

Development and testing of nanomaterials for rechargeable lithium batteries

A. Odani^a, A. Nimberger^a, B. Markovsky^a, E. Sominski^a, E. Levi^a,
V.G. Kumar^a, M. Motiei^a, A. Gedanken^a, P. Dan^b, D. Aurbach^{a,*}

^aDepartment of Chemistry, Bar-Ilan University, Ramat Gan 52900, Israel

^bBattery Division-Tadiran, P.O. Box 75, Kiryat Ekron, Israel

Abstract

The use of nanoparticles in composite electrodes for Li batteries may have considerable kinetic advantages due to the reduction of the diffusion length for lithium insertion in the active mass, and also because of the reduction of the overall charge transfer resistance of the electrodes. We report herein on the synthesis of various types of nanomaterials for rechargeable lithium batteries and their testing as active mass in anodes and cathodes. These include SnO, VO_x, Li_xMnO₂, and various types of carbon nanotubes. Sonochemistry was applied for the synthesis of part of the nanophases. The tools for this study included X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and standard electrochemical techniques (CV, SSCV, chronopotentiometry and impedance spectroscopy).

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Nanomaterials; Rechargeable lithium batteries; Sonochemistry

1. Introduction

Research in the field of rechargeable lithium batteries has progressed a significant extent in the past decade through an increasing demand for power sources for portable electronic devices [1]. The commercially available lithium-ion cells, which are the most-advanced among the rechargeable batteries available so far, employ polycrystalline micron-sized powder as the electrode material, which functions as the Li insertion host. With the advancement of nanotechnology, there is an interest in the replacement of conventional materials by nanomaterials. There is a reasonable chance that as the active mass of electrodes for Li batteries is comprised of smaller particles, they will perform better in terms of kinetics and stability [2,3].

In this research, a few nanomaterials were examined for a possible application as electrode materials in Li-ion batteries. Sonochemistry was used for the synthesis of some nanomaterials. Sonochemistry was one of the major tools for the synthesis of nanophases. It is well known that the application of ultrasound radiation to chemical reactions that produce solid products forms nanoparticles because of

the cavitation phenomenon which characterizes sonochemical reactions in solutions [4–6]. Spinel-LiMn₂O₄ is one of the most promising cathode materials for Li-ion batteries [7]. A simple method to synthesize spinel-LiMn₂O₄ in large amounts, which interestingly produces nanoparticles, has been developed and is reported herein. Other important materials for Li battery cathodes are based on VO_x compounds [8,9]. In this paper, we describe in brief the synthesis, structural and electrochemical studies of a V₃O₇ phase that functions as an intercalation host for both Li⁺ and Mg²⁺ ions.

Anodes for Li-ion cells can be composed of lithiated carbons or lithium alloys. In recent years, Li_xSn alloys were intensively investigated as anode materials for Li batteries [10]. A major problem with Li–Sn compounds as anode materials is the very large volume changes during Li⁺ insertion–deinsertion cycling. Large volume changes can be avoided when the size of the metallic host particles is kept small. We report herein on the study of nano-sized SnO as a Li battery anode material.

Another interesting type of anode material for Li-ion batteries is the multiwall carbon nanotube (MWCNT). During the last decade, numerous attempts were carried out to synthesize different types of carbon nanotubes, part of which were investigated as anode materials in batteries [11,12].

* Corresponding author.

E-mail address: aurbach@mail.biu.ac.il (D. Aurbach).

A main disadvantage of nanotubes in comparison with graphite and coke as raw materials for lithium-ion batteries may be the relatively high cost of production. We describe herein preliminary testing of MWCNT, produced in a very cheap and easy way, as a Li insertion anode material. This paper provides a short review of our efforts to synthesize and test nanomaterials for battery applications. This review is a first release of our preliminary results related to the study of nano-VO_x, nano-LiMn₂O₄ and MWCNT. The study of the SnO nanoparticles was also reported elsewhere [13].

2. Experimental

Sonolysis of SnCl₂ [13] in basic aqueous solutions produced high purity amorphous nanoparticles of SnO. This amorphous tin oxide could be easily transformed to nanocrystalline phases by annealing at 200 °C for 2 h. Nanophases of VO_x were prepared by sonolysis of vanadyl triisopropoxide under Ar in the presence of water. A detailed description of the synthesis and analysis of the LiMn₂O₄ nanoparticles was recently submitted for publication [14]. The most important points are explained in Section 3. Finally, multiwall carbon nanotubes were obtained by reacting Co(CO)₃NO with magnesium and carbon black at high temperatures [15]. Composite electrodes were fabricated, as already reported [16]. The instrumentation for the studies reported herein included a Bruker AXS D8 advanced X-ray diffractometer (using Cu K α , $\lambda = 1.5418$ Å radiation), a Jeol-TEM 100SX microscope, a Mettler DSC-30 in the temperature range of 25–500 °C, a PGSTAT Autolab electrochemical measuring system from Ecco Chemie, Inc. (impedance spectroscopy and voltammetry), a Solartron (Model BTU 1470) multichannel potentiostats (for standard electrochemical measurements), and computerized multi-

channel battery testers from Maccor and Arbin, Inc. (USA). All the electrochemical measurements and preparation were carried out under a highly pure argon atmosphere (O₂ and H₂O levels <5 ppm) in VAC, Inc. glove boxes.

3. Results and discussion

3.1. Nano-LiMn₂O₄

In the framework of the present study, we developed a method to produce highly pure nanocrystalline LiMn₂O₄. This method includes two critical stages: reaction between MnO₂, LiOH and glucose in an aqueous solution at 80 °C (several hours), followed by calcination at 750 °C (1 day). It should be emphasized that the use of glucose as a mild reducing agent enabled lithiation of the MnO₂ at relatively low temperatures to Li_xMnO₂ ($x \approx 0.5$) compounds that could be easily extracted from the aqueous solution, and then, upon calcination, were transformed to highly pure nanocrystalline Li_{0.96}Mn₂O₄. The use of a reducing agent in order to lithiate the MnO₂ before calcination and conduct the reaction in the previously mentioned two stages was found to be critical for obtaining both pure and nanocrystalline material. The powder-X-ray diffraction (XRD) pattern of the material is shown in Fig. 1 along with a transmission electron microscopy (TEM) micrograph as an insert, and it exhibits an excellent match to the reported powder-XRD patterns of spinel-LiMn₂O₄ (lattice constant, $a = 8.23$ Å). TEM micrograph of the calcined material show that they comprise 60–100 nm sharp-edged nanocrystals.

Typical chronopotentiograms (potential (E) versus time (t) curves) of composite electrodes comprising this active mass (together with 10% graphite particles and 10% PVdF in EC–DMC/LiAsF₆), obtained during prolonged galvanostatic charge–discharge cycling are displayed in the left

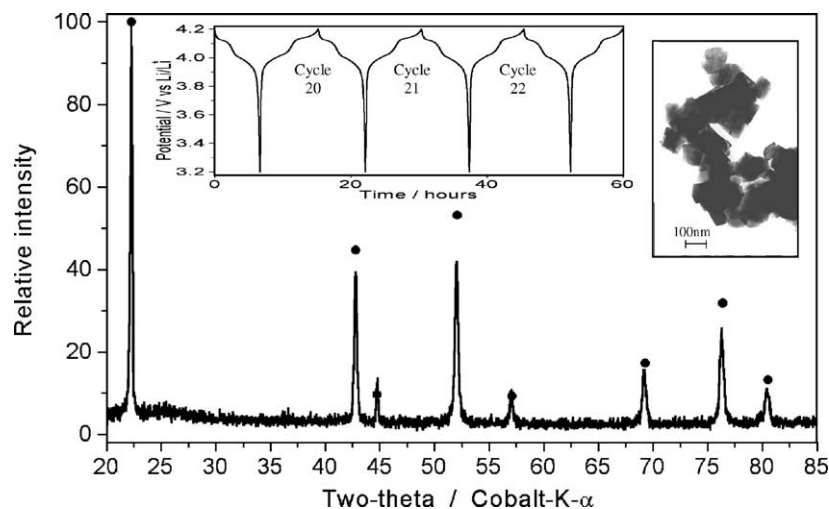


Fig. 1. Powder-XRD patterns of the material obtained by the calcination of the Li–Mn–O powder (● refers to the standard lines for spinel-LiMn₂O₄). Right inset: TEM micrograph of the particles. Left inset: Typical potential profile (potential (E) vs. time (t) curves) of the composite electrodes (galvanostatic cycling, C/7, 30 °C, EC–DMC (1:1)/1 M LiAsF₆).

insert of Fig. 1. The nano-spinel- LiMn_2O_4 electrodes exhibit stable 4 V spinel electrochemical characteristics upon cycling (i.e. two potential plateaus which reflect the phase transitions that the insertion of Li into this material involves) with a stable capacity of $\sim 70 \text{ mAh g}^{-1}$, although the first cycle charge-capacity is usually 150 mAh g^{-1} (not shown here). The long-term capacity values are much less than what is expected for spinel- LiMn_2O_4 material with a perfect structure [11]. This finding is surprising in light of the high purity of the active mass as confirmed by XRD (Fig. 1) and solid state Li NMR [14]. We assume that the relatively low capacity obtained, relates to the small particle size, which causes problems for an efficient electrical contact of the entire active mass to the current collector. It is quite possible that we address herein a general problem in the use of nanomaterials in composite electrodes, namely, a lack of sufficient electrical contact when the active mass is electronically insulating. Further studies of this issue are in progress.

3.2. Vanadium oxide cathodes

We succeeded in producing nanocrystalline VO_x compounds within the framework of the present work. Sonolysis of vanadyl triisopropoxide, as described in the Section 2, produces nano- $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$. In Fig. 2a we present the XRD patterns of the as-prepared sonochemical product. The peaks are broadened due to the small particles. Their size was calculated by XRD measurements to be on average about 6 nm. The XRD patterns fit $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$. Differential scanning calorimetry (DSC) measurements show an exothermic peak at 400°C , which relates to the transformation of the V_3O_7 to V_2O_3 (see the patterns of the thermal reaction

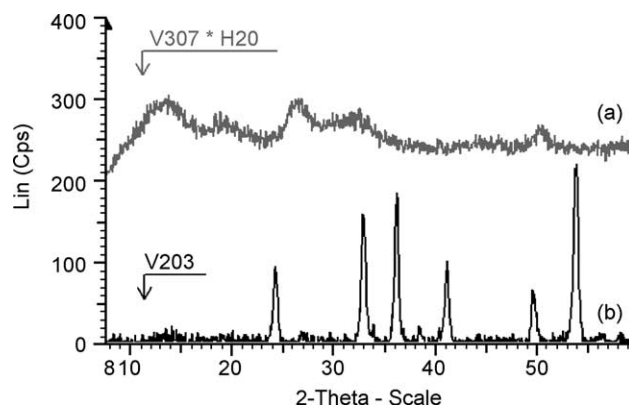


Fig. 2. XRD patterns of the sonochemical product VO_x : (a) as-prepared; (b) after heating to 400°C .

product in Fig. 2b which fit very well to V_2O_3). It was possible to also obtain nanocrystalline V_2O_5 by controlled oxidation of the V_3O_7 material (beyond the scope of this paper). The nanocrystalline V_3O_7 material was tested as an active mass in composite cathodes for Li and Mg batteries. The tests included electrochemical Li and Mg insertion in a polar aprotic solution (galvanostatic and voltammetric measurements), followed by element analysis. It was found that this material inserts reversibly both Li and Mg. We present herein preliminary results of the electrochemical tests.

Fig. 3 shows a cyclic voltammogram of a composite $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ electrode in an $\text{Mg}(\text{ClO}_4)_2/\text{ACN}$ solution, which reflects a capacity of 150 mAh g^{-1} in reversible insertion of magnesium ions (also concluded by elemental analysis). The insert in Fig. 3 shows a cyclic voltammogram of a $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ electrode in a LiClO_4/PC solution. A reversible capacity higher than 100 mAh g^{-1} could be obtained in these tests.

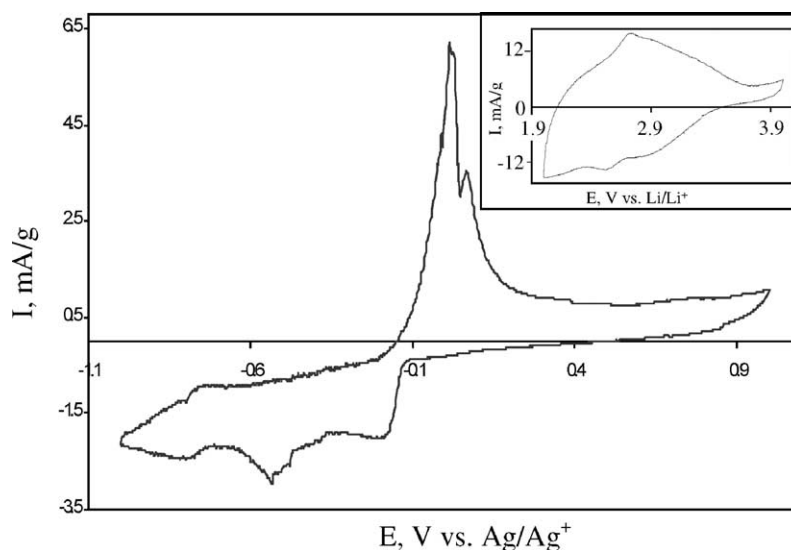


Fig. 3. A cyclic voltammogram of a composite electrode comprised of VO_x as-prepared in a $1 \text{ M Mg}(\text{ClO}_4)_2/\text{ACN}$ solution at a scan rate of 0.05 mV s^{-1} (Ag/Ag^+ as a reference electrode and Pt-foil as a counter electrode). The insert shows a cyclic voltammogram of the same type of electrode in a lithium cell ($1 \text{ M LiClO}_4/\text{PC}$ and Li: reference and counter electrodes).

It is clear that the nano- V_3O_7 thus obtained is not suitable as a cathode material for Li batteries due to the low capacity. However, the fact that this material can insert magnesium reversibly is highly interesting and hence, this material deserves further study in connection with Mg electrochemistry and Mg batteries.

3.3. Nanoparticles of SnO as an anode material

The SnO nanoparticles obtained by sonochemistry are amorphous and could be crystallized by annealing at 200 °C for 2 h. From TEM measurements of the SnO nanoparticles, their size was estimated to be 4–6 and 20 nm for the amorphous and the nanocrystalline phases, respectively. We tested both amorphous and nanocrystalline SnO as the active mass for negative electrodes in secondary Li batteries.

The performance of these electrodes depended on the following parameters: active mass structure (amorphous or crystalline nanophase), conductive additive (graphite or carbon black), the amount of binder and conductive additive, electrode morphology in terms compactness and the electrolyte solution chosen.

The optimal composition of the composite electrodes was found to be 80% SnO nanocrystalline particles, 10% PVdF binder, and 10% conductive carbon particles (graphite).

It was also established that unpressed electrodes demonstrated better cyclability and lower capacity fading than electrodes with a compact (pressed) active mass. The optimal electrolyte solution was found to be $LiPF_6/EC-DMC$. Typical potential–capacity profiles of composite nanocrystalline SnO electrodes in galvanostatic cycling are presented in Fig. 4.

XRD patterns of pristine SnO and cycled electrodes, showed that the tin nanoparticles aggregate during cycling (note that metallic tin particles embedded in a Li_2O matrix are the products of delithiation of these electrodes). It was confirmed that all of the SnO is indeed converted to tin, and hence, all the active mass of the electrode is accessible to

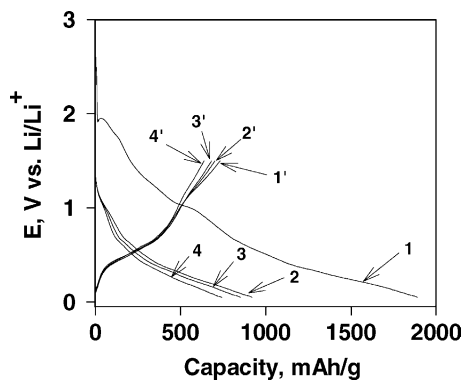


Fig. 4. Typical chronopotentiograms obtained with SnO electrodes in galvanostatic cycling ($C/10$ rate). The electrode compositions, mode of preparation, and electrolyte used are as follows: a nanocrystalline phase, graphite additive, unpressed, $EC-DMC/1\ M\ LiPF_6$. The number of charge–discharge cycles is indicated.

the electrochemical process. It was also confirmed that the capacity fading of electrodes composed of SnO nanoparticles was lower compared with electrodes comprised of micron-sized SnO particles. The preparation, analysis and the electrochemical studies of the nano-sized SnO particles that we investigated, are described in detail in [13].

3.4. Multiwall carbon nanotubes as anode materials

Recently, Gedanken and co-workers developed a very simple and cheap method to produce multiwall carbon nanotubes and nanoflasks. The nanotubes thus formed contain cobalt nanorods [15]. Fig. 5 shows typical TEM micrographs of the earlier described carbon nanotubes and nanoflasks. Two types of nanotubes, short (0.5 μm) and long (over 5 μm) can be observed. Their thickness deviates between 50 and 150 nm. Within the framework of the present work, these carbon nanotubes were tested as an anode material for Li-ion batteries. Preliminary results are presented in Fig. 6, which shows two consecutive slow scan rate ($8\ \mu V\ s^{-1}$) voltammograms measured with a composite electrode containing 90% nanotubes and 10% PVdF in an $EC-DMC/LiPF_6$ solution. The shape of these voltammograms suggests that Li insertion into the nanotubes includes staging as in graphite [1] (four sets of CV peaks, two of which are well distinguishable in Fig. 6), and absorption by less ordered carbon structures (the peaks in Fig. 6 are superimposed on broad reversible waves). Further studies of the exact Li insertion mechanisms into the MWCNT are in progress and are beyond the scope of this paper. At the present stage of the study, it was possible to obtain a reversible capacity around 250 $mAh\ g^{-1}$ with these electrodes. It was found that application of pressure to the electrodes during their fabrication is detrimental to their performance, because when the nanotubes are condensed there are problems in the electrical contact between the solution and the entire active mass.

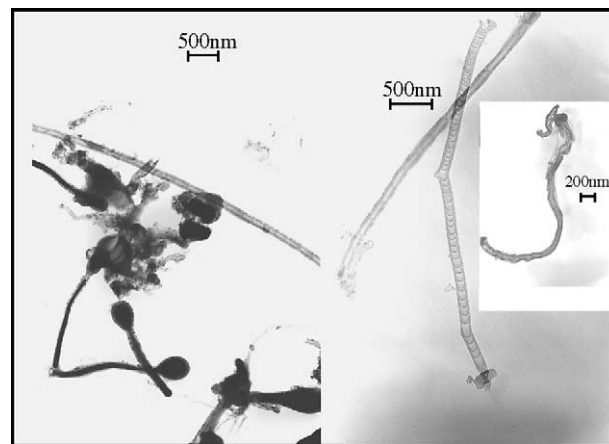


Fig. 5. TEM micrographs of different types of carbon nanotubes. Co nanorods are indicated. Scale bars appear on each micrograph.

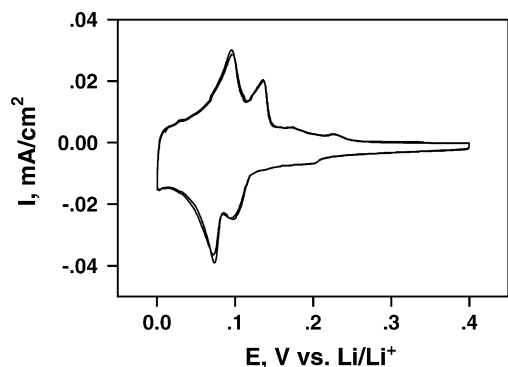


Fig. 6. Slow scan rate CVs measured with unpressed composite carbon nanotube electrodes ($0.4 \rightarrow 0.0$ V vs. Li/Li^+), $8 \mu\text{V s}^{-1}$, EC-DMC (1:1)/1 M LiPF_6 .

4. Conclusion

All the previously synthesized materials were found to be electrochemically active in reversible Li insertion in non-aqueous Li salt solutions. Composite electrodes comprised of nanocrystalline SnO could reach a capacity almost close to the theoretical one. The initial capacity of the cathodes comprised of the nanocrystalline spinel- $\text{Li}_x\text{Mn}_2\text{O}_4$ that we prepared was also close to the theoretical one. Regarding the VO_x material, we obtained $\text{V}_3\text{O}_7 \cdot \text{H}_2\text{O}$ nanoparticles that could insert both lithium and magnesium in non-aqueous Li or Mg salt solutions. The behavior of composite electrodes comprised of the carbon nanotubes was very similar in its electroanalytical response to that of graphite electrodes. Li insertion into the MWCNTs occurs by stages at relatively fast kinetics, but at a lower capacity than that of graphite (yet $>250 \text{ mAh g}^{-1}$). The performance of Li insertion electrodes comprised of the above materials was found to be highly sensitive to the experimental parameters, namely, the application of pressure to the electrodes during their preparation,

the amount of binder and conductive additives, as well as the composition of the electrolyte solution chosen.

Acknowledgements

Partial support for this work was obtained by the EC under contract number EKN6-CT-2001-00509.

References

- [1] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novak, *Adv. Mater.* 10 (1998) 725.
- [2] M. Winter, P. Novak, A. Monnier, *J. Electrochem. Soc.* 145 (1998) 428.
- [3] N.C. Li, C.R. Martin, B. Scrosati, *Electrochem. Solid State Lett.* 3 (2000) 316.
- [4] K.S. Suslick, D.J. Casadonate, M.L.H. Green, M.E. Thompson, *Ultrasonics* 25 (1987) 1.
- [5] N.A. Dhas, A. Gedanken, *Chem. Mater.* 9 (1997) 3144.
- [6] P. Jeevanandam, Y. Koltypin, A. Gedanken, Y. Mastai, *J. Mater. Chem.* 10 (2000) 511.
- [7] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359.
- [8] M.M. Thackeray, in: J.O. Besenhard (Ed.), *Handbook of Battery Materials (Part 3)*, Wiley, New York, 1999.
- [9] D. Aurbach, B. Markovsky, G. Salitra, Y. Cohen, E. Shembel, R. Apostolova, V. Nagirny, *J. Power Sources* 97–98 (2001) 486.
- [10] R.A. Huggins, *Solid State Ionics* 115 (1998) 57.
- [11] E. Frackowiak, S. Gautier, H. Gaucher, S. Bonnamy, F. Beguin, *Carbon* 37 (1999) 61.
- [12] Z.H. Yang, H.Q. Wu, *Solid State Ionics* 143 (2001) 173.
- [13] D. Aurbach, A. Nimberger, B. Markovsky, E. Sominsky, A. Gedanken, *Chem. Mater.* 14 (2002) 4155.
- [14] V.G. Kumar, S. Ben-David, D.M. Pickup, E.R.H. Van-Eck, A. Gedanken, D. Aurbach, *Chem. Mater.*, submitted for publication.
- [15] S.W. Liu, J.J. Zhu, Y. Mastai, I. Felner, A. Gedanken, *Chem. Mater.* 12 (2000) 2205.
- [16] J.J. Zhu, Z.H. Lu, S.T. Aruna, D. Aurbach, A. Gedanken, *Chem. Mater.* 12 (2000) 2557.