

Review

## Review on electrode–electrolyte solution interactions, related to cathode materials for Li-ion batteries

Doron Aurbach<sup>a,\*</sup>, Boris Markovsky<sup>a</sup>, Gregory Salitra<sup>a</sup>, Elena Markevich<sup>a</sup>, Yossi Talyossef<sup>a</sup>,  
Maxim Koltypin<sup>a</sup>, Linda Nazar<sup>b</sup>, Brian Ellis<sup>b</sup>, Daniella Kovacheva<sup>c</sup>

<sup>a</sup> Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

<sup>b</sup> Department of Chemistry, University of Waterloo, Waterloo, Canada

<sup>c</sup> IGIC, Bulgarian Academy of Science, Sofia, Bulgaria

Available online 27 November 2006

### Abstract

In this paper we review some critical aspects related to interactions between cathode materials and electrolyte solutions in lithium-ion batteries. Previous results are briefly summarized, together with the presentation of new results. This review deals with the basic anodic stability of commonly-used electrolyte solutions for Li-ion batteries (mostly based on alkyl carbonate solvents). We discuss herein the surface chemistry of the following cathode materials:  $\text{LiCoO}_2$ ,  $\text{V}_2\text{O}_5$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ ,  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , and  $\text{LiFePO}_4$ . The methods applied included solution studies by ICP, Raman, X-ray photoelectron and FTIR spectroscopies, and electron microscopy, all in conjunction with electrochemical techniques. General phenomena are the possible dissolution of transition metal ions from these materials, which leads to changes in the active mass and a retardation in the electrode kinetics due to the formation of blocking surface films. These phenomena are significant mostly at elevated temperatures and in electrolyte solutions containing acidic species. Water-contaminated  $\text{LiPF}_6$  solutions can reach a high concentration of acidic species (e.g., HF), which is detrimental to the performance of materials such as  $\text{LiCoO}_2$  and  $\text{LiFePO}_4$ . Both  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  and  $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ , even when used as nanomaterials, show a high stability in commonly-used electrolyte solutions at high temperatures. This stability is attributed to unique surface chemistry that is correlated to the presence of Ni ions in the lattice.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Cathodes; Surface chemistry; Impedance; Capacity fading; Electrolyte solutions

### Contents

1. Introduction .....	491
2. Experimental .....	492
3. Results and discussion .....	493
3.1. On the anodic stability of the electrolyte solutions .....	493
3.2. On the surface chemistry of $\text{LiCoO}_2$ electrodes .....	493
3.3. On $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes .....	495
3.4. On $\text{LiFePO}_4$ electrodes .....	497
4. Conclusions .....	498
References .....	499

### 1. Introduction

In recent years, rechargeable Li-ion battery systems have become a prominent technology in the global battery market.

These batteries offer the highest energy density available to date for rechargeable batteries. While currently produced Li-ion batteries power mostly small devices such as cellular phones, portable computers and mobile electro-optic equipment, intensive world-wide efforts are taking place to push the technology even further to much more demanding applications such as large and fast batteries for electric vehicles.

\* Corresponding author. Tel.: +972 3 5318309; fax: +972 5351250.  
E-mail address: [aurbach@mail.biu.ac.il](mailto:aurbach@mail.biu.ac.il) (D. Aurbach).

The major factor that determines the energy density, rate capability (i.e., power density), and cost of Li-ion batteries is the cathode. The current predominant cathode material is LiCoO<sub>2</sub>, which is very expensive, possesses limited practical capacity (<140 mAh g<sup>-1</sup>) and rates, and suffers from stability problems at elevated temperatures in the common electrolyte solutions (e.g., a LiPF<sub>6</sub> salt in a mixture of alkyl carbonate solvents). Consequently, intensive R&D work on new cathode materials for Li-ion batteries is being carried out today by hundreds of research groups throughout the world. The major cathode materials currently being explored are LiMn<sub>2</sub>O<sub>4</sub> spinel [1], LiFePO<sub>4</sub> [2], LiMn<sub>1-x-y</sub>Ni<sub>x</sub>Co<sub>y</sub>O<sub>2</sub> [3], LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> [4], LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> spinel [5], LiNi<sub>1-x</sub>MO<sub>2</sub> (M = a third metal, Co, Al) [6], Li<sub>x</sub>VO<sub>y</sub> [7], and Li<sub>x</sub>M<sub>y</sub>VO<sub>z</sub> (M = a third metal such as Ca, Cu) [8]. Much attention is given to the development of reliable synthetic routes for these materials, their structural analysis and basic electrochemical behavior. Furthermore, the scientific community studying these cathode materials is reaching a very high level of precision in structural analysis, using synchrotron, X-ray radiation (for *in situ* XRD [9], XANES [10], EXAFS [11]), high resolution electron microscopy/electron diffraction [12], and solid-state NMR [13].

All cathode materials of interest for Li-ion batteries are reactive with the commonly-used electrolyte solutions, thus developing a rich surface chemistry [14]. There is strong evidence that most of the above-mentioned lithiated transition metal oxides are covered by surface films in solutions, due to spontaneous reactions with solution components [15]. Hence, the electrochemical behavior of most cathode materials may depend very strongly on their surface chemistry in solutions and phenomena such as surface film formation. Similar to Li and Li-C anodes, many types of cathodes for Li-ion batteries can also be considered as SEI [16] electrodes (i.e., covered by a Li-ion conducting interphase [16]). There are many possible reactions of Li<sub>x</sub>MO<sub>y</sub> materials with solutions that contain alkyl carbonate solvents and Li salts such as LiPF<sub>6</sub>. These include acid–base interactions between the Li<sub>x</sub>MO<sub>y</sub> and trace HF, which are inevitably present in LiPF<sub>6</sub> solutions, nucleophilic attack of the electrophilic alkyl carbonate molecules by oxygen ions on the transition metal oxide, surface-induced polymerization of cyclic alkyl carbonates to polycarbonates, and redox reactions with solution species (both reduction and oxidation processes that may lead to a change in the oxidation state of the transition metal, and to dissolution of transition metal ions into the solution). In contrast to the precision that can be achieved in the bulk analysis of the cathode materials, their rigorous surface analysis is much more difficult, because very thin surface films may be formed whose composition and structure can be profoundly influenced by contaminants in the solutions (even at the ppm level).

This paper describes some recent studies related to the surface chemistry of several cathode materials of interest. These include LiCoO<sub>2</sub>, LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub>, LiMn<sub>0.5</sub>Ni<sub>0.5</sub>O<sub>2</sub>, Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>, and olivines. Surface-sensitive techniques such as FTIR, Raman, XPS, and electron microscopy were used in conjunction with bulk analytical techniques (ICP, XRD) and electrochemical methods (voltammetry, chronopotentiometry, and impedance

spectroscopy). The effect of the particles' size on their reactivity (i.e., micro *versus* nano) was also explored.

## 2. Experimental

The LiCoO<sub>2</sub> used was a commercial product (OMG Inc., the particle size was several microns). Microparticulate LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>4</sub> was obtained from LG Chem. [17] (spinel structure, particle size of 2–3 μm). Microparticles (several microns in size) of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> were synthesized from LiOH, Mn, and Ni acetates via a solution reaction followed by solid-state/high temperature calcinations step, according to a published procedure [18]. Nanoparticles of LiNi<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>2</sub> and LiMn<sub>1.5</sub>Ni<sub>0.5</sub>O<sub>2</sub> were synthesized by the self-combustion reaction (SCR) modified by Kovacheva and co-workers [19]. Three LiFePO<sub>4</sub> olivine compounds were synthesized as summarized below:

1. “Sol–gel” LiFePO<sub>4</sub> (denoted as Sample 1) was produced by reacting stoichiometric amounts of Li<sub>3</sub>PO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and FeC<sub>6</sub>H<sub>5</sub>O·2H<sub>2</sub>O under flowing argon at 600 °C for 15 h, followed by a treatment under 7% H<sub>2</sub>/N<sub>2</sub> at 600 °C for 1 h. The final product contains 3% carbon. Aside from the carbon, the material was phase-pure as determined by XRD: no detectable iron phosphide or other impurities were present.
2. “Solid-state” LiFePO<sub>4</sub> (denoted as Sample 2) was produced by ball-milling stoichiometric amounts of FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, and Li<sub>2</sub>CO<sub>3</sub>, firing the mixture at 600 °C for 12 h, and then again at 700 °C in a flowing 7% H<sub>2</sub>/N<sub>2</sub> stream. The final product contains 3% C, surface FeP, and/or Fe<sub>2</sub>P as determined by a combination of elemental analysis, TGA, and XRD. The contributions of the phosphides were estimated to be <5%.
3. “Hydrothermal” LiFePO<sub>4</sub> (denoted as Sample 3) was produced by reacting H<sub>3</sub>PO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>, LiOH, and ascorbic acid in an autoclave (Parr pressure bomb) for 15 h at 190 °C. The solid product was sintered at 600 °C for 6 h under flowing argon. The material contains traces of Fe<sub>2</sub>P<sub>2</sub>O<sub>7</sub> and 1.8% carbon.

Thin film V<sub>2</sub>O<sub>5</sub> electrodes were produced by sputtering V<sub>2</sub>O<sub>5</sub> from pellets onto inert metal current collectors (e.g., gold foils) by high voltage ionization at high vacuum [20], as well as composite electrodes comprising nanoparticles of V<sub>2</sub>O<sub>5</sub>. The latter were produced in two stages: the formation of carbon-coated V<sub>2</sub>O<sub>3</sub> nanoparticles by the RAPET method [21], followed by heating them in air up to 400 °C, which formed nanoparticles of V<sub>2</sub>O<sub>5</sub> partially covered by a thin film of carbon layer [22].

In general, two types of electrodes were studied:

1. Composite electrodes comprising the active mass (≈80% by weight), carbon black, and polyvinylidene difluoride (PVdF) binder (≈10% by weight each) on Al foil current collectors.

Download English Version:

<https://daneshyari.com/en/article/1291555>

Download Persian Version:

<https://daneshyari.com/article/1291555>

[Daneshyari.com](https://daneshyari.com)