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THE EFFECT OF Li_2O ON COMPOSITE LTAP AND WINDOWS GLASSES

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ABSTRACT

THE EFFECT OF LI_2O ON COMPOSITE LTAP AND WINDOWS GLASSES . Research on The Effect of Li_2O on Composite LTAP and Windows Glasses have been done. Windows glasses contain of Sodium Lime Silica Glasses and Na_2O 11,6%, CaO 8,1% and SiO_2 58,7%. LTAP (Lithium Titanium Alumunium Phosphate) material mixed in the slurry of powder windows glasses with composition of weight procentage 75%. The temperatures process for sintering of samples is above of glass transition at 600 ^{0}C. Then samples quenched with liquid nitrogen. The variation of Li_2O addition on samples are 0, 2,5, 5 and 7,5% weight. XRD pattern of all samples has a same phenomenon of crystallization phases, i.e. LTAP with lithium silica from $Li_5Si_2O_7$, Li_2SiO_3, Li_4SiO_4 and $Li_2Si_2O_5$. Optimum addition oh Li_2O is 7,5 % weight Li2O that gift a conductivity of 1,479 x 10^{-7} S/cm and high value on density and smallest porosity

Key words : Sodium Lime Silica Glasses, Windows Glasses, Glass Transition, Lithium Oxide, LTAP

ABSTRAK

PENGARUH LI_2O PADA KOMPOSIT LTAP DAN GELAS KACA JENDELA. Penelitian tentang Pengaruh Li_2O pada Komposit LTAP dan Gelas Kaca Jendela telah dilakukan. Gelas kaca jendela atau *Soda Lime Silica* mengandung Na_2O 11,6%, CaO 8,1% and SiO_2 58,7%. LTAP (Lithium Titanium Alumunium Posfat) dicampurkan dengan komposisi 75% berat dalam *slurry* gelas kaca dan kemudian di*sinter*. suhu *sintering* berada di atas suhu transisi gelas 600 ^{0}C. Sampel selanjutnya didinginkan secara cepat dengan nitrogen cair. *XRD patron* sampel mempunyai beberapa fase, yaitu LTAP dan senyawa *lithium silica* berupa $Li_5Si_2O_7$, Li_2SiO_3, Li_4SiO_4 dan $Li_2Si_2O_5$. Penambahan Li_2O optimum pada 7,5 % berat Li_2O yang mempunyai kondukitivitas 1,479 x 10^{-7} S/cm dan nilai densitas tertinggi dan porositas terendah.

Kata kunci : Sodium Lime Silica Glasses, Gelas kaca jendela, Transisi gelas, Litium oksida, LTAP

INTRODUCTION

Lithium batteries work with a phenomenon of intercalation process from the transfer of lithium ion. This process accour in process of charging and discharging, like in Figure 1 [1]. Intercalation work in the electrodes of lithium batteries. A electrolyte deals of lithium battery is a medium for a migration of lithium ion.

The used electrolyte of lithium batteries is general in a basic of liquids materials in the market lithium batteries. Lithium per chlorate (Li_4ClO_4) is common used [2]. In the new development of lithium batteries, solid polymer electrolyte (SPE) used as a composite material from ceramic and polymer material [2]. High current capacity of lithium batteries needs high temperature resistant material, because a process of charging and discharging increases batteries temperature that is more quickly with high current capacity. High current batteries is usage in industry of automotive and UPS for communication.

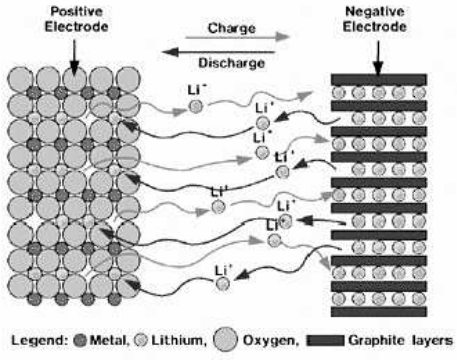

Figure 1. Schematics process of charging and discharging in lithium battery [1].

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One electrolyte candidate of $LiTi_2(PO_4)_3$ (LTP) have high enough ionic conductivity which is around 10^{-7} Scm^{-1} [3]. Because LTP has NASICON crystal structure making its cationic free to move among interstitial place in the network. NASICON crystal structure is shown by Figure 2 [4]. This material LTP is basic structure of LTAP ($Li_{1,3}Ti_{1,7}Al_{0,3}(PO_4)_3$). In this experiment solid electrolyte is searched for target of above. Solid electrolyte is a composite material from LTAP with glasses metric. The raw material of glasses is windows glasses that are in technical term as Sodium Lime Silica.

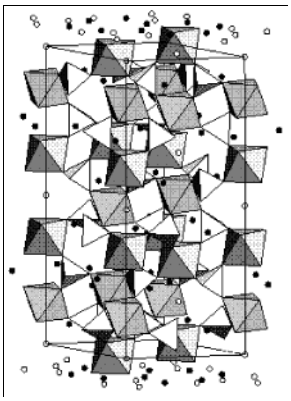
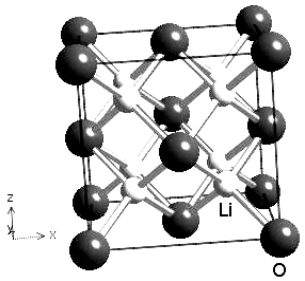


Figure 2. Model of NASICON Structure [4].

Li_2O is included solid electrolyte base on lithium and have anti fluorite structure able to yield great number of cationic vacation. Diffusion Li_2O can be done into structure and only causing a little expansion of glasses interface. One theory expresses that pregnant glass more than 5-mole % Li_2O can generate rich interface of lithium ionic [5]. The addition of Li_2O is to make glass becoming conductivity materials, because Li-ion can used as ion modified networks on windows glasses. This effect like as Na and Ca ion on silica glass. Structure Li_2O crystal form shown by Figure 3 [5]. In the previously experiment addition of Li_2O give a good interaction within windows glasses[6]. The conductivity of windows glasses increase more than one thousand times. Great deals of Li_2O diffuse on window glasses, and the others react with silica oxide. The optimum addition of Li_2O is 7,5% weight.



Gambar 3. Structure of Li_2O [5].

Commercial glass is silicate, with SiO_2 tetrahedral structure added by some modification ion. Crystal silicate structure can be differentiated by between crystalline form with amorphous form or glass. Glass can be considered sometime to be very viscous dilution because a glass is non-crystalline materials or amorphous. At high temperature above Tm, glass represents real dilution. Atoms have freedom move and can shift. When commercial glass in a state of melting to be made cool swiftly, hence decrease of thermal happened because of atoms perform a restructuring and form more efficient heap. This construction (Figure 4) representing the nature of typically from all liquid phases, but with quicker refrigeration happened change of sudden expansion coefficient. Under certain temperature is so-called glass transition temperature, or glass temperature, T_g, where there are not restructuring from atom and decreasing because of small thermal vibration.

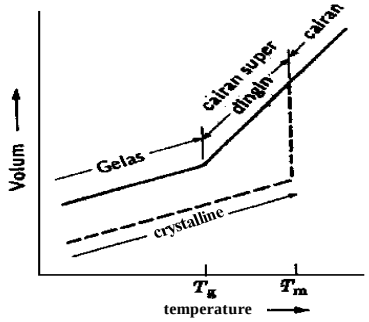


Figure 4. Change of dilution volume at quenching [7].

Transition glass material temperature is simply referred as also with temperature, where at that moment material which is its molecule, have very small mobility. At temperature under T_g materials have the character of brittle and stiff and above Tg materials have the character of more elastic. The elastic character of glasses is useful as glue to make a metric of composite electrolyte from windows glasses. The temperature process of sintering is above T_g of windows glasses in this experiment

Table 1. Temperature Glass Transition (Tg) Some Glass Materials [8].

Type	Tg(^oC) measured	Tg (^oC)
Silica glass	~1200	-
Pyreks	550	350
Windows glass	550	270

EXPERIMENTAL METHOD

Li_2O obtained from Merck produced carbonate lithium (Li_2CO_3) through calcinations process at temperature 700 ^oC in 2 hour to discharge CO_2. Equation reaction of process mentioned as following:

$$Li_2CO_3 \qquad Li_2O + CO_2 \quad \text{.....} \quad (1)$$

Li_2O added at slurry of windows glasses in weight percentages of 7.5%.

Process to make LTP use powder metallurgy technique. Raw material able to be seen in equation of chemical reaction 2, which produced by Merck, namely Li_2CO_3, TiO_2 and $(NH_4)_2HPO_4$. The calcinations temperature is 900 ^{0}C during 2 hours, then sintering at temperature 1100 ^{0}C during 8 hours [9].

$$0{,}5Li_2CO_3 + 2TiO_2 + Al_2O_3 + 3(NH_4)_2HPO_4 \rightarrow LiTi_2(PO_4)_3 + 0{,}5CO_2 + 6NH_3 + 3H_2O + 5/4\,O_2 \quad \text{.....} \quad (2)$$

The used raw materials for windows glasses are common or commercial clear glass. The XRF analyses of this glass gift types and content of compound, namely Na_2O 11.6%, CaO 8.1%, MgO 3.58%, Al_2O_3 0.19%, K_2O 0.053% and SiO_2 58.7%[9]. Samples are mixture materials from windows glasses 25% weight and LTAP with 75% weight. Variation of Li_2O are 0, 2, 5, 5 and 7,5% weight from windows glasses.

At former experiment, temperature process sintering above Tg obtained at 600 ^{0}C [10]. Samples of mixture materials sintered at temperature 600 ^{0}C during 1 hour, then quenched in liquid nitrogen. The samples have make with method of tape casting. Samples are in form of palette with the size of diameter 1.5 cm and thick 0.5 cm. The samples analyzed with XRD, porosity and density.

The samples measured conductivity with method of complex impedance or Electrochemical Impedance Spectroscopy (EIS). This measure use Solartron 1260. A simple electrochemical cell acts like a resistance and a capacitor where make a series or parallel circuit. R_{tot} represents a resistance from electrolyte and C_{dl} represents double layers capacitor. Notation for complex impedance is [11]:

$$Z = Z' + iZ'' \quad \text{with} \quad i = \sqrt{-1} \quad \text{.....} \quad (3)$$

and

$$|Z| = \left(Z'^2 + Z''^2\right)^{1/2} \quad \text{.....} \quad (4)$$

Thus notation of complex impedance equation is for an electrochemical cell:

$$Z = R_{tot} - i/\omega . C_{dl}. \quad \text{.....} \quad (5)$$

To get R_{tot} value, hence we have to get Z"= 0 by extrapolation form semicircle to X-axis. From Z value = Rtot, we earn to determine conductivity of materials by using equation:

$$R = \rho \frac{l}{A} \quad \text{.....} \quad (6)$$

with: R = R_{tot} = resistance from extrapolation (ohm)
ρ = specific resistance (ohm.m)
l = thickness of sample (m)
A = square of sample (m^2)

RESULTS

Product of quenched samples investigated by XRD is shown in Figure 7 with Figure 6 from pattern of LTAP. Phase's which has been identificated contain $Li_5Si_2O_7$, Li_2SiO_3, $Li_2Si_2O_5$ and Li_4SiO_4 is shown in Figure 7.

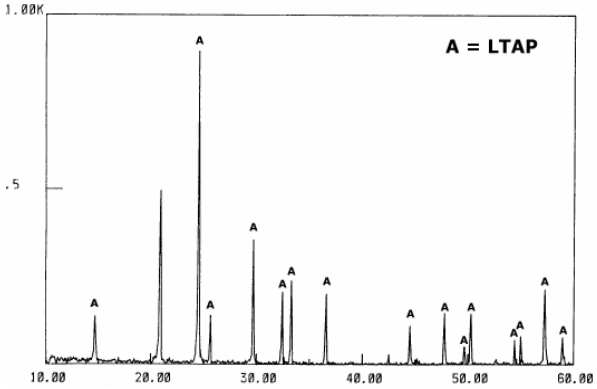


Figure 6. XRD patterns of LTAP sample.

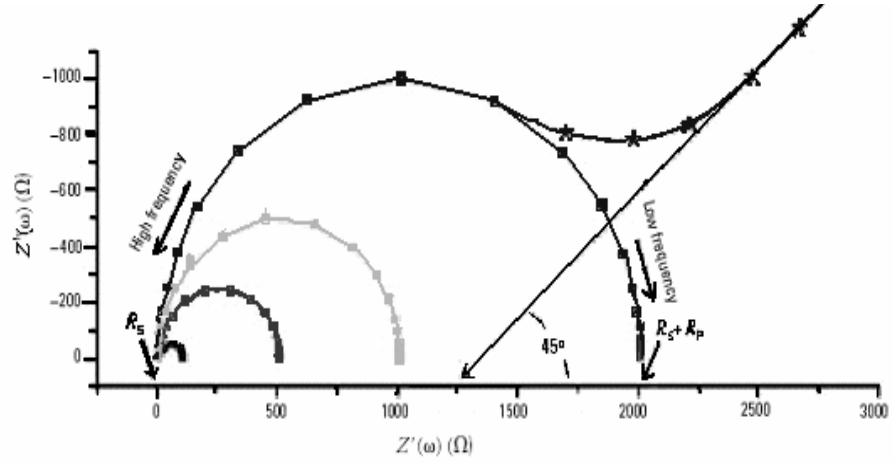


Figure 5. Nquist plotting from Electrochemical Impedance Spectroscopy1 [1].

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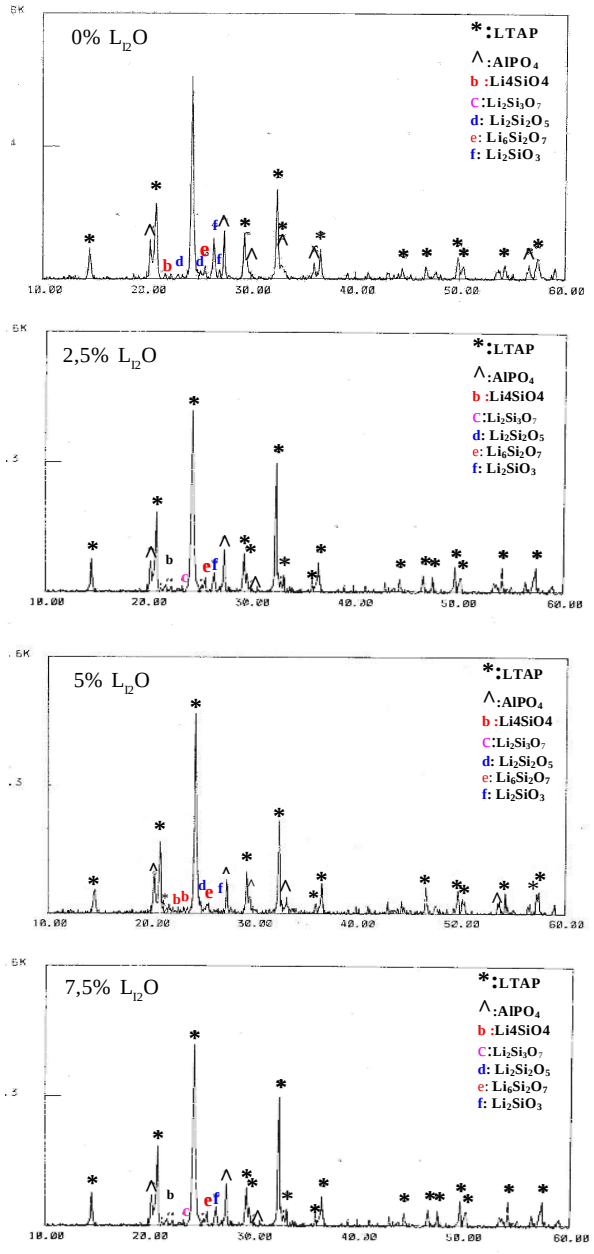


Figure 7. XRD pattern of composite with variation Li_2O

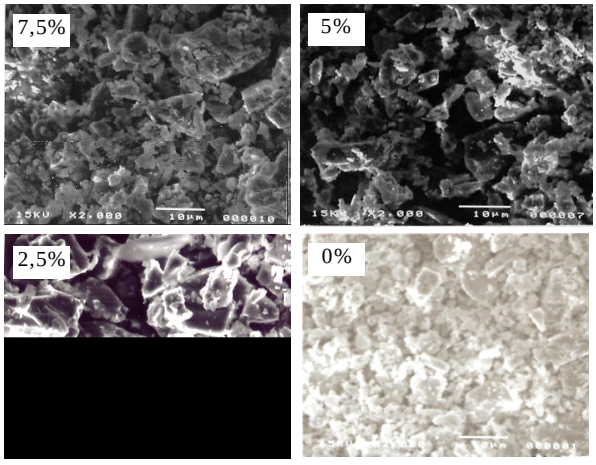


Figure 8. SEM of composite with variation Li_2O.

The porosity and density of produced samples are shown in Figure 9. Porosity and density measured with method of Archimides [11].

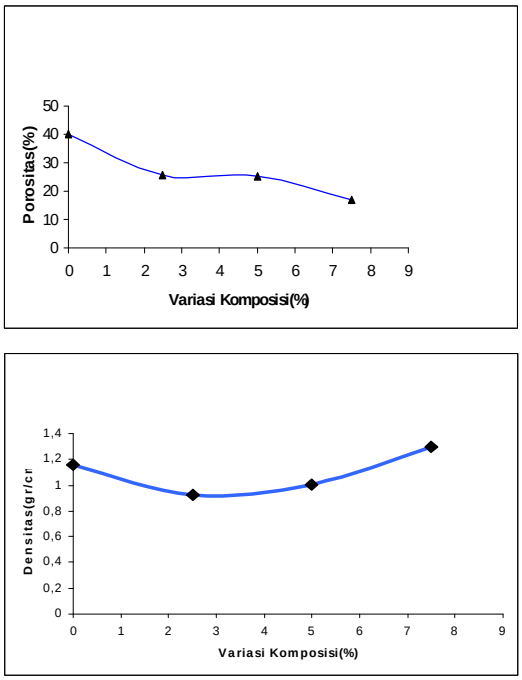
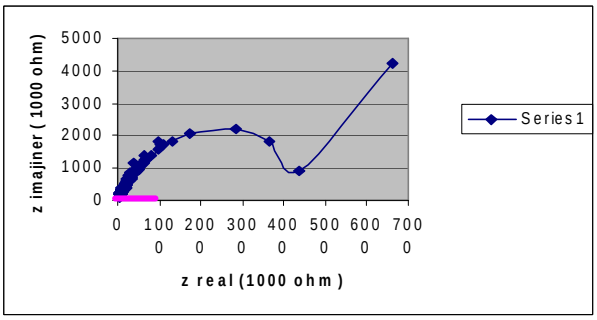
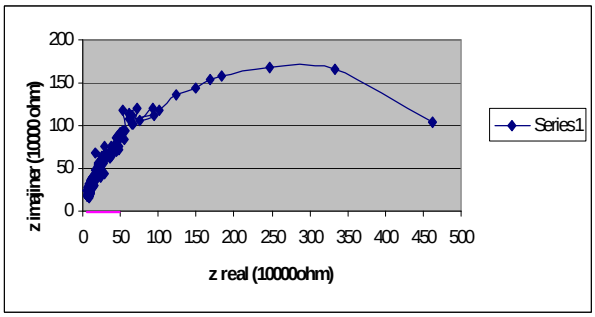


Figure 9. Density and Porosity of composite with variation Li_2O.

Conductivity of samples measured by complex impedance in frequency range of 10Hz to 10KHz, give the cole graphics in Figure 10. The cole graphics of samples gives phenomena of Warburg gradient.

From extrapolation in the X-axis on Figure 10, resistance of self-material and ionic can calculated with Equation 6. The results of conductivity of all samples can be seen in Figure 11.





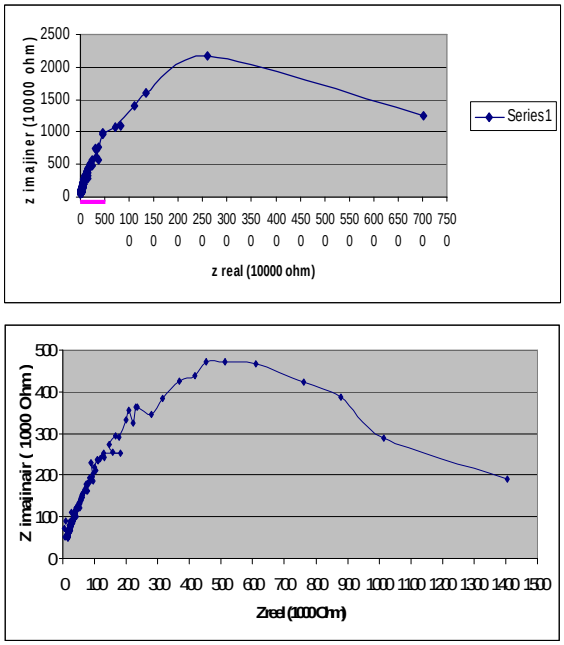


Figure 10. Cole-cole plot from impedance measured samples.

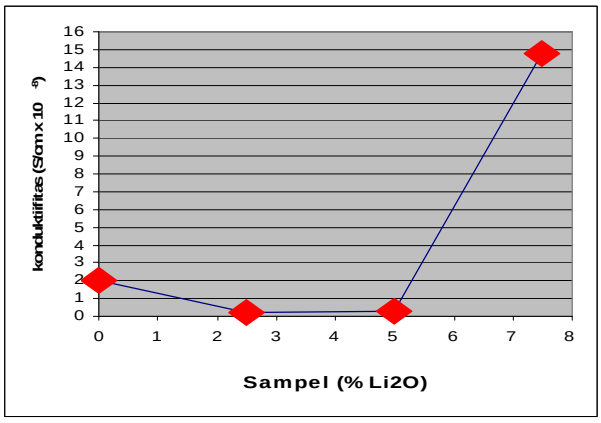


Figure 11. Conductivity samples with variation of addition Li_2O

DISCUSSION

The peaks of sodium lime silica in the form of $Na_2Ca_3Si_2O_8$ cannot clearly been seen. The crystal phase peaks of sodium lime silica are detected, but the peaks aren't highest intensity (100%). So crystalline sodium lime silica can been declared no anything peaks.. The phases investigated by XRD changes with variation Li_2O on the composite LTAP and glass matrix. Great deals of Li_2O diffuse on windows glasses. Compound of Windows glasses like to become a glass of Li_2O-Na_2O-CaO-SiO_2 system. Other deal of Li_2O start to react with the glass materials forming various compounds of lithium silicate, i.e. $Li_5Si_2O_7$, Li_2SiO_3, Li_4SiO_4 and $Li_2Si_2O_5$.

Lithium hydrate do not detected in XRD pattern and has not influence in measurement of conductivity. At liquids nitrogen during quenching, aqueous vapor to air and it cannot react with lithium ions in samples. This is good phenomenon to produce an electrolyte materials.

All samples produce glue concept of viscous glasses works best in this experiment with great deals of amorphous phases. This phenomenon can be seen on result of SEM. Window glass as raw material can good follow in the sintering and quenching process to make glue for crystalline phases. And Li_2O gifs support role in this function of the glasses. All samples with addition of Li_2O like stronger than sample without addition. Windows glasses can thus good used as a matrix for a composite with method of this process.

Porosity of samples is in order of 20 to 40 % as shown in Figure 9. Density of samples is in order of 0.9 to 1.3 g/cm^3. The greatest porosity is a sample without addition of Li_2O therefore sample is brittle. The smallest porosity is sample with addition of 7.5 wt% Li_2O. The sample has also the greatest density of 1.3 g/cm^3. In density comparison with soda lime silica of floating glass, namely 2,44 g/cm^3, density of samples decrease with phases changing that density is round 2.25 g/cm^3 without porous [13]. Crystalline phases of lithium silicate cause this decreasing with difference of crystalline size.

The level of porosity and density is still bad to make electrolyte materials. Size of powder raw materials give an important role for this target. In this experiment the size of powder raw materials is 200 mesh about 80 µm. These must be less to make lowest porosity and high density.

Electrolyte materials for lithium batteries can transfer lithium ion with high conductivity. All samples give the results as seen in Figure 11. Conductivity of samples is in order of 10^{-7} S/cm. Type reaction of Li_2O and silica gifs great effect in this conductivity. Li – silica with greater number of lithium have greater conductivity than lower number of lithium. Conductivity of LTP is in order of 10^{-7} S/cm.

Specific resistivity of soda lime silica from floating glass, that is also usage as windows glass, is 5 x 10^9 Ohms/cm [13]. Conductivity in Equation 5 is inverse with specific resistivity. Then conductivity of soda lime silica is about 2 x 10^{-10} S/cm. In comparison between samples and soda lime silica, conductivity of samples is occurred improvement till thousand times. This is significant repair in conductivity character of soda lime silica. Highest conductivity is 1.475 x 10^{-7}S/cm from Li_2O addition of 7.5% weight.

CONCLUSION

This experiment gives a good result to produce electrolyte materials and give conclusion as follows

1. LTAP as material do not change in composite making of electrolyte
2. Permanent glass glass upon which matrix in making of electrolyte of lithium battery remain to be amorphous

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3. Lithium Hydrate do not showing by refrigeration with Liquid Nitrogen function better
4. Great deals of Lithium Oxide diffuse on windows glass to be form NaO-LiO-CaO-SiO system, and the others form compound of lithium silica, i.e. $Li_5Si_2O_7$, Li_2SiO_3, Li_4SiO_4 and $Li_2Si_2O_5$,
5. Optimum addition oh Li_2O is 7,5 % weight Li2O that gift a conductivity of 1,479 x 10^{-7} S/cm and high value on density and smallest porosity.

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