Sol-Gel Synthesis and Characterization of Nanocrystalline Spinel LiMn_2O_4 For Battery Applications

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Abstract Nanocrystalline spinel LiMn_2O_4 was synthesized by sol-gel method using aqueous solution of metal acetates ($\text{LiOAc} \cdot \text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$) and citric acid as chelating agent. X-ray diffraction measurement showed the peaks at 2θ values corresponding to (111), (311), (222), (400), (331) and (440) planes of cubic spinel LiMn_2O_4 nanoparticles with average size ~ 25 nm. FT IR shows all the characteristic peaks of the cubic spinel. TG/DTA measurement showed the weight loss between 100-250 $^\circ\text{C}$ and 300-500 $^\circ\text{C}$ which correspond the endothermic and exothermic processes. An exothermic peak observed at around 400 $^\circ\text{C}$ is due to the thermal decomposition of the ingredients to form LiMn_2O_4 . FE-SEM measurement revealed the formation of small polycrystalline particles of almost spherical morphology with size between 20-30 nm.

Keywords Lithium Batteries, Sol-gel Method, TG/DTA, Polycrystalline Nanoparticles

I. Introduction

Development of efficient devices intensively for energy conversion and storage are the major challenges to our society. Among all, the energy conversion by dye sensitized solar cells (DSSCs) and energy storage in lithium-ion batteries have brought the enormous attention of scientific community. Amongst various energy and power technologies, rechargeable Li-ion batteries (LIB) are a representative of those based on electrochemical energy storage and conversion. Rechargeable lithium ion batteries possess many advantages over traditional rechargeable batteries. They include high voltage, high energy-to-weight ratio, that is energy density, long cyclic life, no memory effect and slow loss of charge when not in service. For these reasons, lithium-ion batteries (LIB) are currently the most popular type of battery for powering portable electronic devices. Diverse range of new applications, such as electric vehicles (EVs), hybrid electric vehicles (HEVs), power tools, uninterrupted power sources (UPS), stationary storage

batteries (SSBS), microchips and next generation wireless communication devices are the major driving force behind these research efforts to enhance the ultimate battery performance.

Most of lithium batteries used in portable and hybrid electronic devices employ transition metal oxides such as LiCoO_2 , LiMn_2O_4 or mixed metal analogs such as $\text{Li}(\text{Ni}, \text{Mn}, \text{Co})\text{O}_2$ as the active cathode materials [1–7]. Spinel LiMn_2O_4 is a better alternative to LiCoO_2 due to its non-toxic nature, inexpensive and ease of preparation. Several approaches for the synthesis of LiMn_2O_4 have been investigated such as co-precipitation [8, 9], solid state synthesis [10-12], sol-gel [13, 14] melt impregnation [15] and Pechini process [16]. Compared to the other synthetic methods, sol-gel (wet chemistry) is a promising technique to synthesize materials at lower temperature to obtain controlled particles size that is evenly distributed and in situ conductive coatings by addition of suitable precursors [17]. Most commonly, organic solvents (gels) like citric acid, ascorbic acid and ethylene glycol are used as chelating agents in the sol-gel process for synthesizing cathode materials [18].

In this paper, we report the citric acid assisted sol-gel synthesized nanocrystalline spinel LiMn_2O_4 material for Li-ion batteries. In section 2, the details of synthesis of LiMn_2O_4 nanoparticles have been presented. The experimental results of prepared nanoparticles are discussed in Section 3. Finally, Section 4 concludes the paper.

2. Experimental

The samples were prepared by the sol-gel method using $\text{Li}(\text{CH}_3\text{COO}) \cdot \text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and citric acid as raw materials. In a typical synthesis, 0.01 mol of $\text{Li}(\text{CH}_3\text{COO}) \cdot \text{H}_2\text{O}$, 0.02 mol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in distilled water and then added aqueous solution of citric acid (0.03 mol) under continuous stirring. After the salts were completely dissolved, the solution was heated at 80 $^\circ\text{C}$ for 2h. After evaporation of water at 80 -100 $^\circ\text{C}$, the as-prepared sol became viscous gel. The gel was put into drying oven at 120 $^\circ\text{C}$ for 3 h to become dry gel. The dry gel

was calcinated at 550°C for 3h.

The XRD analysis was performed by a Philips PW1710 diffractometer, a $\text{Cu K}\alpha$ ($\lambda = 1.5406\text{\AA}$) radiation source and Ni filter with continuous acquisition in $10\text{--}80^\circ 2\theta$ range, $0.05^\circ 2\theta \text{ s}^{-1}$ scan rate. The TG/DTA was carried out by Mettler Toledo TGA/SDTA A851 from room temperature (RT) to 700°C (heating rate 5°C min^{-1}) in O_2 flux. The infrared spectra were recorded using Fourier-transformed infrared spectrophotometer (FT/IR-610, JASCO) in transmission mode in the wave number region between 4000 and 500 cm^{-1} . The morphology and particle size of LiMn_2O_4 was measured by field emission scanning electron microscope (HITACHI S-4800).

3. Results and Discussion

Figure 1 shows the XRD pattern of LiMn_2O_4 nanoparticles synthesized by a conventional sol-gel method. Pattern shows the peaks at 2θ values corresponding to (111), (311), (222), (400), (331) and (440) planes of single phase cubic spinel crystal structure with a space group of $\text{Fd}\bar{3}\text{m}$.

Figure 1. XRD pattern of LiMn_2O_4 particles prepared by sol-gel method

Average size of the particles was found to be $\sim 25 \text{ nm}$ calculated using Debye Scherer equation $D = 0.9 \lambda / (\beta \cos \theta)$, where λ is the wavelength of X-ray beam ($\text{Cu K}\alpha = 1.5406\text{\AA}$), β is the full width at half maximum of the (hkl) diffraction peak and θ is the Bragg angle. The obtained XRD pattern of the LiMn_2O_4 was found in good agreement with others published reports [8-16].

The thermal decomposition of LiMn_2O_4 nanoparticles is shown in Figure 2. The TGA curve of LiMn_2O_4 shows two main steps of mass loss. The mass loss between $100\text{--}250^\circ\text{C}$ is attributed to the physically adsorbed water from the precursor mixture. The corresponding DTA curve indicates that these processes are endothermic at temperature 165 and 266°C .

Further, TG curve shows steep weight loss in between 300 and 500°C . The corresponding DTA curve indicates that these processes are exothermic around 400°C . This effect is due to the thermal decomposition of the ingredients to form LiMn_2O_4 . In this region, the weight loss is observed to be high due to degradation of acetate ions and citric acid.

Figure 2. TG/DTA profile of LiMn_2O_4 particles prepared by sol-gel method

Figure 3 shows the FTIR spectra of LiMn_2O_4 nanoparticles recorded in between 500 and 4000 cm^{-1} . The spectrum exhibits other bands at 1442 , 1352 , 1182 , 1023 , 723 and a shoulder at 653 cm^{-1} . The characteristic peaks below 1500 cm^{-1} confirms the presence of metal oxygen vibrational frequencies. A weaker band around $\sim 1600 \text{ cm}^{-1}$ and a stronger band around 1400 cm^{-1} represents the asymmetric and symmetric stretching of --COO^- group.

Figure 3. FTIR spectra of LiMn_2O_4 particles prepared by sol-gel method

Figure 4. SEM image of LiMn_2O_4 particles prepared by sol-gel method

Figure 4 depicts the morphological features of as-prepared spinel LiMn_2O_4 nanoparticles. FE-SEM analysis reveals that

LiMn_2O_4 fired at 550°C consists of even particles with average about 20-30 nm. It seems that the citric acid in the starting powder not only played a role as a chelating agent but also effectively suppressed the excessive grain growth. The particles of LiMn_2O_4 consist of many small polycrystalline particles with almost spherical morphologies.

4. Conclusion

We have reported the synthesis of nanocrystalline LiMn_2O_4 material by sol-gel method using citric acid as chelating agent. XRD, SEM FTIR and TG/DTA were employed to study the structural, chemical and thermogravimetric/differential thermal properties of prepared nanoparticles. The XRD analysis showed well crystallized LiMn_2O_4 nanoparticles of size ~ 25 nm for the sample calcinated at 550°C . TG/DTA measurement showed the weight loss between 100 - 250°C and 300 and 500°C whereas peak at 400°C is attributed to the thermal decomposition of the ingredients to form LiMn_2O_4 . The formation of small polycrystalline particles of almost spherical morphology with size between 20-30 nm were confirmed by FE-SEM. Finally, this study is helpful for the production of LiMn_2O_4 nanoparticles as cathode material for rechargeable lithium-ion batteries.

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