

Short communication

# Synthesis of nano-crystalline $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$ powder by a novel sol–gel thermolysis process for Li-ion polymer battery

A. Subramania\*, N. Angayarkanni, T. Vasudevan

*Advanced Materials Research Lab, Department of Industrial Chemistry, Alagappa University, Karaikudi, Tamil Nadu 630 003, India*

Received 14 June 2005; accepted 12 October 2005

Available online 29 November 2005

## Abstract

Cubic spinel nano-crystalline  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.10, 0.15, 0.20, 0.25$ ) powders are prepared at low temperature by means of a facile gel-polymer thermolysis process by calcining the prepared precursor samples at  $340^\circ\text{C}$  to obtain the products. X-ray diffraction and scanning electron microscopic analyses confirm that the products consists of nano-crystalline particles with uniform distribution. The effect of calcinations on the crystallinity of the cubic spinel  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  powder is examined by differential scanning calorimetric analysis. In order to asses the electrochemical reversibility of the cathode material, cyclic voltametry studies are performed by fabricating button cells with the configuration of carbon/MPPE/ $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$ .

© 2005 Elsevier B.V. All rights reserved.

*Keywords:* Lithium-ion batteries; Sol–gel thermolysis; Strontium-doped lithium manganate; Cubic spinel compound; Electrochemical reversibility

## 1. Introduction

Recently, lithium rechargeable batteries have gained importance by virtue of their various advantages of high voltage, good low-temperature performance and easy handling. They are being used in applications that range from cell phones and toys to electric vehicles [1,2]. Carbonaceous materials used for the anode and lithium transition metal oxides for the cathode. Among the various metal oxides, spinel  $\text{LiMn}_2\text{O}_4$  [3] offers considerable benefits, in terms of high specific capacity, toxicity and low cost. On the other hand,  $\text{LiMn}_2\text{O}_4$  suffers from capacity fading that limits its reversibility. In order to overcome this problem, substitution of some of the manganese with additional lithium ( $\text{Li}_{1+x}\text{Mn}_{2-x}\text{O}_4$ ) [4] or metal cations  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  ( $M = \text{Ni}, \text{Cu}, \text{Cr}, \text{Co}$  and  $\text{Al}$ ) [5] has been explored. Thackeray and Co-workers [5] have pointed out that the substitution of metal cations for Mn enhances the stability of spinels [6]. The electrochemical behaviour of these materials also depends on the method of synthesis.

Several techniques such as sol–gel [7], self-propagating combustion [8], precipitation [9] and emulsion drying [10] have been

adopted for the synthesis of nano-crystalline materials. Among these, self-propagating combustion synthesis is the most widely used method. Nevertheless, this method has the drawback of producing highly agglomerated particles. To remove this drawback, a low-temperature Pechini process [11] has been introduced and yields a phase-pure product with controlled stoichiometry. In the Pechini process, a mixed solution of citric acid and ethylene glycol in a 1:4 molar ratio is used for dissolving the reactants and several steps are involved to obtain the polymeric precursor. All these steps are tedious and must be performed carefully. The process includes the removal of excess of ethylene glycol under reduced pressure to cause polymerization.

Hence, this investigation, reports a sol–gel thermolysis method that is quite suitable for the larger-scale synthesis of well-dispersed nano-crystalline  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  powder of high purity. This sol–gel thermolysis is a novel and unique combination of a thermal process and a chemical gelation process. The organic polymer(s) not only acts as an excellent fuel, but also controls the size during the formation of the sol–gel and prevents the particles from aggregating during the thermolysis of dry gel due to its long chain structure. In this context, it should be mentioned that reports are available using poly (vinyl alcohol) combinations for the synthesis of various nano-crystalline materials [12]. The method investigated have may, however, provide a wider scope for tailorability,

\* Corresponding author. Tel.: +91 4565 228836; fax: +91 4565 225202.  
E-mail address: [a.subramania@yahoo.co.in](mailto:a.subramania@yahoo.co.in) (A. Subramania).

and for precise control of the particle-size and morphology of nano-crystalline powders. The present investigation involves the synthesis of nano-crystalline  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  powders through the use of urea and PVA. The structural properties of the synthesized products are characterized by X-ray diffraction (XRD) analysis. The effect of calcination on the crystallinity and grain size of the cubic spinel  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  powders is examined by differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), respectively. Finally, the electrochemical reversibility of the synthesized products is also tested.

## 2. Experimental

### 2.1. Synthesis of $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$ powders

The nano-crystalline cubic spinel  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x = 0.10, 0.15, 0.20, 0.25$ ) powders were prepared by a sol–gel thermolysis process. Analar grade  $\text{LiNO}_3$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2$  were taken as the starting materials in stoichiometric amounts with urea and polyvinyl alcohol and made into a homogeneous solution with distilled water. Each resulting solution was then heated to  $100^\circ\text{C}$  to obtain a viscous solution (sol).

The viscous solution was again heated (to  $120^\circ\text{C}$ ) for 3 h to obtain the precursor sample (gel). The precursor sample was then pyrolysed at  $340^\circ\text{C}$  for 3 h in air to obtain a cubic spinel  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  powder. The synthesis procedure is described in the flowchart shown in Fig. 1. The resultant products were collected and subjected to both physical and electrochemical studies.

### 2.2. Physical characterization

#### 2.2.1. Thermal studies

The thermal decomposition behaviour of the precursor sample was studied by Mettler-DSC (TA 3000) at a heating rate of  $10^\circ\text{C min}^{-1}$  under an ordinary atmosphere.

#### 2.2.2. XRD studies

The purity and structural conformity of the product was confirmed by JEOL X-ray diffraction analysis (JDX-8030) using  $\text{Cu K}\alpha$  radiation. The diffraction patterns were obtained at  $25^\circ\text{C}$  in the range  $10^\circ \leq 2\theta \leq 75^\circ$ . The step size and scan rate were set at  $0.1$  and  $2^\circ\text{C min}^{-1}$ , respectively.

#### 2.2.3. SEM analysis

To investigate the particle nature and size of the product, scanning electron micrograph was taken with a JEOL—Scanning electron microscope (JSM-840A).

### 2.3. Electrochemical characterization

In order to assess the cycling behaviour of the synthesized cathode materials, cyclic voltammetry studies were conducted by fabricating 2016 coin-type electrochemical cells with the configuration of  $\text{C}/\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  and employing a  $\text{Li}^+$  ion

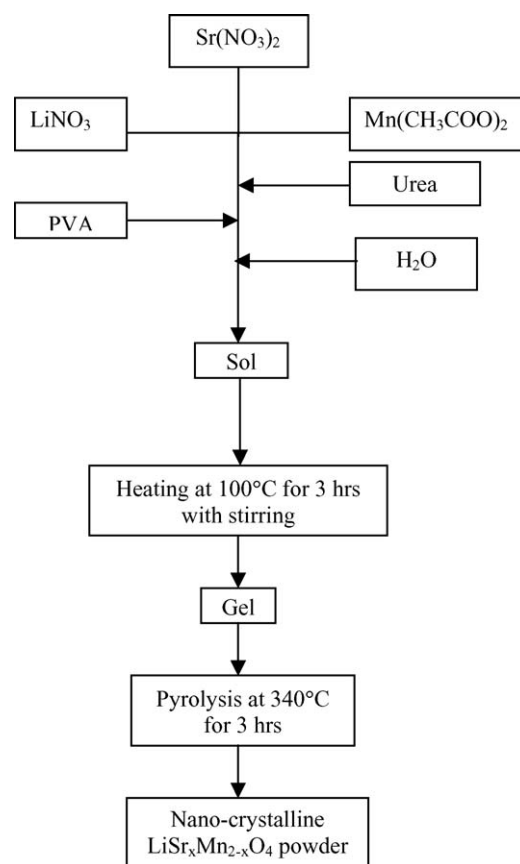


Fig. 1. Flow chart for preparation of  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  by sol–gel thermolysis.

conducting, PAN-based, microporous, polymer electrolyte. The cathode was prepared by mixing  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  powder, acetylene black and a colloidal Teflon binder in a 85:10:5 weight ratio. The above composite material was mixed with alcohol and the mixture was placed in a die and pressed on to an expanded aluminium grid at a pressure of  $5 \text{ tonnes cm}^{-2}$  using a hydraulic press to yield circular pellet electrodes. The pellets were then dried at  $120^\circ\text{C}$  in an air oven. Cyclic voltammograms were recorded at a slow scan rate of  $1 \text{ mV s}^{-1}$  over the potential range 3.0–5.0 V using an EG & G Electrochemical analyzer.

## 3. Results and discussion

### 3.1. Thermal studies

The DSC curve for  $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  is shown in Fig. 2. This curve optimizes the required temperature for phase formation and crystallization of the precursor sample. Two exothermic peaks are observed. A large exothermic peak is observed at  $250.45^\circ\text{C}$  due to the combustion nature of urea and the polymer. On further heating, a second small exothermic peak is observed; it commences at  $304.03^\circ\text{C}$  with ends at  $336.29^\circ\text{C}$ . This indicates that the compound begins to decompose at a very low temperature and the exothermic combustion of urea and PVA supplies heat that is sufficient to initiate the formation of a nano-crystalline powder. The exothermic peak at  $336.29^\circ\text{C}$  indicates

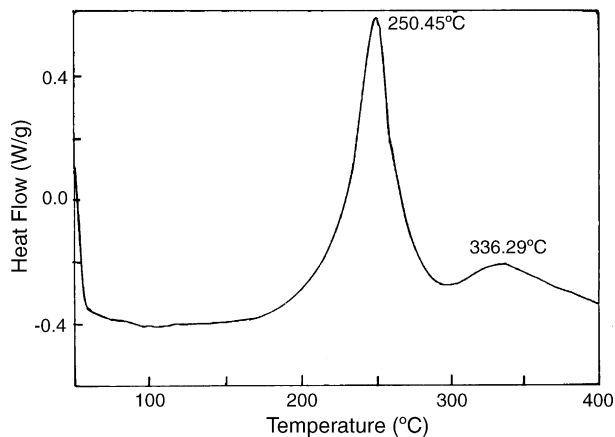


Fig. 2. DSC scan for precursor sample of  $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$ .

complete phase formation and crystallization of the cubic spinel powder.

### 3.2. XRD studies

The X-ray diffractograms for the cubic spinels  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.10, 0.15, 0.20, 0.25$ ) reveal the formation of highly crystalline product with high phase purity upon calcination at  $340^\circ\text{C}$  as shown in Fig. 3. There are no residues present in the diffractograms and this demonstrates that the products have single-phase structures without any noticeable residual impurities. Compared with  $\text{LiMn}_2\text{O}_4$ , the lattice parameters of  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  slightly decrease with increase in substitution of  $\text{Sr}^{2+}$  content and hence the Bragg planes (440) and (531) are shifted slightly towards lower  $2\theta$  angles. The variation of the cubic lattice parameters of  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  as a function of Sr content is shown in Fig. 3. It is obvious that the slight decreases in the lattice parameters are due to an increase in the replacement of Mn by  $\text{Sr}^{2+}$ . This raises the average Mn valency from  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  and also the  $\text{Sr}^{2+}$  replaces  $\text{Mn}^{3+}$  in the 16d octahedral sites. Hence, a strong Bragg plane (220) is not observed at  $2\theta=30^\circ$ .

### 3.3. SEM studies

An electron micrograph of the cubic spinel  $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  powder is presented in Fig. 4. This shows the formation of spherical grains of sub-micron size. The large voids indicate that the product is porous in nature. This feature facilitates easy access of battery electrolyte and thereby increases the number of active sites which is desirable for good battery activity.

### 3.4. Electrochemical studies

The cyclic voltammograms reveal the reversible intercalation/de-intercalation of  $\text{Li}^+$  ions, as shown in Fig. 5(a)–(d). Among the various  $\text{Sr}^{2+}$ -doped  $\text{LiMn}_2\text{O}_4$  cathode materials,  $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  gives a high open-circuit potential of 5.0 V upon removing  $\text{Li}^+$  and also has very good reversibility.

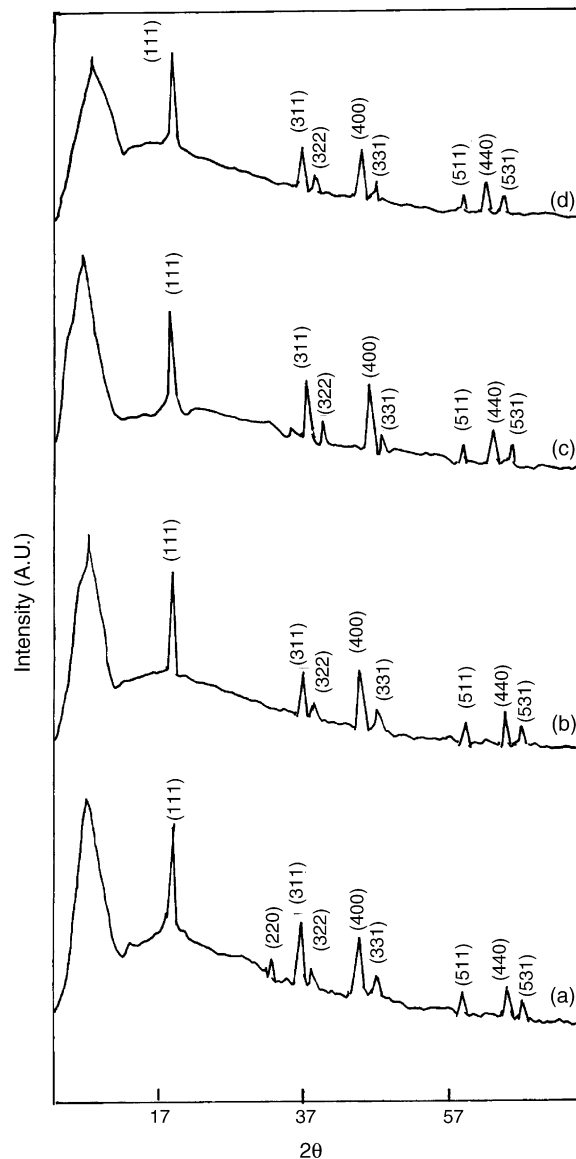


Fig. 3. X-ray diffraction patterns for cubic spinel  $\text{LiSr}_x\text{Mn}_{2-x}\text{O}_4$  ( $x=0.10, 0.15, 0.20, 0.25$ ) obtained by sol-gel thermolysis.

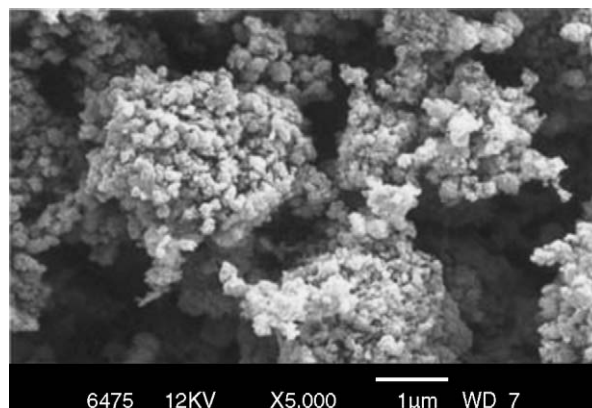


Fig. 4. Scanning electron micrograph of  $\text{LiSr}_{0.25}\text{Mn}_{1.75}\text{O}_4$  powder.

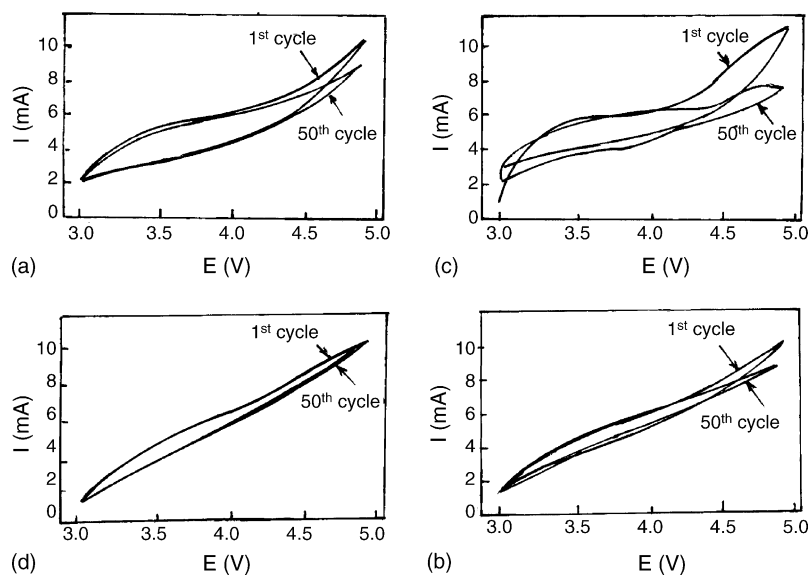


Fig. 5. Cyclic voltammograms of C/LiSr<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> cells employing a Li<sup>+</sup> ion conducting PAN-based, microporous polymer electrolyte at a scan rate of 1 mV s<sup>-1</sup> (a) LiSr<sub>0.10</sub>Mn<sub>1.90</sub>O<sub>4</sub>, (b) LiSr<sub>0.15</sub>Mn<sub>1.85</sub>O<sub>4</sub>, (c) LiSr<sub>0.20</sub>Mn<sub>1.80</sub>O<sub>4</sub>, (d) LiSr<sub>0.25</sub>Mn<sub>1.75</sub>O<sub>4</sub>.

#### 4. Conclusions

The synthesis of nano-crystalline, Sr-doped LiMn<sub>2</sub>O<sub>4</sub> powders using sol–gel thermolysis appears to be a more feasible method for large-scale production at a very low temperature of 340 °C. LiSr<sub>0.25</sub>Mn<sub>1.75</sub>O<sub>4</sub> yields a high open-circuit voltage of 5.0 V upon removing Li<sup>+</sup> ions and has very good reversibility. The particle size of the products obtained by this method is at the sub-micron level. The preparative process also yields a phase-pure product with controlled stoichiometry. Hence, LiSr<sub>x</sub>Mn<sub>2-x</sub>O<sub>4</sub> powder obtained by sol–gel thermolysis process could be used as an effective cathode material for Li-ion batteries.

#### Acknowledgements

The authors are grateful to the DST, New Delhi, for financial support.

#### References

- [1] T. Nagamura, K. Tozawa, Prog. Batteries Sol. Cells 9 (1999) 209.
- [2] B. Scrosati, Nature 373 (1993) 557.
- [3] C.Y. Wan, Y. Nuli, Q. Wu, M. Yan, Z. Jiang, J. Appl. Electrochem. 33 (2003) 107.
- [4] G.G. Amatucci, N. Perera, T. Zheng, L. Plitz, J.M. Tarascon, J. Power Sources 81 (1999) 39.
- [5] A. Eftekhari, J. Power Sources 124 (2003) 182.
- [6] R.J. Gummow, A. Dekock, M.M. Thackeray, Solid State Ionics 69 (1994) 59.
- [7] B.J. Hwang, R. Santhanam, D.G. Liu, J. Power Sources 101 (2001) 86.
- [8] D. Kovacheva, H. Gadjov, K. Petrov, S. Mandel, J. Mater. Chem. 12 (2002) 1184.
- [9] K.M. Shaju, G.V. Subba Rao, B.V.R. Chowdari, J. Electrochim. Acta 48 (2002) 145.
- [10] S.T. Myung, H.T. Chung, S. Komaba, N. Kumagai, H.-B. Gu, J. Power Sources 90 (2003) 103.
- [11] W. Liu, G.C. Farrington, F. Chaput, B. Dunn, J. Electrochem. Soc. 143 (1996) 879.
- [12] S.H. Cho, J.S. Yoo, J.D. Lee, J. Electrochem. Soc. 145 (1998) 1017.