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Preparation of LiMn_2O_4 Nanorods and Nanoparticles for Lithium-ion Battery Applications

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Abstract

Spinel LiMn_2O_4 nanorods were prepared by rapid two steps synthesis process, which involves a novel microwave hydrothermal synthesis and followed by a solid-state reaction. LiMn_2O_4 nanoparticles were prepared by pechini process. X-ray diffraction (XRD) studies of the prepared samples confirmed the formation of crystalline pure spinel phase of LiMn_2O_4 nanoparticles and nanorods. Fourier transform infrared (FTIR) studies of the prepared samples confirmed the formation of the LiMn_2O_4 structured nanoparticles and nanorods. Scanning electron microscopy (SEM) micrographs of the prepared samples showed the formation of the LiMn_2O_4 nanorods and nanoparticles. Electrical conductivities studies of LiMn_2O_4 nanorods and nanoparticles were studied through impedance spectroscopy measurements.

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Keywords: LiMn_2O_4 ; nanorods and nanoparticles; XRD; FTIR; SEM; Impedance; Electrical conductivity.

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1. Introduction

Lithium ion batteries, which have high energy density and long cycle life, are considered to be one of the most promising energy storage systems for portable electronic devices such as cellular phones, camcorders, i-Pods, laptop computers, etc. [1,2]. Three dimensional open structured spinel LiMn_2O_4 is found to be a potential cathode material to replace layered LiCoO_2 in lithium-ion battery applications, because of its high reduction potential, low cost, high abundance, non-toxicity, etc. [3-5]. However, the application of spinel LiMn_2O_4 in high power systems such as electric vehicles (EVs) and hybrid electric vehicles (HEVs) requires fast kinetic properties. Nanostructured materials with different morphologies, such as spherical nanoparticles, nanorods, nanowires, nanosheets, etc., are found to be effective in enhancing the kinetic properties of the spinel LiMn_2O_4 electrode [6,7].

The synthesis process plays a major role in determining the physical and chemical properties of nanostructured materials. In the past decade, so many synthesis routes have been developed for the preparation of LiMn_2O_4 nanoparticles like sol-gel, combustion, hydrothermal, microwave hydrothermal, etc. [8-10]. In the present work, LiMn_2O_4 nanoparticles and nanorods were prepared by two different methods. LiMn_2O_4 nanoparticles were prepared by Pechini process and LiMn_2O_4 nanorods were synthesized by two steps process: the first step involves the microwave hydrothermal synthesis to prepare $\beta\text{-MnO}_2$ nanorods and the second step involves a solid state reaction between as prepared $\beta\text{-MnO}_2$ nanorods and lithium hydroxide monohydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$) to form the LiMn_2O_4 nanorods. The prepared samples were characterized by XRD, FTIR spectroscopy, SEM and impedance spectroscopy techniques.

2. EXPERIMENTAL

2.1 Synthesis of LiMn_2O_4 nanoparticles

Stoichiometric quantities of LiNO_3 (S.d. Fine-Chem. Ltd) and $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (Qualigens) were dissolved in citric acid (Qualigens) and ethylene glycol (Merck chemicals) solution. The molar ratio of total metal ions to citric acid was kept as 1:1 and the molar ratio of total metal ions to ethylene glycol was kept as 1:2. Standard (16N concentrated) nitric acid (NA) was added to the starting solution (SS) by keeping the volume ratio of SS: NA = 5:1. The resulting transparent yellow color solution was evaporated at 80 °C under constant stirring condition. Continuous evaporation of the solution leads to the formation of dark yellowish resin and it was dried at 170 °C for 24 hours to obtain the polymeric intermediate. The polymeric intermediate was grounded and calcined at 500 °C for 12 hours to obtain LiMn_2O_4 nanoparticles.

2.2 Synthesis of LiMn_2O_4 nanorods

In the first step, 0.004:0.004 molar ratio of $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (Merck) and $\text{Na}_2\text{S}_2\text{O}_8$ (Aldrich) were dissolved in 35 ml of de-ionized water under mild magnetic stirring condition at room temperature. The obtained clear solution was transferred to a 100 ml teflon liner vessel container and the vessel was covered with a high strength sleeve made of advanced composite material. The sealed vessel was placed inside a microwave accelerated reaction system (MARS, CEM corporation, USA) and maintained at 120 °C for 90 minutes. After the reaction, the obtained product was washed several times with the distilled water followed by acetone to remove sulphate ions and remnants by centrifugation process. The final product was dried at 120 °C for 12 h in vacuum oven to obtain $\beta\text{-MnO}_2$ nanorods. In the second step, 1:2 molar ratio of $\text{LiOH}\cdot\text{H}_2\text{O}$ and the prepared $\beta\text{-MnO}_2$ nanorods were dispersed in 5ml of ethanol solution and grounded for several hours to form a fine mixture solution, and dried at ambient conditions. This process was repeated for three to four times to form a well mixed powder. The final mixed powder was calcined at 700 °C for 10 h in air atmosphere and obtained the spinel LiMn_2O_4 nanorods.

2.3. Characterization

The phase identification of LiMn_2O_4 nanorods and nanoparticles were carried out using Philips PANalytical, X'Pert Pro X-ray diffractometer operated at 40 kV and 30 mA with monochromatic X-ray source of CuK_α radiation having

a wavelength (λ) of 1.541060 Å. The X-ray diffraction patterns were recorded in the 2θ range of $10 < 2\theta < 70^\circ$ with a scan rate of 0.02° at room temperature. The structure of the LiMn_2O_4 nanorods and nanoparticles was identified by recording FTIR using Shimadzu FTIR-8000 spectrometer. The microstructure of the LiMn_2O_4 nanorods and nanoparticles samples were examined using scanning electron microscopy (SEM) of the Hitachi, S-3400N model with an accelerating operating voltage of 20 kV. The electrical conductivities of the LiMn_2O_4 nanorods and nanoparticles samples were evaluated by analyzing the measured impedance data. The powder samples of LiMn_2O_4 nanorods and nanoparticles were made in the form of a pellet and silver paste was applied on both sides of the pellets. The prepared pellets were sintered at 100°C for 1 h. The impedance spectra of the sample pellets were recorded at ambient conditions using Novocontrol, Alpha A high performance frequency analyzer.

3. Results and Discussion

3.1. X-Ray Diffraction Results and Analysis

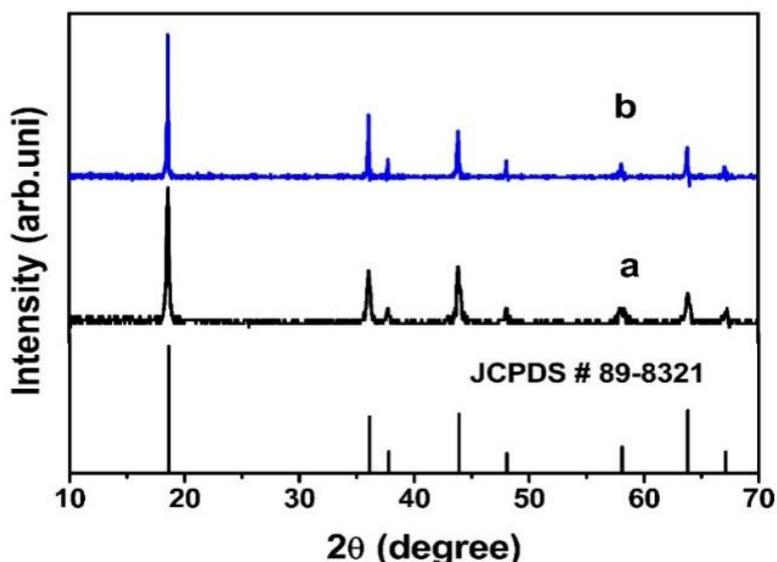


Fig.1. XRD patterns of LiMn_2O_4 (a) Nanoparticles and (b) Nanorods.

Fig.1 shows the X-ray powder diffraction patterns of LiMn_2O_4 nanoparticles and nanorods. From fig.1 (a) and (b), the well-defined X-ray diffraction patterns indicate the crystalline nature of the both samples. The formation of phase pure spinel LiMn_2O_4 with cubic structure and $Fd3m$ space group was confirmed by comparing the obtained XRD pattern with the standard JCPDS data (Card No. 898321). From fig.1b, it also confirmed that there is no $\beta\text{-MnO}_2$ peaks were observed in the X-ray diffraction pattern of spinel LiMn_2O_4 nanorods, which indicates that the reaction between $\beta\text{-MnO}_2$ and $\text{LiOH}\cdot\text{H}_2\text{O}$ at 700°C produced the phase pure spinel LiMn_2O_4 nanorods.

3.2. FTIR Results and Analysis

FTIR spectra of LiMn_2O_4 nanoparticles and nanorods are shown in fig.2 (a) and (b). From fig.2 (a) and (b), the LiMn_2O_4 samples exhibit two sharp infrared bands observed at 612 cm^{-1} and 510 cm^{-1} , which are assigned to the O-Mn-O vibrations in spinel LiMn_2O_4 structure [11]. Hence, the obtained FTIR spectra confirm the formation of spinel structure in both the LiMn_2O_4 nanoparticles and nanorods samples.

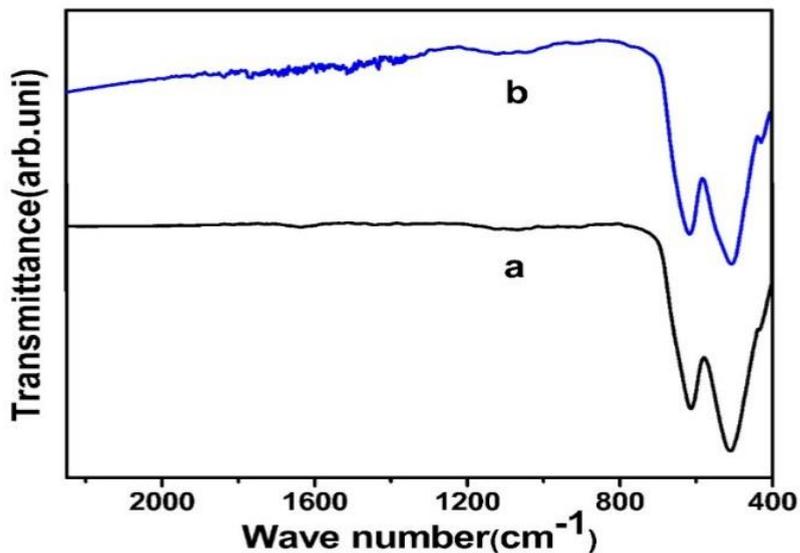


Fig.2. FTIR spectra of LiMn₂O₄ (a) nanoparticles, and (b) Nanorods.

3.3.SEM Analysis

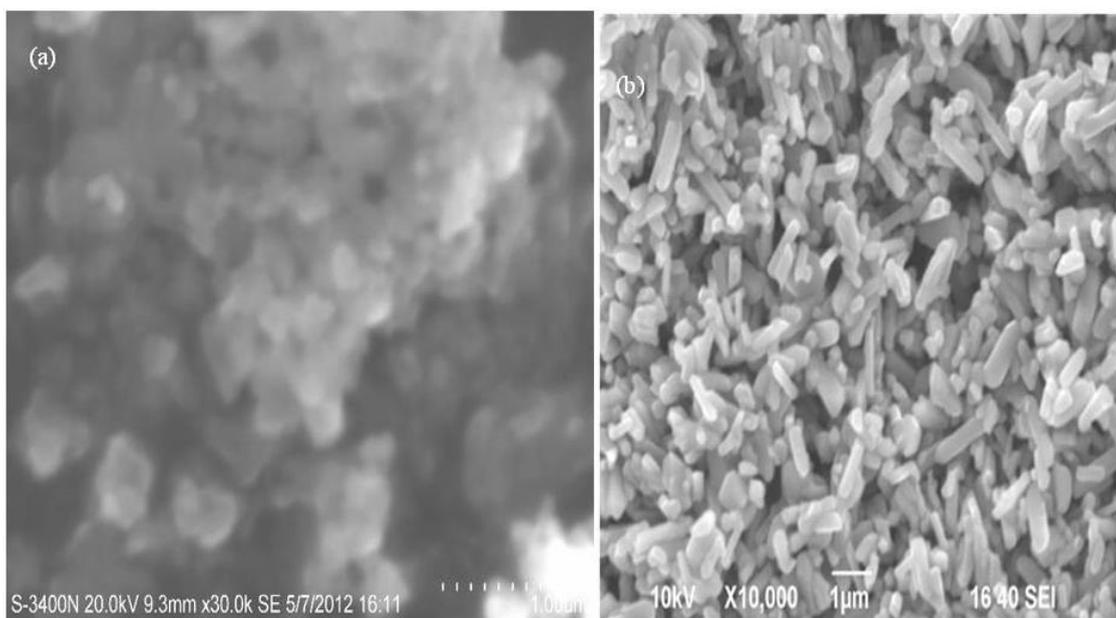


Fig.3 (a) SEM images of LiMn₂O₄ nanoparticles (b) nanorods.

Fig.3 shows the scanning electron micrographs (SEM) of as prepared LiMn₂O₄ powder samples. The SEM micrograph of LiMn₂O₄ sample (fig.3(a)) prepared by Pechini process shows the formation of agglomerated spherical nano size particles with a distribution around 300 nm. The SEM image (fig.3(b)) of LiMn₂O₄ synthesized by rapid two steps synthesis process shows the nanorods morphology with an average diameter of 190 nm and length about of 0.9-1.3 µm. The nanorods morphology remained even after 700 °C temperature.

3.4. Electrical Conductivity Studies

The impedance spectra of spinel LiMn_2O_4 nanoparticles and nanorods recorded at room temperature are shown in fig.4. From fig.4, the impedance plots exhibit two semicircles in the measured frequency range. The semicircles in the high frequency and low frequency regions represent the bulk and grain boundary effects of the samples, respectively [12,13]. The observed impedance spectra were fitted by using *winfit* software and obtained an equivalent circuit shown as inset in fig.4 for both the spinel LiMn_2O_4 nanoparticles and nanorods samples. The obtained equivalent circuit confirms that the high frequency and low frequency semicircles are due to parallel combination of resistive (R) and capacitive (C) elements of the samples at grain interior and grain boundary, respectively.

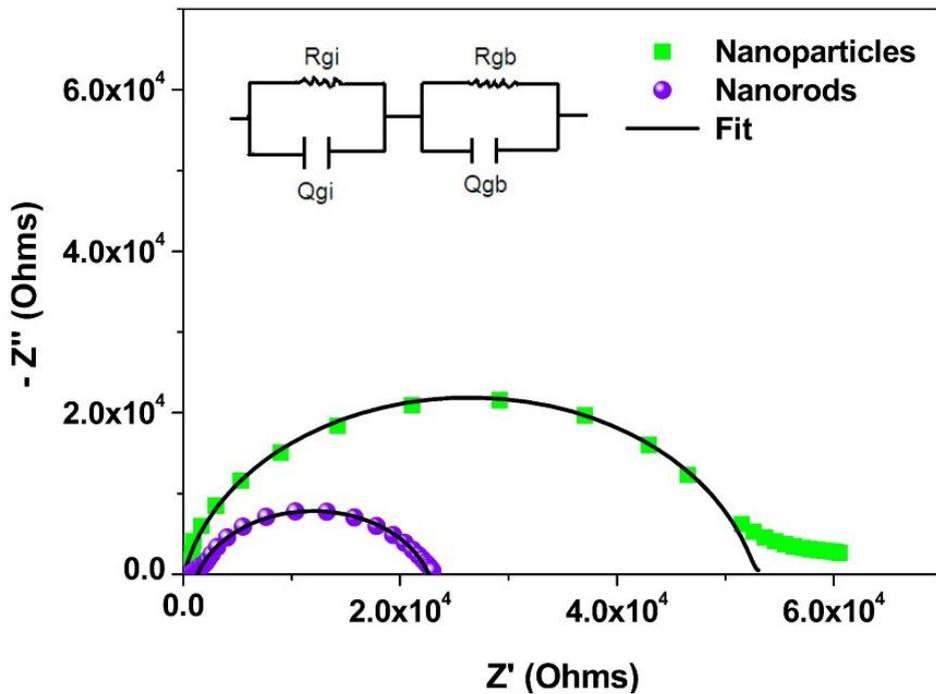


Fig.4. Impedance spectra of LiMn_2O_4 nanoparticles and nanorods

The bulk and grain boundary resistances of the two samples were evaluated by fitting the impedance spectrum using the *winfit* software. The electrical conductivities of nanoparticles and nanorods powder samples were evaluated from the following equation

$$\sigma = \frac{t}{R_{gi}A} + \frac{t}{R_{gb}A}$$

Where, σ is the electrical conductivity, t is thickness of the sample pellet, R_{gi} and R_{gb} are grain interior and grain boundary resistances, and A is the area of the pellet sample. The room temperature electrical conductivities of LiMn_2O_4 nanoparticles and nanorods are found to be 5.65×10^{-5} and $3.13 \times 10^{-4} \text{ Scm}^{-1}$, respectively. LiMn_2O_4 nanorods show the higher conductivity comparing to the prepared LiMn_2O_4 nanoparticles.

4. Conclusions

Spinel LiMn_2O_4 nanorods and nanoparticles were successfully synthesized by Pechini process and rapid two steps process respectively. The X-ray diffraction studies confirmed the formation of phase pure spinel LiMn_2O_4 with cubic structure. The well defined nanorods and nanoparticles morphology of LiMn_2O_4 samples were confirmed from SEM images. The electrical conductivities of the prepared LiMn_2O_4 nanorods and nanoparticles are found to be $3.13 \times 10^{-4} \text{ Scm}^{-1}$ and $5.65 \times 10^{-5} \text{ Scm}^{-1}$ respectively at room temperature.

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