: Comparison of the energy *vs.* density of states showing the relative Fermi level of the $Co^{4+/3+}$ redox couple for $LiCoO_2$, the $Ni^{4+/3+}$ redox couple for LiNi0.8Co0.2O_2, the Mn4+/3+ redox couple for LiMn2O_4 and the $Ni^{3+/2+}$ redox couple for $LiNiPO_4$.

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