



STUDIES ON ION CONDUCTION MECHANISM IN $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ CATHODE MATERIALS

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ABSTRACT

Lithium rich and deficient, $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ ($x = 0, \pm 0.1, -0.2$ and $y = 0, \pm 0.05, +0.1$) cathode materials were prepared by conventional solid state reaction method. Vibrational studies of the prepared materials were analyzed by using FTIR spectroscopy. Electrical and dielectric properties of the materials were measured using AC impedance spectroscopy in the frequency range 7 MHz-1Hz over the temperature range of 303-343 K. The sample $\text{Li}_{0.9}\text{Ni}_{0.45}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ shows maximum conductivity of $1.02 \times 10^{-4} \text{ S cm}^{-1}$ at ambient temperature. All samples obey Arrhenius rule. Dielectric properties of the cathode materials on the influence of Li, Ni composition and temperature were also discussed.

Key words: Conductivity, Arrhenius behaviour, Hopping frequency.

INTRODUCTION

Lithium cobalt oxide (LiCoO_2) is a very attractive cathode material because of its high theoretical capacity of 274 mAh/g, high theoretical volumetric capacity of 1363 mAh/cm³, oxidation potential of 4.1 V vs Li/Li^+ and good cycling performance. However, it has major limitations like high cost, toxic, thermal instability. Partial substitution of Ni with Co was found to be an effective way to minimize those limitations¹. Moreover, improvements in the capacity of modern Li ion batteries continue to be made possible by enhancing the electronic conductivities and ionic diffusivities in cathode and anode materials². According to Literature, Li deficit cathode materials exhibit high conductivity³. At the same time, Lithium rich metal oxide cathode materials are of great interest because, when excess Li ions introduced, beyond the limitations of one Li ion per MO_2 formula, exceptionally high reversible capacities and energy densities can be achieved⁴. Main drawback of LiCoO_2 is that can deliver only 140 mAh/g capacity (half of its theoretical capacity), which is attributed to the intrinsic structural instability of the material when more

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than half the Li ions are extracted⁵. Doping of small amount of additional metal like Mg⁶ is an effective way to stabilize the crystal structure. Hence we wish to prepare Li rich and deficient, Mg doped LiNiCoO₂ with the parallel variation of Ni concentration and to study its electrical and dielectric behaviour in detailed manner.

EXPERIMENTAL

Li_{1+x}Ni_{0.4+y}Co_{0.3}Mg_{0.3}O₂ cathode materials were prepared by conventional solid state reaction method. LiNO₃.6H₂O (Himedia > 99.99%), NiNO₃.6H₂O (Himedia >99.99%), CoNO₃. 6H₂O (Alpha Aisher >99%) and MgNO₃.6H₂O (Spectrum >98 %) were used as raw materials. The appropriate amounts of raw materials were taken and the material was ground well. The mixture was kept in a furnace at 800°C for 11 hrs. After slow cooling to temperature, particles were collected and again ground well to get homogenous powder. To take impedance measurement, powder samples were pelletized then the pellet was sintered to at 600°C for 5 hrs to increase the stability of the pellet. The silver was coated on both sides of pellet, which has been acted as blocking electrodes. FTIR spectrum of the cathode material was recorded in the range of 550-2000 cm⁻¹ using JASCO FT/IR-4100 spectrometer. AC impedance spectroscopic measurements were carried out using Biologic SP-300 electrochemical work station and temperature is varied upto 70° C from room temperature within the frequency range of 1 Hz- 7 M Hz with the amplitude voltage of 10 mV

FTIR analysis

Fig. 1 shows the FTIR spectra of Li_{1+x}Ni_{0.4+y}Co_{0.3}Mg_{0.3}O₂ cathode materials. All samples show absorption peak around 573, 863, 1435 and 1487 cm⁻¹.

The peak arises around 573 is due to LiCoO₂ phase and other minor peaks present between 550-600 cm⁻¹ were attributed to Ni-O bonds. According to the recent report, even though the precursors did not have any carbonate origin, it will obtain on during synthesis process⁷. Similar phenomenon is observed here and it is reflected in FTIR spectrum. The peak, which is observed around 863 cm⁻¹ is ascribed to (CO₃)²⁻ bending. The peaks, which are appeared between wave number 1400-1500 cm⁻¹ were assigned to asymmetric C-O stretching.

Conductance spectra analysis

The ac impedance measurement is taken for all the samples over the wide range of frequencies and different temperatures. Fig. 2 shows the conductance spectra of prepared samples.

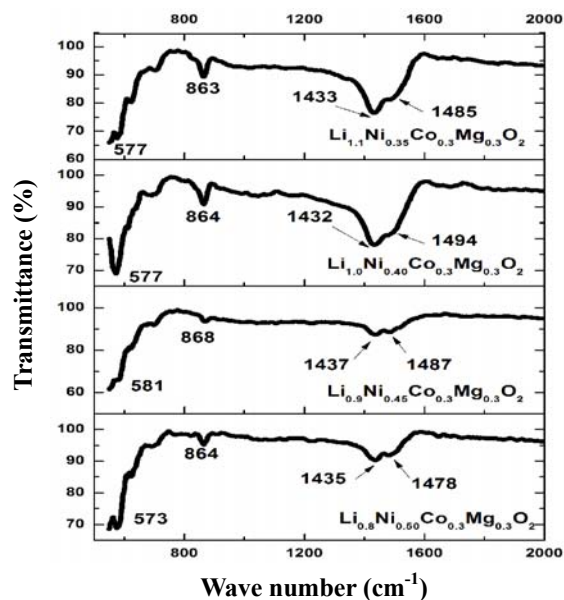


Fig. 1: FTIR spectra of $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ cathode materials

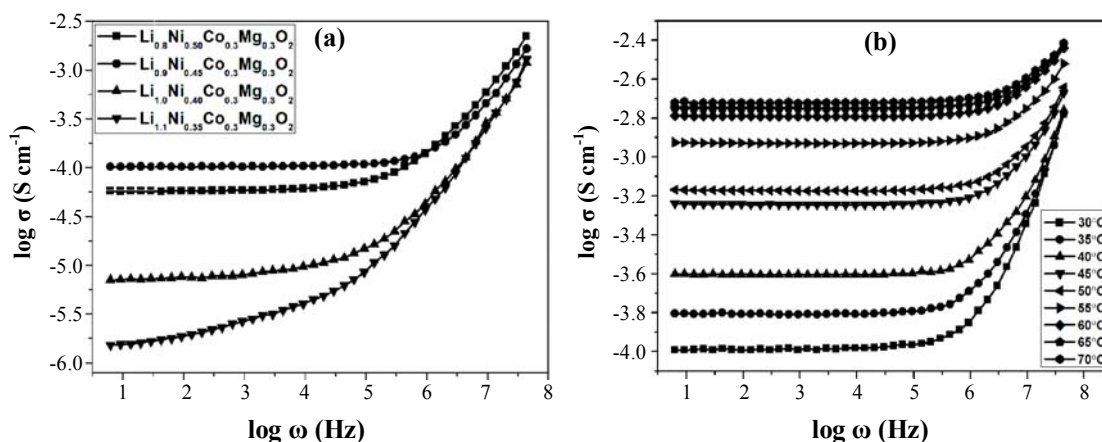


Fig. 2: Conductance spectra for (a) $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ materials at RT
(b) $\text{Li}_{0.9}\text{Ni}_{0.45}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ for the temperature range RT-70°C

Conductance spectra consist of two regions such as low frequency plateau region and high frequency dispersive region. Plateau region corresponds to the dc conductivity of the material and it is due to long range translational transport of Li ions in response to the applied field⁸ and the dispersion region is characterized by random hopping of mobile ion⁹. The dc conductivity values were obtained by extrapolating the plateau region to vertical axis and obtained conductivity values are given in Table 1.

Table 1: Conductivity and Activation energy of $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$

S. No.	Sample designation	Conductivity σ (S cm^{-1})		Activation energy (eV)	
		at RT	at 343 K	E_a	E_H
1.	$\text{Li}_{0.8}\text{Ni}_{0.50}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$	1.94×10^{-5}	2.71×10^{-4}	0.64	0.52
2.	$\text{Li}_{0.9}\text{Ni}_{0.45}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$	1.02×10^{-4}	1.92×10^{-3}	0.70	0.67
3.	$\text{Li}_{1.0}\text{Ni}_{0.40}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$	6.95×10^{-6}	4.08×10^{-5}	0.54	0.41
4.	$\text{Li}_{1.1}\text{Ni}_{0.45}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$	1.46×10^{-6}	1.37×10^{-5}	0.50	0.46

From Fig. 2 (a), it is known that conductivity increases upon the increase of Ni content or otherwise for decrement of Li content. This result is well matched with the literature¹⁰. Li deficit sample $\text{Li}_{0.9}\text{Ni}_{0.45}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ shows the maximum conductivity of the order of 10^{-4} and for the further increment of Ni concentration and decrement of Li composition causes the decrement of conductivity. It may be due to the fact that much amount of Ni ions start to collapse the layered structure and lead to reduce in conductivity value. From Fig. 2 (b) it is known that conductivity increases for the increment of temperature. From table it is clear that, invariably for all samples conductivity get increased to one order at the temperature of 70°C.

Temperature dependent conductivity

The temperature dependent dc electrical conductivity and hopping frequency of the prepared cathode materials are shown in Fig. 3.

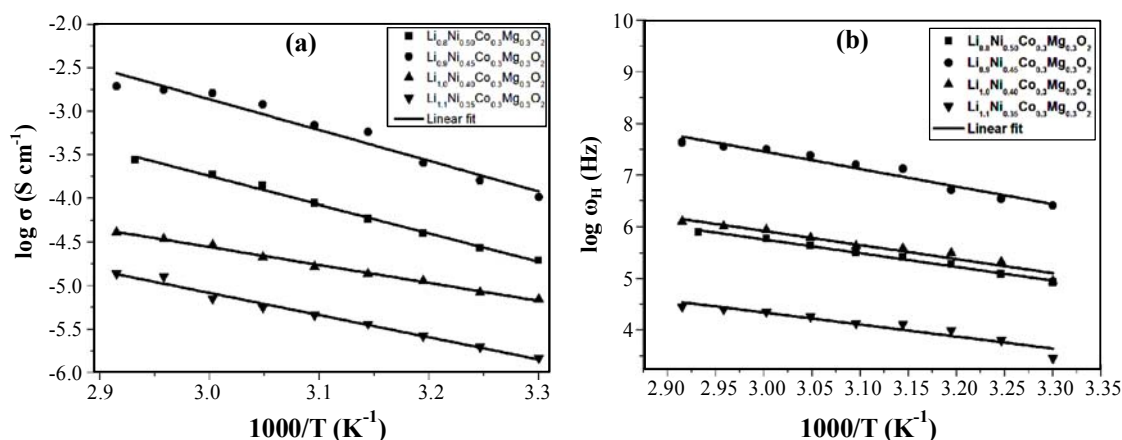


Fig. 3: Temperature dependence of (a) dc conductivity (b) hopping frequency for $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ ($x=0, \pm 0.1, -0.2$ and $y=0, \pm 0.05, +0.1$)

The activation energy, E_a of the bulk conductivity is calculated using Arrhenius relation, $\sigma(T) = \sigma_0 \exp(E_a/KT)$ Where σ_0 is pre exponential factor and K is Boltzmann constant. The conductivity increases with temperature, which is associated with decrease in bulk resistance. For material, conductivity dispersion takes place at particular frequency that frequency is named as hopping frequency (ω_H)¹¹. Hopping frequency has been obtained directly from conductivity data (i.e the frequency where two times of dc conductivity exists) From Fig. 3 (b), it is known that ω_H increases with increase of temperature and obeys Arrhenius relation, $\omega_H = \omega_0 \exp(-E_H/KT)$. Where ω_0 is pre-exponential factor of the hopping frequency and E_H is activation energy for hopping. The activation energy is calculated using slope obtained from graphs and it is given in table 1. From the table, it is known that E_a is greater than E_H . Hence the supplied thermal energy is not only used for ion migration but also utilised for charge carrier creation¹².

Dielectric loss analysis

Fig. 4 shows the variation of logarithmic dielectric loss with respect to logarithmic frequency.

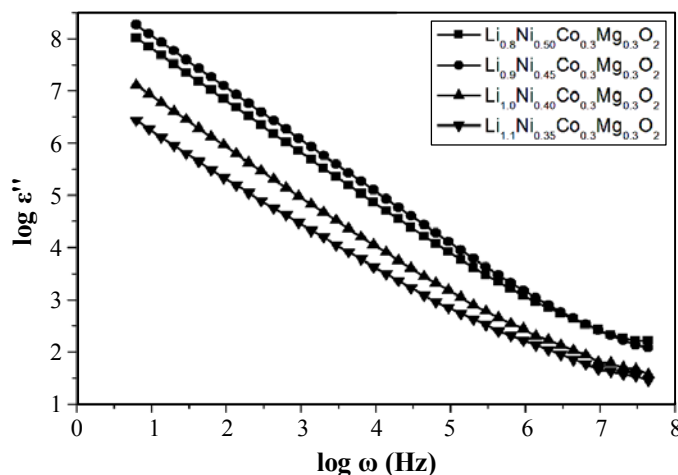


Fig. 4: Dielectric loss for (a) $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ materials at RT

From Fig. 4, it is known that dielectric loss increases with the decrement of frequency and the sample $\text{Li}_{0.9}\text{Ni}_{0.45}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ shows high dielectric loss value and so proving that having large number of charge carriers. Fig. 4 (b) shows dielectric loss increases with temperature. The slope of $\log \epsilon''$ versus $\log \omega$ is found to be -0.8 to -0.9. It indicates that the dc conduction is predominant in the present samples¹².

CONCLUSION

A series of cathode materials $\text{Li}_{1+x}\text{Ni}_{0.4+y}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ ($x = 0, \pm 0.1, -0.2$ and $y = 0, \pm 0.05, +0.1$) were prepared by solid state reaction method. Formation of carbonate ion is confirmed through FTIR spectra. Using AC impedance study it is identified that the sample $\text{Li}_{0.9}\text{Ni}_{0.45}\text{Co}_{0.3}\text{Mg}_{0.3}\text{O}_2$ exhibits maximum conductivity of the order of $10^{-4} \text{ S cm}^{-1}$ at room temperature. All samples follow Arrhenius behaviour and calculated activation energies reveal that thermal energy is used for the migration of charge carriers as well as creation of charge carriers. Dielectric study reveals that systems contain large number of free charge carriers and dc conductivity is predominant.

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