

AC Conductivity, Dielectric and Electric Modulus Studies of Nanocrystalline LiCoO₂ Particles

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ABSTRACT

Nanocrystalline LiCoO₂ particles were prepared using acrylamide assisted polymeric citrate process. As prepared powders were characterized using X-ray diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques. The electrical properties like, A.C conductivity, dielectric constant and electric modulus were studied through impedance measurements.

Keywords: Nanocrystalline LiCoO₂ particles, X-ray diffraction, Electrical properties, Dielectric properties.

1 INTRODUCTION

Lithium ion batteries are the major power source for portable electronic devices such as cellular phones, cameras, laptops, camcorders, i-Pods, etc [1]. LiCoO₂ is the most preferred positive electrode material as it is widely used in commercial lithium ion batteries [2]. It is well known that the practical capacity of LiCoO₂ is limited to around 140 mAhg⁻¹; which is nearly half of its theoretical capacity 274 mAhg⁻¹. LiCoO₂ has an ordered rock salt structure (α - NaFeO₂) and belongs to R-3m space group [3]. Unfortunately, the power capability of LIBs is mitigated by slow diffusion in bulk materials. In order to overcome this problem, researchers have been focussing to reduce the particle size. Nanosize particles increase the surface-to-volume ratio and shorten the diffusion lengths of the carriers, which in turn can enhance the conductivity and hence, improve the power density, compared to bulk particles [4].

The preparation of LiCoO₂ cathode material by conventional solid state reaction method involves heating of precursor materials at high temperatures, which results in inhomogeneity, bigger crystalline size, poor stoichiometry, phase impurity, etc [5,6]. Hence, in the present work, LiCoO₂ particles were prepared by acryl amide assisted polymeric citrate process. The synthesized powders were characterized using X-ray powder diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) techniques. The electrical properties like, AC conductivity, dielectric and electric modulus studies were made through impedance measurements.

2 EXPERIMENTAL

LiNO₃(S.d.Fine-Chem.Ltd.),Co(NO₃)₂.6H₂O(SQ grade, Qualigens), citric acid anhydrous (SQ grade,Qualigens) and acryl amide (SQ grade,Qualigens) were used for the synthesis of nanocrystalline LiCoO₂ powders by polymeric citrate process.

Stoichiometric quantities of metal nitrate and citric acid solutions were prepared separately and were mixed by keeping total metal ion to citric acid ratio as 1:1 under constant stirring condition. Stoichiometric amount of acryl amide solution was added to the above solution by keeping total metal ion to acryl amide ratio as 1:1. The resulting pink coloured solution was evaporated at 80 °C for 6 hours and it turned into viscous pink coloured resin. Further, the pink coloured resin was heated at 170 °C for 12 hours and the polymeric intermediate was obtained. The polymeric intermediate was grounded and calcined at 500 °C for 12 hours to obtain nanocrystalline LiCoO₂ powders.

Powder X-ray diffraction patterns were recorded using X'pert PRO MPD, PANalytical (Philips) X-ray powder diffractometer with Cu K α radiation of wavelength 1.54 Å⁰ at a scan rate of 2° per minute and 2 θ values range from 10° to 80°. FTIR spectra were recorded using shimadzu FTIR-8000 spectrometer to identify the structural coordination of the prepared sample. The measurement was carried out in the range from 400 cm⁻¹ to 4000 cm⁻¹ with KBr diluter. The microstructure of prepared sample was imaged using scanning electron microscopy (Hitachi, S-3400N model). The impedance spectra of the prepared sample pellet was recorded using impedance analyzer (Novacontrol, Alpha A high performance frequency analyzer). The AC conductivity, dielectric constant and electric modulus spectra were obtained from the measured impedance data.

3 RESULTS AND DISCUSSION

3.1 XRD

Powder X-ray diffraction patterns of the synthesized LiCoO₂ sample is shown in fig.1. From fig.1, the well defined diffraction peaks indicate the crystalline nature of the synthesized sample. The formation of phase pure LiCoO₂ was confirmed by comparing the observed XRD patterns with the standard JCPDS data. No additional impurity peaks were observed in the diffraction pattern.

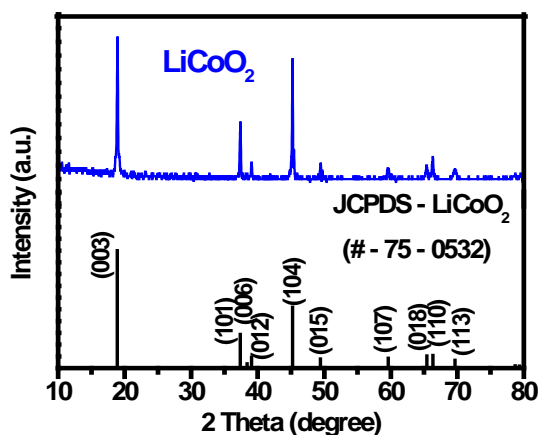


Fig.1 XRD patterns of LiCoO₂ nanoparticles.

The crystallite size of prepared sample was calculated using Scherrer's formula

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where, λ is the X-ray wavelength (1.54 Å) and β is the full-width at half maximum (FWHM) of the diffraction line. The average crystallite size of LiCoO₂ sample is found to be 36 nm.

3.2 FTIR

FTIR spectra of the synthesized LiCoO₂ sample is shown in fig.2.

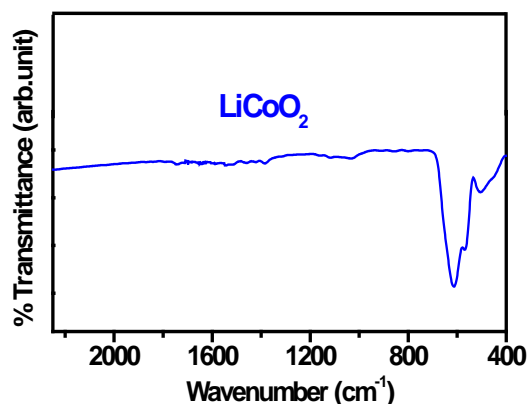


Fig.2 FTIR spectra of LiCoO₂ nanoparticles.

From fig.2, the bands observed at 550-560 cm⁻¹, 580-610 cm⁻¹ with high intensity and at 510 cm⁻¹ with low intensity correspond to the asymmetric stretching modes of [CoO₆] octahedra in LiCoO₂ structure [7]. Hence, FTIR results showed the formation of LiCoO₂ structure and are in good agreement with XRD results.

3.3 SEM

Scanning electron (SEM) micrographs of the synthesized

LiCoO₂ sample is shown in fig.3.

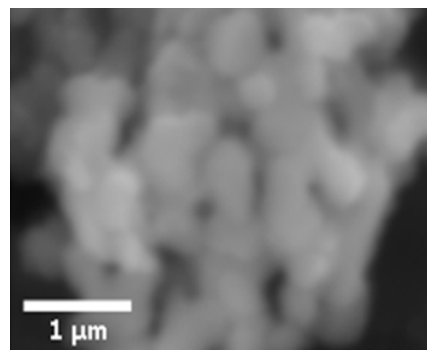


Fig.3 SEM image of LiCoO₂ nanoparticles.

From fig.3, SEM image shows the formation of agglomerated spherical nano particles of LiCoO₂, having the average particle size of 370 nm (300 – 450 nm).

3.4 A.C conductivity

Fig.4 shows the conductivity (σ) vs. Log (ω) plot of the synthesized LiCoO₂ particles at different temperatures.

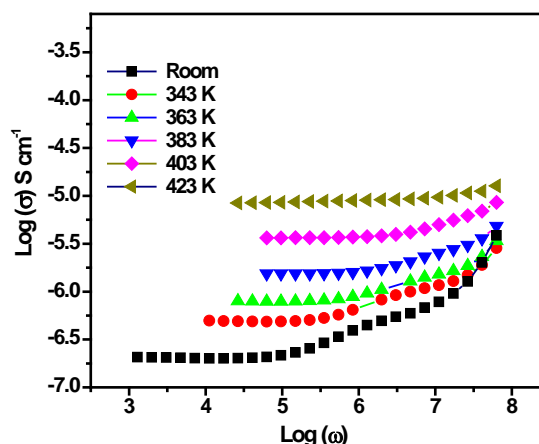


Fig.4 Plot of AC conductivity (σ_{ac}) vs. $\log \omega$ of LiCoO₂ Nanoparticles.

Fig.4, shows a plateau region at low frequencies, which is frequency independent and a dispersive region at high frequencies. The A.C conductivity study of LiCoO₂ is found to obey Jonscher's power law [8]. The Jonscher's power law equation may be written as

$$\sigma(\omega) = \sigma_{DC} + A\omega^n \quad (2)$$

where, n is the frequency exponent in the range $0 < n < 1$. The observed frequency-independent conductivity at low frequencies indicate the DC conductivity of the material. The power law feature $\sigma(\omega) \propto A\omega^n$ is observed at high frequencies. The frequency at which dispersive region begins is called as hopping frequency (ω_p). The extrapolation of the plateau region towards Y-axis gives the

DC conductivity of the material. It is observed that the DC conductivity of the material as well as hopping frequency (ω_p) increases with increase of temperature.

3.5 Dielectric constant

Fig.5 shows the dielectric constant (ϵ') vs. $\text{Log}(\omega)$ plot of the synthesized LiCoO_2 particles at different temperatures.

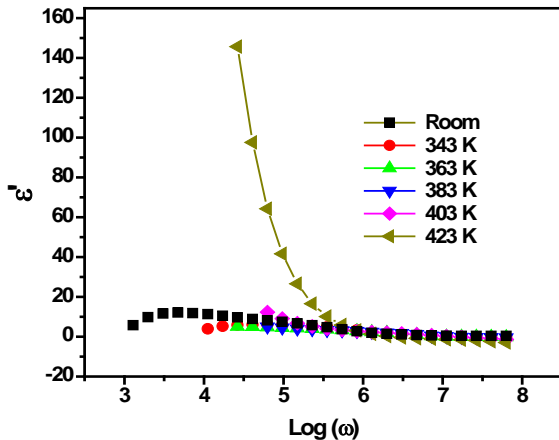


Fig.5 Plot of dielectric constant vs. $\text{log}\omega$ of LiCoO_2 Nanoparticles.

From fig.5, it is observed that the dielectric constant of the material decreases with increase in frequency. The observed high dielectric constant at low frequencies is due to the space charge accumulation at the interface. At higher frequencies, the charged ions cannot follow the rapidly varying oscillating electric field and hence the dielectric constant decreases and becomes constant. The dielectric constant of the material increases with increase of temperature. The initial increase of the dielectric constant at very low frequencies is may be due to the inductive behavior of the material.

3.6 Electric modulus

Fig.6 shows the electric modulus (M'') vs. $\text{Log}(\omega)$ plot of the synthesized LiCoO_2 particles obtained at different temperatures. From fig.6, it is observed that the electric modulus value increases with frequency and becomes saturated (M_∞) at higher frequencies. The shape of each curve is asymmetric of non-Lorentzian type exhibiting a peak at the relaxation frequency (ω_{max}) with a long tail in the shorter relaxation time region [9,10]. The broadness of the curves interpret the distribution of relaxation time for distinguishable physical processes.

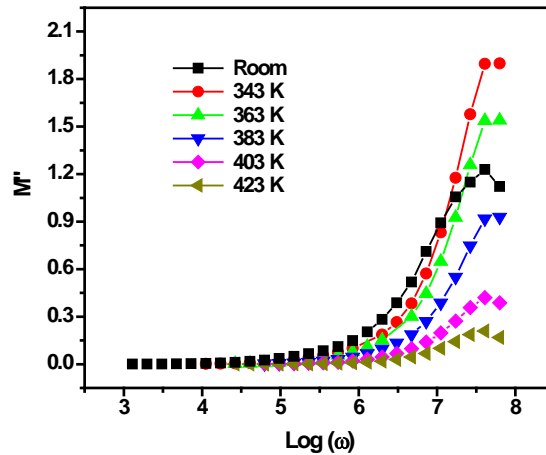


Fig.6 Plot of electric modulus (M'') vs. $\text{log}\omega$ of LiCoO_2 Nanoparticles.

The change in magnitude of M''_{max} with temperature is may be due to the inductive behavior of the sample.

4 CONCLUSIONS

Nanocrystalline LiCoO_2 particles were synthesized using acryl amide assisted polymeric citrate process. XRD and FTIR studies confirm the formation LiCoO_2 phase and structure respectively. The formation of spherical nanoparticles were confirmed from SEM results. The electrical behavior of LiCoO_2 particles with temperature is interpreted through A.C conductivity, dielectric constant and electric modulus studies.

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