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ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF Li[Ni$_{0.5}$ Co$_{0.25}$ Mn$_{0.25}$]O$_2$ CATHODE MATERIAL

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Abstract. In the present study a mixed hydroxide method has been employed to prepare Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ from the precursors and electrical and electrochemical properties have been studied. X-ray diffraction studies of the synthesized powder exhibited predominant (003) orientation corresponding to hexagonal layered structure. The average grain size estimated from SEM data is about 1.0 µm. The impedance measurements have been carried out in the frequency range of 1 Hz – 1 MHz and within the temperature range of 303–373 K. The temperature dependent conductivity was observed to follow the Arrhenius relation and the estimated activation energy is 0.21 eV. The electrochemical performance was studied by cyclic voltametry and charge-discharge measurements.

Keywords: Li[Ni$_{0.5}$ Co$_{0.25}$ Mn$_{0.25}$]O$_2$, mixed hydroxide method, structural, electrical, electrochemical properties.

1. Introduction

Lithium ion batteries occupy a very large portion of the portable battery market because of their high energy density, high theoretical capacity, design flexibility and excellent cycling power capability and are extensively used as electrochemical power sources in a lot of modern equipments, such as mobile telephones, laptop computers, video-cameras and so on [1-5]. Among the lithium-ion secondary battery materials, layered-structured compounds Li[Ni$_{1-y-z}$Co$_y$Mn$_z$]O$_2$ exhibit the good electrochemical performance and safety characteristics [6]. This has motivated the study of other layered compounds that contain less or no cobalt at all such as LiNiO$_2$, LiNi$_{1-y}$Co$_y$O$_2$, LiMnO$_2$, LiNi$_{1-y}$Mn$_y$O$_2$ and LiNi$_{1-x-y}$Mn$_x$Co$_y$O$_2$. Among these, the low content of Co is also beneficial to reduce the cost and toxicity. Li[Ni$_{0.5}$ Co$_{0.25}$ Mn$_{0.25}$]O$_2$ is expected to be the most promising potential cathode material in Li[Ni$_{1-y-z}$Co$_y$Mn$_z$]O$_2$ oxides, due to its high discharge capacity. Li[Ni$_{1-x-y}$Mn$_x$Co$_y$]O$_2$ powders were synthesized by various methods like co-precipitation method, solid-state reaction, solvent evaporation method, *etc.* [7-9]. In the present study, the mixed hydroxide method has been employed for the preparation of Li [Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ and studied its structural, morphological, electrical and electro-chemical properties.

2. Experimental

2.1. Synthesis of Li(Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$)O$_2$

LiOH·H$_2$O (98 % Aldrich), Co(NO$_3$)$_2$·6H$_2$O (98 % Aldrich), Ni(NO$_3$)$_2$·6H$_2$O (98 % Fluka), and Mn(NO$_3$)$_2$·4H$_2$O (97 % Fluka) were used as the starting materials. Li(Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$)O$_2$ samples were prepared by the "mixed hydroxide method" which has been previously developed [10]. 50 ml of the transition metal nitrates aqueous solution were slowly dripped (2 h) into 500 ml of a stirred solution LiOH using a burette. This caused the precipitatation of M(OH)$_2$ (M = Mn, Ni, and Co) with a homogeneous cation distribution. The burette was washed twice and filtered with the additional distilled water to remove any residual Li salts (LiOH and LiNO$_3$). The precipitate was then dried in air at 453 K for 12 h. The dried precipitate was mixed with a stoichiometric amount of LiOH·H$_2$O and ground. The resultant powder was then heated in air to 1173 K for 10 h.

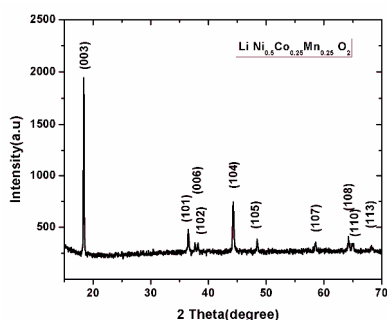### 2.2. Characterization of Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$

The structure of the prepared sample is studied by X-ray diffraction technique (Siefert computerized X-ray diffractometer, model 3003 TT) using CUK$_{\alpha 1}$ radiation ($\lambda = 0.15406$ nm) in the 2Θ range of 15–70°. The particle size and shape were observed by a scanning electron

microscope (SEM, Model: Carl Zeiss EVO50) operated under the high vacuum mode. The composition of the sample is analysed by EDAX system (Oxford instruments, UK). The impedance measurements were performed using a phase sensitive multimeter (Model: PSM 1700,UK) in the range from 1 Hz to 1 MHz at different temperatures. The electrochemical experiments were carried out by designing a conventional type aqueous three-electrode glass cell (Pt/Li[$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$] O_2). The electrochemical work station (CHI 608c, CH Instruments Inc, USA) electrochemical analyzer was employed for the aqueous cell measurements.
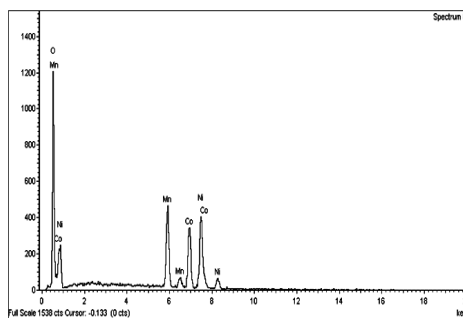
3. Results and Discussion

3.1. Structural Analysis

Fig. 1 shows X-ray diffraction pattern of Li[$Ni_{0.5}Co_{0.25}Mn_{0.25}$]$O_2$. All the peaks can be indexed based on α-NaFeO$_2$ structure. XRD spectrum exhibited different characteristic peaks along with (003)

predominant orientation. In XRD pattern, the integrated peak splits of (006/102) and (108/110) doublets are regarded as an indicator of layered structure materials characteristics [11-12]. Li atoms are on 3a sites, Ni, Mn and Co atoms are randomly placed on 3b sites and oxygen atoms are on 6c sites. This indicates that the sample has a high degree of crystallinity, good hexagonal ordering, and great layered characteristics [13]. The estimated lattice parameters of the sample are: $a = 2.84$ Å, $c = 14.43$ Å.

The chemical analysis of the sample has been carried out using EDAX measurements as shown in Fig. 2. It exhibits the characteristic peaks of Ni, Co, Mn and O present in the sample. It is not possible to detect Li for the obvious reason that X-ray florescence yield is extremely low for Li. The respective peaks due to Ni, Co, Mn and O are indicated along with their respective energy positions. The peaks due to any other elements are not detected, which is a clear indication of the sample chemical purity. SEM analysis revealed that the sample consists of homogeneously distributed micro grains with an average grain size of about 1 µm as shown in Fig. 3.

Fig. 1. XRD spectrum of Li[$Ni_{0.5}Co_{0.25}Mn_{0.25}$]$O_2$ powder

Fig. 2. EDAX spectrum of Li[$Ni_{0.5}Co_{0.25}Mn_{0.25}$]$O_2$ powder
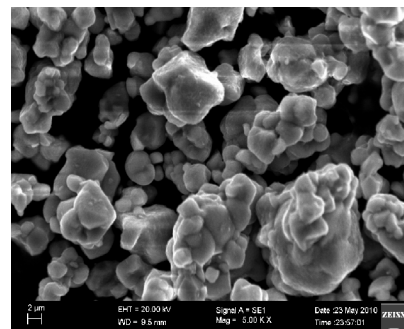
Fig. 3. SEM image of Li[$Ni_{0.5}Co_{0.25}Mn_{0.25}$]$O_2$ powder

3.2. Electrical Analysis

The response of the real and imaginary parts of impedance (Z' and Z'') of Li[$Ni_{0.5}$ $Co_{0.25}$ $Mn_{0.25}$]O_2 as function of frequency(1Hz-1MHz) at different temperatures (room temperature to 373 K) is shown in Figs. 4 and 5.
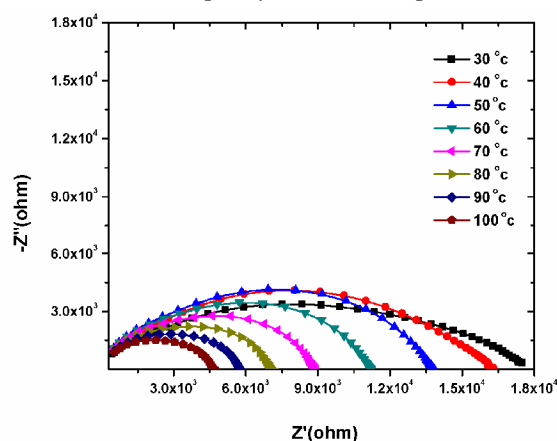
It is observed from Fig. 4 that the magnitude of Z' decreases with the increase in temperature, representing the reduction of grain and grain boundary resistance. Higher impedance value at lower-frequency region indicates the existence of space charge polarization. Z' peak shifts toward higher frequency region with the increase in temperature, revealing the existence of frequency relaxation process. It is observed from Fig. 5 that Z'' increases with the increase in frequency, and on attaining the relaxation frequency it starts to decrease for all temperatures. As the temperature increases, the

magnitude of Z'' decreases and the peak shifts toward higher-frequency region.

The complex impedance data provides information about the relaxation process and gives frequency dependent phenomenon associated with grain boundary regions and intrinsic properties of the material in the system. The cole-cole plots of Li[$Ni_{0.5}Co_{0.25}Mn_{0.25}$]$O_2$ at different temperatures are shown in Fig. 6. These plots allow the resistances to associated grain interiors (bulk), grain boundaries and sample/electrode interfaces to be separated because each of them has different relaxation time, resulting in separate semi circles in the complex impedance plane. The relaxation frequency for the bulk is one or two orders of magnitude higher than the relaxation frequency for grain boundaries and the relaxation frequency resulting from the electrode process is much smaller than the relaxation frequency of grain boundaries [14].
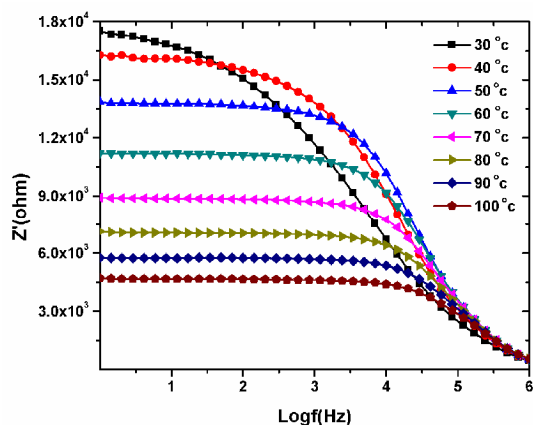
Fig. 4. Variation of real part of impedance with frequency at various temperatures

Fig. 5. Variation of imaginary part of impedance with frequency at various temperatures

Fig. 6. Cole-Cole plots of Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$
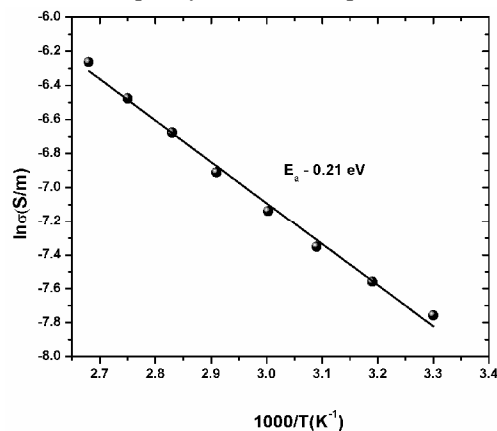
Fig. 7. Temperature dependence of Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ conductivity

In Fig. 6 the complex plane of Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ sample, one semi circle is observed. As the temperature increases, all semicircles become smaller and shift toward higher-frequency region, indicating a reduction of grain (R_g) resistance.

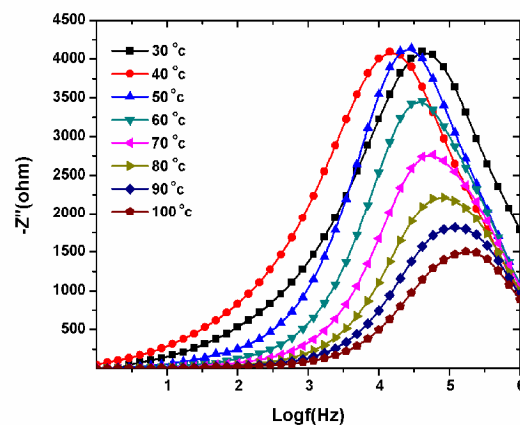The bulk conductivity (σ, S·cm^{-1}) value has been calculated using the following formula [15]:

$$\sigma = L/R_b·A$$

where R_b is a bulk resistance of the sample; L is the pellet thickness and A is the effective area.

The conductivity of the sample is calculated from the above formula and it is observed that the conductivity increases with respect to the temperature and is found to be 1.90·10^{-3} S/m at 373 K.

The temperature dependence of conductivity is shown in Fig. 7. The temperature dependence of ionic conductivity obeys Arrhenius rule:
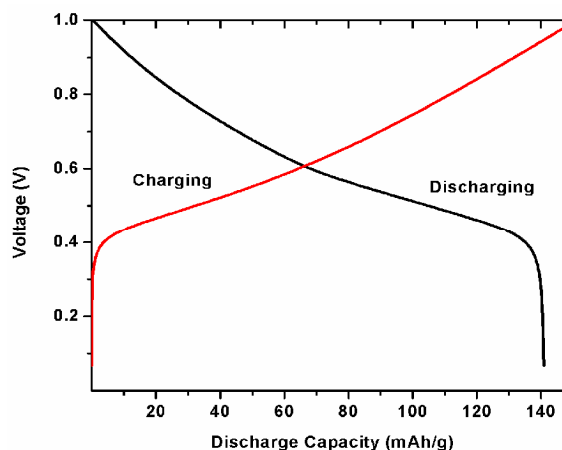
$$\sigma = \sigma_0 \exp (-E_a/KT)$$

where σ_o is a pre-exponential factor; E_a is the activation energy of the conduction; T is temperature in Kelvin and K is the Boltzmann constant.

Fig. 8. Charge-discharge curves of Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$

From the slope, the activation energy can be calculated. The estimated activation energy was found to be 0.21 eV.

3.3. Electrochemical Properties

The electrochemical experiments were carried out by designing a conventional type aqueous three-electrode glass cell (Pt/Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$) suffused in the aqueous electrolyte. Chronopotentiometry was used to determine the specific discharge capacity and cycling capacity of the electrodes. Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ cell in the aqueous media exhibits a discharge capacity of about 140 mAh/g with a good electrochemical cycling performance (Fig. 8).

4. Conclusions

The layered structure Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ cathode material has been synthesized by the mixed hydroxide method. The formation of hexagonal crystal structured Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ with R3m space group has been confirmed from XRD analysis. The estimated grain size of Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ is about 1 μm. The electrical conductivity of the sample has been found to vary from $5.13 \cdot 10^{-4}$ S/m to $1.90 \cdot 10^{-3}$ S/m by the increase of the temperature from room temperature to 373 K. The plot of $\log(\sigma)$ against reciprocal temperature obeys the Arrhenius rule. The estimated activation energy is found to be 0.21 eV. The electrochemical characteristics of Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ in the aqueous region exhibited the discharge capacity of about 140 mAh/g with a good electrochemical cyclic performance [16].

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ЕЛЕКТРИЧНІ ТА ЕЛЕКТРОХІМІЧНІ ВЛАСТИВОСТІ КАТОДНОГО МАТЕРІАЛУ Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$

Анотація. Розроблено метод змішування гідроксидів для приготування Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$ з відповідних продуктів і вивчені його електричні та електрохімічні властивості. За допомогою рентгенівських дифракційних досліджень встановлено, що синтезований порошок має предомінантну (003) орієнтацію, яка відповідає гексагональної шаруватій структурі. За допомогою скануючої електронної мікроскопії встановлено, що середній розмір зерна є понад 1,0 мкм. Вимірювання імпедансу були проведені в діапазоні частот 1 Гц – 1 МГц за температур 303–373 К. Показано, що залежність провідності від температури підпорядковується рівнянню Арреніуса, а розрахункова енергія активації становить 0,21 еВ. Досліджено електрохімічні властивості за допомогою циклічної вольтамперометрії і методу заряду-розряду.

Ключові слова: Li[Ni$_{0.5}$Co$_{0.25}$Mn$_{0.25}$]O$_2$, метод змішування гідроксидів, структурні, електричні, електрохімічні властивості.