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Electrochemistry Study on PVC-$LiClO_4$ Polymer Electrolyte Supported by Bengkulu Natural Bentonite for Lithium Battery

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Abstract – In this research bentonite was used as filler to produce polymer electrolyte (PVC-$LiClO_4$). Some weight variation of bentonite have been made by addition, such as 0% $^{wt}/_{wt}$; 5% $^{wt}/_{wt}$; 10% $^{wt}/_{wt}$; 15% $^{wt}/_{wt}$; 20% $^{wt}/_{wt}$; and 25% $^{wt}/_{wt}$ of bentonite to the mixture of 0,5 gram of PVC and 0,125 gram of $LiClO_4$. Ionic conductivity of polymer electrolyte was tested using impedance spectroscopy. The result of the research was showed that a mixture of PVC-Bentonite(10% $^{wt}/_{wt}$)-$LiClO_4$ gives the highest ionic conductivity (4,86 x 10^{-3} S.Cm^{-1}). This result indicated that the presence of natural bentonite can be used as a filler in the current composite polymer electrolyte and can increase the ionic conductivity of the polymer electrolyte.

Keywords: Polymer electrolyte, bentonite, ionic conductivity, natural inorganic filler.

Introduction

Solid-state lithium polymer batteries may be one of the best choices for electrochemical power source of the future characterized by its high energy densities, good cyclability, reliability and safety. PEO-LiX based polymer electrolytes had received extensive attention, for its potential capability to be used as candidate material for the traditional liquid electrolytes, since Wright *et al.* found that the complex of PEO and alkaline salts had the ability of ionic conductivity in 1973 (Jingyu, 2004). Lithium ion polymer battery is made from lithium ion which holding to polymer electrolyte. There are many research has done to synthesis polymer electrolyte, but filler matrices are synthetic organic polymer which is more expensive than inorganic chemicals (Ahmad, 2009). Biodegradable polymer electrolyte was developed to reduce environmental pollutions. A research using $LiClO_4$ which is dopped to acetic sellulose has been synthesized as biodegradable polymer electrolyte (Sivakumar, 2007). Another biodegradable polymer electrolyte is based on PCL (Poly(ε-caprolalactone)) with PC (polycarbonate) as plastisizer and lithium salts. PCL is synthetic polymer that can degrade in aqueous medium or in contact with microorganisms. Pure PCL/LiClO4 was investigated as a biodegradable solid polymer electrolyte. This polymer showed a wide electrochemical stability window (5.5V *vs.* Li), good mechanical properties, and total biodegradation in soil compost at 60 days (Fonseca, 2007).

Polyvinyl chloride (PVC) is thermoplastic polymer, inert and wide range products with low cost of production. PVC is available as resin with hard or flexible characteristics, usually used by plastisized or prepared in a mixture or heterogeneously dopped with inorganic particles. PVC has been used as a doping in blend of $LiPF_6$ and $LiCF_3SO_3$ salts system.(Subban, 2004). Rajendran (2008) investigated the blend-based polymer electrolyte consisting of polyvinyl chloride (PVC) and polyethylene glycol (PEG) as host polymers and lithium perchlorate ($LiClO_4$) as the complexing salt and TiO_2 as ceramic filler. The conductivity results indicate that the incorporation of ceramic filler up to a certain concentration (15 wt.%) increases the ionic conductivity and have mechanical stability.

Zeolite is microporous material with large surface area, having two dimensional channel and high Lewis acid characteristics. A research with ZSM-5 as filler has been investigated by Jingyu (2004). ZSM-5 is synthetic zeolite which usually used in industry. ZSM-5 have dimensional structure, high activity and selectivity for some reactions, selective on molecular shape and not easy to deactivated (Mustaim, 1997). Jingyu (2004) reported that ZSM-5 as filler in composite polymer electrolyte PEO-$LiClO_4$-LiZSM5 could enhance the ionic conductivity. The addition of ZSM-5 could improve the Li^+ transference number of the CPE effectively. Based on the current results, we would like to explain a development using natural resources such as Bengkulu bentonite. In this work we studied the effect of the addition of bentonite of Bengkulu natural resources as filler in polymer electrolyte PVC-$LiClO_4$. The ionic conductivity measured by impedance spectroscopy.

Materials and Methods

Natural bentonite was taken from Desa Taba Terunjam Kecamatan Karang Tinggi Bengkulu Tengah, polyvynil chloride (PVC MW. 43.000) from Sigma Aldrich, tetrahydrofuran (THF) and $LiClO_4$ from Merck were used as received. Destilled water was available at Chemistry Laboratory, Faculty of Mathematics and Natural Science, University of Bengkulu.

Instrumentation

Balance, magnetic stirrer, glass apparatus pH meter were available at Laboratory of Chemistry, Department of Chemistry, Faculty of Mathematics and Natural Science, University of Bengkulu (Unib).

Procedure

Preparation of Bentonite

Raw bentonite was taken from natural deposit in desa Taba Terunjam Kecamatan Karang Tinggi Bengkulu Tengah and there was no special treatments when it was taken. Raw bentonite from natural deposit was cleaned and grinded into small pieces. The cleaned benonite then washed using aquabidest to neutralize the acidity and dried under the sun shine, which after the bentonite was crushed into powder and filtered to get homogeny particle size. It was stored in desicator till it used.

Preparation and characterization of Polymer Electrolyte PVC-Bentonite-LiCiO$_4$

Briefly, 0,5 g polyvynil chloride (PVC : molecular weight = 43.000) was added into 25 mL of tetrahydrofuran (THF). The mixture then stirred at room temperature for 15 minutes to get homogeneous solution. 0,125 g $LiClO_4$ and bentonite were added into reactor and was stirred at room temperature for 24 hours. Bentonite was added in variety of %wt (5 %, 10 %, 15 %, 20 %, 25 %) of total weight of solid chemicals. The homogen mixture then poured into petridish and dried at ambient temperature. The polymer electrolyte film then stored in desicator before the ionic conductivity measurement. Ionic conductivity was measured using impedance spectoroscopy HIOKI 3522-50 LCR HiTESTER.

Results and Discussion

Bentonite with homogen particle size (53 m) was used to synthesize polymer electrolyte PVC-bentonite-$LiClO_4$. Bentonite was added in variety (0 %; 5 %; 10 %; 15 %; 20 %; 25 %) of total weight PVC + $LiClO_4$. Polyvynil chloride (PVC : molecular weight = 43.000) was added into 25 mL of tetrahydro furan (THF). The mixture then stirred at room temperature to get homogen solution. 0,125 g $LiClO_4$ and bentonite were added into reactor and was stirred at room temperature for 24 hours. In polar solvent, like water, bentonite will be suspended (Lubis, 2007). Bentonite also suspended in THF which is polar solvent. According to Daintith (1990), the suspension is a mixture comprising solid particles suspended in fluid. In this case the solid particle is bentonite and the solution are PVC, THF and $LiClO_4$. After the blend was homogen, it poured into petridish and dried at room temperature. The polymer electrolyte film then stored in desicator before the ionic conductivity measurement. Dried polymer electrolyte films are shown in Figure 1.

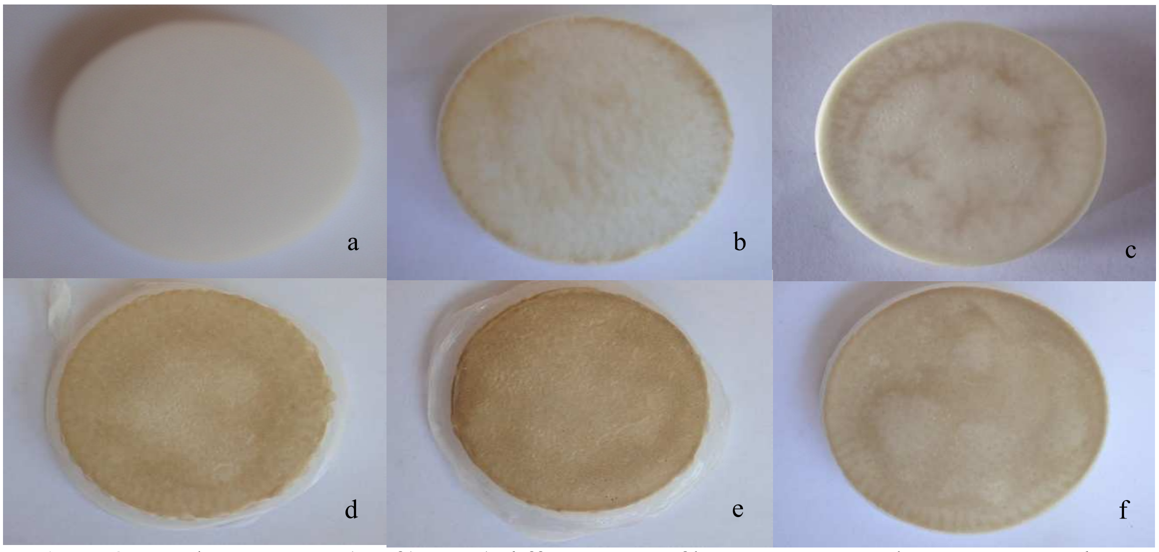

Figure 1. PVC-bentonite- $LiClO_4$ films with different % wt of bentonite (a) 0 % (b) 5 % (c) 10 % (d) 15 % (e) 20 % (f) 25 %

Ionic conductivity of Polymer Electrolyte PVC-Bentonite-LiCiO$_4$

Ionic conductivity of polymer electrolyte PVC-bentonite-$LiClO_4$ was measured using impedance spectroscopy. In this study nafion NR212 was used as reference.Table 1 and Table 2 are shown ionic conductivity of nafion NR212 Dupont and polymer electrolyte PVC-bentonite-$LiClO_4$ respectively. In Table 1 the average ionic conductivity of Nafion NR212 was 7,70 x 10^{-2} S.Cm^{-1}.

Table 1. Ionic conductivity of Nafion NR212 Dupont

Sample	Average Thickness (Mm)	Conductivity (Siemen.Cm^{-1})			Average Conductivity (Siemen.Cm^{-1})
NAFION NR212 Dupont	0,056	7,83 x 10^{-2}	7,57 x 10^{-2}	7,70 x 10^{-2}	7,70 x 10^{-2}

Nafion NR212 was used as reference because nafion polymer having good chemical stability and ionic exchange in the same time. Nafion NR212 are widely used as proton exchange membrane in fuel cell. Bentonite is aluminium or magnesium silicate compound in crystal form with variety content of lime, alkali, and iron and hydrated water. Based on the mineral analysis, most of bentonite is montmorillonite and the rest are kaolinite, Illit, feldspar, gypsum, volcanic ash, calcium carbonate, quartz and other minerals. So it also called as montmorillonite mineral. $LiClO_4$ selected as the salt in this study because it has high solubility in various solvents, did not undergo oxidation at the anode, has a better conductivity than LiF_3CSO_3 and $LiBF_4$, as shown in the results of research on the polymer poly (-caprolactone) (Fonseca,2007), and relatively stable against reduction than $LiPF_6$ (Zhang, 2001).

In the Table 2 ionic conductivity of polymer electrolyte with 0 % - 10 % of bentonite were increase, but the ionic conductivity of polymer electrolyte with 15 % - 25 % of bentonite were decrease. Polymer electrolyte with 10 % of bentonite giving the highest ionic conductivity with 4,86 x 10^{-3} S.Cm^{-1}, and the lowest is polymer electrolyte with 0 % of bentonite with 2,21 x 10^{-4} S.Cm^{-1}. This result indicate that bentonite as natural filler can increase ionic conductivity of polymer electrolyte PVC-$LiClO_4$. Introduction of bentonite filler into polymer electrolyte system will make the electrolyte more amorf and promote more free lithium ion (Li^+) into the system. Bentonite itself is negatif charge, so it has possibility to promote cation exchange. The charge happened because of isomorph substitution.

Table 2. Ionic conductivity of PVC-Bentonit-$LiClO_4$

Sample	Average Thickness (Mm)	Conductivity (Siemen.Cm^{-1})			Average Conductivity (Siemen.Cm^{-1})
0%	0,276	2,46 x 10^{-4}	2,28 x 10^{-4}	-	2,37 x 10^{-4}
5%	0,347	6,01 x 10^{-4}	6,10 x 10^{-4}	6,14 x 10^{-4}	6,08 x 10^{-4}
10%	0,444	4,69 x 10^{-3}	4,89 x 10^{-3}	4,99 x 10^{-3}	4,86 x 10^{-3}
15%	0,391	1,67 x 10^{-3}	1,70 x 10^{-3}	1,66 x 10^{-3}	1,68 x 10^{-3}
20%	0,441	4,98 x 10^{-4}	4,65 x 10^{-4}	5,33 x 10^{-4}	4,99 x 10^{-4}
25%	0,335	-	9,78 x 10^{-4}	9,74 x 10^{-4}	9,76 x 10^{-4}

The addition of bentonite with 10 % of total weight, made the polymer electrolyte has the same number of cation with $LiClO_4$, because Li^+ in $LiClO_4$ removed to coordination system in polymer. Ion Li^+ exchange will decrease isolated hydroxyl level, but H bond will increase. It shows that Li^+ coordinated by octahedral structure of bentonite through atom O of free Al-O-H group or free Si-O-H group. It makes stronger interaction between bentonite and PVC-$LiClO_4$ and the ionic conductivity will increase. Figure 2 show that bentonite particle is porous particle. The size of the particle is 53 m and it spread evenly througout the polymer electrolyte film. Bentonite particle were succesfully introduced to polymer electrolyte PVC-$LiClO_4$ system as seen in Figure 2(b).

Ionic conductivity was decreased with addition of 15 % - 25 % wt bentonite. It seems the addition of bentonite made the system saturated by agglomeration of bentonite and decreasing the movement of ion in polymer chain. Membrane with higher ionic conductivity (> 1.10^{-5} S.cm^{-1}) can be used as fuel cell. It can be used as environmental friendly fuel cell because no polution occured. Based on the result, polymer electrolyte PVC-Bentonite-$LiClO_4$ can be recommended as fuel cell with high ionic conductivity (4.86 . 10^{-3} S.cm^{-1}) it shows that bentonite from Bengkulu can be used as natural filler to increase ionic conductivity of solid polymer electrolyte.

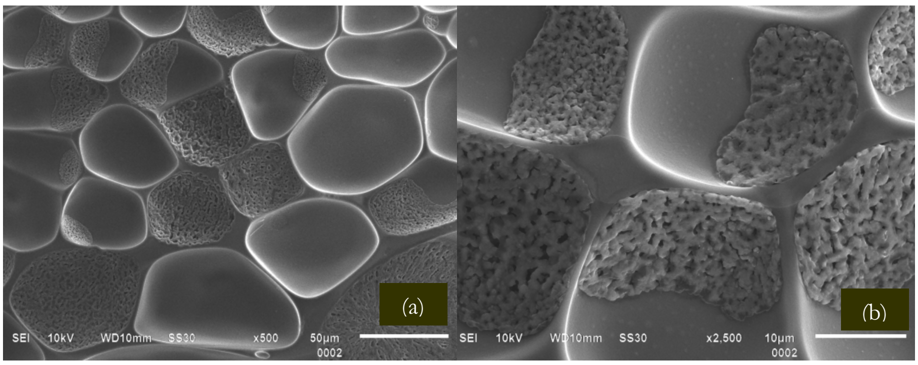

Figure 2. SEM image of PVC-bentonite (10 % wt)-$LiClO_4$ (a) 500 magnification (b) 2500 magnification

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Conclusion

Six different polymer electrolyte systems consisting of PVC–bentonite–LiClO4 (bentonite = 0, 5, 10, 15, 20, 25 wt.%) have been studied. Of the five films, the film with 10 % wt of bentonite is found to be the best on the basis of conductivity. The conductivity of the polymer electrolyte is found as 4.86 x 10^{-3} S cm−1. Hence, natural bentonite look very promising to be used as natural filler in polymer electrolyte systems.

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