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Safei Purnama

Center for Science and Technology of Advanced Materials, National Nuclear Energy Agency, Puspiptek-Serpong, Tangerang 15314, Indonesia

Aziz Khan Jahja

Center for Science and Technology of Advanced Materials, National Nuclear Energy Agency, Puspiptek-Serpong, Tangerang 15314, Indonesia, azizjahja@gmail.com

Takeshi Sakuma

Institute of Applied Beam Science, Ibaraki University, Mito 310-8512, Japan

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Thermal and γ -Ray Irradiation Effects on the Ionic Conductivity of $(\text{LiCl})_x(\text{Montmorillonite})_{1-x}$

Safei Purnama¹, Aziz Khan Jahja^{1*}, and Takeshi Sakuma²

1. Center for Science and Technology of Advanced Materials, National Nuclear Energy Agency, Puspiptek - Serpong, Tangerang 15314, Indonesia
2. Institute of Applied Beam Science, Ibaraki University, Mito 310-8512, Japan

*e-mail: azizjahja@gmail.com

Abstract

Composites of montmorillonite (MMT) - lithium salts have been prepared using a simple process of powders mixing followed by heating. The powders resulting from this method are expected to be ionic conductors with a high ionic conductivity characteristics. This characteristic is also further improved by employing gamma-ray irradiation technique at specified irradiation doses. The best results were obtained for the $(\text{LiCl})_{0.5}(\text{MMT})_{0.5}$ composite with a room temperature ionic conductivity of 2.192 mS/cm, which then increases to ~5 mS/cm after gamma irradiation at a dose of 400 kGy. This value is equivalent to the value of the ionic conductivity of current commercial rechargeable lithium battery, which is ~10 mS/cm. However the commercial battery system is still employing an unsafe organic electrolyte. By employing this lightweight, inexpensive and high-temperature resistant ceramic montmorillonite, the final result of this Research and Development work is expected to provide an alternative solid electrolyte system for rechargeable battery which is safer and more inexpensive especially for secondary battery technology development in Indonesia.

Abstrak

Dampak Suhu Panas dan Iradiasi Sinar γ pada Konduktivitas Ion $(\text{LiCl})_x(\text{Montmorillonite})_{1-x}$. Pembuatan bahan elektrolit padat dilakukan dengan proses sederhana berupa pencampuran serbuk yang diikuti dengan pemanasan yang diharapkan dapat membentuk komposit *montmorillonite* (MMT)-garam Litium yang memiliki karakteristik konduktivitas ionik yang tinggi. Karakteristik ini juga dicoba ditingkatkan lebih jauh dengan menggunakan iradiasi sinar gamma dengan pengaturan dosis radiasi. Hasil terbaik diperoleh untuk komposit $(\text{LiCl})_{0.5}(\text{MMT})_{0.5}$ dengan nilai konduktivitas ionik pada suhu ruang mencapai 2,192 mS/cm yang meningkat menjadi ~5 mS/cm setelah iradiasi gamma dengan dosis 400 kGy. Nilai ini seorde dengan nilai konduktivitas ionik baterai isi ulang yang ada saat ini yang bernilai ~10 mS/cm namun masih menggunakan elektrolit organik yang kurang aman. Dengan penggunaan keramik *montmorillonite* yang ringan, murah serta memiliki kemampuan untuk bertahan pada kondisi suhu tinggi, hasil dari litbang ini diharapkan memberikan prospek salah satu alternatif sistem elektrolit padat baterai isi ulang yang aman dan ekonomis terutama untuk pengembangan teknologi baterai di Indonesia.

Keywords: rechargeable battery, montmorillonite, lithium salt, ionic conductivity, γ -ray irradiation

1. Introduction

Presently, in the field of advanced materials research particular attention has been paid to the research and development of ionic conductors, and especially to the development of ionic conducting compounds as components of a high density energy storage system. What this means then is that the material should be light or small in volume and is able to store a large quantity of energy [2]. The electrical conductivity of solid ionic conductor material or solid electrolytes, is relatively lower than the electrical conductivity of liquid electrolytes which

reaches up to 10^{-1} S/cm at room temperature. Several types of solid electrolytes including polymers, glasses, and ceramics, are currently being investigated, while the electrical conductivity generated in these materials is about 10^{-3} S/cm at room temperature. Therefore there is still a lot of room available for improvement of the electrical conductivity in solid electrolytes until it is on a par with the ionic conductivity of liquid electrolytes.

Lately, electric cars have attracted plenty of attention, in particular of those people who are particularly concerned about the environment and the environmental impact of

conventional fossil fuel. Electric car harness electrical energy that can be stored in the battery system. This electrical energy is converted into other forms of energy which is environmentally friendly, so as to reduce pollution due to vehicular traffic on the road. Moreover, along with the development of electronic devices, the use of the battery also could not be avoided, because the battery is an energy source that is most effective, simple, easily transportable from one location to another as well as economically affordable.

The research focus is now limited to a ceramic-based solid electrolytes namely montmorillonite, and the montmorillonite structure is shown in Figure 1. Ceramic-based solid electrolytes provide an edge with a high level of security, since ceramic is resistant to high temperatures and less reactive to lithium. Ceramics used for the solid electrolyte generally has a framework structure or a layered structure that allows for the easy mobility of ions [3,4]. Ceramic solid electrolyte system will be composed of a ceramic matrix composite with inorganic materials such as lithium salt as a dopant or filler. In its function as a solid electrolyte, the cation dopant/filler serves as a charge carrier and will fill up and move in the space between the layers or diffuses into the layered structure which has defects such as vacancy, interstitials or substitution [3].

The purpose of this study was to synthesize ionic conductor materials which have a low electrical conductivity at room temperature and mix them with the compound material LiCl. In this way the hybrid ionic conductor material $(\text{LiCl})_x(\text{Montmorillonite})_{1-x}$ which has a relatively higher room temperature electrical conductivity is obtained. Montmorillonite is a constituent often found in bentonite clays, local materials that are easily obtainable in Indonesia.

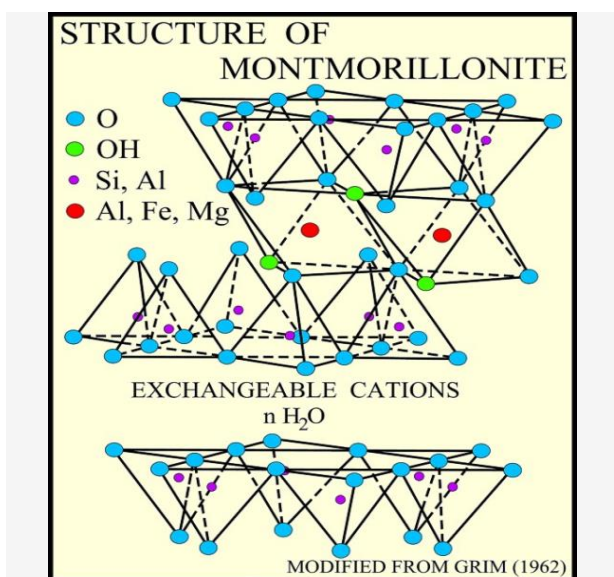


Figure 1. The Structure of Mont Morillonite

2. Methods

Composite materials of solid electrolyte montmorillonite (MMT) - Li salt are synthesized by the powder method for a variety of compositions as shown in Table 1. The starting materials are montmorillonite and alkali salts which were obtained from Sigma Aldrich company.

The manufacturing process is shown schematically in Figure 2. The milling process is accomplished by high energy milling facility (HEM, high energy milling) SPEX 8000 employing both a vial and tungsten carbide balls. The weight ratio between the balls and the sample is 2: 1. Furthermore, the milled powder is then formed into pellets measuring 1.5 cm in diameter and 0.2 cm thick with 3 ton compacting using a hydraulic press before sintering at a temperature of 500-600 °C for 2 hours. The composite pellets are stored in airtight plastic bags for further processing. In order to create the disordered structure effects in the sample, gamma rays irradiation is also performed on the montmorillonite materials and composite materials in addition to the milling process. The irradiation on the montmorillonite materials is carried out at various irradiation dose of 50 kGy, 100kGy, 150 kGy to 200 kGy and 250 kGy respectively, whereas the irradiation procedure on the composite materials is performed at a dose of 400 kGy. The irradiation procedure is performed at the irradiation facility in PAIR-BATAN with ^{60}Co irradiation source and a dose intensity of 700 Gy/h.

Characterization of the structure or composite phase is carried out by analyzing the pattern of X-ray diffraction measurement results obtained with a Philips X-ray diffractometer, at the Center for Science and Technology of Advanced Materials, PSTBM-BATAN. The X-ray diffraction measurement parameters are the wavelength $\lambda = 1,5406 \text{ \AA}$, the cathodic voltage of 30 kV, current of 30 mA, and the angular scanning angle (2θ) in the range of 5° to 60° with a step size of $0,01^\circ$ and time per step is 1.0 seconds. The microstructure was observed using a scanning electron microscope (SEM) and elemental analysis was performed by means of energy dispersive X-ray spectroscopy (EDS) from JEOL at the Center for Science and Technology of Advanced Materials, PSTBM-BATAN. Electrical conductivity measurements were performed using an LCR-meter HIOKI 3522-50 with frequency variation between 0.1 Hz to 100 kHz and a temperature between room temperature to 550 °C. The thermal characterization (DSC) is performed using the DSC instrument Perkin Elmer JADE 7.

Table 1. The Chemical Composition of Solid Electrolyte Composite

Composite type	Composition
$(\text{LiCl})_x(\text{MMT})_{1-x}$	$x = 0; 0,1; 0,2; 0,3; 0,4; 0,5$

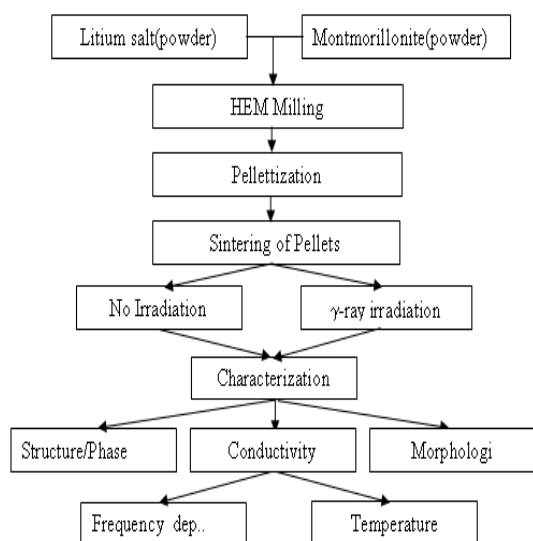


Figure 2. Schematic Flow Chart of Synthesis and Characterization of Li-salt/ MMT Montmorillonite Composite Samples

The methodological steps followed in this work are presented as a flowchart in Figure 2.

3. Results and Discussion

Milling process on montmorillonite and Li salts in general resulted in several mechanical collision processes between the steel milling balls and the powder, in which heat is then generated in the process. Both of these processes will lead to changes in the structure of the two starting materials.

The mechanical process brings about a decrease in the particle sizes of the montmorillonite powder sample, and additionally also causes the structural deformation on the structure of the layer ((T) tetrahedral and (O) octahedral layers). Also in this case, heat which arises during the milling process will lead to the evaporation of water (H_2O) which is trapped in between the layers. This causes the distance between the sheets (~ 1 nm) to shrink and this effect is usually observed in the smaller X-ray diffraction angles of 10° or lower. On the other hand, the size of the Li-salt is smaller than the distance between the layers, therefore some of which will be deformed while some other parts will be pushed in to fill the space between the layer and a buffer or pillars which in turn prevents the decrease in the distance between the sheets due to the evaporation of water, such as observed by other authors studying milling process of Na-montmorillonite and organo-montmorillonite samples.

In the course of sintering, a process of deformation and evaporation of water in montmorillonite occurs. The addition of Li-salt has an impact on both of these processes. The deformation process is reflected in the changes of X-

ray diffraction pattern at larger angles ($2\theta > 10^\circ$) as demonstrated in Figure 3, for the sample $(LiCl)_x(MMT)_{1-x}$. The pattern of the $(LiCl)_x(MMT)_{1-x}$ sample indicates that montmorillonite tends to be amorphous and the LiCl salt diffraction peak decreases with increasing value of x . This mechanism which causes changes in the diffraction pattern can be explained by using the unit cell parameter of the salts and the ionic radii of Li^+ ions and halogen ions. In LiCl compound, the disappearance of the diffraction peak is due to the influx of LiCl salt in between the space layers, which causes the deformation and the ionization of the LiCl fraction which does not fill the space. Li cations are formed to diffuse into tetrahedral and octahedral structures that have been deformed during the milling process. These two processes will increase with the increasing values of x .

The evaporation temperature of water in the space between the layers also shifted to higher temperatures with increasing values of x as shown by the DSC measurement results for $(LiCl)_x(MMT)_{1-x}$ samples shown in Figure 4.

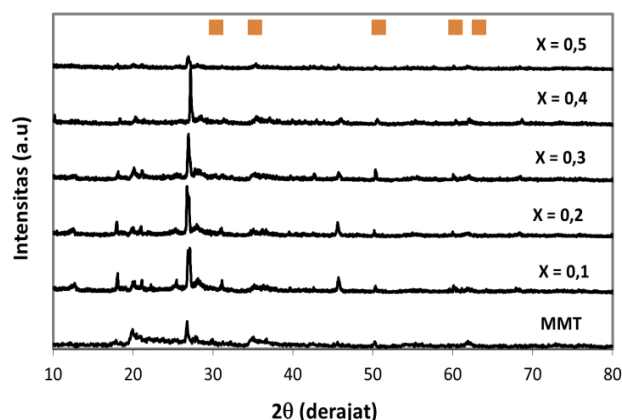


Figure 3. X-ray Diffraction Patterns of $(LiCl)_x(MMT)_{1-x}$ ($x = 0.1, 0.2, 0.3, 0.4, 0.5$) Samples. The (■) Symbol Indicates LiCl Diffraction Peak Positions

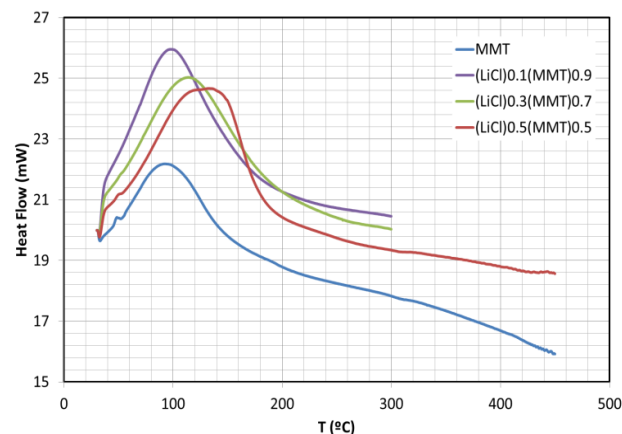


Figure 4. The DSC Curve of $(LiCl)_x(MMT)_{1-x}$ ($x = 0.1, 0.3, 0.5$) Samples

Results of repeated measurements shown in Figure 5. for the $(\text{LiCl})_{0.3}(\text{MMT})_{0.7}$ sample indicates a shift to a higher temperature of approximately $\sim 220^\circ\text{C}$, but with far lower energy which now decreases to only 3% of the energy in the first measurement. This energy change indicates that there are no longer occurrences of water evaporation and hydroxyl groups bonding breakup process on the surface of the layer. Small changes in intensity values only indicate that there is an insignificant alteration in the space between the layers.

Diffusion of Li ions is clearly indicated by changes in the EDS data, wherein the cation fraction of various Fe, Mg and Al elements which were present in the original montmorillonite sample tends to decrease with the increase in the value of x as shown on the EDS graph in Figure 5 and Table 2. The Li diffraction peak does not appear in this graph, because this atom is a light atom which the EDS instrument is not able to detect. However, the table shows the increase in weight % of the Cl element with an increasing value of x . These data show that the Li ions have been dissociated from its salt and undergoing a cationic exchange with the Fe-, Mg- and Al cations. Figure 6 also shows the SEM microgram of the $(\text{LiCl})_x(\text{MMT})_{1-x}$ microstructure morphology

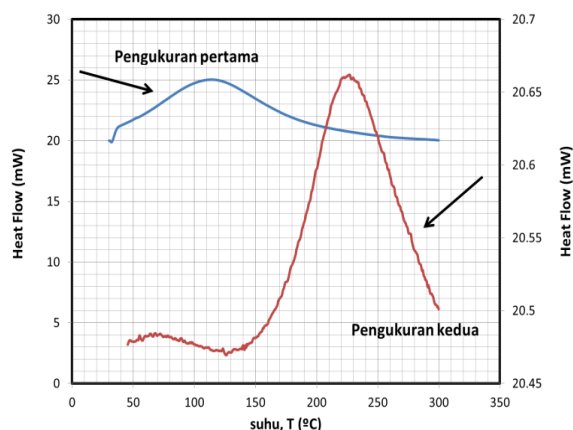


Figure 5. The DSC Curve of $(\text{LiCl})_{0.3}(\text{MMT})_{0.7}$ for Two Consecutive Measurements

Table 2. Elemental analysis of $(\text{LiCl})_x(\text{MMT})_{1-x}$

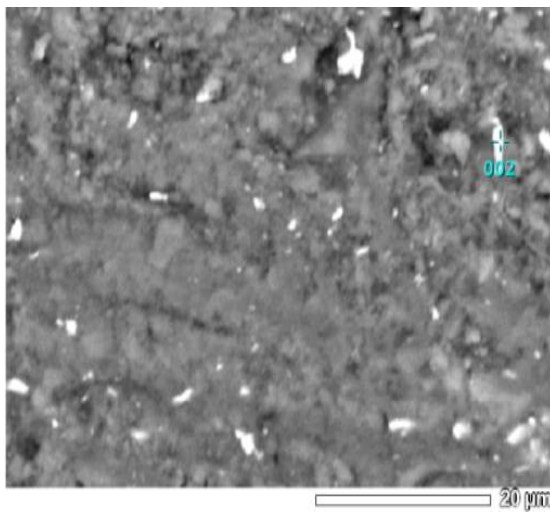
Element	Weight %			
	X = 0	X = 1	X = 3	X = 5
C		3.78	0.50	0.60
O		31.78	38.96	31.26
Mg	v	1.72	0.96	1.21
Al	v	6.90	2.74	8.30
Si	v	14.83	7.09	16.02
Cl		1.05	21.17	31.35
K	v	0.66	0.51	4.57
Ca	v	1.36	5.73	2.14
Fe	v	27.88	8.30	4.55

resulting from the process. In general, the size of the powder sample tends to increase with the increasing values of x , and therefore presents the image of an increasingly homogeneous phase. Since the same magnitude of milling force and milling time are used for all the samples, the observed differences in particle size, seems to support the deduction of the inclusion of the Li-salts and the pillarization in the inter-layer space of the montmorillonite.

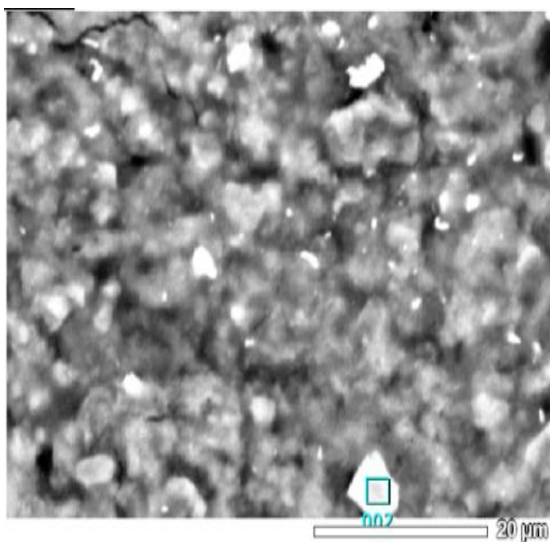
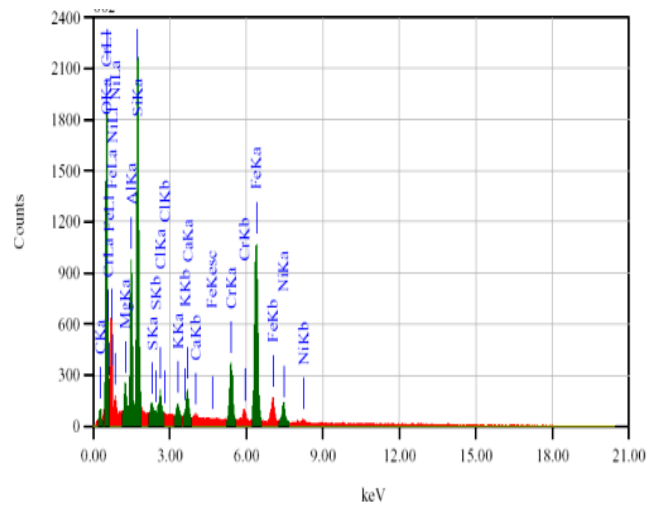
Preirradiation ionic conductivity analysis. The ionic conductivity as a function of frequency measured at room temperature for the $(\text{LiCl})_x(\text{MMT})_{1-x}$ salt sample is shown in Figure 7. The chart is featuring a typical frequency dependence curve of the ionic conductivity. Using Equation (3), the value of the dc current (σ_{DC}) and the result is shown in Figure 8. Ionic conductivity tends to rise with increasing values of x up to a certain value, which turns out to be different depending on the type of salt. For the LiCl salt the conductivity will continue to rise to a maximum value until $x = 0.5$ and decreases after ward for higher values of x . As for the LiI salt, the ionic conductivity would start to decline at $x = 0.3$.

After the theoretical discussion is completed, it follows that the obtained conductivity value is proportional to the number of charge carriers, in this case the Li cations, and to the mobility of the charges. Referring to the previous discussion regarding changes in the LiCl system structure, it could be concluded that the Li cations reside in the space between the layers, within the T-O structure. At lower x values, cations will move from the space between the layers together with the cations diffusing within the T-O structure. Cation number will increase with increasing x values, but the mobility is reduced with the increasing amount of LiCl salt that enters the inter-layer space. As a result, the ionic conductivity values will reach a maximum at a certain x value and then starts to decrease with increasing x values.

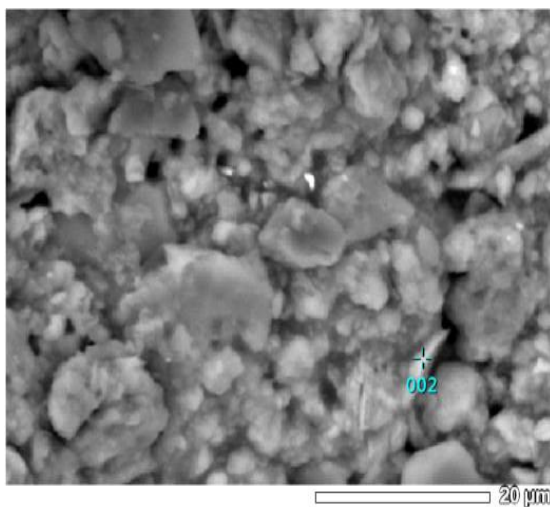
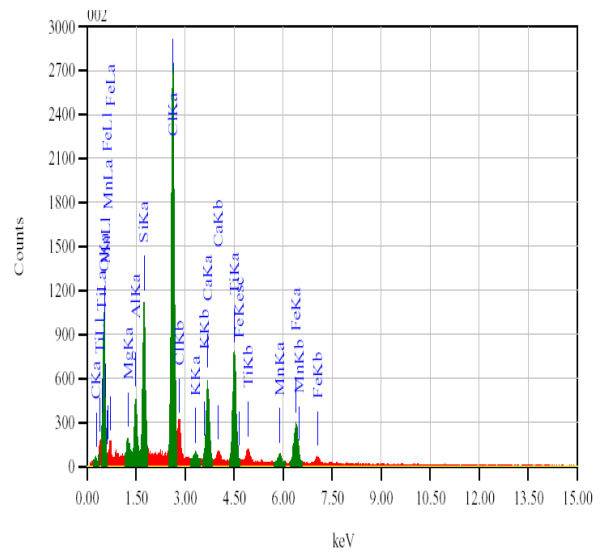
The pre- and post sintering behavior of the ionic conductivity as a function of temperature for the MMT, $(\text{LiCl})_{0.5}(\text{MMT})_{0.5}$ sample is shown in Figure 8. The activation energy (E_a) value is calculated from the slope of the linear plot of $\log \sigma T$ versus the reciprocal of the temperature $\frac{1}{T}$. From the graph it shows that the composite's ionic conductivity activation energy E_a value is lower after sintering compared to the pre sintering value. This means that the lithium cations are more easily activated and are more mobile after undergoing the sintering process. These data support the analysis results which concludes that it is the increasing pillarization effects and the deformation of montmorillonite structure, which enhance the mobility of Li cations. In more detail, the semilog plot tends to form a curve with higher activation energy at higher temperatures. This



(a). $(\text{LiCl})_{0.1}(\text{MMT})_{0.9}$ sample



(b). $(\text{LiCl})_{0.3}(\text{MMT})_{0.7}$ sample



(c). $(\text{LiCl})_{0.5}(\text{MMT})_{0.5}$ sample

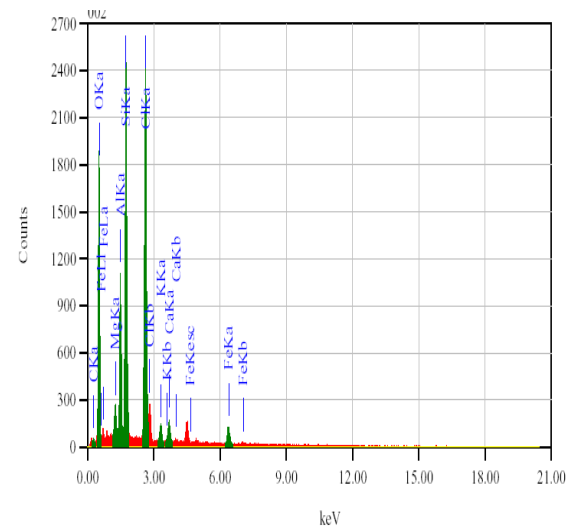


Figure 6. SEM Micrograms and EDS Analysis Result

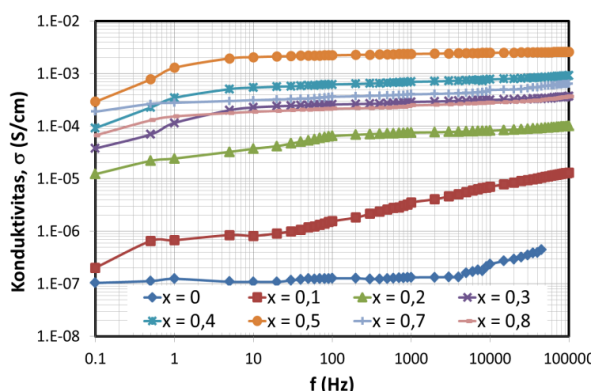


Figure 7. Room Temperature Frequency Dependent (a.c.) Conductivity of $(\text{LiCl})_x(\text{MMT})_{1-x}$ ($x = 0; 0,1; 0,2; 0,3; 0,4; 0,5; 0,7; 0,8$)

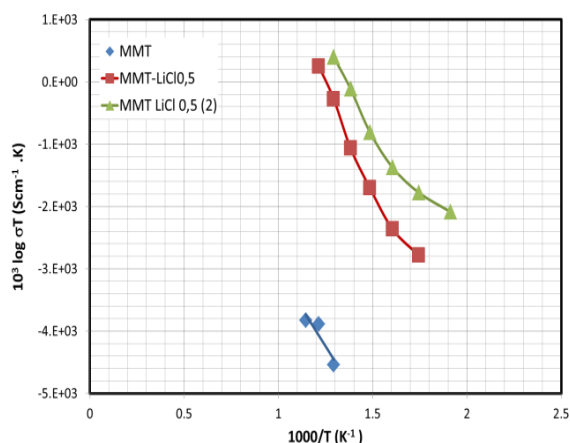


Figure 8. Temperature Dependence of MMT, $(\text{LiCl})_{0.5}(\text{MMT})_{0.5}$ Composite Ionic Conductivity [pre- and post sintering]

observation is consistent with the mechanism related to the increasing ionic mobility at higher temperatures for the solid electrolyte system, and there is no evidence of involvement of other mechanism as was assumed by other authors.

Both the data and discussion presented above seem to support the notion that pillarization effect occurring in the interlayer space of the montmorillonite structure is mainly responsible for the preservation of the cationic mobility and for the increase of the ionic conductivity of the montmorillonite Li- salt composite sample.

Ionic conductivity analysis of irradiated samples. The highest conductivity values are achieved by the $(\text{LiCl})_{0.5}(\text{MMT})_{0.5}$ sample with the radiation dose of 400 kGy. Further study of the effects of a 400 kGy dose of gamma radiation on the $(\text{LiCl})_x(\text{MMT})_{1-x}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) composite system is shown in Figure 9. The diagram shows that the ionic conductivity increases with increasing x values up to the value of x equal 5. And this

conductivity pattern is very similar to the conductivity pattern of the nonirradiated sample. However, the data obtained can not confirm the value of the maximum dose just prior to the onset of the decrease in ionic conductivity montmorillonite ionic conductivity curve as a function of radiation dose is shown in Figure 10, which shows a decrease in ionic conductivity with increasing radiation dose which confirms that the presence of defects does not necessarily improve the conductivity.

Li-salts and Montmorillonite based ionic conductors samples $(\text{LiCl})_x(\text{MMT})_{1-x}$ have been prepared by powder methodology. It could be concluded that the powder method combined with gamma-ray irradiation process are the simplest methods with which to obtain a Li-salt based ceramic solid electrolyte with a characteristically high ionic conductivity. Referring to the various stages used in the synthesis process, there are three aspects that stand out which affect the increase in conductivity. The mere presence of Lithium salt in the sample provides causes: a). An increase in the numbers of available charge carrier, b). The structural deformation of the tetragonal-

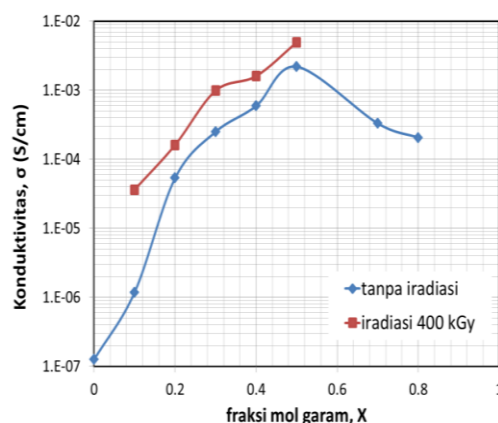


Figure 9. The Ionic Conductivity of $(\text{LiCl})_x(\text{MMT})_{1-x}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) Samples (without irradiation and after the γ -irradiation)

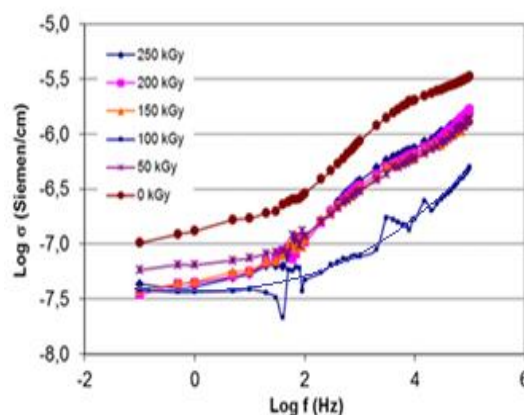


Figure 10. The Montmorillonite Ionic Conductivity as a Function γ -ray Irradiation Dose

octahedral layer in the montmorillonite layered structure either due to the milling process as well as an increase in the number of defects due to irradiation effect, c). Effect of the Li-salt pillarization on the montmorillonite' slayered structure.

In reference to the maximum value of ionic conductivity which reaches ~ 5 mS/cm or half of the conductivity value of an ionic liquid electrolyte rechargeable lithium battery available in the market today; the light weight, inexpensive and high temperature condition resistant montmorillonite ceramic-salt-composite system has a high prospect to become a candidate for an alternative solid electrolyte system which is both safe and economical. However, in order to be employed in an actual rechargeable battery system application, more studies and investigations are needed on the various related parameters such as the amount of electrical capacity that can be stored in the battery, the charge-discharge time and the magnitude of the working voltage that can be generated.

4. Conclusions

Composite materials based on montmorillonite and Li salt in various compositions have been successfully prepared by the powder methodology. From the results of measurement and ionic conductivity data analysis, it is generally found that the addition of Li salt into the montmorillonite matrix has significantly improved the ionic conductivity. The increase in ionic conductivity will depend on the type of and the concentration of the added salt. The best results were obtained for the $(\text{LiCl})_{0.5}(\text{MMT})_{0.5}$ composites with a value of room temperature ionic conductivity of 2.192 mS/cm, which increases to ~ 5 mS/cm after gamma irradiation with a dose of 400 kGy.

Mechanisms of ionic conductivity in a salt-ceramic composite system has been inferred to originate from the salt pillarization effect on the layer-structure of montmorillonite sheet that provides the path for Li^+ ions mobility. Increasing the Li salt concentrations to a certain amount, would result in a better pillarization effect and increases the supply of Li ions, which in turn increases the conductivity. Excessive salt concentration on the other hand, will lower the value of the ionic [12]

conductivity as montmorillonites tend to be amorphous and consequently loose their layered structure. Gamma ray irradiation at the proper dose will increase the number of defects, especially in the tetrahedral and octahedral which subsequently would have a positive effect on the Li^+ ion diffusion process. However, doses that are too high will tend to undermine the structure of the montmorillonite and lower the conductivity values.

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