

STUDY ON STRUCTURAL, MICROSTRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF LITHIUM COBALT OXIDE AND LITHIUM NICKEL OXIDE FOR THE APPLICATIONS OF SOLID OXIDE FUEL CELLS

Moe Min Min Aye¹, Tun Aye², Htet Naing Lwin³ & Win Kyaw⁴

Abstract

Solid Oxide Fuel Cell (SOFC) is an electrochemical device that converts the energy of a chemical reaction directly into electrical energy. SOFC materials of Lithium Cobalt Oxide (LiCoO₂) and Lithium Nickel Oxide (LiNiO₂) were prepared by solid-state reaction method. Structural, microstructural, optical and electrical properties were studied by XRD, SEM, UV-VIS-NIR and electrical conductivity measurement. XRD patterns reveal that the samples analogous to hexagonal structure. The crystallite sizes of the samples were also estimated by using the most intense peaks and obtained as 77.14 nm for LiCoO₂ and 21.40 nm for LiNiO₂ respectively. SEM micrographs indicated that the grain shape of the samples was block shape with clear grain boundary. The energy band gaps E_g were estimated by using the $(\alpha h\nu)^2$ vs. $h\nu$ graphs and obtained as 2.69 eV for LiCoO₂ and 0.52 eV for LiNiO₂. The samples exhibited as the superionic conductors and their activation energies were obtained as 0.4363 eV for LiCoO₂ and 0.4370 eV for LiNiO₂.

Keywords: SOFC, LiCoO₂, LiNiO₂, XRD, SEM, UV-VIS-NIR, electrical conductivity

Introduction

Solid Oxide Fuel Cell (SOFC) is an electrochemical device that converts the energy of a chemical reaction directly into electrical energy. In materials science, fast ion conductors are solids in which ions are highly mobile [Azurdia, (2006)]. These materials are important in the area of solid-state ionic, and are also known as solid electrolytes and superionic conductors. They are mainly useful in batteries and various sensors. Fast ion conductors

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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 [Arico, (2005)].

Lithium transition-metal oxides are functional intercalation compounds for their applications in rechargeable lithium-ion batteries. They have been widely studied in search of structural stability and improved electrochemical performance. LiCoO_2 -based lithium-ion batteries are highly successful commercial products used for powering consumer devices such as laptop computers, video cameras, and cellular phones [Julin, (2003)]. This work deals with the preparation of LiCoO_2 and LiNiO_2 using solid-state reaction method and their structural, microstructural, optical and electrical characteristics were studied by XRD, SEM, UV-VIS-NIR and temperature dependent electrical resistance measurements.

Experimental Details

Preparation of the Samples

Lithium Cobalt Oxide (LiCoO_2) and Lithium Nickel Oxide (LiNiO_2) were prepared by solid state reaction method. The starting materials of Analytical Reagent (AR) grade Lithium Carbonate (Li_2CO_3), Cobalt Oxide (CoO) and Nickel Oxide (NiO) were weighed with molar ratio. The weighed powders were mixed and ground by an agate mortar for 3 h to be homogeneous and to obtain fine powder. The fine powder was annealed at 450°C for 8 h and followed by 800°C for 15 h to be crystalline phase. Flow diagram of the sample preparation procedure of LiCoO_2 and LiNiO_2 is shown in Figure 1. Photographs showing the sample preparation processes are shown in Figures 2(a – i).

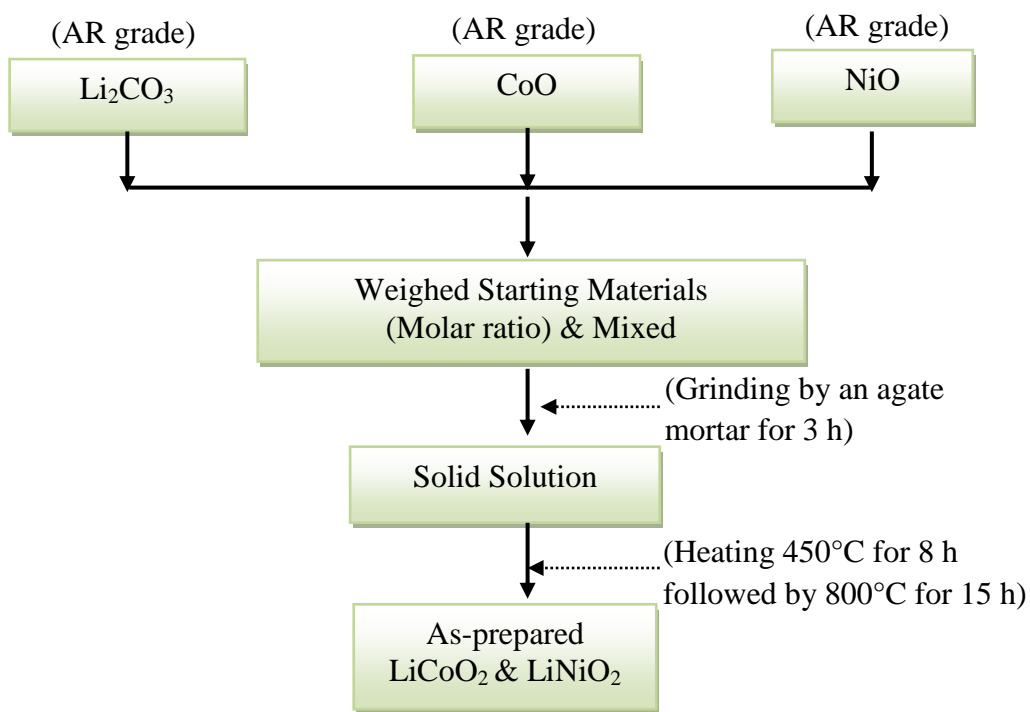


Figure 1: Flow diagram of the sample preparation procedure of LiCoO₂ and LiNiO₂ samples

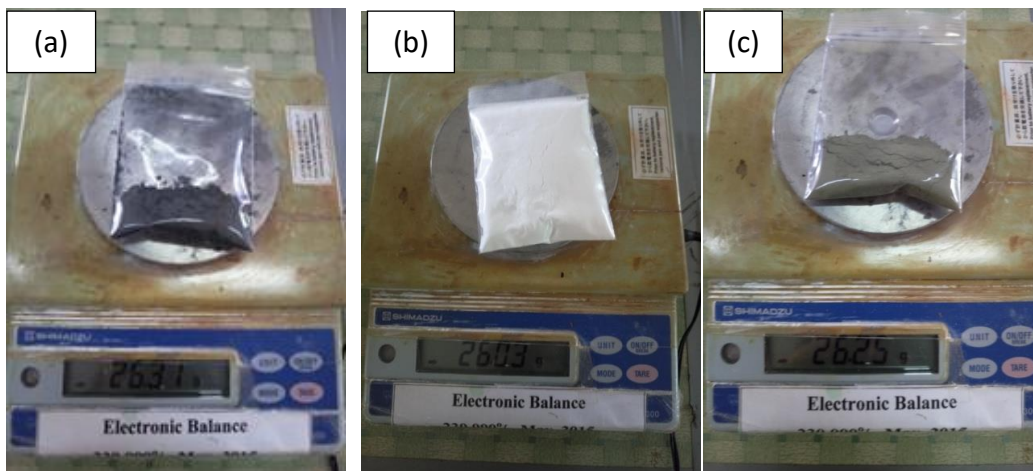


Figure 2: Photographs of the weighing of (a) CoO, (b) Li₂CO₃ and (c) NiO starting materials



Figure 2:(d) Photograph of the weighed Li_2CO_3 , CoO and NiO



Figure 2: Photographs of the JLabTech electric oven (e) at 450°C and (f) at 800°C

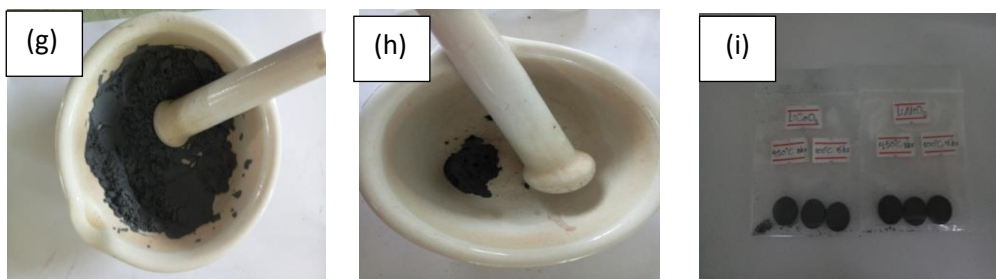


Figure 2: Photographs of the (g) grinding of LiCoO_2 , (h) LiNiO_2 and (i) pellets of LiCoO_2 and LiNiO_2

XRD, SEM and UV-VIS-NIR Measurements

Powder XRD patterns of the samples were observed by Rigaku MiniFlex 600 X-Ray Diffractometer [Department of Physics, University of Yangon]. Microstructural properties of the powder samples were investigated by using JCM-6000Plus Scanning Electron Microscope (SEM) [Department of Physics, West Yangon University] with the accelerating voltage of 15 kV and 7000 times of photo magnification. UV-VIS-NIR (Ultraviolet-Visible-Near Infrared) transmission spectra were collected on PC-controlled SHIMADZU (UV-1800) UV-VIS-NIR Spectrophotometer in the wavelength range of 200 nm – 900 nm.

Temperature Dependent Electrical Resistance Measurement

The LiCoO_2 and LiNiO_2 samples were made into pellets by SPECAC hydraulic pellet-maker using 5 ton (~ 70 MPa). Thicknesses and area of the samples were 2.50 mm and $1.14 \times 10^{-4} \text{ m}^2$. The electrical resistances were observed by using FLUKE 180 digital multi-meter in the temperature range of 303 K – 673 K. DELTA A SERIES DTA-4896 and K-type thermocouple were used as the temperature controller and temperature sensor. Photograph of the experimental setup of temperature dependent electrical resistance measurement is shown in Figure 3.

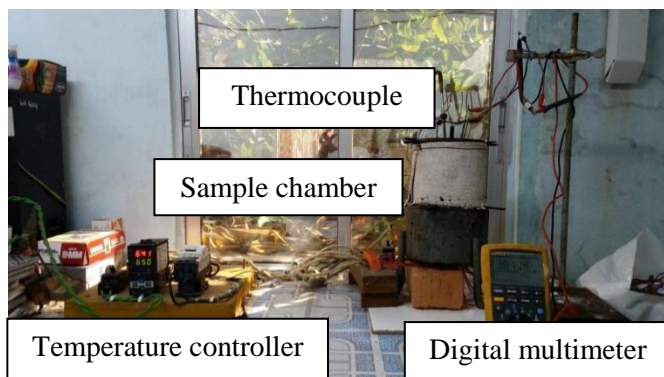


Figure 3: Photograph of the experimental setup of temperature dependent electrical resistance measurement

Results and Discussion

XRD Study

XRD patterns of the sample are shown in Figures 4(a) and (b). The observed XRD lines were identified by using standard JCPDS data library files of

- (i) Lithium Cobalt Oxide, LiCoO_2 , 00-062-0420 for Lithium Cobalt Oxide (LiCoO_2) sample and
- (ii) Lithium Nickel Oxide, LiNiO_2 , 00-062-0468 for Lithium Nickel Oxide (LiNiO_2) sample.

XRD patterns show the formation of single phase hexagonal structure with dominant peak corresponding to (003) reflection in LiCoO_2 sample and (104) reflection in LiNiO_2 sample indicating that the crystallites are preferentially oriented along these planes. The observed lattice parameters of the samples are tabulated in Table 1. Tao, H. et. al. (2010) has reported that the lattice parameters of the $\text{LiCo}_{0.25}\text{Ni}_{0.75}\text{O}_2$ sample are $a = b = 2.90 \text{ \AA}$ and $c = 14.29 \text{ \AA}$ respectively. The obtained lattice parameters in the present study are acceptable compared with the results of Tao, H. et. al. (2011). The crystallite sizes of the samples were 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 (\AA), θ is the diffraction angle of the peak under consideration at FWHM ($^\circ$) and B is the observed FWHM (radians). The obtained crystallite sizes of samples are 77.14 nm for LiCoO_2 and 21.40 nm for LiNiO_2 respectively.

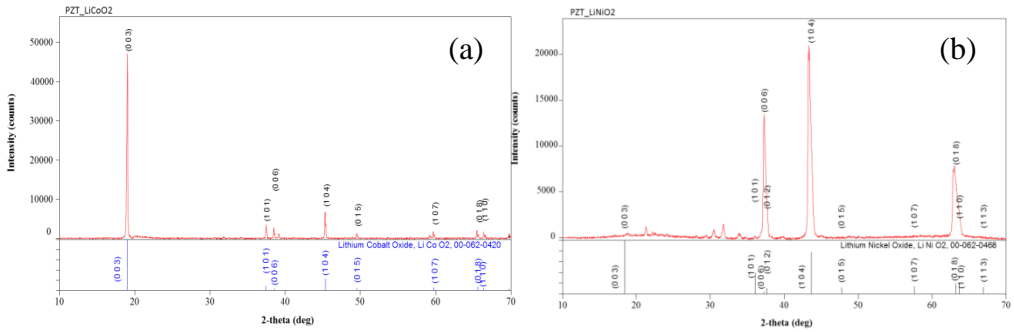


Figure 4: XRD patterns of (a) LiCoO_2 and (b) LiNiO_2

Microstructural Analysis

Grain size and pore structure have a major effect on the properties in polycrystalline materials. SEM micrographs of LiCoO_2 and LiNiO_2 are shown in Figures 5(a) and (b). The image reveals that the grain shape of the samples was block shapes with clear grain boundary.

Table 1: The lattice parameters and crystallite sizes of the LiCoO_2 and LiNiO_2 samples

Sample	Obs. $a=b, c(\text{\AA})$	D (nm)
LiCoO_2	$a=b = 2.8137$ $c = 13.9911$	77.14
LiNiO_2	$a=b = 2.9186$ $c = 14.4427$	21.40

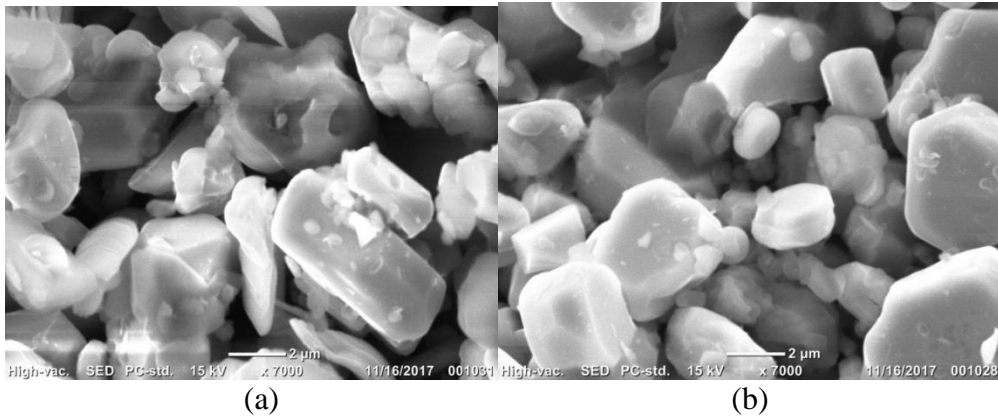


Figure 5: SEM micrograph of (a) LiCoO₂ and (b) LiNiO₂

The grain sizes of the samples are obtained as in the ranges of 0.80 – 5.80 μm for LiCoO₂ and 0.50 – 4.20 μm for LiNiO₂. Some pores appeared in the observed micrographs due to the decomposition of the starting materials. These pores are important role for the movements of ionic materials and it follows the increase in ionic conductivity.

UV-VIS-NIR Spectroscopic Analysis

The effects of Co and Ni on the LiCoO₂ and LiNiO₂ samples on the optical transmission and energy band gaps were examined by UV-VIS-NIR (Ultraviolet-Visible-Near Infrared) transmission spectra. Photons, depending on their energy, interact with matter in a variety of ways. In the present work, only the effect of UV-VIS-NIR (190 nm – 1100 nm) corresponding to the energy (wavelength) region was studied. UV-VIS-NIR transmission and absorption spectra of the samples are shown in Figures 6(a) and (b) for LiCoO₂ and Figures 7(a) and (b) for LiNiO₂ respectively. The intense absorption bands were found in the wavelength ranges of about 250 nm – 1100 nm for LiCoO₂ and 234 nm – 1100 nm for LiNiO₂. It was generally found that the transmission regions of the VIS and NIR light were slightly decreased with the wavelength.

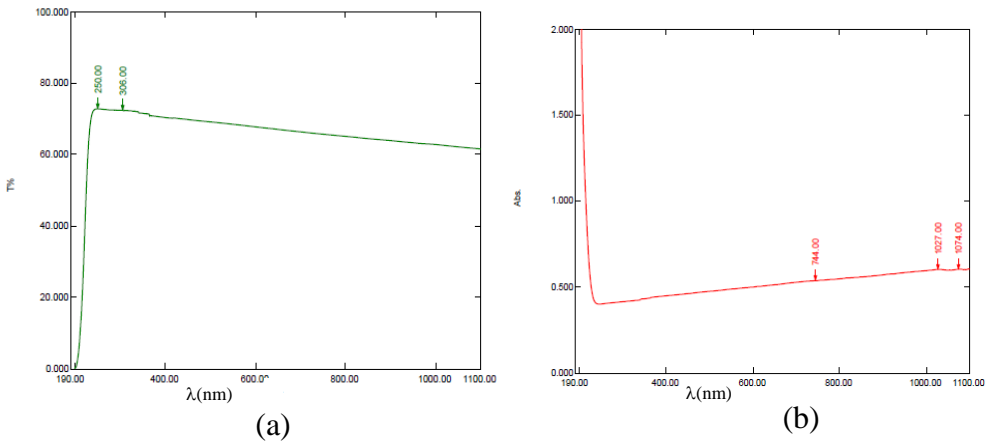


Figure 6: UV-VIS-NIR (a) transmission and (b) absorption spectra of LiCoO_2

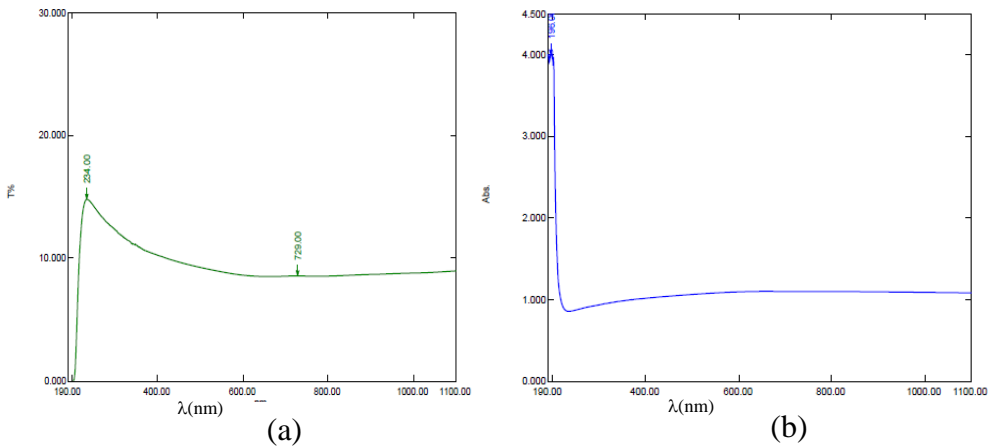


Figure 7: UV-VIS-NIR (a) transmission and (b) absorption spectra of LiNiO_2

It can be deduced that the transmission of UV-VIS-NIR light of Co and Ni effects on the optical transparent in UV than the VIS and NIR regions. The energy band gaps E_g of the samples were determined by using optical percentage transmission with the corresponding wavelength data. To determine the energy band gap, the graph of $(\alpha h\nu)^2$ vs. $h\nu$ was plotted. The intercept of the horizontal line at $\alpha = 0$ gives the value of energy band gap.

The plots of $(\alpha hu)^2$ vs. hu of the samples are shown in Figures 8(a) and (b). The energy band gaps are obtained as 2.69 eV for LiCoO_2 and 0.52 eV for LiNiO_2 respectively. Liu., et. al. (2015) has reported the energy band gap value of LiCoO_2 is 2.70 eV. Also, Chan., et. al. (2011) has reported that the energy band gap value of LiNiO_2 is 0.50 eV. It was found that the obtained energy band gaps are found to be agreed with the results of Liu., et. al. (2015) and Chan., et. al. (2011).

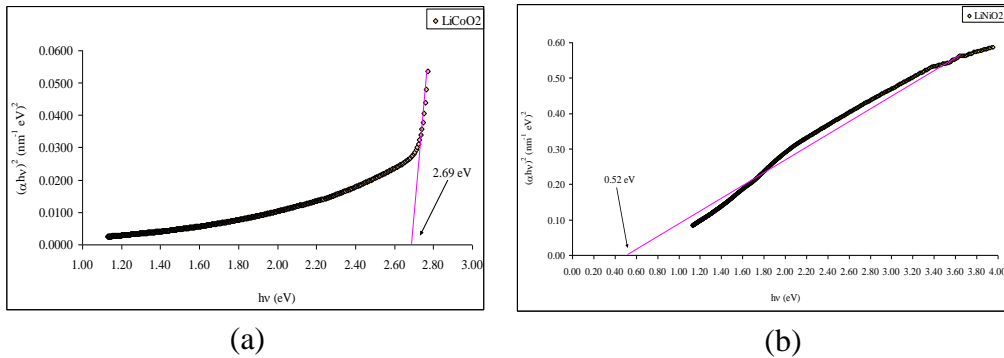


Figure 8: Plots of the $(\alpha hu)^2$ vs. hu graphs of (a) LiCoO_2 and (b) LiNiO_2

Temperature Dependent Electrical Conductivity Study

Electrical conductivity of the solid oxide materials obeys Arrhenius's expression, $\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$ where, σ_0 is the pre-exponential factor, E_a is activation energy (eV), k is Boltzmann's constant and T is absolute temperature (K). Arrhenius's plots of the samples are shown in Figures 9(a) and (b) respectively. The graph shows that the increase in temperature leads to increase in conductivity, which is the normal behaviour of superionic materials and it obeys the well known Arrhenius relation. The higher values of temperature for the samples help the trapped charges to be liberated and participate in the conduction process which results increase in conductivity. According to the conduction mechanism in ceramics, the decrease in resistivity could also be related to the increase in the drift mobility of the thermally activated electrons. The activation energies were evaluated by using the slopes of the $\ln \sigma$ vs $1000/T$ relationship. The obtained activation energies

of the samples were obtained as 0.4363 eV for LiCoO₂ and 0.4370 eV for LiNiO₂.

From the experimental results, the samples exhibited as superionic conductors because their electrical conductivity were $1.04 \times 10^{-3} \text{ S m}^{-1}$ at 423 K (superionic phase temperature T_{SI}) for LiCoO₂ and $1.13 \times 10^{-3} \text{ S m}^{-1}$ at 403 K for LiNiO₂. Since the solid material has the electrical conductivity $\sigma \sim 1 \times 10^{-3} \text{ S m}^{-1}$ called the superionic conductor. A few solids conduct electricity better by ion motion than by electron motion. These unusual materials are technologically important in making batteries. All batteries have two electrodes separated by an electrolyte, which is a material that conducts ions better than electrons.

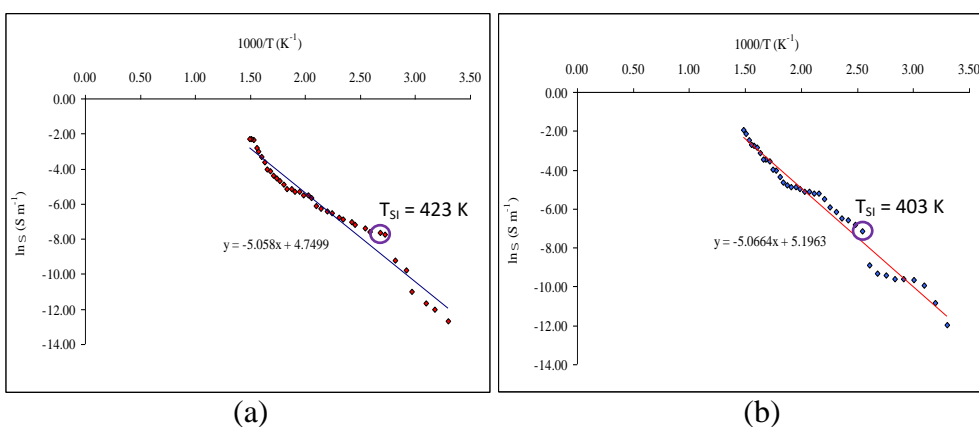


Figure 9: Arrhenius plots of the temperature dependent electrical conductivity of (a) LiCoO₂ and (b) LiNiO₂

Conclusion

Solid oxide materials of LiCoO₂ and LiNiO₂ were successfully prepared by solid state reaction method and their structural, microstructural, optical and electrical conductivity were studied in this work. XRD patterns reveal that the investigated samples analogous to hexagonal structure. The crystallite sizes of the samples were obtained as 77.14 nm for LiCoO₂ and 21.40 nm for LiNiO₂ respectively. From the SEM micrographs, the image reveals that the grain shape of the samples was block shape with clear grain

boundary. Some pores appeared in the observed micrographs due to the decarbonation of the starting materials. From the observed UV-VIS-NIR transmission spectra, the samples demonstrated that less than 100% transmittance of throughout the UV-VIS-NIR region. The energy band gaps E_g were obtained as 2.69 eV for LiCoO_2 and 0.52 eV for LiNiO_2 . The obtained energy band gap values indicated that the samples were semiconducting materials. Temperature dependent electrical resistance measurements showed that the samples exhibited as the superionic conductors. The activation energies were obtained as 0.4363 eV for LiCoO_2 and 0.4370 eV for LiNiO_2 . According to experimental results, the samples can be applied as the solid oxide fuel cell materials because they are semiconducting materials and/or superionic conductors with the activation energies lower than 1 eV.

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