Sol-Gel Synthesis and Characterization of Nanocrystalline Spinel LiMn$_2$O$_4$ For Battery Applications

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Abstract Nanocrystalline spinel LiMn$_2$O$_4$ was synthesized by sol-gel method using aqueous solution of metal acetates (LiOAc·H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$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$_2$O$_4$ 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 0C and 300-500 0C which correspond the endothermic and exothermic processes. An exothermic peak observed at around 400 0C is due to the thermal decomposition of the ingredients to form LiMn$_2$O$_4$. 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$_2$O$_4$ or mixed metal analogs such as Li(Ni, Mn, Co)O$_2$ as the active cathode materials [1–7]. Spinel LiMn$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ material for Li-ion batteries. In section 2, the details of synthesis of LiMn$_2$O$_4$ 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 Li(CH$_3$COO)$_2$·H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$O and citric acid as raw materials. In a typical synthesis, 0.01 mol of Li(CH$_3$COO)$_2$·H$_2$O, 0.02 mol of Mn(CH$_3$COO)$_2$·4H$_2$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 0C for 2h. After evaporation of water at 80 -100 0C, the as-prepared sol became viscous gel. The gel was put into drying oven at 120 0C 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 Cu Kα (λ = 1.5406Å) radiation source and Ni filter with continuous acquisition in 10–80° 2θ range, 0.05° 2θ 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 O₂ 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 LiMn₂O₄ was measured by field emission scanning electron microscope (HITACHI S-4800).

3. Results and Discussion

Figure 1 shows the XRD pattern of LiMn₂O₄ 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 Fd3m.

Average size of the particles was found to be ~ 25 nm calculated using Debye Scherer equation $D = 0.9 \lambda/(\beta \cos \theta)$, where $\lambda$ is the wavelength of X-ray beam (Cu Kα=1.5406Å), $\beta$ is the full width at half maximum of the (hkl) diffraction peak and $\theta$ is the Bragg angle. The obtained XRD pattern of the LiMn₂O₄ was found in good agreement with others published reports [8-16].

The thermal decomposition of LiMn₂O₄ nanoparticles is shown in Figure 2. The TGA curve of LiMn₂O₄ shows two main steps of mass loss. The mass loss between 100-250 °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 LiMn₂O₄. In this region, the weight loss is observed to be high due to degradation of acetate ions and citric acid.

Figure 3 shows the FTIR spectra of LiMn₂O₄ 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 ~ 1600 cm⁻¹ and a stronger band around 1400 cm⁻¹ represents the asymmetric and symmetric stretching of –COO⁻ group.

Figure 4 depicts the morphological features of as-prepared spinel LiMn₂O₄ nanoparticles. FE-SEM analysis reveals that
LiMn$_2$O$_4$ 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$_2$O$_4$ consist of many small polycrystalline particles with almost spherical morphologies.

4. Conclusion

We have reported the synthesis of nanocrystalline LiMn$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$. 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$_2$O$_4$ nanoparticles as cathode material for rechargeable lithium-ion batteries.

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