Synthesis and characterization of Li_2MnO_3 nanoparticles using sol-gel technique for lithium ion battery

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Nanoparticles of Li_2MnO_3 were fabricated by sol-gel method using precursors of lithium acetate and manganese acetate, and citric acid as chelating agent in the stoichiometric ratio. TGA/DTA measurements of the sample in the regions of 30 °C to 176 °C, 176 °C to 422 °C and 422 °C to 462 °C were taken to identify the decomposition temperature and weight loss. The XRD analysis of the sample indicates that the synthesized material is monoclinic crystalline in nature and the calculated lattice parameters are 4.928 Å (a), 8.533 Å (b), and 9.604 Å (c). The surface morphology, particle size and elemental analysis of the samples were observed using SEM and EDAX techniques and the results confirmed the agglomeration of nanoparticles and, as expected, Li_2MnO_3 composition. Half cells of Li_2MnO_3 were assembled and tested at C/10 rate and the maximum capacity of 27 mAh/g was obtained. Charging and discharging processes that occurred at 3 V and 4 V were clearly observed from the cyclic voltammetric experiments. Stability of the electrodes was confirmed by the perfect reversibility of the anodic and cathodic peak positions observed in the cyclic voltammogram of the sample. The Li_2MnO_3 nanoparticles exhibit excellent properties and they are suitable for cathode materials in lithium ion batteries.

Keywords: Li_2MnO_3 ; sol-gel; monoclinic structure; TGA; DTA; XRD; EDAX; Li-ion battery; cyclic voltammetry

1. Introduction

In this electronic era, lithium ion batteries (LIB) have been energizing all our electronic gadgets since Sony Inc. introduced lithium based cathode in 1991. Due to the excellent rate capability, cyclability, and high tap density [1–3], the LiCoO_2 has been widely used as cathode material. LiCoO_2 electrode has the theoretical storage capacity of 273 mAh g^{-1} , but in practice it is 140 mAh g^{-1} . This deviation is due to high-surface reactivity and instability of the delithiated $\text{Li}_{1-x}\text{CoO}_2$ ($x > 0.5$) [4], and cobalt is relatively expensive and toxic in nature. Many engineers and scientists have carried out research to find new cathode material with superior capacity, energy, safety and low cost. In this way, lithium manganese oxide (Li_2MnO_3) was introduced in the year 1996 [5] in commercial

Li-ion cells as positive electrode. Its cyclability is excellent at room temperature and it shows spinel cubic structure. At high temperature, prolonged cycling of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ results in capacity fading [6].

Nowadays, the lithium batteries act as storage devices in hybrid electric vehicles (HEV) and pure electric vehicles. For these vehicles, current energy density of the LIBs should have high value. Nevertheless, the current energy density of LIBs fails to fulfill HEVs or electric vehicles (EVs) requirements [7, 8] due to undesired low energy densities of the commercial LIBs, predominantly. Among the LiB components, cathode material plays a greater role in enhancing the energy density than anode material does, because the capacity and the voltage depend mainly on the electrochemical performance of the cathode material when the carbon is used as the anode material in practice. Several approaches have been adopted to improve the elec-

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trochemical performance of cathode materials at elevated temperatures.

This motivated us to synthesize Li_2MnO_3 as cathode material at nanoscale level by using active material, polyvinylidene fluoride (PVDF), and super P carbon. For instance, surface modification of $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$ and LiCoO_2 with AlF_3 has led to a large discharge capacity with a reasonable cycling at a cut off voltage of 4.5 V. The coating procedure is usually complicated, which makes it very difficult to get the reproducible electrochemical performance, and there exists possible instability of the coating at elevated temperature and especially after expensive cycling. As a consequence, exploring a simple coating-free method to cathode materials with improved performance at elevated temperature is very important, when using batteries for transportation applications is considered. The content of Li_2MnO_3 in these composites is usually high at $x > 0.5$, while Li_2MnO_3 shows a poor cycling performance at elevated temperature due to electrolyte decomposition. Reducing the content of Li_2MnO_3 is thus highly promising but still less accessible. In spite of some progress in the above issues, one still has to face dual primary problems.

2. Experimental

2.1. General view on the preparation of oxidic materials

The electrochemistry of battery-active materials shows a strong correlation with their preparative and processing techniques. Conventional preparative methods for oxides involve solid-state reaction methods with oxides, nitrates, carbonates, etc. as precursors. However, solid-state synthetic methods are both labor-intensive and energy-intensive in that they involve repeated heating and grinding. Moreover, the products are generally large sintered particles. The disadvantages of solid-state methods, such as larger particle size of the products, inhomogeneous distribution, lack of stoichiometry control etc. can be overcome by soft chemistry methods such as sol-gel and co-precipitation which offer products with homogeneous distribution of uniform, submicron size particles with good

stoichiometry control. Therefore several soft chemistry strategies have been adopted for the preparation and processing of such solid oxide materials. Sol-gel processing, one of the promising solution-based methods, has been successfully employed to produce a variety of electrode active materials. However, sol-gel methods usually employ expensive chemicals, which is not attractive from a commercial point of view. Another popular synthesis method is combustion synthesis, which involves highly exothermic redox chemical species in flaming (gas-phase), smouldering (heterogeneous), or explosive reactions.

2.2. Preparation of lithium acetate precursor

The solution was prepared by taking 10.201 g of lithium acetate using a single pan balance (Mettler), having an accuracy of 0.001 mg, transferring it to a required quantity of distilled water and stirring well with a magnetic stirrer.

2.3. Preparation of manganese acetate precursor

The solution was prepared by taking 12.245 g of manganese acetate using a single pan balance, transferring it to a required quantity of distilled water and stirring well with a magnetic stirrer.

2.4. Preparation of chelating agent

28.8195 g of citric acid (salt form) was weighed using a single pan balance and then dissolved in required quantity of distilled water and stirred well.

Stoichiometric quantities of lithium acetate, manganese acetate and citric acid in the ratio of 1:1:3 were taken into three different beakers. In lithium acetate solution, manganese acetate solution was added drop by drop with a constant stirring setup, and the citric acid was added drop by drop gradually with the same rate of stirring. The mixed solution was stirred vigorously with the addition of ammonia (to control pH) and the pH of the solution was monitored using pH meter. The prepared (standardized) solution was again stirred well upon heating to 80 – 90 °C for 4 to 6 hours in a magnetic stirrer, in order to remove the excess of ammonia

and water, till gel formation. The beaker containing gel (metal citrate precipitate) was placed in a hot air oven for 12 hours at 120 °C. Then the beaker was placed in a muffle furnace for 6 hours at 350 °C to eliminate the organic residues in the gel. The soft and solid state form of metal citrate was grinded and annealed at 850 °C for 12 hours in the muffle furnace, then allowed to cool to room temperature. The rate of heating and cooling was maintained at 1 °C/min. The obtained substance was in a form of hard flakes. It was grinded to powder form. Thus, Li_2MnO_3 powder was prepared by sol-gel method using citric acid as a chelating agent.

Fig. 1. Preparation procedure

The chemical composition of the synthesized spinel sample (Li_2MnO_3) was studied by chemical analysis. The thermal decomposition behavior

of the citrate precursor was examined by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) by means of a thermal analysis. The crystalline phase of a material calcined at various temperatures was identified by powder X-ray diffraction using $\text{Cu-K}\alpha$ radiation. The particles morphology of the material was observed by scanning electron microscopy (SEM) with EDAX. The scheme of Li_2MnO_3 procedure is shown in Fig. 1.

3. Results and discussion

The chemistry of Li_2MnO_3 and its derivative is different from those of the materials of the series LiMn_2O_4 , LiNiO_2 and LiMnO_2 . The oxidation states of the transition metals, especially Mn is 3^+ and 4^+ , and the transformation from 3^+ to 4^+ that takes place during discharge process leads to the effect which is known as Jahn-Teller effect. However, the oxidation states of nickel and manganese in the isostructural compositions do not correspond to true solid solutions formed from these materials. The fact that manganese is in its tetravalent state shows that it is electrochemically inactive in the compound. Nickel in 2^+ oxidation state has been shown to undergo a two-electron oxidation in the compound during charging and turned to tetravalent nickel.

3.1. Thermal analysis

The temperature of decomposition of precursors, metal acetates containing lithium, manganese and titanium was studied by using thermogravimetric analysis and differential thermal analysis. Fig. 2 presents the thermal behavior of Li_2MnO_3 synthesized by using citric acid as a chelating agent. The experiments were carried out by heating the sample up to 1000 °C in air atmosphere and at a heating rate of 10 °C. It could be observed from Fig. 2 that the weight loss in the sample occurs in three different stages up to 462 °C. The weight loss at different stages may be due to dehydration, dehydroxylation and decarburization at various temperatures [9]. The process is accompanied by two endothermic peaks and two distinct exothermic peaks. The first distinct weight loss occurs in the temperature range from 30 °C to 176 °C and

this weight loss could be associated with the release of adsorbed water from the acetic acid and acetate precursors. The next weight loss occurs between 176 °C and 422 °C and it could be due to the decomposition and combustion of constituents in the precursors. Another weight loss region occurring between 422 °C and 462 °C may be due to the decomposition of acetate precursor material, combustion of gelling agent and formation or crystallization of Li_2MnO_3 . Above 462 °C there is no appreciable change in the weight that indicates the formation of Li_2MnO_3 spinel which is stable afterwards. A minor endothermic peak around 356 °C and a major exothermic peak around 441 °C, are observed in the sample. The occurrence of exothermic peak at around 441 °C corresponds to the major weight loss within the narrow temperature region which indicates the completion and formation of the compound due to the decomposition of organic and inorganic constituents in the precursors.

Fig. 2. TGA/DTA pattern of Li_2MnO_3

3.2. X-ray diffraction analysis

The XRD pattern of Li_2MnO_3 sample synthesized by sol-gel method using citric acid as chelating agent is depicted in Fig. 3. The diffraction lines clearly show that the sample is in crystalline form [10]. The diffraction peaks have been indexed with non-linear least square fitting (NLLS) in order to obtain their crystallographic parameters. The peak position at 2θ values of 19.05°, 37.62° and

45.24° are indexed as (1 0 2), (2 2 1), (1 0 6) planes, which is in good agreement with those of powder Li_2MnO_3 obtained from the International Center of Diffraction Data Card (JCPDS 73-0152) conforming the formation of crystalline monoclinic structure. The lattice parameters are $a = 4.928 \text{ \AA}$, $b = 8.533 \text{ \AA}$ and $c = 9.604 \text{ \AA}$ and $\alpha = \gamma = 90^\circ$, $\beta = 99.5^\circ$. The obtained results are consistent with the previously reported literature [11].

Fig. 3. X-ray diffraction pattern of Li_2MnO_3

The crystallite size (D) was calculated using Scherrer formula:

$$D = \frac{0.94 \lambda}{\beta \cos \theta} \quad (1)$$

The full width at the half maximum (β) was calculated from the slope of $\beta \cos \theta$ versus $\sin \theta$ plot using the relation:

$$\beta = \frac{\lambda}{D \cos \theta} - \varepsilon \tan \theta \quad (2)$$

The dislocation density (δ) was calculated from the relation:

$$\delta = 1/D^2 \quad (3)$$

The lattice parameters (a , b and c) of the crystals were determined by using the relation:

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \gamma} + \frac{k^2}{b^2 \sin^2 \gamma} - \frac{2hk \cos \gamma}{ab \sin^2 \gamma} + \frac{l^2}{c^2} \quad (4)$$

where (h k l) are the Miller indices of the predominant peaks. The crystallite size, dislocation density and strain of the sample were calculated for the prominent peak (1 0 2) as 34.518 nm, 8.393×10^{14} and 0.0016 respectively. The monoclinic structure of the Li_2MnO_3 sample is shown in Fig. 4.

Fig. 4. Monoclinic structure of Li_2MnO_3

3.3. SEM examination

The surface morphologies of the Li_2MnO_3 sample were analyzed with scanning electron microscopy at a magnification of 10 K. SEM image of the Li_2MnO_3 sample synthesized by sol-gel method is shown in the Fig. 5. The formation of monodispersed and agglomerated particles with a particle size ranging from 2 μm to 4 μm (approximately 0.5 to 2 μm) with clearly visible crystal boundaries is evident from the SEM picture. It also indicates that the material synthesized by the sol-gel method is nonuniform and some particles are spherical in shape. Some faceted crystals are also seen. It is observed that the particles are mainly irregular in shape, and most of them are hemispherical. It could also be observed that some particles exhibit agglomerated morphology and good crystallinity.

Fig. 5. SEM image of Li_2MnO_3 and EDAX spectrum of Li_2MnO_3

3.4. Energy dispersive analysis by X-ray (EDAX)

Energy dispersive analysis by X-ray is an analytical technique used for elemental analysis or chemical characterization of a sample. The technique relies on the interactions of some source of X-ray excitation and the sample, based on the principle that each element has a unique atomic structure allowing unique set of peaks in its X-ray emission spectrum. The experiment was carried out using Bruker EDAX analyzer attached with TESCAN scanning electron microscope. Unfortunately, the content of lithium could not be observed since the instrument could not be used for analyzing the low molecular weight elements. The analysis was carried out for the sample of Li_2MnO_3 prepared by sol-gel method and the results are presented in Fig. 5. The weight percentage of manganese and oxide for the sample are 56.87 % and 46.13 %, respectively.

3.5. Electrochemical studies

Half cells were assembled (CR 2032) using synthesized Li_2MnO_3 as cathode material and Li metal foil as anode. The cathode was prepared by mixing 80 weight percent of active material, 10 weight percent of conducting material (SP carbon) and 10 weight percent of a binder (PVDF). NMP was used as a solvent to prepare a slurry of the above composition and the slurry was applied on the substrate (aluminum foil) and dried at 100 $^{\circ}\text{C}$ for about 12 hours. Lithium foil was used as a counter electrode. Then, the CR2032 type coin cell was assembled in moisture and oxygen controlled glove box.

3.5.1. Electrochemical charge-discharge studies

The galvanostatic charge-discharge experiments were performed in a battery life cycle tester at C/10 rate. The charge cut-off voltage was 4.6 V and the discharge cut-off voltage was 2.8 V. Fig. 6 presents the charge-discharge behavior of the electrode. The charging voltage of the sample prepared by sol-gel method increased rapidly to 3.0 V immediately upon charging and then the voltage increased gradually up to the cut-off voltage of 4.6 V. Total charge input was around 8.00 mAh in the first cycle. The discharge curve indicated the sloping profile up to the cut-off voltage. The delivered discharge capacity of the assembled cell was 6.99 mAh in the first cycle. After that the charge capacity as well as the discharge capacity increased gradually upon continuous cycling. It indicates that the active material was undergoing activation during initial cycles and the discharge capacity increased in subsequent cycles. The cycle life behavior for Li_2MnO_3 samples synthesized by sol-gel method is illustrated in Fig. 7.

Fig. 6. Charge-discharge curves Li_2MnO_3 , (a) charging graph and (b) discharging graph

The cycle life experiments were carried out around 30 times and the discharge capacity increased upon cycling [12]. The sample prepared by sol-gel method showed a rapid increase in discharge capacity upon cycling and maximum capacity.

Fig. 7. Cycle life behavior of Li_2MnO_3

3.5.2. Electrochemical impedance spectroscopy study

Fig. 8. Impedance plot (Nyquist plot) of Li_2MnO_3 prepared by sol-gel method

Electrochemical impedance spectroscopy (EIS) involves the study of variation of impedance of an electrochemical system at a frequency of small amplitude. Electrochemical impedance spectroscopic experiments were carried out in order to ascertain electrochemical kinetic parameters to reveal the relationship between the crystal lattice and electrochemical properties [13]. The experiments were conducted in the range of 100 kHz to 10 MHz with the perturbation amplitude of 10 mV. It was done before cycling (after assembling the coin cells)

and after performing charge discharge experiments. Ten such cycles were carried out to perform the experiments and the results for the sample prepared by sol-gel method (Nyquist plots) are presented in the Fig. 8. All the plots are like asymmetric semi-circle in appearance, similar to a half ellipse in the high frequency region and a straight line inclined at an angle to the real axis in the lower frequency region. The resistance values were determined from the semicircles and the resistance of the electrode made by sol-gel method was found to be 63.1 Ω .

3.5.3. Cyclic voltammetry

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes and the kinetics of heterogeneous electron-transfer reactions as well as on the coupled chemical reactions or adsorption processes. The cyclic voltammetry is often the first experiment performed in an electro-analytical study. In particular, it offers a rapid location of redox potentials of electroactive species and convenient evaluation of the effect of media on the redox process.

In typical cyclic voltammetry, a solution is electrolyzed (oxidized or reduced) by placing it in contact with an electrode surface and then applying to that surface sufficiently positive or negative voltage to force electron transfer. In simple cases, the peak surface is started at a particular voltage with respect to the reference half-cell. The electrode voltage changes to a higher or lower voltage at a linear rate and finally, the voltage changes back to the original value at the same linear rate.

When the surface becomes sufficiently negative or positive, the solution may gain electrons from the surface or transfer electrons to the surface. This results in a measurable current in the electrode circuitry. The result of cyclic voltammetry was obtained in form of a cycle between current and potential (potential on X axis and voltage on Y axis).

Cyclic voltammetry experiments were performed to investigate the reaction mechanism of lithium intercalation/deintercalation on Li_2MnO_3

Fig. 9. Cyclic voltammetry plot for Li_2MnO_3

sample. The experiments were conducted at a scan rate of 0.1 mV/s in the voltage range of 2.5 to 4.6 V after initial activation of the cells. Fig. 9 present the cyclic pattern of Li_2MnO_3 sample prepared by sol-gel method and there are two pairs of clear and strong peaks at 4.0 V region and 3.0 V region. The anodic and cathodic peaks obtained from the cyclic voltammograms clearly indicate the reversible oxidation and reduction reaction mechanism corresponding to the lithium extraction and insertion from the electrode materials. Two distinct and separated pairs of peaks are seen for both oxidation and reduction reaction illustrating that the insertion and extraction of lithium ion occurs in two stages [14] and that it corresponds to the reactions occurring at 4 V. The first peak around 3.85 V is attributed to the removal of lithium ions from the half of the tetrahedral sites in which Li-Li interaction occurs. The second peak observed at about 4.10 V is due to the removal of lithium ions that do not have Li-Li interactions. The areas of two oxidation and reduction peaks are more or less equal which indicates that in each stage lithium ions occupy half of the total available crystallographic sites.

The extraction of lithium in two steps can be explained by its crystallographic structural behavior. There are eight lithium atoms in the unit cell, which can be divided into two types, four of which occupy 8a site inside the unit cell and the remaining four atoms occupy the surface of the unit cell, one at the corner and the three at the center of the crystallographic faces. The lithium ion that is

located at the surface of the unit cell can be extracted easier when compared to the inside of the unit cell, and hence, those lithium can be removed at a lower voltage. As the charging proceeds, the voltage is increased, lithium inside the crystal lattice would be deintercalated too and hence, the splitting of peaks appears in the cyclic voltammogram [15].

4. Conclusions

Based on the synthesis and characterization of Li_2MnO_3 obtained by sol-gel method, the following conclusions can be drawn. The decomposition and temperature of Li_2MnO_3 phase formation have been observed from the TGA/DTA measurements. From the XRD experiments the lattice parameters of the obtained material have been evaluated. The synthesized material is well crystallized, has monoclinic structure and corresponds to the standard pattern of JCPDS – 73-0152 with the space group of C2/C. The morphology and the particle size of the samples have been studied by SEM analysis and the elemental composition was observed by performing EDAX experiments. Half cells were assembled and tested at C/10 rate. The maximum capacity of 27 mAh/g was obtained for the sample prepared by sol-gel method using citric acid as gelling agent. Charging and discharging process that occurred at 3 V and 4 V was clearly observed from the cyclic voltammetric experiments. Stability of the electrodes was confirmed by the perfect reversibility of the anodic and cathodic peak positions in the cyclic voltammograms of the sample.

Acknowledgements

The authors would like to express their sincere thanks to Dr. S R K Prasad (Correspondent, CIT), Dr. R. Prabhakar (Secretary, CIT), Dr. V. Selladurai (Principal, CIT), Mr. Rajiv Rangasamy (Director, CIT), and Dr. N. Muthukumarasamy

(HOD, Physics) for their help and encouragement during work.

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Received 2018-05-28

Accepted 2019-04-23