EFFECT OF FLY ASH-DERIVED SILICA ON THE FUNCTIONAL GROUP INTERACTIONS AND IONIC CONDUCTIVITY OF CHITOSAN/LIOH SOLID POLYMER ELECTROLYTES MEMBRANE

Kartika Sari[1*], Abiyyu Sayyid Muwaffaq[2], dan Evi Yulianti[3]

[1*,2]Department of Physics, Faculty of Mathematics and Natural Science, Universitas Jenderal Soedirman, Purwokerto, 53122, Indonesia

[3]National Research and Innovation Agency (BRIN), PRMM: Advanced Materials Research Center, KST BJ Habibie Serpong, Tangerang, 15314, Indonesia

*Email: kartika.sari@unsoed.ac.id

Abstract. Solid electrolyte membrane based on environmentally friendly materials using SiO_2 dispersed chitosan/LiOH solid electrolyte can be used as one of the materials Coal fly ash waste in the form of silica is being developed. Synthesis and characterization of solid polymer membranes based on chitosan and LiOH with the addition of Silica (SiO_2) from fly ash aims to increase ionic conductivity and stability membrane. Variations in the composition of SiO_2 addition of 2% (S2), 4% (S4), and 6% (S6) on the chitosan mass using the solution casting method. Meanwhile, testing to determine membrane functional groups using Fourier Transform spectroscopy Infrared Spectroscopy (FTIR) and Electrochemical Impedance Spectroscopy (EIS).The FTIR results for samples (S2), (S4), and (S6) show changes in intensity.and peak shifts in the O–H and N–H functional groups at wave numbers 3397, 3430, and 3410 cm^{-1}, respectively. Meanwhile, the CH functional group at wave number 2925, 2939, and 2935 cm^{-1} , respectively. The functional groups C=O and C=C in the numbers waves 1655, 1598, and 1597 cm^{-1} , respectively. For the functional groups Si–O–Si, and Si–O are formed at wave numbers 787, 791, and 790 cm^{-1}, respectively. Cluster The Si–O–Si function, and Si–O indicate the presence of intermolecular interactions between fly silica.ash dispersed on chitosan and LiOH membranes. There is a shift in the number waves cause functional groups to change, so that the mobility of charge carriers samples (2), (S4), and (S6) increased. The addition of silica fly ash can improve chemical structure and increase the interactions between molecules. Thus, the polymer membrane SiO_2 dispersed chitosan/LiOH solid electrolyte can be used as one of the materials safe and efficient solid electrolyte for lithium batteries.

Keywords: Chitosan/LiOH, Silica fly ash, Solid Electrolyte Polymer Membrane.

1. Introduction

At the moment Lithium-ion batteries have advantages such as high energy density high, long service life, and light weight compared to other batteries. This battery has many used in electronic devices and electric vehicles [1]. The disadvantages use of batteries with organic solvent-based liquid electrolytes in lithium-ion batteries use of batteries with organic solvent-based liquid electrolytes in lithium-ion batteries to overcome this problem, a solid polymer electrolyte (SPE) membrane is used more stable and safe to use [2], [3]. The potential of natural polymers and biopolymers is used as environmentally friendly SPE components, and support the principles of a circular economy [4]. Chitosan is a natural material that is widely used for manufacturing of solid polymer membrane batteries [5].

Chitosan is a multifunctional biopolymer with broad biological activities. Chitosan has antimicrobial and antioxidant properties and can act as a drug carrier [6]. Chitosan modifications have been widely developed to overcome the limitations of its solubility. Chitosan is used in polymer electrolyte gels for lithium-ion batteries. The combination of chitosan with lignocellulose increases mechanical strength and stability.thermal. In addition, the development of chitosan-graft-polyaniline copolymer as a binder as conductive. This modification provides high electrical conductivity as well as mechanical strength.on silicon electrodes [7]. Modification of chitosan with Lithium Hydroxide (LiOH) widely used in energy storage systems due to its chemical stability and potential electrochemistry. LiOH serves as the main product that supports the delithiation cycle with high efficiency [8]. LiOH can be regenerated through the processefficient electrochemical process of CO_2 adsorbent, in a circular system. Therefore, the use of LiOH in chitosan membrane systems has the potential to increase conductivity.onic and strengthen the electrochemical properties of solid electrolyte polymer materials. Fly ash silica doping is used to increase the ionic conductivity of the membrane [9].

Silica in fly ash is one of the cement industry wastes that has the potential to be used for used as a reinforcing material in batteries. Silica in fly ash has a structure nanopores that can stabilize the electrode, prevent volume expansion, and increase ionic conductivity [10]. Meanwhile, the extraction 2 from biomass waste such as corn leaves have also shown electrochemical capacity performance.promising. Therefore, silica fly ash can be used as an additive in chitosan-LiOH membrane to improve mechanical stability, ion adsorption capacity, and efficiency conductivity in solid electrolyte systems [11], [12]. This research focuses on the synthesis of chitosan/LiOH solid electrolyte polymer membranes dispersed with silica fly ash.The variations of silica were used 2%, 4%, and 6% (w/w) of the chitosan mass. It is hoped that with the presence of silica fly ash dispersed in the polymer electrolyte membrane solid chitosan/LiOH, which can increase the ionic conductivity value. The method that carried out in the synthesis of solid electrolyte polymer membranes is the solution casting method. The characterization is used Fourier Transform Infrared Spectroscopy (FTIR) for identify the presence of functional groups and Electrochemical Impedance Spectroscopy (EIS) to determine the nquist plot on the chitosan/LiOH/polymer electrolyte membrane.

2. Methods

The tools used in the research were digital scales, beakers, measuring cups, cups,petri dish, sieve/mesh, magnetic stirrer, magnetic bar, oven/spatula dryer, FTIR test equipment. Meanwhile, the materials used are chitosan, Silica Fly-ash, Lithium Hydroxide (LiOH), Sodium Hydroxide (NaOH), distilled water, CH_3COOH 1%, parchment, plastic wrap, plastic clips, aluminum foil and silica gel. Manufacturing and testing of polymer membrane synthesis SiO_2 dispersed chitosan/LiOH electrolyte was carried out in the Core and Materials Physics Laboratory, Department of Physics, Faculty of Mathematics and Natural Sciences, Jenderal University Soedirman Purwokerto, as well as the Advanced Materials Research Center (PRMM) of the Research and Innovation Agency National (BRIN) Tangerang.

Preparation Synthesis Electrolyte Membrane

The research design for the synthesis of chitosan/LiOH membranes dispersed with SiO_2 is shown in Figure 1. The steps of the synthesis of the Chitosan/LiOH membranes were dispersed by silica nanoparticles of fly ash.

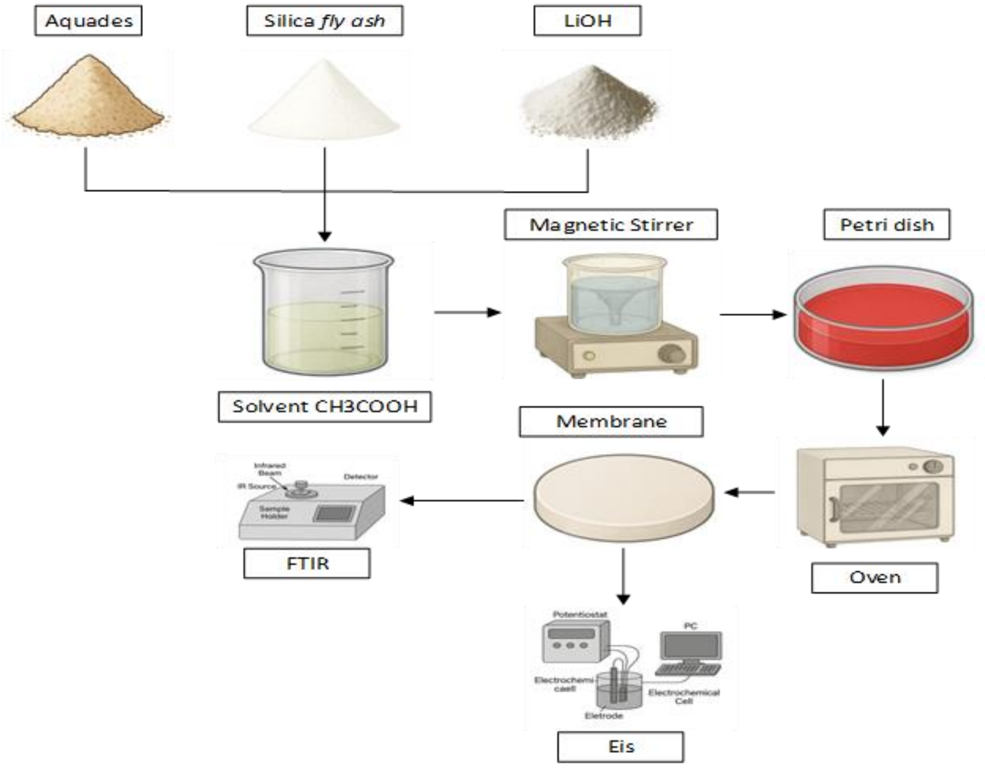


Figure 1. Design and Synthesis of Chitosan/LiOH/SiO_2 Polymer Electrolyte Membrane

Polymer membrane synthesis was carried out with silica fly ash compositions of 2%, 4%, and 6% (w/w) of the chitosan mass. Then, the sample was dissolved in 100 ml of 1% CH3COOH and tirred using a magnetic stirrer at a speed of 750 rpm for 1 hour. Chitosan 2 grams were added to the solution and stirred for 2 hours until homogeneous. 10% (w/w) of LiOH salt is added and stirred for 3 hours until homogeneous. Then, the solution is poured into a petri dish and dried using an oven until a membrane is formed. The membrane that has been formed is characterized using Fourier Transform Infra-Red (FTIR) and Electrochemical Impedance Spectroscopy (EIS).

Characterization Polymer Electrolyte Membranes

1. Fourier Transform Infrared Spectroscopy (FTIR)

Analysis of the structure of solid electrolyte polymer membranes was carried out using the technique Fourier Transform Infrared (FTIR) spectroscopy in the wavelength range 4000–400 cm^{-1}. The characterization aims to identify the functional groups present in Chitosan/LiOH/(SiO2) membrane surface. This FTIR test was carried out in the Laboratory Center for Advanced Nuclear Materials Technology Research (PRT-BMN), Nuclear Energy Research Organization (ORTN), National Research and Innovation Agency (BRIN).

2. Electrochemical Impedance Spectroscopy (EIS)

Impedance analysis of solid electrolyte polymer membrane using electrochemical Impedance Spectroscopy (EIS) Hioki LCR-300 at 1 MHz. EIS testing carried out at the Advanced Nuclear Materials Technology Research Center Laboratory (PRT-BMN) Nuclear Energy Research Organization (OR-TN), National Research and Innovation Agency (BRIN).

3. Results And Discussion

The results of this research are in the form of a dispersed Chitosan/LiOH solid electrolyte polymer membrane. SiO_2 with a composition of 2% (S2), 4% (S4), and 6% (S6). Characterization using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR test results are shown in Figure 2.

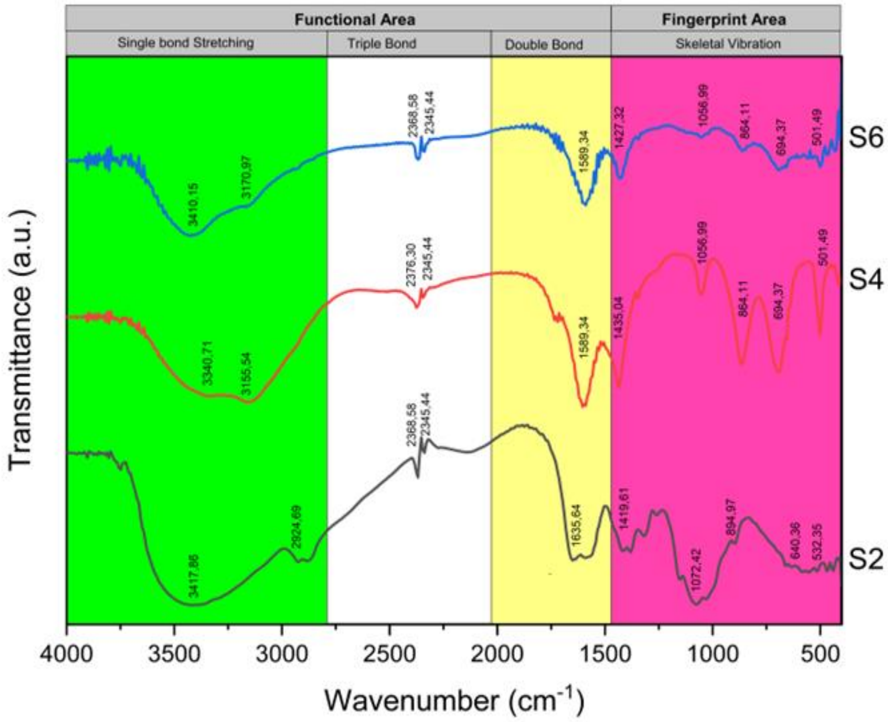


Figure 2. FTIR spectra for Chitosan/LiOH polymer electrolyte membranes dispersed with SiO_2 at 2%, 4%, and 6%

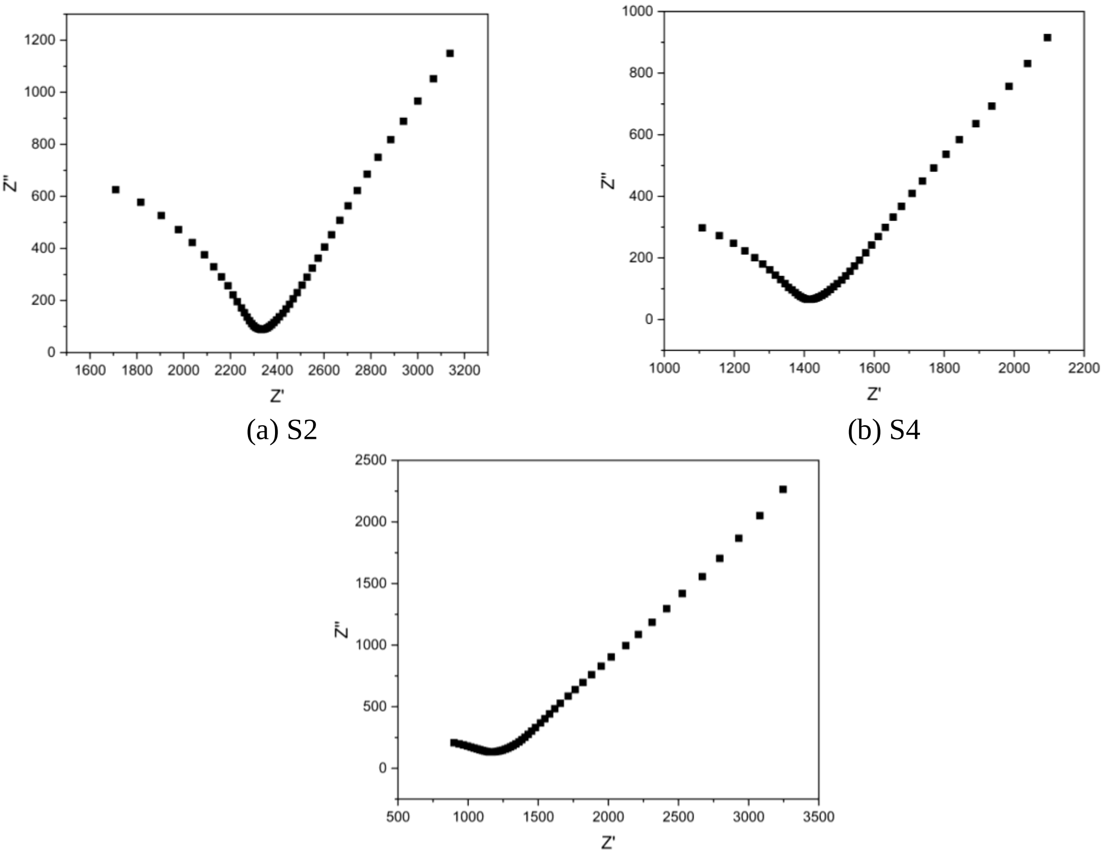
Figure 2 shows the results of the FTIR spectra of the Chitosan/LiOH polymer electrolyte membrane Dispersed SiO_2. Functional group analysis of dispersed chitosan/LiOH polymer electrolyte membranes SiO_2 in Table 1. FTIR characterization of polymer electrolyte membranes based on chitosan/LiOH dispersed with SiO_2 at concentrations of 2%, 4%, and 6% showed changes chemical structure and interactions between functional groups that affect electrochemical performance membrane, especially its ionic conductivity. At high wave numbers (4000–3000) cm^{-1}, a broad absorption band located in the range of (3397–3401) cm^{-1} indicates the presence of stretching vibrations of the O–H and N–H groups derived from chitosan. Small shifts in increasing concentration of SiO_2 indicates the occurrence of hydrogen interactions between the groups hydroxyl groups of chitosan and silanol groups (Si–OH) of silica. This interaction can increase intermolecular bonds and helps form a conductive path for Li^- ions through hopping mechanism, thus supporting the increase of ionic conductivity.

The C–H stretching vibrations that appear stable in the range of (2925–2936) cm^{-1} indicate carbon chain stability in chitosan. A significant shift occurs at the wave number (1655–1595) cm^{-1} which is related to the vibration of the C=O or C=C group. The decrease in the value of the number The wave shows an increase in electrostatic interactions between the carbonyl group and the Li^- ion. or silica particles. Meanwhile, the C–H bending vibration is located at around 1456 cm^{-1} does not appear to have shifted, indicating that this structural part is not is greatly influenced by the composition of silica. However, the fingerprint region between (1300–500) cm^{-1} shows the membrane structure. C–O vibrations (1041–1045) cm^{-1}, Si–O–Si (787–791) cm^{-1} and Si–O (about 563 cm^{-1}) bond strongly with increasing silica composition,and shows the presence of good distribution of SiO_2 in the chitosan matrix.

Table 1. Functional group spectra and wave numbers of Chitosan/LiOH/SiO_2 membranes

No	Functional Groups	Wave Number (cm^{-1})			Vibrations Type
		Kit/LiOH/SiO_2 2%	Kit/LiOH/SiO_2 4%	Kit/LiOH/SiO_2 6%	
1	O-H/N-H	3397	3430.71	3410.15	Stretching
2	C-H	2925.54	2939.34	2935.44	Stretching
3	C=O / C=C	1655.34	1598.44	1597.66	Stretching
4	C-H Bending	1456.34	1456.34	1456.34	Bending
5	C-O	1041.18	1045.98	1045.62	Bending
6	Si-O-Si	787.88	791.46	790.57	Stretching
7	Si-O	563.44	563.44	563.44	Stretching

The presence of Si–O–Si and Si–O groups has an impact on ionic conductivity, because the structure porous silica can create a more efficient lithium ion conduction path, while strengthen the mechanical and thermal stability of the membrane. Thus, increasing the intensity These bands can be interpreted as evidence of the role of silica in creating the network.onductive that supports ion mobility. The FTIR characterization results show that The addition of SiO2 in the right composition not only enriches the chemical structure membrane, but also enhances the functional interactions between active components. This contribute directly to the increase in ionic conductivity as shown in Figure 3.



(a) S2 (b) S4

(c) S6

Figure 3. Nquist Plot for Chitosan/LiOH polymer electrolyte membrane dispersed with SiO_2 at 2%, 4%, and 6%

Figure 3 shows the electrochemical impedance (EIS) results of the Chitosan/LiOH membrane.dispersed SiO_2 with variations in silica concentration of 2%, 4%, and 6%. EIS results shows the differences in resistance characteristics and conduction mechanisms. For sample S2 shows an imperfect arc-shaped curve with an impedance value real impedance (Z') ranges from 1000 to 2200 Ohm and the maximum imaginary impedance value (Z") around 300 Ohms. This indicates that the material still has internal resistance. high and limited ion conduction paths. The curve is gentle and does not form perfect semicircle indicates that the ionic relaxation process is still not optimal and there is a wide distribution of relaxation times, so that the ionic conductivity of this material is classified as low. For the S4 membrane, the curve shows a shift to become more linear and not shows a clear arc. The apparent impedance range increases to about 700 up to more than 3000 Ohm, while the Z" value does not show a sharp peak. This occurs increase in total resistance due to possible overload of SiO_2 which inhibits ion movement in the polymer matrix. The shape of the curve is more like a straight line shows the dominance of capacitive behavior and high polar resistance, and shows lack of morphological structure for ion transfer pathways. Meanwhile, at a composition of 6% silica, The EIS curve shows a more perfect semicircle shape with a Z' value between 1600 to 3200 Ohm and the maximum Z" is close to 1200 Ohm.

The presence of ionic relaxation processes and more regular charge distribution. Although the resistance value is still relatively high, a more defined curve shape indicates that the interaction between lithium ions (Li-) with a more stable polymer matrix. The addition of silica in this amount seems to work enhance the internal structure of the material and support the formation of conductive paths.better than the previous composition.Overall, the increase in SiO2 concentration from 2% to 6% shows a significant influence on the structure and electrochemical performance of the system.The 6% composition shows the best impedance characteristics among the three,with more efficient ionic relaxation and semicircle curves approaching ideal characteristics electrochemical system. The resistance is still relatively high, so modification is recommended.further, such as the addition of conductive materials (e.g. rGO or activated carbon), for lowering resistance and increasing overall ionic conductivity.

4. Conclusion

This research successfully synthesized a chitosan-based solid electrolyte polymer membrane and LiOH with the addition of silica from fly ash of 2%, 4%, and 6%. FTIR characterization shows the presence of changes in functional groups which indicate interactions between chitosan, LiOH, and silica. The addition of silica fly ash causes a shift in the wave number in the O–H, N–H, C=O, and Si–O groups which strengthen molecular interactions as well increase the potential of ion conductive pathways. EIS results show that the silica composition of 6% produces the best impedance profile, characterized by a semicircle curve shape more defined, indicating a more efficient ionic relaxation process. Although resistance is still quite high, the addition of silica fly ash has been shown to increase stability chemistry, internal structure, and ionic conductivity of the membrane. Thus, the membrane Chitosan/LiOH dispersed silica fly ash has great potential as a solid electrolyte safe and efficient for lithium-ion battery applications.

5. Acknowledgement

The author would like to thank Universitas Jenderal Soedirman through BLU Funding for Unsoed Basic Research Scheme in 2024.

References

[1] K. K. Rajeev, E. Kim, J. Nam, S. Lee, J. Mun, and T. H. Kim, “Chitosan-grafted-polyaniline copolymer as an electrically conductive and mechanically stable binder for high-performance Si anodes in Li-ion batteries,” *Electrochim. Acta*, vol. 333, 2020, doi: 10.1016/j.electacta.2019.135532.

[2] K. Sari, A. N. M. Haryadi, N. Khusaenah, Sudaryanto, E. Yulianti, and A. B. S. Utomo, "Modification of Chitosan/PEG4000 dispersed with Lithium Triflate (LiCF3SO3) as a solid polymer electrolyte for the secondary battery," *Commun. Sci. Technol.*, vol. 9, no. 2, pp. 243–251, 2024, doi: 10.21924/cst.9.2.2024.1496.

[3] R. Borah, F. R. Hughson, J. Johnston, and T. Nann, "On battery materials and methods," *Mater. Today Adv.*, vol. 6, p. 100046, 2020, doi: 10.1016/j.mtadv.2019.100046.

[4] F. A. Perdana, "Baterai Lithium," *INKUIRI J. Pendidik. IPA*, vol. 9, no. 2, p. 113, 2021, doi: 10.20961/inkuiri.v9i2.50082.

[5] K. Sari, S. Sunardi, A. B. S. Utomo, P. L. Toruan, E. Yulianti, and M. Mashadi, "Sifat Optik Dan Permitivitas Listrik Membran Polimer Padat Kitosan/Peo," *Sainmatika J. Ilm. Mat. dan Ilmu Pengetah. Alam*, vol. 17, no. 2, p. 97, 2020, doi: 10.31851/sainmatika.v17i2.4987.

[6] T. Paramitha, R. R. Fatimah, and A. H. A. Tachtiar, "Extraction of Silica (SiO2) from corn leaves waste as anode in Lithium-Ion Batteries," *J. Phys. Conf. Ser.*, vol. 2945, no. 1, 2025, doi: 10.1088/1742-6596/2945/1/012020.

[7] S. Abdullah *et al.*, "Characterization of Solid Polymer Electrolyte Membrane made of Methylcellulose and Ammonium Nitrate," *J. Phys. Conf. Ser.*, vol. 1532, no. 1, 2020, doi: 10.1088/1742-6596/1532/1/012017.

[8] C. Z. Zhao *et al.*, "Liquid phase therapy to solid electrolyte–electrode interface in solid-state Li metal batteries: A review," *Energy Storage Mater.*, vol. 24, no. March, pp. 75–84, 2020, doi: 10.1016/j.ensm.2019.07.026.

[9] K. Sari, A. Setiabudi, R. Halifah, N. A. Q. A'yun, and Sunardin, "Gugus Fungsi, Struktur Morfologi dan Konduktivitas Ionik Membran Polimer Elektrolit Padat Kitosan/LiOH/ZnO," *Pros. Semin. Nas. Fis.*, vol. 1, no. 1, pp. 190–199, 2022.

[10] E. Lizundia and D. Kundu, "Advances in Natural Biopolymer-Based Electrolytes and Separators for Battery Applications," *Adv. Funct. Mater.*, vol. 31, no. 3, pp. 1–29, 2021, doi: 10.1002/adfm.202005646.

[11] P. Yadav, S. H. Beheshti, A. R. Kathribail, P. Ivanchenko, J. Van Mierlo, and M. Berecibar, "Improved Performance of Solid Polymer Electrolyte for Lithium-Metal Batteries via Hot Press Rolling," *Polymers (Basel).*, vol. 14, no. 3, 2022, doi: 10.3390/polym14030363.

[12] I. Aranaz *et al.*, "Chitosan: An overview of its properties and applications," *Polymers (Basel).*, vol. 13, no. 19, 2021, doi: 10.3390/polym13193256.