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Study of the nanosized Li_2MnO_3: Electrochemical behavior, structure, magnetic properties, and vibrational modes

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ABSTRACT

In this work, we synthesized nano-particles (20–80 nm) of Li_2MnO_3 using the self-combustion reaction and studied the electrochemical activity of electrodes prepared from this nano-material at 30, 45, and 60 °C. It was shown that the first Li-extraction from nano-Li_2MnO_3 occurs at much lower potentials (by 180–360 mV) in comparison with micron-sized Li_2MnO_3 electrodes. This can be associated with the higher surface-to-volume ratio, much shorter the diffusion path and the increased surface concentration of the electrochemically active sites. On the basis of magnetic susceptibility studies of nano-Li_2MnO_3 we proposed a model of disordered surface layer, containing Mn^{3+} or Mn^{2+} ions, both at low spin state, at the surface of these nano-particles. From the results of structural analysis (by X-ray and electron diffraction and vibrational Raman spectroscopy) of galvanostatically cycled nano-Li_2MnO_3 electrodes in Li-cells we came to a conclusion of partial transition of layered $LiMO_2$ to spinel-type ordering.

1. Introduction

Lithium manganese oxides $LiMnO_2$, $Li_{0.33}MnO_2$, $LiMn_2O_4$, $Li_2Mn_4O_9$, Li_2MnO_3, *etc.* are electroactive intercalation host materials in lithium cells. Among this family of oxides, Li_2MnO_3 is one of the most interesting compounds from the point of view of its structure and electrochemical behavior. Indeed, this oxide, in its microcrystalline form, is electrochemically inactive for lithium insertion and extraction between 2.0 and 4.4 V; however it delivers a high theoretical capacity of 460 mAh/g for total Li extraction. Li_2MnO_3 possesses an O3-type structure where interslab octahedral sites are only occupied by Li^+-ions, while Li^+ and Mn^{4+}-ions (in a ratio of 1:2) occupy slab octahedral sites [1]. In lithium and Mn^{4+}-rich two-component integrated $xLi_2MnO_3{\cdot}(1-x)Li(Mn–Ni–Co)O_2$ compounds, which are promising electrode materials for advanced rechargeable batteries, Li_2MnO_3 undergoes delithiation at >4.5 V during charge accompanied by partial oxygen release. These compounds are characterized by the formation of a cation ordering in the transition metal layers, which is very similar to that observed in Li_2MnO_3 [2]. Therefore, Li_2MnO_3 is considered as an interesting model compound and it has attracted much attention by several research groups involved in materials science, electrochemistry, and lithium batteries [3–7].

One of the challenges in the field of rechargeable lithium-ion batteries is the use of nanoparticles for cathode and anode materials. This in general should be considered as favorable for achieving high rate capability, since solid-state Li-ion transport in the bulk materials may be the rate-determining step for the entire intercalation–deintercalation processes. The use of nanoparticles leads to reducing to minimum the diffusion path for the electrons and the Li-ion transport, and to better accommodation of strain during Li^+ extraction/insertion. Furthermore, since the electrochemical active surface area is inversely proportional to the particle size, the electrodes comprising nanoparticles posses significantly larger surface area and have more active sites for the electrochemical reactions [8,9]. Hence for nano-particles, surface effects become more important than the bulk properties and they are still under debate in the literature [10]. In regard of the materials for positive electrodes in lithium cells, it was demonstrated that the cathodes comprising nanoparticles of $LiMn_{0.5}Ni_{0.5}O_2$ [11] and $LiMn_{1.5}Ni_{0.5}O_4$ [12] display faster kinetics than electrodes based on micrometric-size particles. It was also shown that the electrodes prepared from the spinel $LiMn_2O_4$ nanoparticles exhibited

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improved cycling performance, small charge-transfer resistance at the electrode/solution interface, a reduced the Jahn–Teller effect [13], and stabilization of the nano-$LiMn_2O_4$ cathodes in cycling at 60 °C [14]. In the case of nano-crystalline $LiCoO_2$ electrodes, the increased values of the discharge capacity were attributed to shorter diffusion distances that promote faster and more uniform Li^+ intercalation [15]. The dramatic effect of the small grain-size material (<20 nm) on increasing the electrochemical activity (capacity) was established recently for the lithium extraction/insertion reactions of $LiCrO_2$ electrodes [16]. From the other hand, nanoparticles with a relatively high surface area may be reactive with electrolyte solutions based on alkyl carbonate solvents and $LiPF_6$ (which unavoidably contain detrimental contaminants such as HF, trace water, PF_5 and POF_3). Possible reactions with solution species may develop undesirable detrimental side reactions (especially on the high surface area particles) leading to the passivation phenomena and high electrode impedance. In these systems, the irreversible oxidation of alkyl carbonate solvents resulting in the evolution of CO_2 accompanies the electrochemical processes at high anodic potentials.

For more than a decade, our groups have accumulated lots of information and reported numerous papers on the synthesis of nanoparticles of the lithiated transition metal oxides [11,12,14], their magnetic properties [17–21], vibrational modes studied by infra-red and Raman spectroscopy [22–24], and on the electrochemical performance of positive electrodes comprising nanoparticles of the active material in lithium cells [12,25,26]. Based on the literature reports in the field, it can be concluded that the possible use of nano-materials in electrodes for Li-ion batteries should be studied rigorously and specially for each electrode material individually taking into account the balance between the pros and cons [26,27]. In regard of the Li_2MnO_3 nano-particles, we realized that the literature data on their characterization and electrochemical performance are scarce. It was shown, for instance [9,28] that the electrochemical behavior of the nanocrystalline-Li_2MnO_3 electrodes depends upon the particles morphology, specific surface area, and annealing temperature of the as-prepared material. The authors [9] synthesized nano-Li_2MnO_3 by the solid-state reaction and studied the structural transformation of this material between layered $LiMnO_2$ and cubic $LiMn_2O_4$ spinel-type phases.

In the view of the studies related to the nanosized Li_2MnO_3 material, there is the necessity to revise intensely its structural, magnetic, and spectroscopic properties, aging behavior in solutions, and performance in positive electrodes of Li-cells, in comparison with that of the micro-metric Li_2MnO_3. The aim of the present paper was to synthesize nano-Li_2MnO_3 by the simple and inexpensive self-combustion reaction (SCR) and to study its structural and magnetic characteristics, vibrational modes, and the electrochemical behavior of electrodes comprising Li_2MnO_3 nanoparticles, in lithium cells at 30–60 °C. Along with conventional tools like X-ray and electron diffraction, transmission electron microscopy, and Raman spectroscopy, which characterize the samples on the nanometer and molecular scale, respectively, we applied in this work magnetic measurements that are the most sensitive to detect impurities of transition metal ions or local defects at the atomic level in lithiated oxides $LiMO_2$ (M is 3d metal) [29].

2. Experimental

2.1. Synthesis of nano-Li_2MnO_3

For the synthesis of Li_2MnO_3 by the SCR, we used aqueous solution contained the stoichiometric amounts of lithium nitrate and manganese(II) nitrate, which act as the oxidants, and sucrose as the fuel, similarly to the previous reports [14,30]. The oxidant/fuel ratio was 1:1. The as-prepared Li_2MnO_3 material was annealed at 400 °C for 1 h in air. These conditions of annealing (relatively low temperature and duration) were chosen in order to obtain a crystalline product with nano-sized particles since higher temperature of annealing and extended time may result in submicron and micron-sized particles and agglomerates [11,14,30,31]. Micronic size Li_2MnO_3 (used for comparison) was obtained from BASF and already explored [7].

2.2. Specific surface area measurements and chemical analysis of nano-Li_2MnO_3

The active surface area of materials was measured by Brunauer, Emmet and Teller (BET) method (Gemini 2375, Micromeritics, multipoint mode). The specific surface areas of nano- and micro-Li_2MnO_3 particles were ~14.0 and ~0.86 m^2/g, respectively. The nano-Li_2MnO_3 particles were of 20–80 nm, while the particle size of the micron-sized Li_2MnO_3 material was 20–50 μm [7]. The crystallite size estimated from the Debye–Sherrer equation was 30 ± 2 nm and 106 ± 11 nm, respectively for the nano-sized and micron-sized particles. The chemical analysis of the annealed product was carried out using the inductive coupled plasma technique (ICP-AES, spectrometer Ultima-2 from Jobin-Yvon Horiba). The composition of the material was determined as Li_2MnO_3, Mn:Li = 1:2 within the accuracy of the measurement ~98%.

2.3. X-ray diffraction (XRD), transmission electron microscopy (TEM), and electron diffraction measurements

X-ray powder diffraction (XRD) measurements were performed using an AXS D8 Advance diffractometer from Bruker Inc. (Germany) in the 2θ range from 10° to 110°, with a step size of 0.02°, at 15 s/step rate. The analysis of the XRD patterns was carried out using the PowderCell program [32] and the Fullprof program as described elsewhere [33]. TEM examinations of the nano-Li_2MnO_3 particles were performed with a LaB_6-120 kV Tecnai-12 transmission electron microscope and convergent beam electron diffractions (CBED) were taken using a 15 nm probe size. Samples for the TEM studies were prepared by methodology described in Ref. [34].

2.4. Analysis by Raman spectroscopy

Micro-Raman spectroscopy measurements were performed at room temperature using a micro-Raman spectrometer from Renishaw inVia (United Kingdom) equipped with a 514 nm laser, a CCD camera, and an optical Leica microscope. A 50× objective lens to focus the incident beam and an 1800 lines/mm grating were used. For calibration, a silicon standard was used (peak at 520 cm^{-1}). Raman spectra were collected at least from 10 to 15 locations on a sample. The set-up measurements provided 20–30 s of exposure times and 5 accumulations in the range of 200–2000 cm^{-1}. The spot size of the laser was estimated to be around one micron. To avoid possible photodecomposition of the samples, Raman spectra were recorded using low excitation power of 4–20 mW. The data were analyzed using Renishaw Wire 3.3 software.

2.5. Magnetic measurements

The magnetic measurements (susceptibility and magnetization) were performed with two fully automated superconducting quantum interference devices (SQUID) magnetometers (Quantum Design MPMS XL) in the temperature range 4–300 K. Powders were placed into small plastic vial, placed in a holder and finally inserted into the helium cryostat of the SQUID apparatus. The temperature