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Preparation and Characterization of $LiCoMnO_4$ for Lithium-Ion Battery

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Abstract
The $LiCoMnO_4$ spinel compound was prepared by a sol–gel method. Structural measurements were utilized to investigate the characteristics of LCMO powder. The powder crystallizes in the space group Rd-3m, with a trigonal crystallinity structure, according to XRD analysis (hexagonal axes). SEM images showed that the crystalline grains sizes were about 200 nm - 350 nm, which provides large surface area. The sample had soft magnetic characteristics, according to hysteresis behaviour analysis in the Vibrating Sample Magnetometer (VSM). The prepared material is thought to be a candidate for the applications of energy storage in lithium-ion batteries.

Keywords: Lithium-ion battery, sol-gel method, spinel cathodes, $LiCoMnO_4$.

تحضير وتشخيص مادة قطب الكاثود $LiCoMnO_4$ لبطارية ايون الليثيوم

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الخلاصة
في هذا العمل، تم تصنيع مادة قطب الكاثود لبطارية ايون الليثيوم بطريقة (sol–gel) ومن ثم تلدينها. تم اخذ القياسات التركيبية للتحقق من تشخيص مسحوق مركب قطب الكاثود. من خلال فحص حيود الاشعة السينية تم معرفة تبلور المركب في مجموعة الفضاء Rd–3m مع هيكل بلوري الثلاثي (محاور سداسية). وطبقا لفحص المجهر الالكتروني الماسح فان حجم الحبيبات البلورية يتراوح من 200 الى 300 نانومتر. وطبقا لفحص الاهتزازية المغناطيسية فان تحليل الهسترة تم. حصولنا على مواد ذات حلقة هسترة ضيقة.

1. Introduction

The evolution of Li ion batteries with production of high power and energy density for hybrid and electric vehicles presents enormous challenge [1]. Because of its low expense, acceptable electrochemical performance, and remarkable thermally stabilization, spinel $LiMn_2O_4$ has been widely investigated as active cathode material. Its energy density, on the other hand, is not particularly high. Partially replacing Mn with transition metals with greater potential couplings could result in increased energy density and discharge plateaus [2]. A flat discharge plateau of the $LiNi_{0.5}Mn_{1.5}O_4$ became a favourable material form the many doping derivatives; about 4.7 (Volt) vs. Li/Li^+ and an 18% greater energy density than $LiMn_2O_4$. The doping Co derivative $LiCoMnO_4$ with redox couple of the Co^{3+}/Co^{4+} has a potential greater

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than $LiNi_{0.5}Mn_{1.5}O_4$ around ~5.0 (Volt) vs. Li/Li^+ [2-4]. $LiCoMnO_4$ is expected to have a greater energy density than $LiNi_{0.5}Mn_{1.5}O_4$ due to its higher redox potential and similar theoretical specific capacity. Kawai et al. were the first to report $LiCoMnO_4$ in 1998 [5]. Previous research has primarily focused on structural changes at high temperatures Previous research has primarily focused on structural changes at high temperatures, where above 600 ^oC, there was an oxygen deficiency that was accompanied by the reversibly change from spinel to rock salt, and the manganese ions were reduced from Mn^{4+} to Mn^{3+} in $LiCoMnO_{4-\delta}$ [6-10].

Sol-gel synthesis is a wet chemical method that is commonly used to create metal oxides or other particular compositions at low temperatures. Materials having a range of morphologies, such as porous structures, thin fibres, dense powders, and thin films, can be created using sol-gel synthesis [11-12]. Nevertheless, there have been few investigations on the morphological control of $LiCoMnO_4$ and electrochemical performance. $LiCoMnO_4$ cathode materials made by synthesis methods of sol-gel or solid-state reactions tend together forming largest particles, obstructing Li^+ diffusion. The single crystals of micrometer-sized $LiCoMnO_4$ synthesized via sol-gel method utilizing $LiCH_3COO•2H_2O$ as a starting material is reported in the present study, and including structural measurements and sample properties.

2. Experimental Part

Sol-gel synthesis method was used to prepare $LiCoMnO_4$ cathode material. A 100 mL of distilled water containing dissolved amounts of 2.80g $Co(CH_3COO)_2·4H_2O$ (98%, fluka, India), 2.33g $Mn(CH_3COO)_2·4H_2O$ (99%, fluka, India), 1.074g $LiCH_3COO·2H_2O$ (99%, fluka, India), and 8.45g citric acid ($C_6H_8O_7·H_2O$) (99%, fluka, India), 1.074g $LiCH_3COO·2H_2O$ (Aldrich 99.95%), was heated and stirred at 120 °C until a gel is formed. A muffle furnace was used for heating of gel at 380°C for 12 hours, and the next step is the calcination at 800°C for 24 hours in an O_2 atmosphere. The cooling and heating rates above 350°C established at 1 °C min^{-1}.

The LiCoMnO4 sample was investigated by X-ray diffraction (XRD-6000) employing 2Ɵ and operating at 40 kV and 30 mA, X-ray Cu K (1.540600 °A). The topographies of the LCMO sample were investigated using a Field Emission Scanning Electron Microscope (FE-SEM); MIRA3 TESCAN. A vibrating sample magnetometer (VSM) was used to determine the magnetic characteristics (Model VSMF 7407).

3. Results and Discussions

The pattern of the XRD of $LiCoMnO_4$ powder is shown in Figure 1. The pattern was identified as a single phase of a spinel-type structure with a cubic crystal system and space group Fd-3m with a high degree of crystallinity, where the main peaks at 13.25°, 34.15° corresponding to (111), (220) indicates the formation of pure $LiCoMnO_4$, which mean there is no impurity phase, as agreed with previous researchers [14-16]. The shapely octahedral single-crystal morphology of $LiCoMnO_4$ with {111} faces which can be observed in the SEM images.

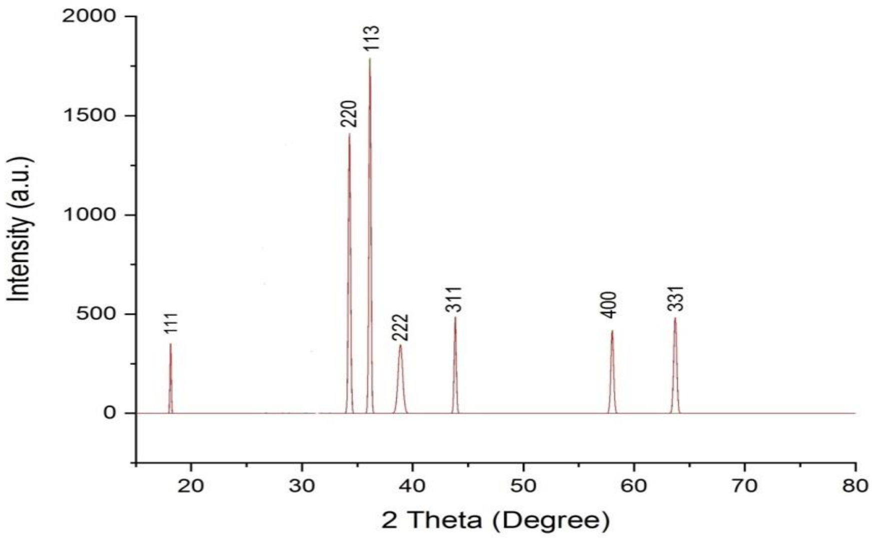

Figure 1-XRD pattern of LCMO cathode active material

The topography and particle distribution of LCMO were described using SEM images, as seen in Figure 2a–c. The $LiCoMnO_4$ film consists of octahedral or small triangle crystalline grains. The crystalline grains sizes are about 200 nm - 350 nm. The grains had triangle shape which is due to the cubic spinel structure with the (111) orientation.

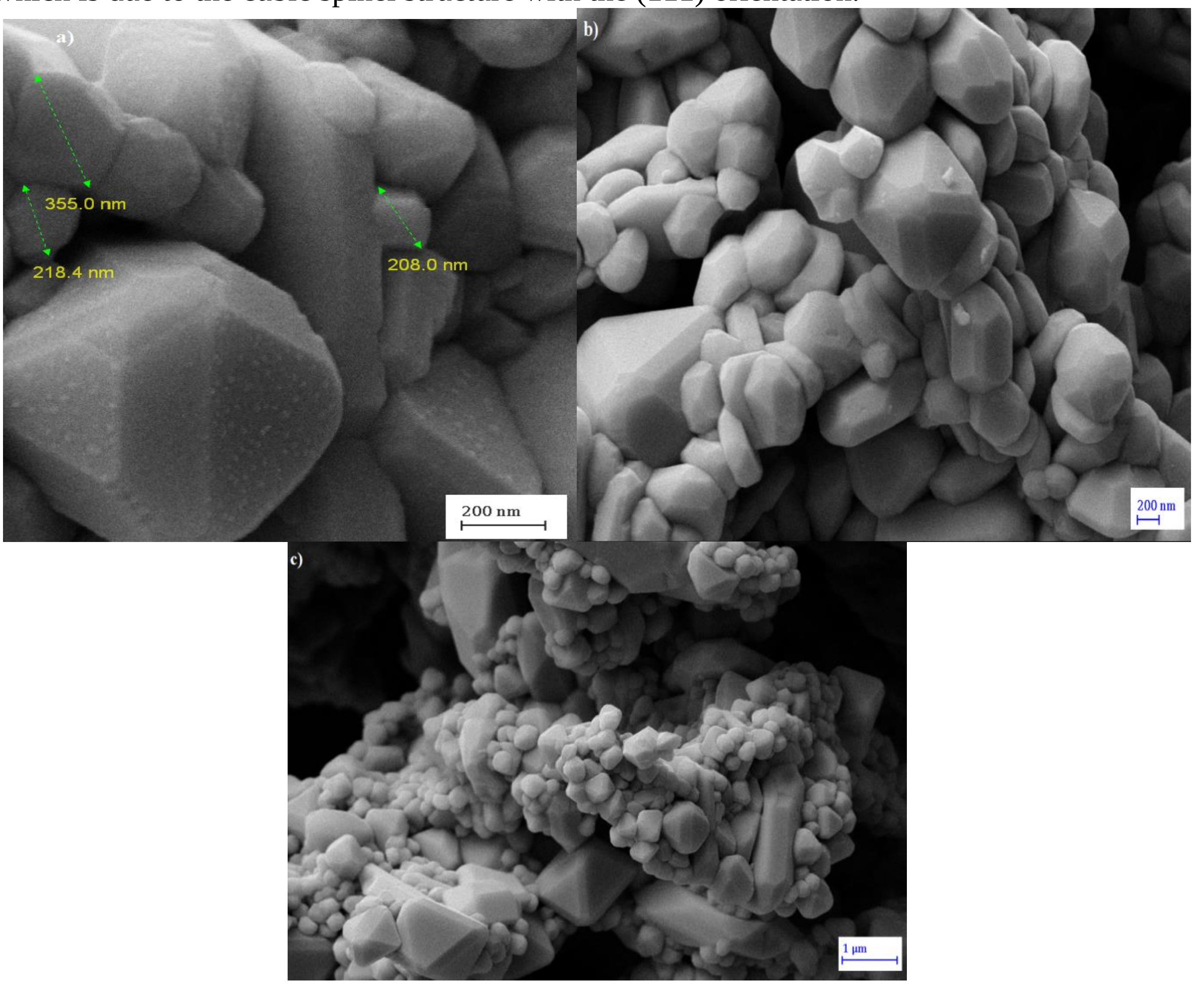

Figure -2a-c FE-SEM images of LCMO cathode active material

As shown in Figure 3, to detect the constituents of the material, we employed X-ray energy dispersive spectroscopy (EDS). Co, Mn, O, and C were identified to have weight percentages of 30.9, 18.3, 18.5 and 4.5.

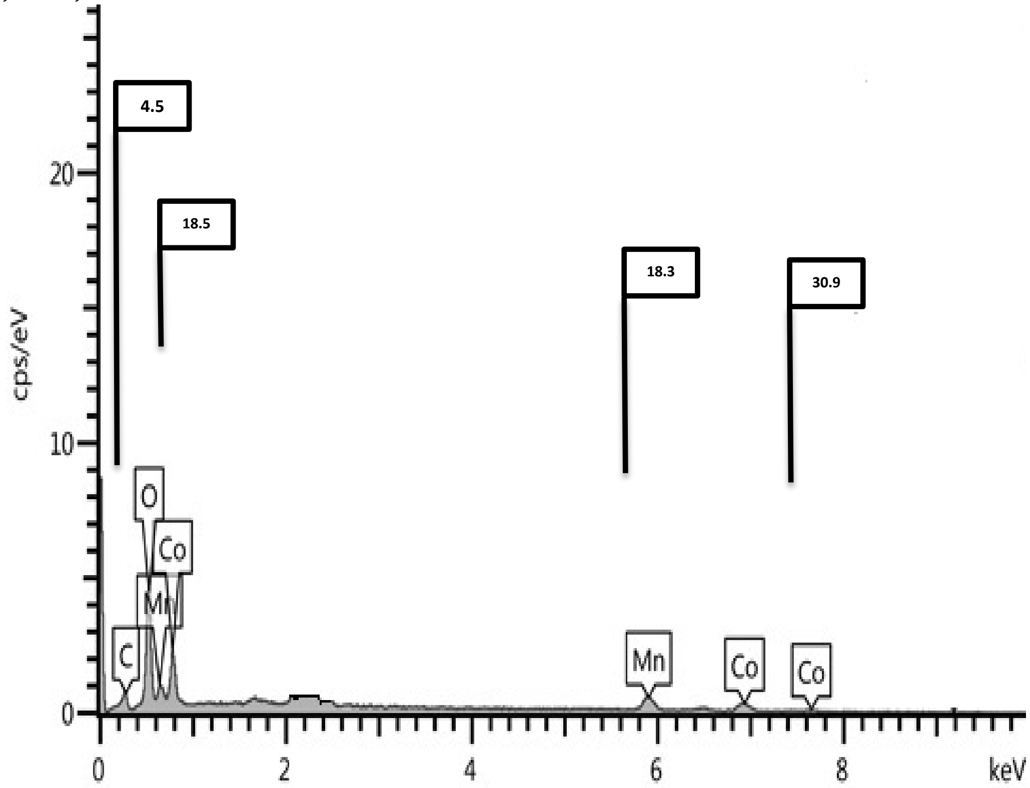

Figure 3-EDX of $LiCoMnO_4$ cathode active material

Figure 4 shows the measured hysteresis loops $LiCoMnO_4$ powder at annealing temperature 800 °C. A paramagnetic behaviour of the $LiCoMnO_4$ powder is shown by the comparing of the hysteresis loops of $LiCoMnO_4$ material measured at R.T. with standard curves formed from mixed magnetic systems. It can be shown from the data that $LiCoMnO_4$ material is paramagnetic material, and the magnetization parameter determined at 0.4 emu/g in ± 15,000 Oe (1 Oe ≅ 80 A/m) applied field which agreed with other results [14]. Such phenomenon is mainly caused by an enhanced scattering of the charge carriers in the LCMO sample annealed at 800 °C, in which higher density of magnetic disorders exists at the grain boundaries, acting as a barrier to the charge carriers [14].

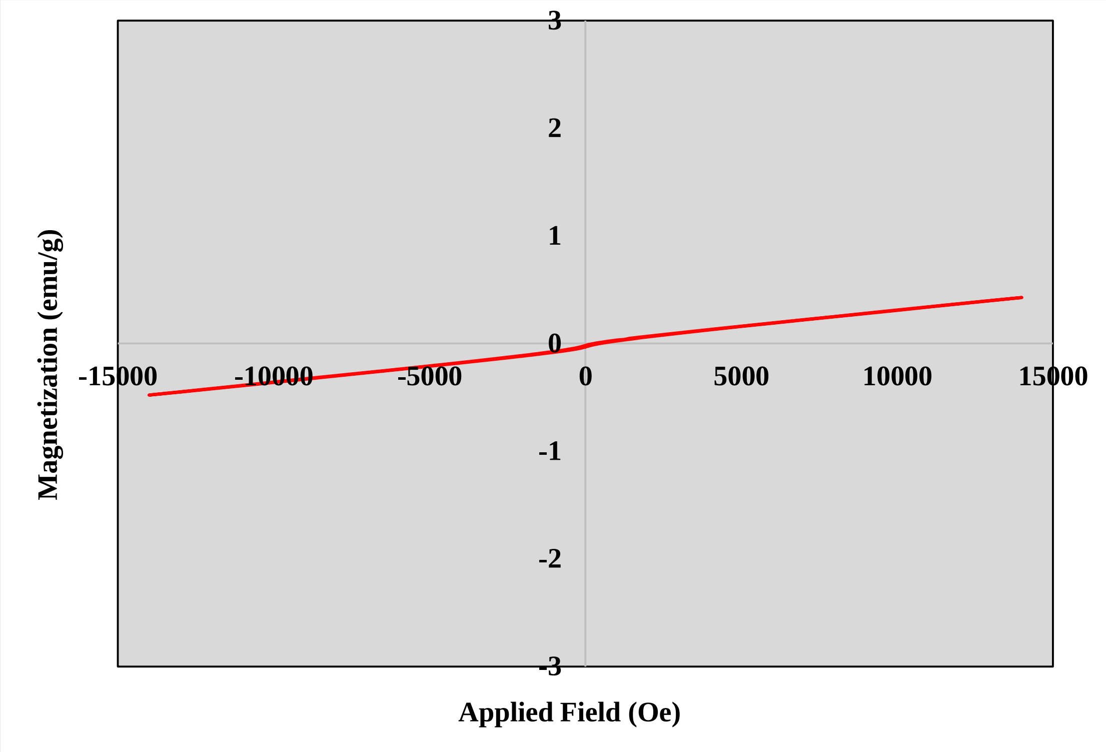

Figure 4-The loops hysteresis of LCMO powder annealed at 800 °C

4. Conclusion

$LiCoMnO_4$ with spinel structure have been successfully prepared by sol-gel method with new precursor agents. The composition and structure of these materials have been investigated; XRD pattern confirmed the formation of pure $LiCoMnO_4$ with no impurity phase. The high crystallinity and structure with average particle size of 200-350 nm, which offer high surface area ratio and reveals a pure particle formation. The changes in the magnetic properties of LCMO can be attributed to the modification of the particle sizes and depends on the calcination temperature.The prepared material is thought to be a candidate for the applications of energy storage in lithium-ion batteries.

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