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PAPERS PUBLISHED IN THE INTERNATIONAL / NATIONAL JOURNALS

- Synthesis of nano-crystalline LiSr_xMn_{2-x}O_4 powder by a novel sol-gel thermolysis process for Li-ion polymer battery.
  A.Subramania, N.Angayarkanni and T.Vasudevan.

- Combustion synthesis of inverse spinel LiNiVO_4 nano-particles using gelatine as the new fuel.
  A.Subramania, N.Angayarkanni, S.N.Karthick and T.Vasudevan
  Materials Letters, 60 (2006) 3023

- A Microwave-induced combustion method for the synthesis of nano-crystalline Ni- and Mn-doped LiCoO_2 for Li-ion battery.
  A.Subramania, N.Angayarkanni, S.Lakshmidevi, R.Gangadharan and T.Vasudevan,

- Synthesis and electrochemical characterization of nano-crystalline LiCoO_2 powder by a novel sol-gel thermolysis process for Li-ion batteries
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- Synthesis and characterization of LiMg_yMn_{2-y}O_4 cathode materials by a modified Pechini process for lithium batteries
  A.Subramania, N.Angayarkanni, A.R. Sathiyapriya R.Gangadharan and T.Vasudevan
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• Effect of PVA with various combustion fuels in sol-gel thermolysis process for the synthesis of LiMn$_2$O$_4$ nanoparticles for Li-ion batteries.

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*Materials Chemistry and Physics, (in press)*

• A novel polyaspartate precursor method for the synthesis of LiCa$_y$Mn$_{2-y}$O$_4$ nanoparticles for Li-ion batteries

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• Development of a newer nanocrystalline yttrium doped LiMn$_2$O$_4$ cathode material for high performance Li-ion polymer battery

A.Subramania and N.Angayarkanni

*Electrochimica Acta, (Communicated)*

**PAPERS PRESENTED IN INTERNATIONAL / NATIONAL CONFERENCES**

• Synthesis of Nano-crystalline LiSr$_x$Mn$_{2-x}$O$_4$ powder by modified pechini process for Li-ion Polymer Battery.

A.Subramania, N.Angayarkanni, N.Sridevi, R.Gangadharan and T.Vasudevan


• Synthesis of nano-crystalline LiCoO$_2$ powder by combustion assisted sol-gel technique for Li-ion batteries.

A.Subramania, S.Lakshmi Devi, N.Angayarkanni, R.Ganesan and T.Vasudevan

• Synthesis of nano-crystalline LiCdₓMn₂₋ₓO₄ cathode materials by using a new combustion fuel for Li-ion polymer battery.
A.Subramania, N.Angayarkanni, R.Gangadharan and T.Vasudevan

• A novel polymer-pyrolysis approach to synthesize nano-crystalline LiMn₂O₄ for lithium-ion batteries
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International Conference on Recent Advancements in Chemistry. (ALPS-2006), Vellore, on Jan.5-6, 2006.

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A.Subramania, N.Angayarkanni and T.Vasudevan,
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- Synthesis of LiMn$_2$O$_4$ nanoparticles by solution combustion method using hexamine as fuel
Effect of PVA with various combustion fuels in sol–gel thermolysis process for the synthesis of LiMn$_2$O$_4$ nanoparticles for Li-ion batteries

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Abstract

LiMn$_2$O$_4$-based spinels are of great interest as positive electrode materials for lithium-ion batteries. The single-phase LiMn$_2$O$_4$ nanoparticles have been synthesized by a novel sol–gel thermolysis process using poly vinyl alcohol (PVA) with three different combustion fuels such as urea, hexamine and citric acid to know the effect on structure, particle size and electrochemical properties of LiMn$_2$O$_4$ nanoparticles. Among the three combinations, the polymeric gel precursor obtained by using PVA–urea has generated complete crystallization at lower temperature than other two combinations are confirmed by TG/DTA analysis. But all the three combinations generate phase pure LiMn$_2$O$_4$ nanoparticles are confirmed by XRD studies. The particle size and electrochemical properties are confirmed by TEM analysis and charge/discharge studies, respectively. It reveals that LiMn$_2$O$_4$ obtained by using PVA–urea has smaller nanoparticles and better electrochemical performance than the nanoparticles obtained by using other two combinations such as PVA–hexamine and PVA–citric acid.

Keywords: Sol–gel thermolysis; Lithium manganate; Cubic spinel compound; Poly vinyl alcohol; Li-ion batteries

1. Introduction

Lithium ion batteries are well regarded as a new promising power sources for both portable electronic devices and zero emission vehicles (ZEV) due to their longer cycle life and higher energy density than other rechargeable battery systems. Currently LiCoO$_2$ [1], LiNiO$_2$ [2] and LiFePO$_4$ [3] are the main positive electrode materials for lithium-ion batteries. In comparison with layered LiNiO$_2$ and LiCoO$_2$ spinel LiMn$_2$O$_4$ has some advantages such as lower cost, higher abundance of Mn in the earth, high safety and lower toxicity [4]. The electrochemical properties of the electrode materials are strongly dependent on the physical and chemical properties like crystalline size, stoichiometry, homogeneity, etc. [5]. Synthesis process plays a major role in improving the physicochemical properties of the electrode material [6].

LiMn$_2$O$_4$ powders are typically prepared by a solid-state thermal reaction method [7]. This method requires long-range diffusion of metal ions, may result in non-homogeneity, larger particles and poor control of stoichiometry. To overcome the above drawbacks several techniques such as sol–gel [8], self-propagating combustion [9], precipitation [10] and emulsion [11] have been adopted for the synthesis of nano-crystalline materials. Among these, self-propagating combustion synthesis is the most widely used method. This method has the drawback of producing highly agglomerated particles. When this method is used along with a polymer, it is possible to produce well-dispersed nano-materials. The organic polymer employed can serve both as a fuel for nanoparticles formation as well as a dispersing medium which limits the agglomeration of particles. In this context, we have reported very recently the synthesis of nano-crystalline LiSr$_3$Mn$_{2-x}$O$_4$ by sol–gel thermolysis process using poly vinyl alcohol (PVA) and urea combination [12].

Thus, the present work was carried out to compare the effect of PVA with various combustion fuels such as urea, hexamine and citric acid for the synthesis of nano-crystalline LiMn$_2$O$_4$ powder. The physical and electrochemical characterizations were also carried out for the synthesized LiMn$_2$O$_4$ nanoparticles.

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2. Experimental

2.1. Synthesis of LiMn₂O₄ nanoparticles

The nano-crystalline cubic spinel LiMn₂O₄ powders were prepared by a sol-gel thermolysis process using three different fuel combinations such as PVA-urea, PVA-hexamine and PVA-citric acid. The stoichiometric amount of anhydrous LiNO₃ and Mn(CH₃COO)₂ were taken as the starting materials with PVA and urea combination and made into a homogeneous solution (sol) with distilled water. The resulting sol was then heated to 100°C for 2 h to obtain the polymeric gel precursor sample. The precursor sample was then pyrolysed at 415°C for 3 h in air to obtain cubic spinel LiMn₂O₄. Similarly nano-crystalline LiMn₂O₄ powders were prepared by using PVA-hexamine and PVA-citric acid combinations as described in the flow chart shown in Fig. 1. The resultant products were collected and subjected to both physical and electrochemical characterizations.

2.2. Physical characterization

The thermal decomposition behavior of the LiMn₂O₄ precursor samples were made using a simultaneous TG-DTA thermal analyzer (STA-1500) at the heating rate of 10°C/min under ambient atmosphere. X-ray diffraction measurements were made from JEOL (JDX 8030)-X-ray diffractometer using nickel filtered Cu Kα radiation to identify the crystalline phase of the synthesized materials. The shape and size of microstructure of the particles were observed using JEOL-(JEM-100SX)-Transmission electron microscope.

2.3. Electrochemical characterization

The electrochemical properties of the synthesized powders were examined by fabricating 2016 coin type electrochemical cell in the configuration of C/LiMn₂O₄ employing Li⁺ ion conducting PAN based micro porous polymer electrolyte. The cathode was prepared by mixing LiMn₂O₄ powder, acetylene black and colloidal teflon binder in the 85:10:5 weight ratios. The composite material was mixed with alcohol and the mixture was pressed in a die on an expanded aluminium grid at a pressure of 5 tons/cm² using a hydraulic press to yield circular pellet electrodes. The pellets were then dried at 120°C in an air oven. The charge and discharge cycling was performed galvanostatically at the current density of 0.2 mA/cm² in the voltage range of 3.2-4.7 V.

3. Results and discussion

3.1. Thermal analysis

Fig. 2(a-c) shows the TG–DTA results of LiMn₂O₄ precursors obtained by using PVA-urea, PVA-hexamine and PVA-citric acid combinations, respectively. It can be seen from Fig. 2(a) that the mass loss of the polymeric gel precursor occurs in three steps, at 20–155, 155–365 and 365–400°C and terminates at 400°C. The mass loss in the temperature range of 20–155°C corresponds to the removal of superficial water on
Fig. 2(b and c) show the phase formation of LiMn$_2$O$_4$ begins at around 305 and 312°C followed by the complete decomposition of precursor occurred at 425 and 450°C, respectively. The above discussion revealed that the phase formation and/or complete crystallization of LiMn$_2$O$_4$ precursor of PVA–urea combination occurs at lower temperature than that of the other two combinations.

### 3.2. XRDs studies

The XRD patterns of LiMn$_2$O$_4$ powders synthesized by using PVA–urea, PVA–hexamine and PVA–citric acid are shown in Fig. 3(a–c), respectively. The XRD patterns show that the spinel LiMn$_2$O$_4$ powder has pure and crystalline in nature in all the three combinations. Impurity phases such as Li$_2$CO$_3$ and Mn$_2$O$_3$ are often formed in other low temperature synthesis techniques [13] are not observed. The main diffraction peaks of cubic spinel LiMn$_2$O$_4$ phase, such as (1 1 1), (3 1 1) and (4 0 0) are well developed. This means that lithium ions occupied tetrahedral 8a sites and manganese also occupied octahedral 16d sites. Furthermore, the diffraction peak intensity ratio between (1 1 1) and (3 1 1) or (4 0 0) is high in accord with that of LiMn$_2$O$_4$ in the JCPDS data [14]. The lattice parameter of the three combinations is agreed well with those of other research groups [15–19].

### 3.3. TEM analysis

The TEM photograph of LiMn$_2$O$_4$ nanoparticles obtained by using PVA–urea, PVA–hexamine and PVA–citric acid combinations are shown in Fig. 4(a–c), respectively. The TEM pictures of all three combinations clearly show that nanoparticles are uniformly distributed throughout the matrix with spherical morphology. The particle size histograms were obtained from TEM analysis and a representative histogram of PVA–urea combination is shown in Fig. 5. It reveals that the average particle size of the gel precursor, which is accompanied by small endothermic peak at around 140°C in the DTA curve. As the process of heating is continued, the mass loss increases, owing to the combustion nature of the polymeric gel precursor. The huge mass loss in the temperature range of 155–365°C is associated with the combustion nature of inorganic and organic constituents of the precursor such as nitrates, urea and PVA accompanied by exothermic peaks at around 274 and 320°C in the DTA curve. The small weight loss in the temperature range of 365–400°C indicates the combustion of remaining organic constituents of the precursor, accompanied by huge exothermic peak at around 390°C in the DTA curve. At higher temperature >400°C, there is no mass loss. This indicates that the decomposition of precursor completed at 400°C.

Fig. 3. XRD patterns of the cubic spinel LiMn$_2$O$_4$ powders synthesized by sol–gel thermolysis process using (a) PVA–urea, (b) PVA–hexamine and (c) PVA–citric acid.

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Fig. 4. TEM photograph of LiMn$_2$O$_4$ samples prepared by using (a) PVA–urea, (b) PVA–hexamine and (c) PVA–citric acid combinations.

Fig. 5. Particle size histogram of LiMn$_2$O$_4$ powder synthesized by sol–gel thermolysis process using PVA–urea obtained from TEM studies.

Fig. 6. Charge/discharge curve for the LiMn$_2$O$_4$ synthesized by using (a) PVA–urea, (b) PVA–hexamine and (c) PVA–citric acid.
Table 1

<table>
<thead>
<tr>
<th>PVA-urea</th>
<th>PVA-hexamine</th>
<th>PVA-citric acid</th>
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<td>~37</td>
<td>~54</td>
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<td>~42</td>
<td>~60</td>
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is around ~42 nm whereas for PVA–hexamine and PVA–citric acid combinations, the average particles size is around ~60 and ~71 nm, respectively. It is further evident by measuring the particle size of the synthesized powder from the XRD data using Scherer equation [20] is shown in Table 1.

3.4. Electrochemical characterization

The charge/discharge curves at the 1st and 50th cycle for LiMn$_2$O$_4$ synthesized by using PVA–urea, PVA–hexamine and PVA–citric acid combinations are shown in Fig. 6(a–c), respectively. The initial discharge capacity for nanocrystalline LiMn$_2$O$_4$ powder synthesized by using PVA–urea, PVA–hexamine and PVA–citric acid combination is 137, 135 and 136 mAh/g, respectively. The initial discharge capacity for these three systems is nearer to each other. There is no appreciable difference. The discharge capacity versus cycle number of C/LiMn$_2$O$_4$ of three systems is shown in Fig. 7. At 50th cycle the capacity loss observed for PVA–urea system is only 9%, whereas that for PVA–hexamine and PVA–citric acid systems are 13% and 15%, respectively. The above discussion revealed that the nano-crystalline LiMn$_2$O$_4$ powder synthesized by using PVA–urea combination has very good reversibility when compared to other two. Because the smaller particle size of LiMn$_2$O$_4$ facilitates rapid diffusion of Li$^+$ ions which leads to good battery performance [21,22].

4. Conclusion

Nanocrystalline phase pure LiMn$_2$O$_4$ powders have been synthesized in bulk quantities by sol–gel thermolysis process using PVA–urea, PVA–hexamine and PVA–citric acid combinations. Thermal studies and TEM studies show that PVA–urea combination yield LiMn$_2$O$_4$ at lower temperature with smaller nanoparticles than other two combinations. An electrochemical investigation also shows that the product obtained by using PVA–urea combination yield better capacity retention than the materials prepared by using other two combinations. Hence, PVA–urea is the effective combination in sol–gel thermolysis process for the synthesis of cubic spinel powder and the compound obtained by using this combination is an effective cathode active material for Li-ion battery applications.

Acknowledgement

The authors gratefully acknowledge the DST, New Delhi for financial support.

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Fig. 7. Relationship between the discharge capacity and cycle number of the cell C/LiMn$_2$O$_4$ of three systems is shown in Fig. 7. At 50th cycle the capacity loss observed for PVA–urea system is only 9%, whereas that for PVA–hexamine and PVA–citric acid systems are 13% and 15%, respectively. The above discussion revealed that the nano-crystalline LiMn$_2$O$_4$ powder synthesized by using PVA–urea combination has very good reversibility when compared to other two. Because the smaller particle size of LiMn$_2$O$_4$ facilitates rapid diffusion of Li$^+$ ions which leads to good battery performance [21,22].
A novel polyaspartate precursor method for the synthesis of LiCa$_{y}$Mn$_{2-y}$O$_{4}$ nanoparticles for Li-ion batteries

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Abstract

Cubic spinel LiCa$_{y}$Mn$_{2-y}$O$_{4}$ nanoparticles were synthesized using nitrates of Li$^{+}$, Ca$^{2+}$ and acetate of Mn$^{2+}$ with aspartic acid as a polymerizable combustion fuel. They were dissolved in distilled water and then concentrated by heating to form a viscous resin which was transformed into a foam-like mass by drying at 120°C. Phase pure LiCa$_{y}$Mn$_{2-y}$O$_{4}$ powders were obtained by combustion of these foams. The decomposition temperature of the polyaspartate precursor was investigated by TG/DTA analysis. The structural property of the synthesized LiCa$_{y}$Mn$_{2-y}$O$_{4}$ powders was confirmed by x-ray diffraction studies. The average particle size of the synthesized powders was calculated from the x-ray data using the Scherrer equation. TEM analysis was also carried out to confirm the particle size and surface morphology of the synthesized LiCa$_{y}$Mn$_{2-y}$O$_{4}$ powder. Finally, electrochemical charge–discharge studies were carried out by assembling 2016 type electrochemical button cells using carbon as the anode and the synthesized LiCa$_{y}$Mn$_{2-y}$O$_{4}$ as the cathode with microporous polymer electrolyte.

1. Introduction

Over the past decade, spinel LiMn$_{2}$O$_{4}$ has been studied extensively as a cathode material for rechargeable lithium and lithium ion batteries due to its economical and environmental advantages [1]. Unfortunately, its application has been limited by a severe capacity fade, particularly at elevated temperature, which is mainly due to Jahn–Teller distortion [2–4]. Substitution of other cations, such as Sr, Mg, Ni, Cu, Cr, Co, Al etc [5–7], for manganese as well as the modification of the preparation methods have been found to improve the cyclability of LiMn$_{2}$O$_{4}$ cathode [8]. So far, spinel lithium manganese oxide and its substituted form have mainly been prepared by self propagating high temperature synthesis [9–11]. This method has the drawback of producing highly agglomerated particles. To overcome this drawback, another synthetic procedure has been adopted that yields nanoparticles without any agglomeration even at low temperature: the so-called polymer precursor method. In this method, a metal ion solution containing polymeric or polymerizable organic molecules is heated to form a gel and then thermally decomposed to the metal oxide powders. The metal ions are uniformly distributed in the polymer gel and are attached to the polymer molecules through functional groups, such as OH and COOH, present in the polymer structure. Polyacrylic acid, poly vinyl alcohol and urea formaldehyde are polymeric materials and sucrose, acrylamide, acrylic acid etc are polymerizable materials that are used for the synthesis of metal oxide powders [12–16]. Another synthesis procedure that yields finely divided powder is the so-called combustion route. By this solution combustion route, metal oxide had been prepared using urea, citric acid, sucrose, glycine etc as fuels [17–19].

Hence in the present work, we have introduced a novel polymerizable fuel, aspartic acid, for the synthesis of newer LiCa$_{y}$Mn$_{2-y}$O$_{4}$ cathode material by combining the principles of polymer precursor synthesis and combustion synthesis. The structural properties of the synthesized products were characterized by XRD. The effect of calcination on the crystallinity of the cubic spinel LiCa$_{y}$Mn$_{2-y}$O$_{4}$
powders was confirmed by TG/DTA analysis. The surface morphology and particle size of the synthesized products were confirmed by TEM analysis. The particle size was calculated from XRD data using the Scherrer formula. Finally, the electrochemical charge-discharge characteristics were characterized by fabricating coin type electrochemical cells in a carbon/polymer electrolyte/LiCa_{y}Mn_{2-y}O_{4} configuration.

2. Experimental details

2.1. Synthesis of LiCa_{y}Mn_{2-y}O_{4} powders

The cubic spinel LiCa_{y}Mn_{2-y}O_{4} (0.05 ≤ y ≤ 0.20) powders were prepared by a polyaspartate precursor method using aspartic acid as a polymerizable fuel. Stoichiometric amounts of oxidizers, such as lithium nitrate, calcium nitrate and manganese acetate, were taken along with aspartic acid and made into a homogeneous solution.

According to a concept developed in propellant chemistry (7), the oxidizing valency (O) of LiNO_{3} was −5, Ca(NO_{3})_{2} was −10 and Mn(CH_{3}COO)_{2} was +16, and the reducing valency (F) of aspartic acid was +15. The amount of aspartic acid required was calculated for LiCa_{0.10}Mn_{1.90}O_{4}

\[ 1 \times (-5) + (-10 \times 1 \times 0.10) + (16 \times 1 \times 1.90) + 15n = 0, \]

\[ n = 1.626 \text{ M}. \]

Therefore, the required amount of aspartic acid was 1.626 M. The same procedure was followed for other ratios such as 0.05, 0.15 and 0.20. The polymerization of aspartic acid was initiated by thermal treatment to form the polyaspartate precursor. Hence, under heating at 100°C, the above homogeneous solution was dried to form a well distributed polyaspartate of Li, Ca and Mn precursor and the dried mass was calcined at 430°C for 5 h to give nanocrystalline LiCa_{y}Mn_{2-y}O_{4} powder. A flow chart for the synthesis of LiCa_{y}Mn_{2-y}O_{4} is shown in figure 1. The resultant products were collected and subjected to both physical and electrochemical studies.

2.2. Thermal studies

Thermal analysis of the precursor sample was carried out using a JEOL (STA-1500) TG/DTA thermal analyser at a heating rate of 10°C min⁻¹ under ambient atmosphere to determine the optimum temperature for phase formation and/or complete crystallization of the precursor sample.

2.3. XRD studies

The purity and structure of the products were confirmed by a JEOL (JDX-8030) x-ray diffraction analyser using Cu Kα radiation. The diffraction patterns were obtained at 25°C in the range of 10° ≤ 2θ ≤ 75° in the step scans. The step size and scan rate were set at 0.1 and 2°C min⁻¹ respectively.

2.4. TEM analysis

To investigate the particle nature and size of the products, TEM photographs were taken using a JEOL (Model: 200CX) transmission electron microscope.

2.5. Electrochemical characterization

LiCa_{y}Mn_{2-y}O_{4} powders were electrochemically characterized by fabricating 2016 type electrochemical button cells in a C/LiCa_{y}Mn_{2-y}O_{4} configuration using a Li⁺ ion conducting PVdF-co-HFP based micro-porous polymer electrolyte. The cathode was prepared by mixing LiCa_{y}Mn_{2-y}O_{4} powder, acetylene black and colloidal teflon binder in 85:10:5 weight ratios. The above composite material was mixed with alcohol and the mixture was pressed in a die onto an expanded aluminium grid at a pressure of 5 tons cm⁻² using a hydraulic press to yield circular pellet electrodes. The pellets were then dried at 120°C in an air oven. The charge-discharge studies were performed galvanostatically at the current density of 0.2 mA cm⁻² within the voltage range of 3.2-4.7 V using a WonATech battery cycle life tester.

The capacity and cyclability of the cathode materials were calculated based on the results of the charge-discharge studies.

3. Results and discussion

3.1. Polymeric precursor

Polyaspartic acid is a long chain linkage of aspartic acid (amino acid). Hence, it has a dual nature. It can act as an excellent fuel as well as a good dispersing agent [20, 21]. In the polyaspartate precursor, metallic Li, Ca and Mn ions are dispersed homogeneously throughout the polymer matrix. Such a structure effectively controls the particle size to give nanocrystalline particles. Moreover,
this uniform immobilization of metallic ions in the polymer chain favours the formation of uniformly distributed solid solutions of metallic oxides and also avoids the agglomeration of nanoparticles during the combustion process.

3.2. Thermal analysis

Figure 2 shows the thermogram of LiCa_{0.20}Mn_{1.80}O_4 precursor. The DTA curve shows one endothermic peak and two exothermic peaks. The broad endothermic peak begins to appear at around 97 °C and terminates at around 171 °C, and the weight loss observed in the TG curve between 29 and 207 °C is due to the loss of water molecules present in the gel precursor. The first huge exothermic peak occurred at 278 °C, with a huge mass loss of 62%, and is indicative of total combustion of the inorganic and organic moieties present in the precursor. This reaction generates an enormous amount of heat energy, which presumably facilitates the oxidation-decomposition reaction under the influence of atmospheric oxygen to form the oxide product LiCa_{0.20}Mn_{1.80}O_4. The second small exothermic peak at 411 °C, with a small weight loss, is associated with the combustion of the remaining organic constituents in the precursor. At higher temperature (~450 °C), there is no mass loss. This indicates that the decomposition of the precursor is completed at 450 °C.

3.3. XRD studies

The XRD patterns of LiCa_{y}Mn_{2-y}O_4 (with y = 0.05, 0.10, 0.15, 0.20) are shown in figure 3. The x-ray diffractograms reveal the formation of a highly crystalline phase of the product with high phase purity. There is no residue present in the diffractogram, proving that the product obtained has a single-phase structure without any noticeable residual impurities. The lattice parameters of LiCa_{y}Mn_{2-y}O_4 slightly decrease with increasing substitution of Ca^{2+} content, as shown in figure 4, and hence the Bragg planes (440) and (531) are slightly shifted towards lower 2θ angles. Increasing replacement of Mn by Ca^{2+} increases the average Mn valency from Mn^{4+} to Mn^{3+}, and the Ca^{2+} also replaces Mn^{3+} in the 16d octahedral site, as we do not observe the (220) Bragg line at about 2θ = 30°.

3.4. TEM analysis

Figures 5 and 6 show a TEM photograph and its particle size histogram of the synthesized LiCa_{0.20}Mn_{1.80}O_4 respectively. They show that the morphology of the synthesized powder is regular in shape and that there is no agglomeration, with an average particle size of around 61 nm. For comparison, we measured the particle size of the synthesized powders from the XRD data using the Scherrer equation. It shows that the powder is nano-crystalline particles and the particle size is 55 nm. This result supports our TEM observation. This indicates that the obtained LiCa_{y}Mn_{2-y}O_4 has good battery activity.

3.5. Electrochemical characterization

Figure 7 shows the charge-discharge curve at the first cycle of C || LiCa_{y}Mn_{2-y}O_4 (y = 0.05, 0.10, 0.15, 0.20). The initial discharge capacity decreases with increasing Ca content. This is due to the decrease in the amount of Mn^{4+} ions in the substituted spinel phase. The discharge capacity versus cycle...
Figure 5. TEM photograph of LiCa$_{0.30}$Mn$_{1.80}$O$_4$ powder.

Figure 6. Particle size histogram of LiCa$_{0.30}$Mn$_{1.80}$O$_4$ obtained from TEM.

Figure 7. Charge–discharge curves for C || LiCa$_y$Mn$_{1-y}$O$_4$ cell.

Figure 8. Relationship between the discharge capacity and cycle number of C || LiCa$_y$Mn$_{1-y}$O$_4$ cells and C || LiMn$_2$O$_4$ cells.

4. Conclusion
The following conclusions are drawn from the present investigation.

(1) X-ray diffraction studies show that the cubic spinel compound synthesized using aspartic acid is a single-phase compound without any impurities.

(2) TEM analysis clearly indicates that the synthesized products are in the nano-level without any agglomeration due to the dual nature of aspartic acid.

(3) Electrochemical studies show that Ca doped LiMn$_2$O$_4$ synthesized using aspartic acid has very good electrochemical performance.

(4) Among the various substitutions, $y = 0.10$ i.e., LiCa$_{0.10}$Mn$_{1.90}$O$_4$ shows excellent cycling performance.

In conclusion, aspartic acid is an excellent fuel as well as a very good dispersing agent for the synthesis of cubic spinel LiCa$_y$Mn$_{1-y}$O$_4$ powder. LiCa$_y$Mn$_{1-y}$O$_4$ synthesized using aspartic acid could be used as an effective cathode material for Li-ion batteries.

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Short communication

Synthesis of nano-crystalline LiSr_\(x\)Mn_{2-x}O_4 powder by a novel sol–gel thermolysis process for Li-ion polymer battery

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Abstract

Cubic spinel nano-crystalline LiSr_\(x\)Mn_{2-x}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 °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 LiSr_\(x\)Mn_{2-x}O_4 powder is examined by differential scanning colorimetric analysis. In order to assess the electrochemical reversibility of the cathode material, cyclic voltametry studies are performed by fabricating button cells with the configuration of carbon/MPPE/LiSr_\(x\)Mn_{2-x}O_4.

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Keywords: Lithium-ion batteries; Sol–gel thermolysis; Strontium-doped lithium manganese; 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 LiMn_2O_4 [3] offers considerable benefits, in terms of high specific capacity, toxicity and low cost. On the other hand, LiMn_2O_4 suffers from capacity fading that limits its reversibility. In order to overcome this problem, substitution of some of the manganese with additional lithium (Li_{1+x}Mn_{2-x}O_4) [4] or metal cations LiM_xMn_{2-x}O_4 (M = Ni, Cu, Cr, Co and 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 LiSr_\(x\)Mn_{2-x}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,
and for precise control of the particle-size and morphology of nano-crystalline powders. The present investigation involves the synthesis of nano-crystalline LiSr_xMn_{2-x}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 LiSr_xMn_{2-x}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 LiSr_xMn_{2-x}O_4 powders

The nano-crystalline cubic spinel LiSr_xMn_{2-x}O_4 (x = 0.10, 0.15, 0.20, 0.25) powders were prepared by a sol-gel thermolysis process. Analar grade LiNO_3, Sr(NO_3)_2, Mn(CH_3COO)_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°C to obtain a viscous solution (sol).

The viscous solution was again heated (to 120°C) for 3 h to obtain the precursor sample (gel). The precursor sample was then pyrolysed at 340°C for 3 h in air to obtain a cubic spinel LiSr_xMn_{2-x}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°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 Cu Kα radiation. The diffraction patterns were obtained at 25°C in the range 10° ≤ 2θ ≤ 75°. The step size and scan rate were set at 0.1 and 2°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 C/LiSr_xMn_{2-x}O_4 and employing a Li^+ ion conducting, PAN-based, microporous, polymer electrolyte. The cathode was prepared by mixing LiSr_xMn_{2-x}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 tonnes cm^{-2} using a hydraulic press to yield circular pellet electrodes. The pellets were then dried at 120°C in an air oven. Cyclic voltammograms were recorded at a slow scan rate of 1 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 LiSr_{0.25}Mn_{1.75}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°C due to the combustion nature of urea and the polyvinyl alcohol. On further heating, a second small exothermic peak is observed; it commences at 304.03°C with ends at 336.29°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°C indicates
complete phase formation and crystallization of the cubic spinel powder.

3.2. XRD studies

The X-ray diffractograms for the cubic spinels LiSr$_x$Mn$_{2-x}$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°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 LiMn$_2$O$_4$, the lattice parameters of LiSr$_x$Mn$_{2-x}$O$_4$ slightly decrease with increase in substitution of Sr$^{2+}$ content and hence the Bragg planes (4 4 0) and (5 3 1) are shifted slightly towards lower 2θ angles. The variation of the cubic lattice parameters of LiSr$_x$Mn$_{2-x}$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 Sr$^{2+}$. This raises the average Mn valency from Mn$^{3+}$ to Mn$^{4+}$ and also the Sr$^{2+}$ replaces Mn$^{3+}$ in the 16d octahedral sites. Hence, a strong Bragg plane (2 2 0) is not observed at 2θ = 30°.

3.3. SEM studies

An electron micrograph of the cubic spinel LiSr$_{0.25}$Mn$_{1.75}$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 Li$^+$ ions, as shown in Fig. 5(a)-(d). Among the various Sr$^{2+}$-doped LiMn$_2$O$_4$ cathode materials, LiSr$_{0.25}$Mn$_{1.75}$O$_4$ gives a high open-circuit potential of 5.0 V upon removing Li$^+$ and also has very good reversibility.
4. Conclusions

The synthesis of nano-crystalline, Sr-doped LiMn$_2$O$_4$ 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$_{0.25}$Mn$_{1.75}$O$_4$ yields a high open-circuit voltage of 5.0 V upon removing Li$^+$ 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$_{x}$Mn$_{2-x}$O$_4$ powder obtained by sol–gel thermolysis process could be used as an effective cathode material for Li-ion batteries.

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References

Combustion synthesis of inverse spinel \( \text{LiNiVO}_4 \) nano-particles using gelatine as the new fuel

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Abstract

An inverse spinel type \( \text{LiNiVO}_4 \) nano-particles have been synthesized to be used as cathode active material for Li-ion batteries by adopting combustion method using gelatine as the new fuel, which act as an excellent combustion fuel as well as very good dispersing agent. The optimum temperature for the phase formation and/or complete crystallization of the precursor sample is found out by TG/DTA analysis. The structural property of the synthesized product is characterized by X-ray diffraction and FTIR spectroscopy studies. The morphology and the particle size of the synthesized powder is analyzed by TEM studies. The electrochemical reversibility and the charge/discharge studies of the synthesized \( \text{LiNiVO}_4 \) are examined by fabricating lithium-ion polymer cell in the configuration of \( \text{C/LiNiVO}_4 \) employing \( \text{Li}^+ \) ion conducting PVdF-HFP based micro-porous polymer electrolyte.

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Keywords: Combustion synthesis; Gelatine; Lithium nickel vanadate; Inverse spinel compound; Li-ion batteries

1. Introduction

Over the past decade tremendous research has been conducted on cathode materials for their use in Li-ion batteries. Among them, \( \text{LiNiVO}_4 \) and \( \text{LiCoVO}_4 \) have been proposed as cathode active materials for modern rechargeable Li-ion batteries [1]. These inverse spinel materials are very attractive due to their theoretical capacity of about 148 mAh g\(^{-1}\) and high voltage in the range of 4.2–4.8 V over the other transition metal oxides such as \( \text{LiCoO}_2 \) [2], \( \text{LiNiO}_2 \) [3] and \( \text{LiMn}_2\text{O}_4 \) [4] and their upper voltage limits are in the range of 4.1–4.5 V. Of late, attempts are being made to obtain phase pure \( \text{LiNiVO}_4 \) by many researchers since synthesis is the key step towards the successful development of materials with good physical as well as electrochemical properties. Hence maximum efforts need to be put forth in selecting techniques for the synthesis of better performing \( \text{LiNiVO}_4 \). Several methods such as solid-state thermal reaction, hydrothermal, coprecipitation and combustion [5–8] have been adopted for the synthesis of these oxide materials. Among them, combustion technique is the most widely used method. Nevertheless, this technique has the drawback of producing highly agglomerated particles. To overcome this drawback, we have reported very recently a low temperature sol–gel thermolysis technique for the large-scale synthesis of well-dispersed nanocrystalline cubic spinel \( \text{LiSr}_2\text{Mn}_2\text{O}_4 \) powder using urea and poly vinyl alcohol [9].

In this paper, we report at the very first, the synthesis of \( \text{LiNiVO}_4 \) nano-particles in a very pure state by gelatine combustion technique. This gelatine plays an important role during the synthesis, which act as an excellent fuel as well as very good dispersing agent rather than all other conventional fuels to control the particle size and also prevents the particles from aggregation during the combustion process. The optimum temperature for the phase formation and/or complete crystallization of the precursor sample is found out by TG/DTA analysis. The structural property of the synthesized product is characterized by X-ray diffraction and FT-IR spectroscopy studies. The morphology and the particle size of the synthesized powder is analyzed by transmission electron microscope (TEM). Finally the electrochemical reversibility and charge-
discharge study of LiNiVO$_4$ nano-particles are tested by fabricating a Li-ion cell using PVdF-HFP based micro-porous polymer electrolyte.

2. Experimental details

The inverse spinel LiNiVO$_4$ nano-particles was prepared by combustion process using gelatine as the new fuel. Analar grade LiNO$_3$, Ni(NO$_3$)$_2$, NH$_4$VO$_3$ were used as the starting materials in the stoichiometric amount besides gelatine and made into a homogeneous solution using distilled water and then the solution was heated to boiling at 100 °C, a green-yellow paste was obtained. The paste was then allowed to decompose at around 200 °C. On decomposition, combustible gases NO$_3$ and ammonia are generated and resulting a black-brown mass which is referred to as precursor. The precursor was further heated to 490 °C yields a black mass and subsequently turns to yellow due to oxidation of trivalent vanadium (V$^{3+}$) to pentavalent vanadium (V$^{5+}$).

Thermal analysis of the precursor sample was made using a simultaneous TG/DTA Thermal analyzer (Model: STA-1500, PL Thermal Sciences, UK) at a heating rate of 10 °C/min under air atmosphere to find out the phase formation and/or complete crystallization temperature of the precursor sample.

X-ray diffraction measurements were made from JEOL X-ray diffractometer (Model: JDX-8030) using Cu-Ka radiation to identify the phase purity and structure conformity of the synthesized LiNiVO$_4$ powder. The diffraction patterns were taken at 25 °C in the range of 0° ≤ 2θ ≤ 70 ° in step scans. The step size and scan rate were set at 0.1° and 2°/min respectively.

FTIR spectrum was recorded with Perkin Elmer FTIR spectroscopy (Model: Paragon 500) using KBr pellets in the range of 400-1000 cm$^{-1}$.

The synthesized LiNiVO$_4$ nano-particles was analyzed by JEOL Transmission electron microscope (Model: 200CX) operated at 200 kV to examine the morphology and the particle size of the synthesized product.

The cyclic voltammetry and the charge/discharge studies were carried out on the synthesized LiNiVO$_4$ nano-particles by fabricating 2016 coin type electrochemical cell in the configuration of C/LiNiVO$_4$ employing Li$^+$ ion conducting PVdF-HFP based microporous polymer electrolyte. The cathode was made by mixing LiNiVO$_4$ nano particles, acetylene black and colloidal Teflon binder in the 85:10:5 weight ratios by wetting with alcohol. The mixture was pressed in a circular die on to an expanded aluminum grid at a pressure of 5 tons/cm$^2$ using a hydraulic press, yields a circular pellet electrode. This pellet was then dried at 120 °C in an oven. The electrochemical reversibility and charge-discharge studies of the fabricated cell was performed in between 3.0 and 5.0 V at a constant drain of 1 mV/S and 0.2 mA respectively using WPG-100 Potentiostat/Galvanostat (Wonatech) cycle life tester.

3. Results and discussion

Gelatine contains a large number of glycine. It is prepared by the thermal denaturation of collagen, isolated from animal skin and bones. It can also be extracted from fish skins. Due to long chain linkage of amino acids, gelatine has the dual nature, it can act as an excellent fuel as well as very good dispersing agent as in sol-gel thermolysis process [9]. Hence Li, Ni and V ions are trapped homogeneously through out the gelatine matrix and effectively control the particle size to get the nano-size particles of LiNiVO$_4$ and keep the nano-particles free from agglomeration during the combustion process. It can be assumed that the overall structure of gelatineous precursor is illustrated in Fig. 1.

The TG and DTA measurements were carried out for the precursor LiNiVO$_4$ sample in order to find out the exact phase formation and/or complete crystallization temperature of the synthesized LiNiVO$_4$ powder. The TG and DTA curves for the precursor LiNiVO$_4$ are shown in Fig. 2. The DTA curve shows one distinguishable endothermic transformation and one exothermic transformations. The endothermic
transformation process that appeared at about 100 °C can obviously be attributed to the removal of water molecule present in the precursor sample. The first exothermic whose onset begins at 230 °C with a peak maximum at 268.15 °C accompanied by 25% mass loss was deduced from TG analysis. As the process of heating is continued, the mass loss increases, owing to the combustion nature of the precursor complex. The combustion nature of gelatine together with the nitrate present in the precursor gave rise to enormous heat energy for initiating the crystallization of LiNiVO₄. At higher temperature of >475 °C there is no mass loss. This indicates that the decomposition of precursor completed at 475 °C.

The XRD pattern was observed for the synthesised LiNiVO₄ is shown in Fig. 3. The X-ray diffractogram displays (311) Bragg peak at about 36°. The diffractogram also displays a weak (111) Bragg peak and a strong (220) line both of which indicate the inverse spinel structure of LiNiVO₄. The increase in intensity of (220) line at the expense of (111) line is due to the presence of vanadium on the tetrahedral 8a site. The intensity ratio of I(220)/I(311) is 0.5 shows the highly crystalline nature of the product [10]. The XRD pattern of the obtained LiNiVO₄ powder completely matched that of an inverse spinel structure listed in a JCPDS file and evidently there is no residues present in the diffractogram which confirm that the product obtained by using gelatine has the single phase structure without any noticeable impurities. The possible contamination of NiO impurity peak at 2θ=43.5° is absolutely absent in the obtained product. Thus the exclusion of NiO contaminant is the final product as observed by Prabaharan et al. [8], has been made possible through the usage of gelatine as the fuel. Peaks corresponding to Li₃VO₄ phase at 2θ=16.2°, 24.5°, 22.8° and 24.3° were also found to be absent. The lattice constant value of synthesized product was measured to be 8.218 Å, which is in good agreement with the standard value of 8.219 Å [11].

Fig. 4 shows the FTIR spectrum of LiNiVO₄ powder obtained in the wave length range of 400–1000 cm⁻¹. The bands observed at 630, 700 and 810 cm⁻¹ have been assigned to stretching vibrations of VO₄ tetrahedrons, and are found to be the characteristics vibrational bands of an inverse spinel structure [12]. The bands observed in the 400–750 cm⁻¹ region has been largely associated with the bending vibrations of VO₄ tetrahedrons or the vibrations of NiO₆ and LiO₆ octahedral environments. The bonding of Li and Ni with each oxygen atom in VO₄ tetrahedral brings about some asymmetry, but with out disturbing the overall cubic symmetry of the fundamental unit cell. Hence, the broad bands located around 810 and 850 cm⁻¹ corresponds to the asymmetric stretching modes in distorted VO₄ tetrahedrons [13]. Also two weak bands around 440 and 420 cm⁻¹ have been assigned to asymmetric stretching of Li–O in LiO₆ environment [14]. These two peaks are more prominent for LiNiVO₄. The bands in the high frequency region are assigned to the vibration between oxygen and the highest valence cation. As a result, the weak band around 900 cm⁻¹ is assigned to be symmetric stretching in VO₄.

Fig. 5 shows the TEM image of LiNiVO₄ powder calcined at 475 °C. It shows that the powder is composed of ultrafine particles with uniformly distributed size ca. 40–60 nm. No doubt, such nano size
particles would facilitate reducing the diffusion length of the lithium ions for intercalation and deintercalation. Fig. 6 shows the particle size distribution of LiNiVO₄ powder. It can be seen that the average particle size is around 40 nm. For comparison, we measured the particle size of the synthesized powder from the XRD data using Scherer equation. It shows that the powder is nanocrystalline particles and the particle size is ~35 nm. This result supports our observation through TEM that the gelatine combustion technique produced larger nanoparticles.

Fig. 7 shows the cyclic voltammogram of C/LiNiVO₄ cell in the voltage range of 3–5 V at a sweep rate of 1 mV/s. The CV response shows that the electrochemical lithium insertion/deinsertion process and the charge/discharge behaviour remains almost unchanged and confirms the considerable reversibility of the cell.

The reversibility of the electrochemical process is further demonstrated by the charge–discharge studies in between 3 and 5 V at a constant current density of 0.2 mA cm⁻² is shown in Fig. 8. It shows that the initial capacity of LiNiVO₄ is 102 mA h g⁻¹ against the theoretical value of 148 mA h g⁻¹ and retaining almost 65% of its initial capacity at the 20th cycle. However this discharge capacity value may seen to be far behind the theoretical value but it is much better than already reported values [12,15–17]. This may be due to the improved morphological feature of the nano-particles.

4. Conclusion

In summary, gelatine is found to be an effective fuel as well as very good dispersing agent for the synthesis of inverse spinel LiNiVO₄ nano-particles. Due to this dual character of gelatine the crystalline powder is formed even at low temperature with no aggregation during the combustion process. An electrochemical investigation shows that the product obtained by this method yields better capacity than the materials prepared using other combustion fuels reported in the literature. Hence, gelatine used for the synthesis of inverse spinel powder is an effective combustion fuel and the compound obtained using this fuel could be used as an effective cathode active material for Li-ion battery applications.

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References

Synthesis and characterization of LiMg$_2$Mn$_{2-y}$O$_4$ cathode materials by a modified Pechini process for lithium batteries

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Abstract. Cubic spinels of composition, LiMg$_2$Mn$_{2-y}$O$_4$, with $y = 0.0, 0.05, 0.1, 0.15$ and $0.2$, were synthesized by a modified Pechini process using polyethylene glycol and citric acid. The phase formation and/or crystallization of the precursors were studied by thermal analysis. Products were characterized by X-ray diffraction and SEM analysis. Coin cells were fabricated with lithium as the anode and LiMg$_2$Mn$_{2-y}$O$_4$ as the cathode in an electrolyte of 1M LiPF$_6$ in a 1:1 (v/v) mixture of EC and DEC. The charge–discharge studies were performed and the results were compared with materials prepared by a solid state thermal method.

Keywords. Lithium batteries; cathode material; modified Pechini process; cubic spinel materials.

1. Introduction

Among the various insertion compounds used in lithium batteries, LiMn$_2$O$_4$ spinel is attractive as a positive electrode material due to its low cost and less toxic nature (Ozhuku et al 1990; Guyomard and Tarason 1994). However, LiMn$_2$O$_4$ suffers from capacity fade, which limits its cyclability. The capacity fading is due to John–Teller distortion effect (Gummow et al 1994) and lattice instability of pure spinel compounds at higher oxidation levels (Yamada 1996). But doped spinels have no such distortion effect. Hence capacity fading is independent of temperature. In order to overcome these problems, substitution of some of the manganese with additional lithium (Li$_{1+x}$Mn$_{2-x}$O$_4$) or with several cations (Li$_{1-x}$M$_{x}$Mn$_{2-y}$O$_4$, where $M = \text{Ni, Co, Cr and Al}$) (Morita et al 2001; Lee et al 2004) has been widely explored. The electrochemical behaviour of these materials also depends upon the method of synthesis (Gummow et al 1994). In recent years, several low temperature techniques such as sol–gel (Hwang et al 2001), combustion (Kovacheva et al 2002), precipitation (Shaju et al 2002) and emulsion drying (Myung et al 2000) have also been used for the synthesis of LiMn$_2$O$_4$ spinels. Although these methods offer a greater degree of homogeneity, they require careful manipulation which may increase the cost of production and it may also require high temperature heating (above 800°C) for 10–12 h to get the final product.

Very recently, Pechini process (U.S. Pat. 1967) has been used for the synthesis of LiMn$_2$O$_4$ because it eliminates some drawbacks inherent in the other low temperature processes and also gives high purity products with controlled stoichiometries. Other low temperature processes are not always effective at maintaining a homogeneous reactant distribution during heating; the result is that undesirable phase can form at the beginning of calcinations (Bach et al 1990; Barboux et al 1991). But in Pechini process a 1:4 molar ratio of citric acid and ethylene glycol is used and several steps are involved to get the polymeric precursor. All these steps are tedious and care must be taken in every step including in the removal of any excess ethylene glycol by heating to about 180°C under reduced pressure. As ethylene glycol is eliminated, polyesterification occurs (Liu et al 1996). In order to eliminate the above drawbacks of the Pechini process, in the present investigation, a modified Pechini process is introduced in which both citric acid and PEG are directly used in the reaction process.

Hence in the present study, we have shown the possibility of synthesizing substituted LiMn$_2$O$_4$ by a modified Pechini process. The electrochemical behaviour of cathode materials during charging and discharging were also investigated. These results were compared with materials prepared by a solid-state thermal method.

2. Experimental

2.1 Synthesis

Nano-crystalline cubic spinel, LiMg$_2$Mn$_{2-y}$O$_4$ ($y = 0.10, 0.15, 0.20, 0.25$) powders, were prepared by a modified Pechini process. AnalR grade LiNO$_3$, Mg(NO$_3$)$_2$ and Mn(CH$_3$COO)$_2$ were used as the starting materials. In this method, stoichiometric amount of LiNO$_3$, Mg(NO$_3$)$_2$ and

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Mn(CH₃COO)₂ were taken and made into a homogeneous solution with distilled water. In the above solution, required quantity of citric acid and polyethylene glycol were added and then the solution was heated to 100°C to make it viscous. Interestingly polyethylene glycol acts as a dispersing agent as well as secondary fuel.

According to a concept developed in propellant chemistry (Jain et al. 1981), the oxidizing valency (O) of LiNO₃ was -5, Mg(NO₃)₂ -10 and Mn(CH₃COO)₂ +16 and the reducing valency (F) of citric acid was +18. The amount of citric acid required was calculated for LiMg₀.₂₀Mn₁.₈₀O₄ system by using this concept to get

\[ 1 \times (-5) + (-10 \times 1 \times 0.10) + (16 \times 1 \times 1.90) + 18n = 0, \quad n = 1.35 \text{M}. \]

Therefore, the required amount of citric acid was 1.35 M. But the amount of PEG optimized empirically was equivalent to the amount of citric acid taken. The same procedure was followed for other ratios such as 0.15, 0.20 and 0.25.

The viscous solution so obtained was further heated to 140°C for 3 h for esterification reaction. This precursor was then pyrolysed at 340°C for 3 h in air. In this way cubic spinel LiMg₂Mn₂₋₀₄ powder was obtained. The resultant products were collected and subjected to both physical characterization and electrochemical studies.

### 2.2 Physical characteristics

X-ray diffraction measurements were made from JEOL (JDX 8030) X-ray diffractometer using nickel filtered Cu-Kα radiation to identify the crystalline phase of the synthesized materials. The thermal decomposition behaviour of the precursor sample, LiMg₂₀Mn₁.₈₀O₄, was made using a simultaneous TG/DTA thermal analyser (STA-1500 Model) at the heating rate of 10°C/min under ambient atmosphere. The microstructure of the powder was observed using JEOL (JSM-840 A) scanning electron microscope.

### 2.3 Electrochemical characteristics

LiMg₂Mn₂₋₀₄ powders were electrochemically characterized by fabricating 2016 coin cells which consisted of lithium anode, LiMg₂Mn₂₋₀₄ powder cathode, polypropylene separator and a solution of 1 M LiPF₆ in 1 : 1 (v/v) ratio of EC and DEC electrolyte. The cathode was made of a mixture containing LiMg₂Mn₂₋₀₄ powder, acetylene black and polyvinylidene fluoride (PVdF) binder in N-methyl-2-pyrrolidone (NMP) in the 80 : 10 : 10 weight ratio. This mixture was spread over an expanded micro-grid and was then pressed at a pressure of 5 tons/cm² and dried at 120°C for 5 h in an oven. The cells were assembled in an argon filled dry box. The charge and discharge cycling was performed galvanostatically at the current density of 0.2 mA/cm² within voltages of 3.2-4.5 V.

### 3. Results and discussion

The optimum temperature of phase formation and/or crystallization of the LiMg₂₀Mn₁.₈₀O₄ precursor sample is 490-17°C which is confirmed by thermal analysis as shown in figure 1. This result displays two discrete weight loss regions occurring at 381.5°C and 490.2°C. An exothermic peak is observed at about 381-49° accompanied by a noticeable weight loss of 2.5%. With continuous heating, the mass loss increases, owing to the combustion nature of citric acid together with nitrate precursor complexes and resulting in second exotherm whose onset begins at 490-2°C with an end at 534.5°C accompanied by huge mass loss of 70-4%. This indicates that the compound begins to decompose at lower temperatures and the exothermic combustion of citric acid supplying adequate heat energy for initiating the crystallization of LiMg₂Mn₂₋₀₄ powder. There are two distinguishable exothermic transformations deduced from the DTA data. The exotherm occurring at 490-2°C indicates phase formation and/or crystallization of the cubic spinel, LiMg₂Mn₂₋₀₄.

Figure 2 shows X-ray diffraction patterns of a series of powders with different \( x \) in LiMgₓMn₂₋₀₄ materials calcined at 550°C for 5 h in air. All these samples were identified as a single phase cubic spinel with a space group, \( Fd3m \). The lattice constant values of LiMgₓMn₂₋₀₄ samples were presented in table 1. As compared with LiMn₂O₄, the lattice parameters of LiMgₓMn₂₋₀₄ slightly decreased with increase in substitution of Mg²⁺ content (Liu et al. 1996; Idemoto et al. 1999) and hence the Bragg planes (440) and (531) were slightly shifted towards lower 2θ angle. Figure 3 represents the variation of the cubic lattice parameters of LiMgₓMn₂₋₀₄ as a function of the Mg content. It is obvious that a slight decrease in lattice parameter was observed due to the partial replacement of Mn by Mg²⁺. This increases the average Mn
valency from Mn\(^{3+}\) to Mn\(^{4+}\). Also the Mg\(^{2+}\) replaces Mn\(^{3+}\) in the 16\(d\) octahedral site and hence the strong Bragg plane (220) was not observed at \(2\theta = 30^\circ\), which is extremely sensitive to the occupancy of the 8\(a\) tetrahedral site (Juliene et al 2001).

The 4 V discharge capacities of the cathodes of various compositions obtained in the first cycle (figure 4) along with the theoretical values are shown in table 2. The initial discharge capacities of Li/LiMn\(_2\)O\(_4\) (\(y = 0\)) is 137 mAh/g.

The initial discharge capacities of Li/LiMg\(_y\)Mn\(_{2-y}\)O\(_4\) from \(y = 0\) to 0.25 are 132 mAh/g, 118 mAh/g, 100 mAh/g and 90 mAh/g, respectively. Since deintercalation of Li\(^+\) from the spinel structure must be electrically compensated by oxidation of Mn\(^{3+}\) to Mn\(^{4+}\). This suggests that even for substituted spinel phases, only the amount of Mn\(^{3+}\) contributes to the discharge capacity. So the initial capacity of LiMg\(_y\)Mn\(_{2-y}\)O\(_4\) (0 \(\leq y \leq 0.25\)) is limited by the initial amount of Mn\(^{3+}\) in the 16\(d\) sites. The discharge capacity versus cycle number of Li/LiMg\(_y\)Mn\(_{2-y}\)O\(_4\) with \(y = 0\) to 0.25 is shown in figure 5. The capacity loss observed for undoped LiMn\(_2\)O\(_4\) is about 25% after 25 cycles, whereas that for Li/LiMg\(_y\)Mn\(_{2-y}\)O\(_4\) from \(y = 0.05\) to 0.25 are 12%, 2-33%, 7% and 9.5%, respectively. This can be achieved by the substitution of Mg\(^{2+}\) into the Mn site accompanied

Figure 2. X-ray diffraction patterns for cubic spinel, LiMg\(_y\)Mn\(_{2-y}\)O\(_4\), where (a) \(y = 0.0\), (b) \(y = 0.05\), (c) \(y = 0.10\), (d) \(y = 0.15\) and (e) \(y = 0.20\) obtained by modified Pechini process.

Figure 3. Variation of lattice constant of LiMg\(_y\)Mn\(_{2-y}\)O\(_4\) as a function of Mg content.

Table 1. Comparison between the standard and experimentally observed lattice constant values of cubic spinel, LiMg\(_y\)Mn\(_{2-y}\)O\(_4\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Standard lattice constant value (Å)</th>
<th>Experimentally observed lattice constant value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn(_2)O(_4)</td>
<td>8.2358</td>
<td>8.2293</td>
</tr>
<tr>
<td>LiMg(<em>{0.05})Mn(</em>{1.95})O(_4)</td>
<td>8.2356</td>
<td>8.2287</td>
</tr>
<tr>
<td>LiMg(<em>{0.1})Mn(</em>{1.9})O(_4)</td>
<td>8.2338</td>
<td>8.2205</td>
</tr>
<tr>
<td>LiMg(<em>{0.15})Mn(</em>{1.85})O(_4)</td>
<td>8.2191</td>
<td>8.2123</td>
</tr>
<tr>
<td>LiMg(<em>{0.2})Mn(</em>{1.8})O(_4)</td>
<td>8.2154</td>
<td>8.1976</td>
</tr>
</tbody>
</table>
Table 2. 4 V capacities of various compositions (mAh/g).

<table>
<thead>
<tr>
<th>Formula</th>
<th>Practical capacity</th>
<th>Theoretical capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMnO₄</td>
<td>137</td>
<td>148-2</td>
</tr>
<tr>
<td>LiMg.05Mn.95O₄</td>
<td>132</td>
<td>134-5</td>
</tr>
<tr>
<td>LiMg.10Mn.90O₄</td>
<td>118</td>
<td>120-61</td>
</tr>
<tr>
<td>LiMg.15Mn.85O₄</td>
<td>100</td>
<td>106-45</td>
</tr>
<tr>
<td>LiMg.20Mn.80O₄</td>
<td>90</td>
<td>92-046</td>
</tr>
</tbody>
</table>

Figure 4. Electrochemical features of Li/LiMgₓMn₂₋₀.₄ cells with y = 0.0, 0.05, 0.10, 0.15, 0.20 during first charge-discharge cycle in the voltage range of 3-2 and 4-5 V at a current density of 0.2 mA/cm².

Figure 5. Relationship between the discharge capacity and cycle number of Li/LiMgₓMn₂₋₀.₄ cells in the voltage range of 3-2-4-5 V at a current density of 0-2 mA/cm².

by the oxidation of Mn³⁺ into Mn⁴⁺ resulting in an increase in the average valency of Mn which suppresses the John–Teller distortion. Li et al (1996) also reported that the doped materials enhance the stability of the octahedral sites in the spinel skeleton structure. Hence, the electrochemical stability of LiMn₂O₄ is less than that of the Mg substituted LiMn₂O₄. These results were in good agreement with the reported results (Jeong et al 2001). Among the various compositions, LiMg₀.₁₀Mn₁.₉₀O₄ shows better reversibility, because the suppression of John–Teller distortion is high in 0.10 substitution than 0-05 substitution. Moreover, electrochemical inactive Mn⁴⁺ species is low in 0-10 substitution than in 0-15, 0-20 and 0-25 substitutions. Figure 6 shows the scanning electron microscope (SEM) pattern of LiMg₀.₁₀Mn₁.₉₀O₄ powder calcined at 550°C for 5 h in air. The photograph confirms the formation of spherical grains of sub-micron nature of lithium magnesium manganate with an average size of < 50 nm accompanied by controlled grain growth.

4. Conclusions

The following conclusions were drawn from the present study:

(i) The modified Pechini process is found to be an easy method for the synthesis of cubic spinel, LiMgₓMn₂₋₀.₄ powders, at moderate temperature.
Synthesis of LiMg$_y$Mn$_{2-y}$O$_4$ cathode materials

(II) X-ray diffraction analysis confirms the phase purity and the structure of the synthesized products.

(III) Thermal analysis indicates the exact phase formation and/or crystallization temperature of the LiMg$_{0.20}$Mn$_{1.80}$O$_4$ sample. It is found that the product undergoes complete crystallization at 535°C.

(IV) The SEM analysis confirms the formation of spherical grains of < 50 nm accompanied by controlled grain growth of the powder.

(V) The charge-discharge behaviour of the synthesized LiMg$_{0.10}$Mn$_{0.90}$O$_4$ sample shows the initial discharge capacity of 118 mAh/g and its capacity loss at even 25th cycle is only 2.33%.

Thus the modified Pechini process used in this investigation is found to be a very useful process for synthesizing Mg-doped LiMn$_2$O$_4$ spinel at moderate temperature which has good cyclability. Hence, the compound could be used as an effective cathode material for high voltage rechargeable lithium batteries.

Acknowledgements

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