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The Deep Eutectic Solvent in Used Batteries as an Electrolyte Additive for Potential Chitosan Solid Electrolyte Membrane

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Abstract. The electrolyte or ion conductor acts as a bridge to transfer the ions the electrodes generate. In general, electrolytes are in the form of liquids. However, liquid electrolytes have drawbacks, including needing to be more practical and leaking quickly. Therefore, people switch to solid matrix electrolytes as battery electrolytes. An ideal solid electrolyte membrane must have chemical stability, thermal stability, high ionic conductivity, high flexibility, low cost, and abundant material availability. Lithium extraction from used batteries using Deep Eutectic Solvent (DES) was found to be an intelligent solvent. Mixing the method with lithium salt on a chitosan membrane can increase conductivity. This study aims to determine the lowest resistance value and highest conductivity of solid polymer electrolytes using Li_2CO_3 from used batteries. After separating the Lithium-Cobalt component from the used battery, it was extracted with deep DES solvent and precipitated using Na_2CO_3 to produce the Li_2CO_3 compound. Polymer electrolyte was synthesized by mixing polyvinyl alcohol and adding 0.2 grams, 0.4 grams, 0.6 grams, 0.8 grams, and 1 gram of chitosan. Li_2CO_3 variables are 0.2 grams, 0.4 grams, 0.6 grams, 0.8 grams, and 1 gram. The results showed that the higher content of chitosan and Li_2CO_3 led to an increase in ionic conductivity. These results concluded that the best solid electrolyte membrane was obtained with a variation ratio of 0.2 grams of chitosan with the addition of 1 gram of Li_2CO_3.

Keywords: Chitosan, Conductivity, Deep Eutectic Solvent, Lithium-Ion, Solid Electrolyte Membrane

INTRODUCTION

The demand for batteries in electronic goods such as notebooks, cellphones, and electric vehicles has become so real and ubiquitous in recent years. Batteries are one of the most effective and reliable energy storage sources (Dehghani-Sanij et al., 2019). Interestingly, one of the improvements the commercial batteries that are widely used and famous is lithium-ion batteries (LIBs). LIBs are quite adequate among other energy storage systems in terms of durability and power or energy densities (Diouf et al.,, 2015; Li et al., 2018). Batteries consist of two essential components electrolytes as inactive and electrodes as active materials (Kasnatscheew et al., 2018). Electrolytes or

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Ionic conductors act as bridges to transfer the ions generated by the electrodes. Their bulk properties, such as ionic conductivity are important (Wang et al., 2015). Most available lithium-ion batteries (LIBs) rely on liquid electrolytes as the ion-conducting phase (Busche et al., 2016; Daniel et al., 2012). Composed of solvents, anions, and solvents solvated lithium ions (Li+), and can be defined as "Li+ solvated electrolytes" (Chang et al., 2020; Xu, 2004). In the lithium-ion battery section, there is a separator. The separator is an electrically insulating material engineered to have pores that allow lithium ions to move between the two battery electrodes during the charging and discharging processes. The primary function of the separator is to ensure ion flow and prevent short circuits in the battery cells. Some of its products still use conventional raw materials, including polyethylene (PE) and polypropylene (PP). The separator still uses liquid electrolytes. Currently, a semi-solid polymer electrolyte is being developed, as well as a separator, namely semicrystalline polyvinylidene fluoride (PVdF); this polymer has high polarity and high electrolyte absorption (Putro et al., 2016).

The electrolyte is an essential part of the electrochemical cell in operation and the completeness system. In addition, the electrolyte must conduct and generate electrons to run the electrochemical cell. The electrolyte in rechargeable lithium batteries falls into the liquid electrolyte category because solid electrolytes' low conductivity, very dry polymers, and liquid electrolytes predominate in most electrochemical systems (Suyati et al., 2010). Liquid electrolytes provide high conductivity and perfect wetting of electrode surfaces, they usually suffer from insufficient electrochemical and thermal stabilities, low ion selectivity, and poor safety (Manthiram et al., 2017; Quartarone et al., 2011). Furthermore, due to easily corrode and leakage, it induce a very big potential safety hazard such as short circuit, combustion, bursting, and other problems (Jiamiao et al., 2020). Replacement of liquid electrolytes with a solid electrolyte in battery becomes a consideration of the new developments and challenges (Manthiram et al., 2017). A solid-state electrolyte composed of a polymer membrane blended with Li salt (Li et al., 2018). Beside that, solid-state batteries have high chemical stability, good safety (Kim et al., 2019), non-leakage, electrochemical stability, and easy handling (Yang et al., 2017). Beside that, there are disadvantages of solid electrolytes, one of which is having low ionic conductivity and low lithium ion displacement inversely proportional to liquid electrolytes (Pratiwi, 2018; Zulfikar et al., 2009).

The chitin from the exoskeleton of crustaceans such as shrimps can produce chitosan. Chitosan has biocompatible, biodegradable and non-toxic properties. In addition, chitosan is also an alkaline polyelectrolyte and has good chemical, mechanical and thermal stability (NK et al., 2015; Zulfikar et al., 2009). Chitosan is a linear polymer formed by d-glucosamine and N-acetyl-d-glucosamine (Ngo et al., 2014; Sánchez-Machado et al., 2019; Santhosh et al., 2006). Chitosan is one type of natural polymer that has the potential to act as a solid electrolyte and the second most abundant biopolymer in nature after cellulose (Pratiwi, 2018; Yulianti et al., 2013). Isolation of Chitin from Shrimp shells has been through several processes: deproteination (separation of proteins), demineralization (separation of minerals), and deacetylation processes. Chitosan was synthesized through a deacetylation process using the Knorr method. In the deacetylation process, they added 60% NaOH with a ratio of 1:20 (w/v). Heating and stirring were carried out at a temperature of 100-110ºC for 4 hours with a stirring speed of 50 rpm to obtain solids which were then washed with distilled water several times until the pH was neutral. The solid is then dried in an oven at 80ºC for 24 hours, cooled in a desiccator, and weighed to a constant weight. So in this study, the yield of chitin was 36.76%. Chitosan was produced as much as 47.305 g from the initial chitin powder used in the 70.521 g deacetylation process creamy white powder appearance (Agustina et al., 2015; Khan et al., 2002; Pribadi et al., 2003).

There are disadvantages of solid electrolytes, one of which is having low ionic conductivity (Pratiwi, 2018). On the other hand, polymers that are developed into electrolyte membranes must meet the requirements of having high ionic conductivity (>10-5 S cm-1) (Lou et al., 2021; Meyer, 1998). Chitosan is a natural polymer with the potential as a solid electrolyte (Pratiwi, 2018; Yulianti et al., 2013). Therefore, innovating the addition of lithium ions can increase the conductivity value of solid chitosan polymers, which can be made by modifying the addition of lithium salts or Li_2CO_3 (Hsb, 2017). The mixing method with lithium salts can increase the conductivity of chitosan membranes up to 100,000 times (Sudaryanto et al., 2012). The extraction of Li_2CO_3, which will be added to the chitosan polymer, comes from extracts (Lithium-Cobalt) from used Li-ion batteries using DES (Deep Eutectic Solvents) (Tran et al., 2019). Deep Eutectic solvents can be used as solvents for various processes and have the advantage of being inexpensive (Hansen et al., 2020; Xu et al., 2017).

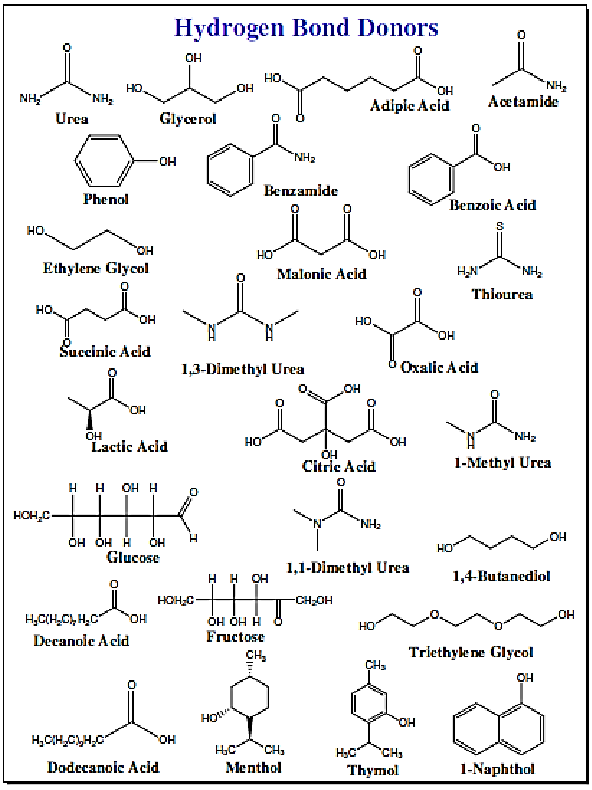

Fig. 1: DES hydrogen bond donors (Hansen et al., 2020). Copyright 2020, American Chemical Society.

DESs as a class of Ils, because they share many of the same general characteristics, make them excellent candidates for potentially replacing volatile organic compounds (VOCs) used widely throughout the research and industry (Hansen et al., 2020). However, Ionic Liquid Solvent (ILS) has high toxicity and price; a new generation solvent called Deep Eutectic Solvent (DES) is inexpensive (Xu et al., 2017); biodegradable (Khandelwal et al., 2016; Radošević et al., 2015), non-toxic (Halder et al., 2019; Juneidi et al., 2016; Radošević et al., 2015) and easy to prepare (Hansen et al., 2020). DESs are eutectic mixtures of salts and hydrogen bond donors (HBDs) with melting points low enough to be used as solvents. A eutectic liquid is generally formed by two solids at eutectic temperature, following a thermal equilibrium (Hammond et al., 2016). DESs are a class of compounds capable of dissolving metal oxides (Albler et al., 2017) and biodegradable compounds (Radošević et al., 2015). The most commonly used and studied DESs comprise components typical of a 'type III eutectic mixture (Abbott et al., 2007). Data of type III DESs used in previous studies species that can act as a hydrogen bond acceptor/donor or as Bronsted-Lowry acids/bases are valid potential candidates for DESs (Fig. 1 and Fig. 2) (Hansen et al., 2020).

One of the most widely used components for the formation of DES is choline chloride (CHCl). CHCl is the quaternary ammonium salt, consisting of the choline cation and the chloride anion, which is inexpensive, biodegradable, and non-toxic. When combined with safe components as hydrogen bond donors such as urea, renewable carboxylic acids (e.g., oxalic, citric, succinic, or amino acids), or renewable polyols (e.g., glycerol, carbohydrates), CHCl is capable of rapidly forming dec. Although most DES comprises CHCl as an ionic species, DES cannot be considered an ILS because DES does not consist entirely of ionic species and can also be obtained from non-ionic species (Abbott et al., 2003; Hansen et al., 2020). A DESs composed of choline chloride and ethylene glycol (ChCl: Ethylene Glycol) was used to extract metal ions from LCO, which were then precipitated and converted into Co_3O_4—a common precursor for the synthesis of LCO (Tran et al., 2019). Previous researchers have done using Deep Eutectic Solvents (DES) to extract the cathode (Lithium-Cobalt) from used Li-ion batteries with a temperature of 180°C and stirring time of 24 hours has an extraction efficiency of 99,3 % (Tran et al., 2019). The addition of Li_2CO_3 in the manufacture of composite sheet with Li_2CO_3 at 0%, 4%, 6% and 8% obtained electrical conductivity respectively 1.87 x $10^{(-3)}$S/cm , 7.92 x $10^{(-7)}$S/cm, 1.75 x $10^{(-3)}$S/cm, 4.28 x $10^{(-3)}$ S/cm. It can be concluded that the higher the Li_2CO_3 presentation, the value of electrolyte and ionic resistance will decrease so that the conductivity value is higher (Hsb, 2017).

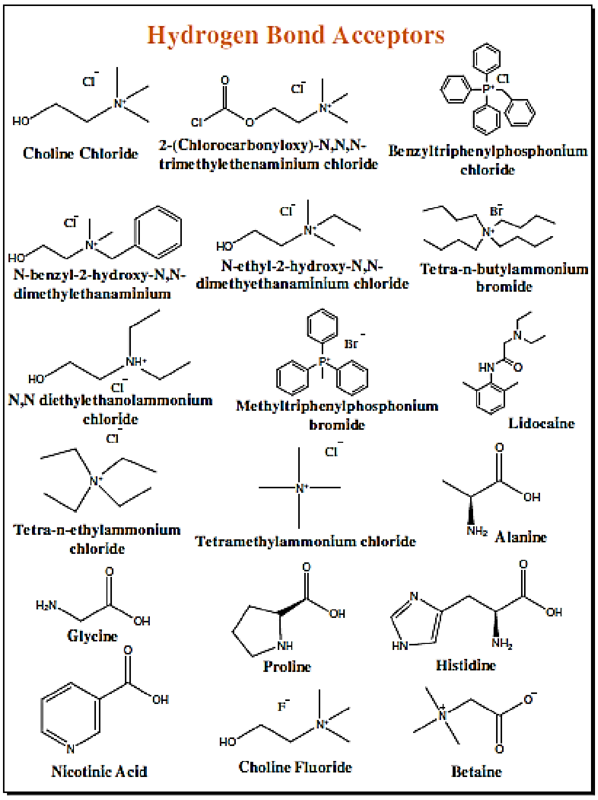

Fig. 2: DES hydrogen bond acceptors (Hansen et al., 2020). Copyright 2020, American Chemical Society.

Based on existing studies, chitosan can be made as a polymer electrolyte by modifying the addition of lithium salts or Li_2CO_3 from used lithium-ion batteries by extraction using DES. The advantages of using used lithium batteries are reuse, easyly obtain, and low production costs. Using Li+ solvated electrolytes from battery electrolytes to increase the ionic conductivity of materials. This study aims to determine the lowest resistance value and highest conductivity of solid electrolyte polymer using Li_2CO_3 from used batteries.

MATERIALS AND METHODS

Materials

The primary materials, including the battery used, were secondary lithium-ion batteries with the Samsung brand and chitosan from shrimp shell waste in Pabean Fish Market Surabaya. Materials components for the formation of DES are Ethylene Glycol 99,9% from Mitra kimia pro analis shop and Choline Chloride 60% product from Cangzhou Tianyu Ltd. The other materials were polyvinyl alcohol from CV Aloin Labora; acetic acid 99,7% from PT Smart Lab Indonesia; sodium hydroxide 99% and sodium carbonate 99% Merck brand, also aquadest.

Deep Eutectic Solvent (DES) Production

Choline Chloride (ChCl) and Ethylene Glycol were mixed into a glass beaker with a 1:4 molar ratio. They were stirred at 600 rpm with a magnetic stirrer and heated at 60°C until a transparent liquid was formed.

Solid-Liquid Extraction Process of Used Batteries

The material in the form of used batteries is separated from its components, and then the electrode solids containing lithium, and cobalt are pulverized to form fine powders. Lithium, Cobalt and DES are mixed into a beaker glass with a solid-per-liquid (S/L) ratio of 150 g/L. Carry out stirring with a long stirring time of 2.5 hours n with a rotation speed of 250 rpm and a temperature of 150°C. The addition of 10 grams of Na_2CO_3 was then filtered, and the residue obtained was baked in the oven at 200°C for 2 hours.

Chitosan Solid Electrolyte Membrane Production

Chitosan with weight variations of 0.2 grams, 0.4 grams, 0.6 grams, 0.8 grams, and 1 gram and 5 grams of polyvinyl alcohol were dissolved in 100 ml 2% acetic acid then homogenized for 2 hours at 80°C. The solution was left to stand until the temperature reached 25°C. Slowly adding Li_2CO_3 dissolved in 30 ml of 0.2 gram aquadest, 0.4 gram, 0.6 gram, 0.8 gram, and 1 gram homogenized. After the solution is homogeneous, it is printed on a petridish and dried in the oven for 4 hours at 80°C and 24 hours at room temperature. Removing the chitosan-based solid electrolyte membrane using 2 M NaOH 100 ml. The analysis uses an LCR meter to determine the value of a material's electrical conductivity. The thickness test or thickness of the edible film obtained is measured using a micrometer or caliper.

RESULTS AND DISCUSSION

The Thickness of the Solid Electrolyte Membrane

The thickness of the edible film data obtained was measured using a micrometer with an accuracy of 0.001 mm at five different places (Nofiandi et al., 2021). Table 1 shows that, for the 0.2 gram Li_2CO_3 polymer, the highest polymer thickness value was found in adding 1 gram of chitosan with a thickness value of 0.63 mm. In contrast, the lowest thickness was found by adding 0.2 grams of chitosan with a thickness value of 0.08 mm. Then for the 0.4 gram Li_2CO_3 polymer, the highest film thickness value was found by adding 1 gram of chitosan with a thickness value of 0.65 mm. In comparison, the lowest thickness was found by adding 0.2 grams of chitosan with a thickness value of 0.15 mm. Furthermore, the 0.6-gram Li_2CO_3 polymer found the highest film thickness value by adding 1 gram of chitosan with a thickness value of 0.75 mm. At the same time, the lowest thickness was found by adding 0.2 grams of chitosan with a thickness value of 0.19 mm.

Table 1. The thickness of the solid electrolyte membrane

	Thickness (mm) Chitosan				
Li_2CO_3 gr	0.2 gr	0.4 gr	0.6 gr	0.8 gr	1 gr
0.2	0.08	0.31	0.44	0.54	0.63
0.4	0.15	0.034	0.45	0.56	0.65
0.6	0.19	0.035	0.47	0.61	0.75
0.8	0.25	0.036	0.48	0.62	0.76
1.0	0.28	0.036	0.51	0.62	0.76

Figure 3 displays the plot of the effect of addition of Li_2CO_3 on the thickness of the solid electrolyte membrane. With the addition of chitosan, the film thickness value will also increase. This affects the more compounds given, the higher the thickness value of a film (Supeni et al., 2015).

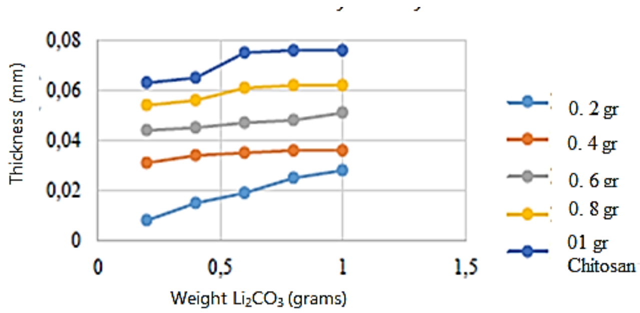

Fig. 3: Effect of addition Li_2CO_3 on The Thickness of the Solid Electrolyte Membrane

The highest thickness value in Li_2CO_3 1 gram is 0.76 mm, while the lowest in Li_2CO_3 0.2 gram is 0.08 mm. One of the requirements for polymer electrolytes is the ease of making thin (~ 40 m) sizes (Arora et al., 2004).

The Thickness Comparison of the Solid Electrolyte Membrane with Japanese Industrial Standard

The highest thickness value is 0.76 mm, and the lowest is 0.08 mm. If it is adjusted to the standard mechanical properties of the edible film, based on Japanese Industrial Standards (JIS), the maximum thickness of the edible film is 0.25 mm (see Table 2). This value is the closest to the standard because many of the thickness test results we got are below 0.25 mm. This is related to the amount of substance added to the edible film. It can be seen from the graph that the addition of Li_2CO_3 does not affect the thickness value significantly.

Table 2. Edible film characteristics based on standards (JIS Z 1707:2019)

No.	Charavteristics	Value
1.	Thickness (mm)	≤0.25
2.	Percent Elongation (%)	≥70
3.	Tensile Strength (Kgf/Cm^2)	≥40
4.	WVTR (g/m^2.h)	
	Grade 1	<0.0416
	Grade 2	0.0416-0.2083
	Grade 3	0.2084-0.8333
	Grade 4	0.8334-4.16
	Grade 5	>4.16

Resistance of Solid Electrolyte Membrane

Table 3 shows the resistance of the solid electrolyte membrane. The electrolyte membrane resistance (Ω) shows that 0.8 grams chitosan polymer, the highest polymer resistance value was found in adding 0.2 grams of Li_2CO_3 with a resistance value of 22.14 Ω. While the lowest resistance is found in adding 1 gram of Li_2CO_3 with a resistance value of 3.047 Ω. Then, for 1 gram of chitosan polymer, the highest polymer resistance value was found in the addition of 0.2 gram of Li_2CO_3 with a resistance value of 23.27 Ω.

While the lowest resistance is found in the addition of 1 gram of Li_2CO_3 with a resistance value of 3.356 Ω. Chitosan shows a decreasing resistance value as Li_2CO_3 increases. The highest resistance value is found in 1 gram of chitosan, while the lowest is in 0.2 gram of chitosan. According to (Afif et al., 2018), the use of too much chitosan causes the polymer shape to become stiff and thick so that it can inhibit the movements of these ions and cause higher resistance.

Table 3. The resistance of the solid electrolyte membrane

	Resistance (Ω) Chitosan				
Li_2CO_3 gr	**0.2 gr**	**0.4 gr**	**0.6 gr**	**0.8 gr**	**1 gr**
0.2	16.2	21.56	21.9	22.14	23.27
0.4	11.48	11.79	12.07	12.41	14.30
0.6	8.025	8.909	10.71	10.75	10.84
0.8	3.515	3.825	4.737	5.131	7.094
1.0	1.684	2.791	3.011	3.047	3.356

Ionic Conductivity of Solid Electrolyte Membrane

Table 4 displays Ionic conductivity of the solid electrolyte membrane. Chitosan polymer 0.8 grams highest polymer ionic conductivity value is found in adding 1 gram of Li_2CO_3 with a conductivity value of 0.00509 S/cm. In comparison, the lowest conductivity was found in adding 0.2 grams of Li_2CO_3 with a conductivity value of 0.00061 S/cm. Then, for Chitosan 1 polymer, the highest polymer ionic conductivity value was found by adding 1 gram of Li_2CO_3 with a conductivity value of 0.00566 S/cm. Meanwhile, the lowest conductivity was found in adding 0.2 grams of Li_2CO_3 with a conductivity value of 0.00068 S/cm. For polymers of various weight variations, Chitosan showed a higher conductivity value with increasing Li_2CO_3.

Table 4. Ionic conductivity of the solid electrolyte membrane

	Ion Conductivity (S/cm) Chitosan				
Li_2CO_3 gr	**0.2 gr**	**0.4 gr**	**0.6 gr**	**0.8 gr**	**1 gr**
0.2	0.00012	0.00036	0.00050	0.00061	0.00068
0.4	0.00033	0.00072	0.00093	0.000113	0.000114
0.6	0.0059	0.0098	0.00110	0.00142	0.00173
0.8	0.00178	0.00235	0.00253	0.00302	0.00268
1.0	0.00416	0.00322	0.00423	0.00509	0.00566

Figure 4 shows that the relationship between the weight of Li_2CO_3 is directly proportional. The increase in conductivity acco mpanied by the presence of lithium ions is due to lithium being the lightest metal element and having a shallow redox potential (E(Li+/Li) = -3.04 V), which allows cells to have high voltage and large energy density. In addition, Li+ ions have a small ionic radius which is advantageous for diffusion in solids and, in this case, is a polymer electrolyte membrane (Gonggo et al., 2017). The graph shows that the lowest ionic conductivity value is found in 0.2 gram Li_2CO_3 polymer, with a variation of 0.2-gram chitosan and an ionic conductivity value of 0.00012 S/cm. Also, the highest ionic conductivity is found in 1 gram Li_2CO_3 polymer, with 1 gram chitosan variation and ionic conductivity of 0.00566 S/cm.

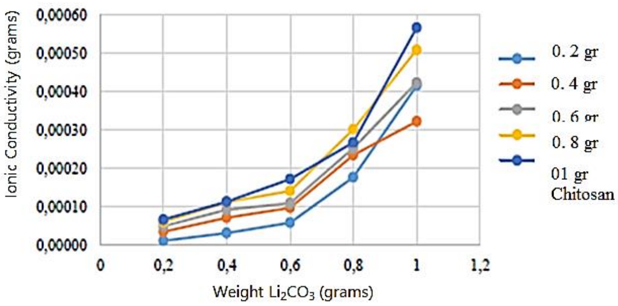

Fig. 4: Effect of addition of Li_2CO_3 on the ionic conductivity of electrolytic

The Ionic Conductivity Comparison of the Solid Electrolyte Membrane with Literature

Table 5 shows that ionic conductivity, as with previous research, were the highest $1.2x10^{-4}$ and $5.66x10^{-3}$. Ionic liquids have been introduced into the polymer electrolyte membranes to promote the anhydrous conductivity to reach a significant level, of approximately 10^{-2}. However, the conductivity values obtained 10^{-4} and 10^{-3} were insufficient and poor under anhydrous coniditions as the proton hopping sites on the go were ineffective (Putro et al., 2016; Zhao et al., 2015).

Table 5. Ionic conductivity comparison

Souce	Ion Conductivity (S/cm)
This Research	Highest : $1.2x10^{-4}$ Lowest : $5.66x10^{-3}$
Lou, et al., 2021	$>10^{-5}$
Muliawati et al., 2021	Highest : $6.7x10^{-4}$ Lowest : 9x10-2
Handayani et al., 2018	Highest : $9.5x10^{-2}$ Lowest : $1.2x10^{-2}$
Ye et al., 2013	$10.3x10^{-2}$ and $8.6x10^{-2}$

CONCLUSIONS

In this research, we extracted lithium from a lithium-ion secondary battery as an addition to the value of ion conductivity in polymer membranes from chitosan as a condition for fulfilling polymer electrolyte membranes. The results found that the conductivity values of various variables based on reference literature were still in the range of common ion conductivity values. In testing, the characteristics of polymer membranes from various variables continue to increase. Some of the data conclusions obtained from this research are summarized in a balanced comparison between the higher the chitosan content in the polymer electrolyte and the higher the Li_2CO_3 content will increase the polymer thickness value. Meanwhile, if the chitosan content is low and the Li_2CO_3 content is high, it will decrease the resistance value and increase the ionic conductivity of the polymer electrolyte. The higher the chitosan content and the higher the Li_2CO_3 content will increase the polymer battery voltage. According to JIS standards, the best ratio for obtaining membrane thickness is the ratio of chitosan 0.2 g with the addition of Li_2CO_3, a maximum of 0.8 gr. The best ratio is still in the average to get the value of ionic conductivity is the ratio of the amount of chitosan 0.2 g with the addition of Li_2CO_3, a maximum of 1 gr. Although tremendous progress has been achieved with the extraction of spent batteries with DES solvent as a character enhancer of ion conductivity values, further potential prospects are still being made for the best fulfillment of the characteristics of polymer-electrolyte solid membranes recommended use in batteries.

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