STUDY ON TEMPERATURE DEPENDENCE SUPERIONIC CONDUCTIVITY OF SOLID ELECTROLYTE LITHIUM-COBALT-NICKEL OXIDES

Nyo Nyo Myint¹, Aye Aye Lwin², Win Kyaw³ and Soe Myint⁴

Abstract

Superionic conductors or solid electrolyte materials are mainly useful in batteries and various sensors. In the present work, Lithium-Cobalt-Nickel Oxide, $\text{LiCo}_{1-x}\text{Ni}_xO_2$, (where x = 0.00 - 1.00 with the step of 0.25) were prepared by solid state reaction method. Lithium Hydroxide Monohydrate (LiOH.H₂O), Cobalt Oxide (CoO) and Nickel Oxide (NiO) with desired stoichiometric compositions were used as the starting materials. X-ray diffraction (XRD) patterns indicated that the samples belong to hexagonal structure from the observed diffractograms were compared with the JCPDS data. To confirm the phase formation of the samples, Fourier Transform Infrared (FTIR) spectroscopic method was used to analyze the vibrational characteristics. Temperature dependence electrical conductivities of the samples were investigated in the temperature range of 303 K – 773 K. It was found that the samples exhibited as the superionic conductors in the high temperature.

Keywords: LiCo_{1-x}Ni_xO₂, XRD, hexagonal, FTIR, superionic conductors.

Introduction

Solid-State Ionics, thrust area of research in the branch of Materials Science, deals mainly with the solid materials which exhibit rapid/fast ion transport through the bulk [Arico, (2005)]. The ionic conductivity of these solids is exceptionally high and comparable to that of liquid/aqueous electrolytes [Azurdia, (2006)]. Hence, they can be potentially used as excellent alternates of liquid/aqueous electrolytes to fabricate solid-state electrochemical devices viz. batteries [Julian, (2003)]. Research in the field of fine grain mixed oxide systems has gained immense importance because of their potential applications in many areas of technology [Kumar, (2009)].

In materials science, fast ion conductors are solids in which ions are highly mobile. These materials are important in the area of solid-state ionics, and are also known as solid electrolytes and superionic conductors. These materials are mainly useful in batteries and various sensors [Fey, (2002)]. Fast ion conductors are used primarily in solid oxide fuel cells. As solid electrolytes they allow the movement of ions without the need for a liquid or soft membrane separating the electrodes. The phenomenon relies on the hopping of ions through an otherwise rigid structure [Fey, (2003)].

Lithium transition-metal oxides are functional intercalation compounds for their applications in rechargeable lithium-ion batteries [Wang, (2010)]. They have been widely studied in search of structural stability and improved electrochemical performance [Tao, (2011)]. This work deals with the Lithium-Cobalt-Nickel Oxides, $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ prepared by solid state reaction method and their structural, vibrational and temperature dependence superionic conductivity are reported.

¹ Dr, Associate Professor, Department of Physics, Yenanchaung Degree College

² Dr, Associate Professor, Department of Physics, Loikaw University

^{3.} Dr, Associate Professor, Department of Physics, Pyay University

⁴ Dr, Professor and Head, Department of Physics, Yenanchaung Degree College

Materials and Method

Preparation of the Sample

Lithium-Cobalt-Nickel Oxide, $LiCo_{1-x}Ni_xO_2$, (where x = 0.00, 0.25, 0.50, 0.75 and 1.00) were prepared by using the starting materials of Analytical Reagent (AR) grade LiOH.H₂O, Co_3O_4 and NiO. Flow diagram of the sample preparation procedure is shown in Figure 1.



Figure 1 Flow diagram of the sample preparation procedure of LiCo_{1-x}Ni_xO₂

XRD, FTIR and Temperature Dependent Electrical Resistance Measurements

X-ray diffraction (XRD) analysis of the powder samples was performed to investigate the crystal structure, lattice parameters and crystallite sizes. The XRD patterns were observed by RIGAKU MULTIFLEX X-ray Diffractometer using CuK_{α} ($\lambda = 1.54056$ Å) radiation in the diffraction angle range of 10° - 70° [Universities' Research Centre (URC), University of Yangon].

Vibrational frequencies of a molecule can be probed by using infrared and Raman spectroscopy. Infrared (IR) spectroscopy is an important relatively inexpensive and efficient analytical method for characterizing materials. FTIR transmission spectra of the samples were observed by PC-controlled SHIMADZU FTIR-8400 Spectrophotometer using Potassium Bromide, KBr pellet at room temperature.

For the temperature dependent electrical resistance measurement, the samples were made into pellets by SPECAC hydraulic press using 5 ton (~70 MPa). The area and thickness of the pellets were 1.14×10^{-4} m² and 4.77 mm respectively. The electrical resistances of the samples were observed by using FLUKE 189 digital multi-meter in the temperature range of 303 K – 773 K by the use of Autonics TCN4L – 24R Temperature Controller.

Results and Discussion

Structure Analysis

XRD patterns of the samples are shown in Figure 2. The observed XRD lines were identified by using standard JCPDS data library files of (i) Cat. No. $50-0653>LiCoO_2 - Lithium$ Cobalt Oxide for x = 0.00 sample, (ii) Cat. No. $50-0653>LiCoO_2 - Lithium$ Cobalt Oxide and Cat. No. 89-3601 > Lithium Nickel Oxide for x = 0.25, 0.50 and 0.75 samples and (iii) Cat. No. 88-1605>Li₀₆₈Ni_{1.32}O₂ - Lithium Nickel Oxide and Cat. No. 89-3601 > Lithium Nickel Oxide for x = 1.00 sample. XRD patterns show the formation of single phase hexagonal structure with dominant peak corresponding to (003) reflection in x = 0.00 - 0.75 samples and (104) reflection in x = 1.00 sample indicating that the crystallites are preferentially oriented along these planes.

The lattice parameters are evaluated by using the equation, $\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$, where d

is interplanar spacing (Å), *a*, *c* are the lattice parameters and (hkl) is the Miller indices. The lattice parameters (a = b and *c*) of the LiCoO₂ sample were found to be increased with increase in Ni concentration due to the lattice substitution of Ni on Co. Tao, et. al. (2011) has reported that the lattice parameters of the LiCo_{0.25}Ni_{0.75}O₂ sample are a = b = 2.90 Å and c = 14.29 Å respectively. Thus, the obtained lattice parameters in the present study are found to be agreed with the results of Tao, et. al. (2011). The crystallite sizes of the samples are estimated by using the Scherrer formula, $D = \frac{0.9\lambda}{B\cos\theta}$, where D is the crystallite size (nm), λ is the wavelength of

incident X-ray (Å), θ is the diffraction angle of the peak under consideration at FWHM (°) and B is the observed FWHM (radians). To examine the nanosized LiCo_{1-x}Ni_xO₂ materials, the FWHM of the observed peaks of the XRD patterns were used to calculate the average crystallite sizes. The lattice parameters and the crystallite sizes are also presented in Table 1. The obtained crystallite sizes decreased with increase in Ni concentration and as shown in Figure 3.



Figure 2 XRD patterns of $LiCo_{1-x}Ni_xO_2$ where (a) x = 0.00, (b) x = 0.25



Figure 2 XRD patterns of $LiCo_{1-x}Ni_xO_2$ where (c) x = 0.50, (d) x = 0.75 and (e) x = 1.00

Sample	Obs. <i>a=b</i> , <i>c</i>	Cal. <i>a=b</i> , <i>c</i>	D
(Contents x of Ni)	(Å)	(Å)	(nm)
0.00	a = b = 2.82	a = b = 2.62	82.72
	<i>c</i> = 13.96	c = 14.09	
0.25	a=b=2.82	a=b=2.77	65.86
	c = 14.07	c = 14.17	
0.50	a = b = 2.85	a=b=2.72	45.81
	<i>c</i> = 14.19	<i>c</i> = 14.21	
0.75	a=b=2.87	a=b=2.87	32.85
	c = 14.30	c = 14.30	
1.00	a = b = 2.94	a=b=2.94	21.26
	c = 14.41	<i>c</i> = 14.43	

Table 1 The lattice parameters and crystallite sizes of LiCo_{1-x}Ni_xO₂



Figure 3 Variation of crystallite size with increase in Ni concentration of LiCo_{1-x}Ni_xO₂

Vibrational Analysis

According to the molecular vibrational theory, a diatomic molecule has two types of normal vibrations: (1) transverse-optical and (2) longitudinal-optical vibrations and also a non-linear tri-atomic molecule, has three types of vibrations: (1) v_1 -mode (symmetric-stretching), (2) v_2 -mode (bending) and (3) v_3 -mode (asymmetric-stretching) respectively [Ross, (1972)]. FTIR transmission spectra of the samples are shown in Figure 4. Vibrational characteristics and mode assignments of constituent molecules of the samples are tabulated in Table 2.



Figure 4 FTIR transmission spectra of $LiCo_{1-x}Ni_xO_2$ where (a) x = 0.00, (b) x = 0.25, (c) x = 0.50, (d) x = 0.75 and (e) x = 1.00

The obtained data (observed wavenumbers) are found experimentally that the LiCo₁₋ _xNi_xO₂ molecular networks emitted frequencies with $\overline{\lambda} = \overline{\nu}$ = wavenumbers. The collected wavenumbers and their corresponding vibrational characteristics of molecules (wavelength, frequency, oscillation time and energy) of the crystal are tabulated in Table 3. According to experimental results, the samples are high frequency oscillators due to their frequencies are found to be $\nu > 10^{12}$ Hz.

Table	2	(a)	Wavenumbers	and	corresponding	vibrational	characteristics	and	mode
		a	ssignments of Li	Co _{1-x}	Ni _x O ₂ where x =	0.00			

Wavenumbers (cm ⁻¹)	Characteristics and Mode Assignment	Molecules
517	v _{TO} -stretching	LiCoO ₂
941	v_{TO} -stretching	LiCoO ₂
984	vro-stretching	LiCoO ₂

Table 2(b)Wavenumbers and corresponding vibrational characteristics and mode
assignments of $LiCo_{1-x}Ni_xO_2$ where x = 0.25

Wavenumbers	Characteristics and	Molecules
(cm ⁻¹)	Mode Assignment	
426	v _{TO} -stretching	LiNiO ₂
478	v_{TO} -stretching	LiNiO ₂
513	v_{TO} -stretching	LiCoO ₂
831	v _{LO} -stretching	LiNiO ₂
980	v _{LO} -stretching	LiCoO ₂

Table 2(c)Wavenumbers and corresponding vibrational characteristics and mode
assignments of $LiCo_{1-x}Ni_xO_2$ where x = 0.50

Wavenumbers (cm ⁻¹)	Characteristics and Mode Assignment	Molecules
530	v _{TO} -stretching	LiCoO ₂
983	v _{LO} -stretching	LiCoO ₂
1425	v ₁ -symmetric stretching	LiNiO ₂

Table 2(d) Wavenumbers and corresponding vibrational characteristics and mode assignments of $LiCo_{1-x}Ni_xO_2$ where x = 0.75

Wavenumbers (cm ⁻¹)	Characteristics and Mode Assignment	Molecules
492	v _{TO} -stretching	LiNiO ₂
864	v_{LO} -stretching	LiNiO ₂
941	v_{LO} -stretching	LiCoO ₂
1443	v ₁ -symmetric stretching	LiNiO ₂

Table 2(e)Wavenumbers and corresponding vibrational characteristics and mode
assignments of LiCo1-xNixO2 where x = 1.00

Wavenumbers	Characteristics and	Molecules
(cm^{-1})	Mode Assignment	
492	v_{TO} -stretching	LiNiO ₂
864	v _{LO} -stretching	LiNiO ₂
1441	v ₁ -symmetric stretching	LiNiO ₂
1501	v ₃ -asymmetric stretching	LiNiO ₂

LO = Longitudinal optical & TO = Transverse optical

\overline{v} (cm ⁻¹)	λ (nm)	ν (Hz)	τ (s)	E (eV)
517	19342	1.550E+13	6.452E-14	0.0642
941	10627	2.821E+13	3.545E-14	0.1168
984	10163	2.950E+13	3.390E-14	0.1221

Table 3(a) Wavenumber and calculated wavelength, natural frequency, oscillation time and
energy of LiCo1-xNixO2 where x = 0.00

Table 3 (b) Wavenumber and calculated wavelength, natural frequency, oscillation time and energy of $LiCo_{1-x}Ni_xO_2$ where x = 0.25

\overline{v} (cm ⁻¹)	λ (nm)	ν (Hz)	τ (s)	E (eV)
426	23474	1.277E+13	7.830E-14	0.0529
478	20921	1.433E+13	6.978E-14	0.0593
513	19493	1.538E+13	6.502E-14	0.0637
831	12034	2.491E+13	4.014E-14	0.1032
980	10204	2.938E+13	3.404E-14	0.1216

Table 3 (c) Wavenumber and calculated wavelength, natural frequency, oscillation time and energy of $LiCo_{1-x}Ni_xO_2$ where x = 0.50

\overline{v} (cm ⁻¹)	λ (nm)	ν (Hz)	τ (s)	E (eV)
530	18868	1.589E+13	6.294E-14	0.0658
983	10173	2.947E+13	3.393E-14	0.1220
1425	7018	4.272E+13	2.341E-14	0.1769

Table 3 (d) Wavenumber and calculated wavelength, natural frequency, oscillation time and energy of $LiCo_{1-x}Ni_xO_2$ where x = 0.75

\overline{v} (cm ⁻¹)	λ (nm)	ν (Hz)	τ (s)	E (eV)
492	20325	1.475E+13	6.780E-14	0.0611
864	11574	2.590E+13	3.861E-14	0.1072
941	10627	2.821E+13	3.545E-14	0.1168
1443	6930	4.326E+13	2.312E-14	0.1791

Table 3(e) Wavenumber and calculated wavelength, natural frequency, oscillation time and energy of $LiCo_{1-x}Ni_xO_2$ where x = 1.00

\overline{v} (cm ⁻¹)	λ (nm)	ν (Hz)	τ (s)	E (eV)
492	20325	1.475E+13	6.780E-14	0.0611
864	11574	2.590E+13	3.861E-14	0.1072
1441	6940	4.320E+13	2.315E-14	0.1789
1501	6662	4.500E+13	2.222E-14	0.1863

Electrical Conductivity Study

The electrical nature of a material is characterized by its conductivity (or, inversely, its resistivity) and its dielectric constant and coefficients that indicate the rates of change of these with temperature, frequency at which measurement is made, and so on. For crystalline materials with a range of chemical composition as well as variable physical properties of porosity and fluid content, the values of electrical properties can vary widely. Electrical conductivity σ of the ceramic obeys an Arrhenius expression, $\sigma = \sigma_0 \exp(\frac{-E_a}{kT})$, where, σ_0 is the pre-exponential factor, E_a is activation energy, k is Boltzmann's constant and T is absolute temperature. Arrhenius plots of the variation of dc electrical conductivity of the samples are shown in Figure 5.

According to the theory of ionic conductivity, the slope of the electrical conductivity in each of the figure, e.g., in Figure 5(a) for $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ (x = 0.00) sample, corresponding to the activation energy for creating of defect states due to the ionic motions of the sample. From Figure 5(a), the activation energy E_a can be obtained by using the slope of the $\ln(\sigma)$ versus $10^3/\text{T}$ graph.

 $E_{a}/k = 5.8981 \times 1000$ $E_{a} = 5.8981 \times 1000 \times k$ $E_{a} = 5.8981 \times 1000 \times 1.38\text{E}\text{-}23$ $E_{a} = 8.14 \times 10^{-20} \text{ J}$ $E_{a} = 0.5087 \text{ eV}$

As shown in Figure 5, electrical conductivities of the samples increased with increase in temperature. The obtained activation energies of the samples are listed in Table 4. From the experimental results, the samples exhibited as superionic conductors at high temperature because their electrical conductivities are found as $\sigma \ge 10^{-3}$ S m⁻¹. In the ln $\sigma - 1000/T$ graphs, the starting point of superionic phase indicates with the circle and the superionic phase temperatures T_{SI} presented in Table 4. As shown in tables, the LiCo_{1-x}Ni_xO₂ (x = 0.75) sample is the lowest (superionic phase) temperature 403 K among the investigated samples.



Figure 5 Arrhenius plots of the ln σ versus 1000/T graphs of LiCo_{1-x}Ni_xO₂ where (a) x = 0.00, (b) x = 0.25



Figure 5 Arrhenius plots of the ln σ versus 1000/T graphs of LiCo_{1-x}Ni_xO₂ where (c) x = 0.50, (d) x = 0.75 and (e) x = 1.00

Table 4 The activation energies of the LiCo_{1-x}Ni_xO₂ samples

Sample	Superionic Phase	E_a
(Contents x of Ni)	Temperature T _{SI} (K)	(eV)
0.00	503	0.5087
0.25	653	0.5636
0.50	733	0.5092
0.75	403	0.5278
1.00	643	0.5410

Conclusion

Lithium-Cobalt-Nickel Oxide, $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$, (where x = 0.00, 0.25, 0.50, 0.75 and 1.00) were successfully prepared by solid state reaction method. XRD patterns reveal that the samples analogous to hexagonal structure. The lattice parameters of the $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$ samples increased with increase in Ni concentration. The crystallite sizes of the samples decreased with increase in Ni concentration. FTIR spectra showed that the vibrational characteristics and mode assignments of constituent molecules of the samples. It can be assumed that the phase confirmation of the samples. The samples exhibited as the superionic conductors in the high temperature with the activation energies as in the range of 0.5087 eV – 0.5636 eV (i.e., $E_a < 1 \text{ eV}$) and it indicated that the samples were advanced superionic conductors. According to experimental results, the samples can be used as the solid electrolyte materials.

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