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Science and Technology for Nation Prosperity

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Bengkulu, 6th -7th July 2019

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Nanang Sugianto, S.Si., M.Sc.
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Santi Nurul Kamilah, S.Si., M.Si.
Dyah Setyo Rini, S.Si., M.Sc.
Suhendra, S.Si., MT.

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FOREWORD

All praises be to the Almighty God, for all His grace and guidance, proceeding of the 2nd International Conference on Science and Technology with the theme "Science and Technology for Nation Prosperity" can be completed. This proceeding is a collection of papers held by the Mathematics and Natural Science, University of Bengkulu on 6th – 7th July 2019 at GRAGE Hotel Bengkulu.

Our highest gratitude and appreciation goes to the presenters and authors of the papers, as well as the executive committee who have worked hard so that this proceeding can be published. We also thank the Reviewer Board for reviewing all papers so that the quality of the contents of the paper can be maintained and accounted for. Do not forget to all parties who have provided support for the holding of the international conference and the preparation of this proceeding, we thank you.

We do hope that this conference would bring a great opportunity for all of us to strengthen our contribution to the advancement of our nation.

Finally, I hope this proceeding can provide benefits for all.

Bengkulu, June 2020

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INTERNATIONAL PROCEEDING
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A preliminary study of the structure and electrical properties on transition metal incorporated in Li2CoSiO4 prepared from rice husk silica and cathode waste

A Riyanto[1*], S Sembiring[1], C Widyastuti[1], M T Rangga[1], Junaidi[1], and S Husain[2]

[1] Department of Physics, University of Lampung, Bandar Lampung, Indonesia
[2] Department of Physics, Lambung Mangkurat University, Banjarmasin, Indonesia

[*]Email: agus.riyanto@fmipa.unila.ac.id

Abstract. This work was conducted to study the potential of rice husk silica and lithium battery cathode waste as raw material for making transition metals incorporated in Li_2CoSiO_4. This study includes the phase analysis, element mapping, band gap energy, and electrical conductivity of the sample. The sample was prepared from fine rice husk silica powder and cathode waste powder with a mass ratio of 1:1 using a solid-state reaction method. It was sintered at 900 ^oC with a holding time of 12 hours at peak temperature. The results of the phase analysis show that Li_2CoSiO_4 dominates the phase in the sample, even though there is an impurity phase, i.e., Na_2SO_4. Elements mapping shows that transition metals in the form of Ni and Mn are incorporated evenly on the surface of the sample. It has band gap energy of around 1.4 eV and electrical conductivity around $6.26x10^{-5}$-$6.34x10^{-5}$ S/m at a range frequency of 1-1000 Hz. In further work, it is essential to study the phase, element mapping, and electrical properties of samples sintered at varying temperatures. Besides, electrochemical performance also needs to be tested.

1. Introduction

Dilithium cobalt silicate (Li_2CoSiO_4) compound is one of the polyanion silicate material families developed as a cathode on a lithium-ion battery. It has excellent thermal stability, high structural stability, and safety[1]. Besides, it also has a high theoretical capacity of 325 mAh/g, higher than other polyanion compounds based on phosphate, fluorophosphate, or borate[2]. However, like other polyanion silicate material, Li_2CoSiO_4 has an extremely low electrical conductivity and the slow diffusion rate of lithium ions. It causes the ion insertion/extraction into/from lattice difficult so that the electrochemical performance is not optimal[3]. The various method has been made to improve the performance of these materials, one of which is incorporating transition metals. According to Zhang et al. (2014), this technique has been shown to increase the defect concentration and electrical conductivity of polyanion silicate material so that the lithium-ion diffusion process rises[4].

One obstacle in developing Li_2CoSiO_4 materials incorporated with transition metals is the limitation of raw materials. This limitation can be overcome by utilizing lithium-ion battery cathode waste as a source of lithium, cobalt, and other transition metals. For example, the cathode of the Samsung SDI ICR18650-22F battery is made from a lithiated metal oxide (cobalt, nickel, manganese), which has the potential to be used as raw material. The composition of cobalt on the battery is 4-50%, while nickel and manganese are 0-25% and 0-15%, respectively. Many essential elements of the lithium battery

cathode can be recovered through the acid leaching method. For example, Shun-guan et al. (2012) succeeded in obtaining cobalt and lithium elements in the form of compounds $CoC_2O_4.2H_2O$ and Li_2CO_3 from $LiCoO_2$ cathode waste[5]. By dissolving the cathode $LiCoO_2$ into a solution of H_2SO_4 and H_2O_2, a leaching solution can be obtained. Addition $(NH_4)_2C_2O_4$ to leaching solution can precipitate $CoC_2O_4.2H_2O$ compounds, and the addition of Na_2CO_3 to the filtrate residue will precipitate Li_2CO_3. Meanwhile, silica, as one of the essential compounds in the formation of Li_2CoSiO_4, can be obtained from rice husk. Rice husk silica has a high purity level above 98%, amorphous, and reactive[6], [7]. These characteristics cause rice husk silica to be utilized in making silica-based materials. In our previous study, rice husk silica has been used successfully to produce some high purity ceramic materials, such as cordierite[8]–[10] and forsterite[11]. In other studies, rice husk silica has also been used in the manufacturing of mullite[12], borosilicate[13], and carbosil[14].

In the present work, we prepared transition metal incorporated in Li_2CoSiO_4 by utilizing recycling products from cathode waste of Samsung SDI ICR18650-22F batteries and silica from rice husks. The sample was synthesized using the solid-state reaction method and sintered at 900 ^oC. This study is purposed to analyze the potential of the waste as raw material to manufacture the cathode material. Specifically, this study is aimed to investigate functional groups, phases, elements mapping, band gaps, and electrical conductivity of the sample of transition metal incorporated in Li_2CoSiO_4.

2. Materials and Methods

Silica extraction from rice husk

Rice husk silica extraction refers to our previous studies[8]–[11]. As much as 50 g of rice husk in 500 ml of 5% NaOH solution was boiled to obtain silica sol. It was left at room temperature for 24 hours and then filtered to separate sol and remaining husk. To obtain silica gel, 10% HNO_3 solution was added by dropwise until the sol converts to the silica gel entirely. Furthermore, silica gel was cleaned using deionized water repeatedly and then dried at 110 ^oC for 4 hours until a solid was obtained. It was milled to obtain fine silica powder.

Decomposition of cathode waste

The decomposition process was carried out by adding 300 ml of NH_4OH 4 M solution to 20 g pieces of Samsung SDI ICR18650-22F battery cathode waste and then stirring at 60 °C for 1 hour. The deposits obtained from this process are filtered and then dried at 80 ^oC for 2 hours until the powder was obtained. As much as 10 g of the powder was dissolved in 92 ml of 4 M H_2SO_4 and 8 ml of 4% H_2O_2 under stirring at 70 ^oC for 2 hours. As much as 4 M NaOH solution was added to the solution to pH 7, and then 4 M Na_2CO_3 solution was added to obtain a paste with pH 11. The paste was washed using deionized water and then heated at 100 ^oC for 5 hours. The solid obtained from the heating was ground to get a fine powder (cathode waste powder).

Synthesis of transition metal incorporated in Li_2CoSiO_4

The preparation of transition metal incorporated in Li_2CoSiO_4 was carried out by the solid-state reaction method, namely by mixing 5 g of rice husk silica and 5 g of cathode waste powder. The mixture was then ground and sieved to obtain particles with a size of 250 meshes. Then, it was dissolved in 100 ml of 96% ethanol and stirred at room temperature for 6 hours following by stirring at 60 ^oC for 2 hours. Next, the sample was ground, and then as much as 1.5 g of sample powder was pressed with a pressure of 5 MPa to become a cylindrical pellet with a diameter of 2 cm and thickness 0.3 cm. It was calcined at a temperature of 300 ^oC with a holding time of 3 hours then continued with the sintering at 900 ^oC with a holding time of 12 hours at peak temperature.

Identification of functional groups

FTIR (Prestige 21 Shimadzu) was used to identify functional groups. The measurement was carried out by preparing a sample by grinding around 2 mg of metal incorporated in Li_2CoSiO_4 and 300 mg of

potassium bromide (KBr) in the mortar. The mixture was pressed to form the KBr pellet. The sample scanned at wavenumbers with a range of 4000-300 cm^{-1}.

Crystal structure analysis

Crystal structure analysis was carried out using an x-ray diffractometer (X'Pert Powder PANalytical PW 30/40) with CuKα radiation (λ = 0.15418 Å) produced at a voltage of 40 kV and an electric current of 30 mA. Diffractogram was recorded in the range 2θ 10°-100°.

Morphology investigation and mapping elements

The sample was characterized using SEM/EDS (Hitachi SU-3500) to evaluate the surface morphology and elemental composition.

Band gap calculation

Calculation of band gap values begins by measuring diffuse reflection using UV-Vis Spectrophotometer (Shimadzu 2450). The band gap was calculated using the Kubelka-Munk relation as shown in Equation 1

$$F(R) = K/S = (1-R)^2/2R \quad (1)$$

where S and K are the scattering and absorption coefficients respectively, $F(R)$ is the function of Kubelka-Munk, and R is the diffuse reflection. The band gap (E_g) and the absorption coefficient is related through the Tauc relation. Tauc relation to the direct band gap is given in Equation 2

$$(\alpha h\nu)^{1/n} = A\left(h\nu - E_g\right) \quad (2)$$

where α is the linear absorption coefficient, ν is the light frequency (Hz), A is the proportional constant, and $n = 1/2$ for the direct band gap. When incident radiation scatters are perfectly diffuse manner, the absorption coefficient K becomes equal to 2α. In this case, considering the scattering coefficient S as constant concerning wavelength, the Kubelka-Munk is proportional to the absorption coefficient α, applying Equation 1 can be obtained from the relation such as Equation 3

$$[F(R)h\nu]^2 = A\left(h\nu - E_g\right) \quad (3)$$

Electrical conductivity measurement

Electrical conductivity was measured using LCR meter (HIOKI 3520-52) in the range frequency of 1-1000 Hz. The value of electrical conductivity was calculated using Equation 4

$$\sigma = Gl/A \quad (4)$$

where G is conductance (S), l is length (m), and A is cross-sectional area (m^2).

3. Result and discussion

Figure 1 shows the infrared spectrum of a sample of transitions metal incorporated in Li_2CoSiO_4. The absorption peak observed at 3448 cm^{-1} is related to the stretching vibration of the O-H bond. This absorption band mostly arises from O-H bonds in silanol groups (Si-OH) and water molecules trapped in the sample[15]. The presence of silanol groups is supported by the presence of an absorption band at 1635 cm^{-1}, which is a characteristic peak of Si-OH bond[11]. In the spectrum, there is also the most absorption peak observed at 1111 cm^{-1}, which is related to the asymmetric vibrations of the Si-O-Si group. Meanwhile, the absorption peak at 794 cm^{-1} is associated with the stretching vibration of the Si-O-Si bond[16]. The peak at 1111 cm^{-1} is also related to the stretching vibration of the S-O bond[17]. The peak at 617 cm^{-1} is also associated with the bending vibration of the S-O bond[17]. Other influential absorption bands are at 470 cm^{-1}, which is related to the vibration of the Co-O group originating from CoO_4 bonds[18]. Besides, there are also absorption bands at 370 and 354 cm^{-1}, which are related to the vibration of the Li-O group originating from LiO_4[19].

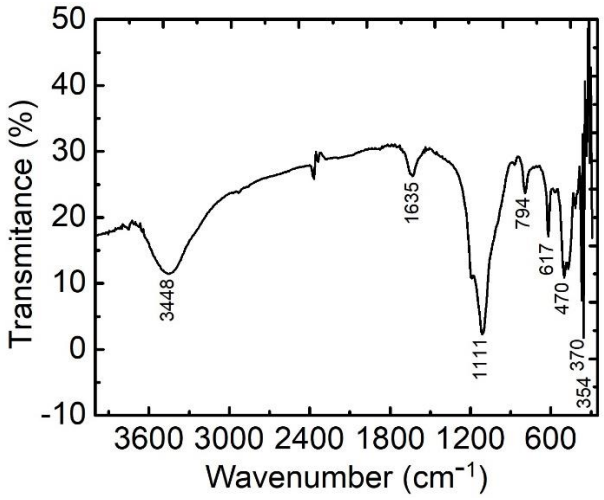

Figure 1 FTIR spectrum of a sample of transition metal incorporated in Li_2CoSiO_4

The diffraction pattern of the sample is shown in Figure 2. XRD qualitative analysis was conducted by comparing diffraction lines with PDF databases using the search-match method. Based on this method, the phase identified in Figure 2 shows the presence of the phase of Li_2CoSiO_4 with the most intense peak located at 2θ 21.73° (PDF 00-070-2351). The phase formation Li_2CoSiO_4 is in agreement with FTIR analysis, which shows the presence of Si-OH, Si-O-Si, Co-O, and Li-O groups. Besides Li_2CoSiO_4, there is also an impurity phase, Na_2SO_4, with the most intense peak located at 2θ 32.12° (PDF 00-036-0397). The impurity phase is predicted to be formed from the raw material used to prepare the sample. The formation of the Li_2CoSiO_4 and Na_2SO_4 phases is also in agreement with the results of the composition analysis on the sample surface, which shows the presence of several related elements, as shown in Figure 3. Figure 3(a) shows the morphology of the sample, which shows the form of dense and without clear grain boundaries. Silicon (Si), cobalt (Co), and oxygen (O) as the main elements forming the structure of Li_2CoSiO_4 are distributed evenly on the surface of the sample, as shown in Figure 3(b)-(d). Transition metal elements also appear to be quite uniformly distributed on the surface of the sample, as shown in 3(e)-(f). The presence of nickel (Ni) and manganese (Mn) in this sample shows that there are transition metals incorporated in the Li_2CoSiO_4 structure. The presence of the Na_2SO_4 phase was also confirmed in the distribution of the elements shown in Figure 3(g)-(h), which showed the presence of sodium (Na) and sulfur (S). However, these elements are in relatively small amounts compared to the constituent of transition metal incorporated in Li_2CoSiO_4.

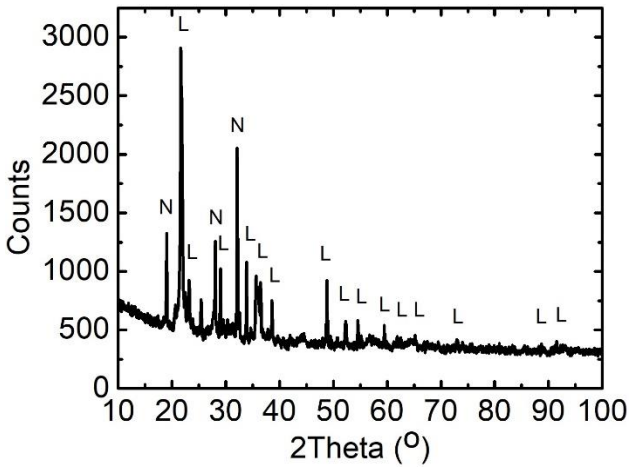

Figure 2 X-ray diffraction pattern of a sample transition metal incorporated in Li_2CoSiO_4, L = Li_2CoSiO_4, and N = Na_2SO_4 (impurity)

The band gap energy of transition metal incorporated in Li_2CoSiO_4 estimated using Tauc plots, as shown in Figure 4(a) shows a small enough value of around 1.4 eV. This small band gap is followed by a high electrical conductivity value, as shown in Figure 4(b). The electrical conductivity of the sample at room temperature in the frequency range 1-1000 Hz looks stable with the lowest value is $6.26x10^{-5}$ S/m, and the highest value is $6.34x10^{-5}$ S/m. This electrical conductivity is much more excellent when compared to the electrical conductivity of pristine Li_2CoSiO_4. The pristine Li_2CoSiO_4 produced from manufacturing raw materials generally only have electrical conductivity in the order of ~ 10^{-12} S/m[20]. The presence of transition metals in the sample has a significant effect on the electrical conductivity of the sample. It can be known from the value of electrical conductivity of transition metal incorporated in Li_2CoSiO_4, which is much higher than that of pure Li_2CoSiO_4. Not only increasing the concentration of defects, but the presence of transition metals Ni and Mn in the sample also triggers an increase in the density of free electrons[4]. As a result, the energy band gap of the sample incorporated with the transition metal becomes narrower, and its electrical conductivity is much higher than that of pure Li_2CoSiO_4. Based on the band gap value and electrical conductivity, the rice husk silica and cathode waste are very potential to be used as a raw material for making transition metal incorporated in Li_2CoSiO_4 for cathode applications.

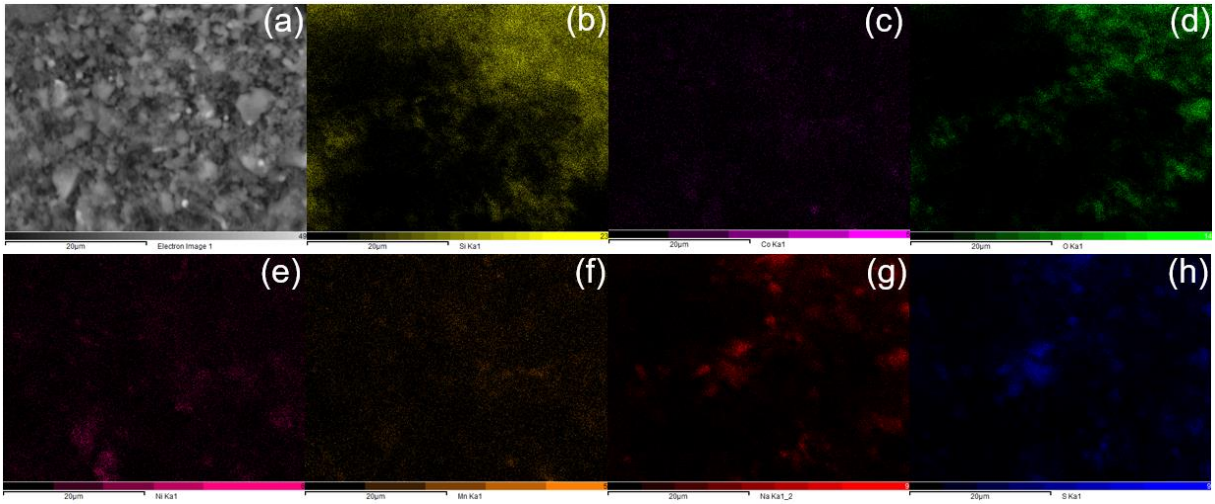

Figure 3 Morphology and elements mapping in a sample transition metal incorporated in Li_2CoSiO_4, (a) morphology of sample, (b) Si, (c) Co, (d) O, (e) Ni, (f) Mn, (g) Na, and (h) S

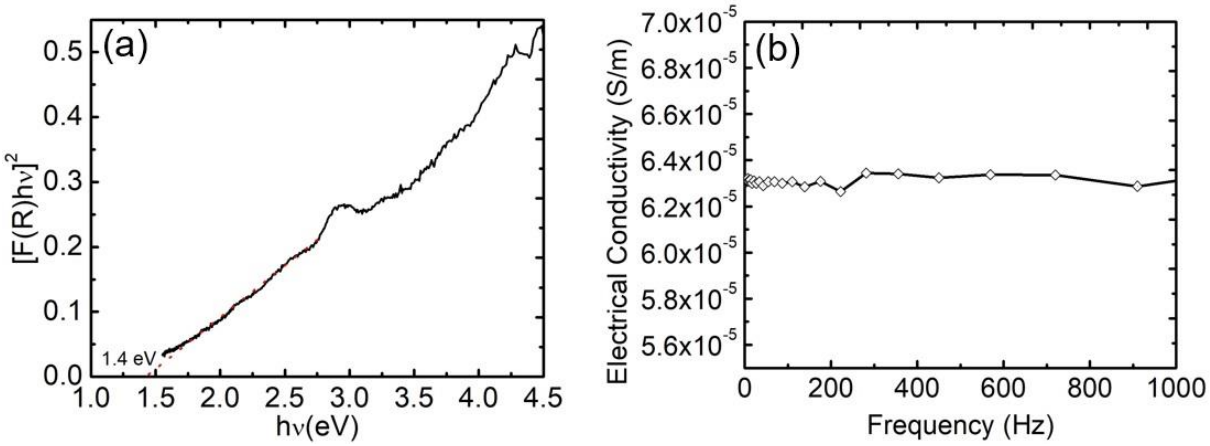

Figure 4 Electrical characteristic of transition metal incorporated in Li_2CoSiO_4, (a) the Tauc plot of band gap energy, and (b) electrical conductivity at a different frequency

4. Conclusion

The functional group identification, phase analysis, and element mapping show that the rice husk silica and cathode waste are very potential used as a raw material to produce a transition metal incorporated in Li_2CoSiO_4, even though still accompanied by impurity. This material also has a small band gap around 1.4 eV and very stable electrical conductivity in room temperature in the range $6.26x10^{-5}$-$6.34x10^{-5}$ S/m in the frequency region 1-1000 Hz. This characteristic makes it very suitable for a cathode of lithium battery application. For further studies, an electrochemical performance test of this sample needs to be carried out. Besides, the phases, element mapping, electrical characteristics, and electrochemical performance of these samples, which sintered at different temperatures, also need to be studied.

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