Reducing the Electrical Conductivity of ZnO/Ag Nanofiller for Solid Polymer Electrolytes Prepared by Laser Ablation in Polylactic Acid Solution

Permono A. Putro*,[1] Nurfina Yudasari,[2] Yulia Irdawati,[2] Ahmad S. Sulaeman,[1] and Akhiruddin Maddu[1]

[1]*Department of Physics, Faculty of Mathematics and Natural Sciences, IPB University, Bogor 16680, Indonesia*
[2]*Research Center for Physics, Indonesian Institute of Sciences, Building 442, Puspitek Serpong, South Tangerang, Banten 15314, Indonesia*

Abstract: Solid polymer electrolytes (SPEs) are vital components of fast appearing technology for energy storage-conversion devices. Here, SPEs based on silver (Ag) and zinc oxide (ZnO) nanoparticles are prepared by laser ablation in polylactic acid (PLA) at room temperature. The comparison study of PLA, PLA-ZnO, PLA-ZnO/Ag, and PLA-Ag -based SPEs is conducted in pursuance of the electrical conductivity obtained from electrochemical impedance spectroscopy (EIS) characterization. EIS provides comprehensive analyses, including DC and AC conductivities, dielectric constant, and electrical modulus of the samples. Our results show that PLA-ZnO exhibits an appreciable value of DC conductivity, which insignificantly decreases by Ag addition into PLA-ZnO/Ag. This study suggests that PLA-ZnO remains stable by Ag incorporation; hence, PLA-ZnO/Ag has a great potential as SPEs.

Keywords: SPEs; PLA-ZnO/Ag; electrical conductivity.

*Corresponding author: permanenputro@apps.ipb.ac.id

Article history: Received 09 December 2020, Accepted 02 February 2021, Published June 2021.
http://dx.doi.org/10.12962/j24604682.v17i2.8135
2460-4682

I. INTRODUCTION

The development of polymer-based nanocomposites transparent films with high electrical and thermal conductivities has become a popular research topic for electronic devices [1]. Polylactic acid (PLA), in particular, has a great potential for replacing petroleum-based polymers because of its thermoplastic nature, biodegradable and biocompatible characteristics, mechanical strength, high elastic modulus, and easy processing [2]. Moreover, the properties of PLA can be improved by incorporating nano-sized carbon, metal, or semiconductors materials that offer several unique features, such as electrical conductivity, thermal stability, and mechanical reinforcement [3–6].

Today, silver (Ag) nanomaterial is regarded as one of the most appealing transparent electrodes due to its excellent conductivity. However, Ag cannot stay stable for a long time when exposed to air [7]. Zinc oxide (ZnO) nanoparticles is a semiconductor compound exhibiting the electrical properties that can be modulated and optimized by controlling the thickness or size of ZnO to be in nanoscale [8]. In typical, the inclusion of Ag in the synthesis of ZnO nanostructures has gained number of attention because of its unique structural, electrical, and optical properties [8, 9].

Laser ablation of a solid target in liquids is a simple and reliable method for generating nanoparticles of almost any metals and semiconductors [10]. Zhao *et al.* [9] succeed to use Ag plate and ZnO to synthesize ZnO/Ag by pulsed laser ablation method in water. ZnO/Ag could form a unique core-shell nanostructure and elaborate its optical and structures characteristics. Anugrahwidya *et al.* [11] also managed to use a similar method reported in [9] with some modifications to obtain ZnO/Ag nanoparticles. Referring to previous studies, so far the preparation of ZnO/Ag by using laser ablation in PLA solution has not been reported. PLA-ZnO/Ag transparent film has great potential for solid polymer electrolytes (SPEs) application, where PLA and ZnO/Ag have a role as host and nanofiller, respectively. In the present study, transparent films based on PLA-Ag, PLA-ZnO, and PLA-ZnO/Ag are prepared by laser ablation. Hereinafter, their properties are characterized by an EIS method to observe the electrical behavior, including ionic conductivity, complex dielectric, and electric modulus. All of those parameters are used to determine an ideal candidate for SPEs applications.

II. METHOD

Dichloromethane (DCM, CH_2C_2) and polylactic acid (PLA, $[C_3H_4O_2]_n$) were purchased from Sigma-Aldrich and NatureWorks America, respectively. The used Ag plate specifically has a thickness of 5 mm and size of 15 × 15 mm, while the ZnO plate has a thickness of 5 mm and size of 10 × 15 mm.

ZnO/Ag nanoparticles were prepared using the similar

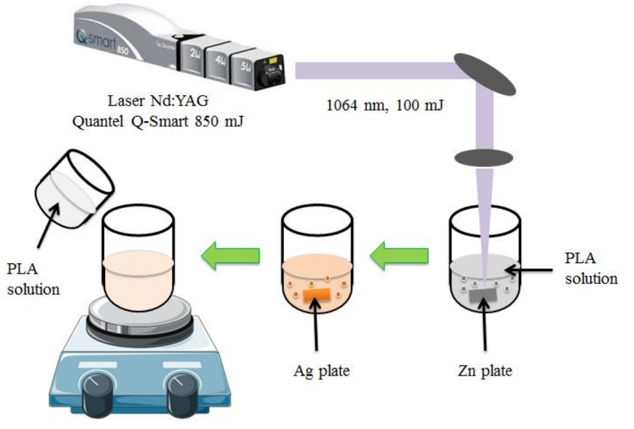

FIG. 1: Synthesis scheme of the ZnO/Ag nanoparticles prepared by laser ablation in PLA solution.

FIG. 2: The photograph of transparent films.

method as reported in previous studies [9, 11] with some modifications. The synthesize procedure conducted by laser ablation in PLA solution consists of three-steps with the experimental set up shown in Fig. 1. In the first step, 2 mol% PLA was prepared by dissolving 2 g PLA granules into 100 mL DMC solution using a hot plate magnetic stirrer at 90^{o}C and 1200 rpm for 30 minutes. For the second step, the laser Nd:YAG was focused on the Zn plate to ablate it for 10 minutes to produce ZnO nanoparticles. The laser was setup at the wavelength of 1064 nm, 100 mJ energy laser, and 160 μs pulsed duration. As for the last step, an Ag plate was ablated by the same pulsed energy of laser for 5 minutes in the obtained solution containing ZnO nanoparticles, which results in ZnO/Ag nanoparticles. Ag nanoparticles were also synthesized by the same method with the laser focused on Ag plate for 5 minutes in 5 mL PLA. 10 ml PLA was then added to the ablated solution. The resulted solution was stirred for 5 minutes and casted on a stainless Teflon. The formed transparent film can be seen at Fig. 2. Characterization was carried out by electrochemical impedance spectroscopy (EIS) to investigate electrical conductivity of all samples.

III. RESULTS AND DISCUSSION

Electrical Conductivity study

The frequency dependent dielectric properties were studied at room temperature in the frequency range 10^2 - 10^6 Hz using LCR meter (HIOKI 3532-50). By measuring the complex impedance (Z), the dielectric constant, dielectric loss, real and imaginary electric modulus can be estimated.

TABLE I: The values of ionic conductivity of PLA, PLA-Ag, PLA-ZnO/Ag and PLA-ZnO.

No.	Sample	DC conductivity (S/cm)
1	PLA	4.354×10^5
2	PLA-ZnO	9.773×10^3
3	PLA-ZnO/Ag	8.814×10^4
4	PLA-Ag	6.820×10^5

The ionic conductivity of all films has been calculated from the bulk resistance (R_b) of the samples at room temperature using Eq. (1) [12, 13].

$$\sigma_\mathrm{DC} = \frac{t}{R_\mathrm{B} A} \tag{1}$$

where σ_DC, t, and A are DC conductivity (S/cm), thickness (cm), and area (cm^2) of the samples, respectively.

Table I summarizes the DC ionic conductivity of the samples, revealing that the conductivity of the PLA-based electrolyte significantly increases with the ZnO addition, while decreases by the Ag inclusion. This indicates that ZnO could improve ions mobility between electrode and electrolyte interface [14], whereas Ag has an effect to reduce it. PLA has the lowest conductivity because of its insulating feature [15]. The data also show that the ZnO/Ag coexistence plays an important role to enhance charge carriers; thus increases the ionic conductivity of the PLA-based electrolyte [16].

Fig. 3 shows the AC conductivity spectra of the samples, which are divided by three regions. The first region is located in low frequency (1.7 - 2 Hz) and attributed to the electrode polarization. The second region is in intermediate frequency (2 - 4 Hz) and related with longrange ion migration and DC conductivity. The final region is at a high frequency dispersion region (4 - 6 Hz); it is ascribed to the increased probability of ion hopping from one site to another [14]. Based on previous study done by Arya *et al.* [14], AC conductivity on the third region can be identified as two processes to clearly explain the ion hopping. The first process is correlated with a forward-backward migration (ω_h) and a forward migration ($\omega > \omega_\mathrm{h}$) in which ions may jump back to the initial chain (ω_h). The second process describes a successful ion hopping to the new chain of polymer ($\omega > \omega_\mathrm{h}$) [14, 17, 18].

The AC conductivity will increase with increasing frequency, which is caused by ion activities in the electrode-electrolyte interface. The low frequency region is known as the busies phase when the charges and charge carriers are collected in electrode-electrolyte interface, thus it will decrease a relaxation process and enhance the dielectric constant [19]. The intermediate frequency is described as an ions diffusion process, where ions may migrate from one chain to another, hence, increases the relaxation process and decreases the dielectric constant as the ions is getting started to pairs [20].

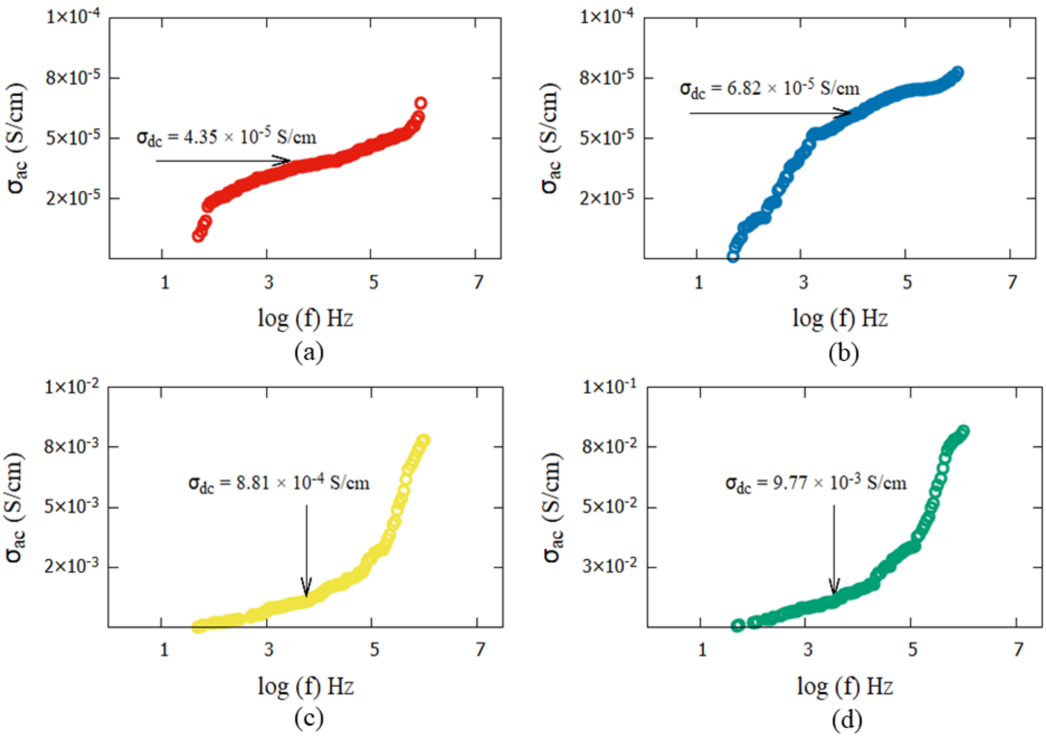

FIG. 3: AC and DC conductivity of (a) PLA, (b) PLA-Ag, (c) PLA-ZnO/Ag, and (d) PLA-ZnO as a function of frequency.

As the result, in the final phase, the ions experience a pairing effect and disperse to another electrode which could also enhance the relaxation process with increasing frequency. As shown in Fig. 3, the ionic conductivity enhancement are influenced by ZnO nanoparticles addition. The conductivity runs into decrement when PLA was added by Ag nanoparticles. However, compare with the pure PLA, the Ag inclusion still increases the PLA ionic conductivity. This indicates that the added Ag is proportional to the resulted free ions in electrode-electrolyte interface [21]. PLA-based polymer with ZnO addition also raise the ionic conductivity significantly, denoting that ZnO results more free ions than Ag.

Dielectric study

We analyzed the complex dielectric constant having real and imaginary parts at room temperature. The real part (ϵ'), also known as dielectric constant) measures the ability of material to stored electric charge, whereas the imaginary part (ϵ'') represents dielectric loss or usually called as dissipation energy in the materials under an applied oscillating electric-field [12, 22, 23]. The ϵ' and ϵ'' are described by Eqs.(2) and (3), respectively.

$$\epsilon' = \frac{Z_i}{\omega C_0(Z_i^2 + Z_r^2)} \tag{2}$$

$$\epsilon'' = \frac{Z_r}{\omega C_0(Z_i^2 + Z_r^2)} \tag{3}$$

where C_0 is the vacuum capacitance which can obtained by $C_0 = \epsilon_0 A/l$, ϵ_0 is the free space dielectric permittivity, l is the thickness, and A is the cross-section area of the capacitor.

Based on Fig. 4(a) and (b), we know that the ϵ' and ϵ'' of PLA have a similar phase from low to high frequency as that explained in Fig. 3. The ϵ' value of PLA reach up to 6×10^4 to achieve the electrode polarization between electrode-electrolyte interface, following the migration of ion with dielectric loss that reach up to 3×10^4 to migrate the ions at low frequency. The polarization and ion migration process occur for a long frequency range following the ion diffusion process. It is indicated with an available space between the points of dielectric spectra [19, 20]. Afterwards, the dispersion process is found at high frequency, where its magnitude reaches a saturation in the higher frequencys dispersive region [18]. This is possibly caused by the molecular dipoles which cannot stay constant with the rapidly changing field [23].

The dielectric spectra of PLA-ZnO are shown in Fig. 4(c) and (d). The ZnO nanoparticle that has been embedded on PLA enhances the dielectric constant and dielectric loss significantly. According to AC conductivity spectra, PLA-ZnO has a higher electrical conductivity. It indicates that the polarization and proliferation of large-mobile free ions occur in electrolyte [21]. However, the shortterm saturation on low frequencies reveals a fast-periodic reversal of the electric field and reduces the ion diffusion. Furthermore, the ions will disperse through the membrane and experiences a saturation phase in higher frequencies. According to previous study [24], Zn^{2+} will improve the ionic transport of polymer electrolyte.

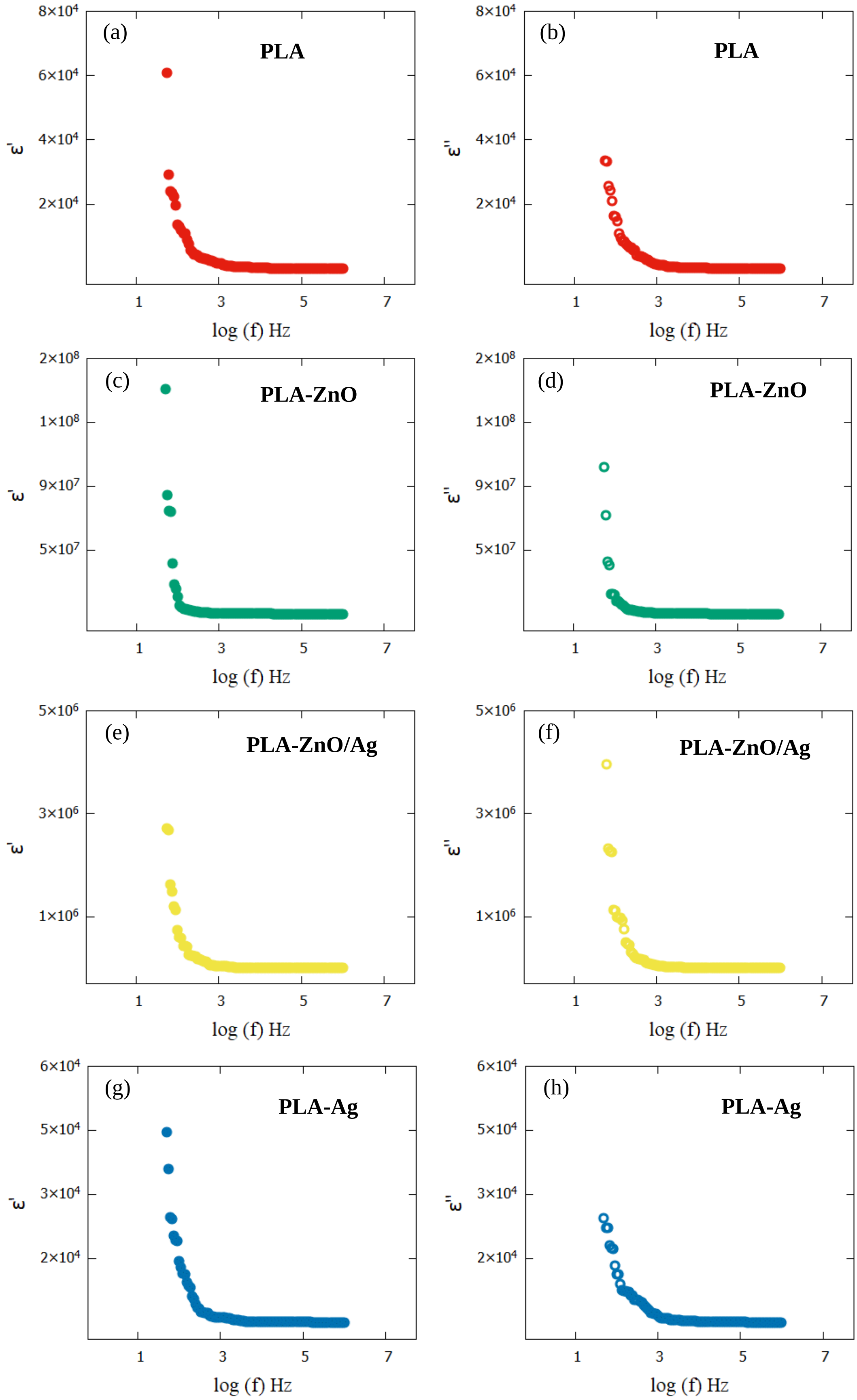

FIG. 4: Dielectric constant (ϵ') and dielectric loss (ϵ'') spectra of PLA, PLA-Ag, PLA-ZnO/Ag, and PLA-ZnO as a function of logarithmic frequency.

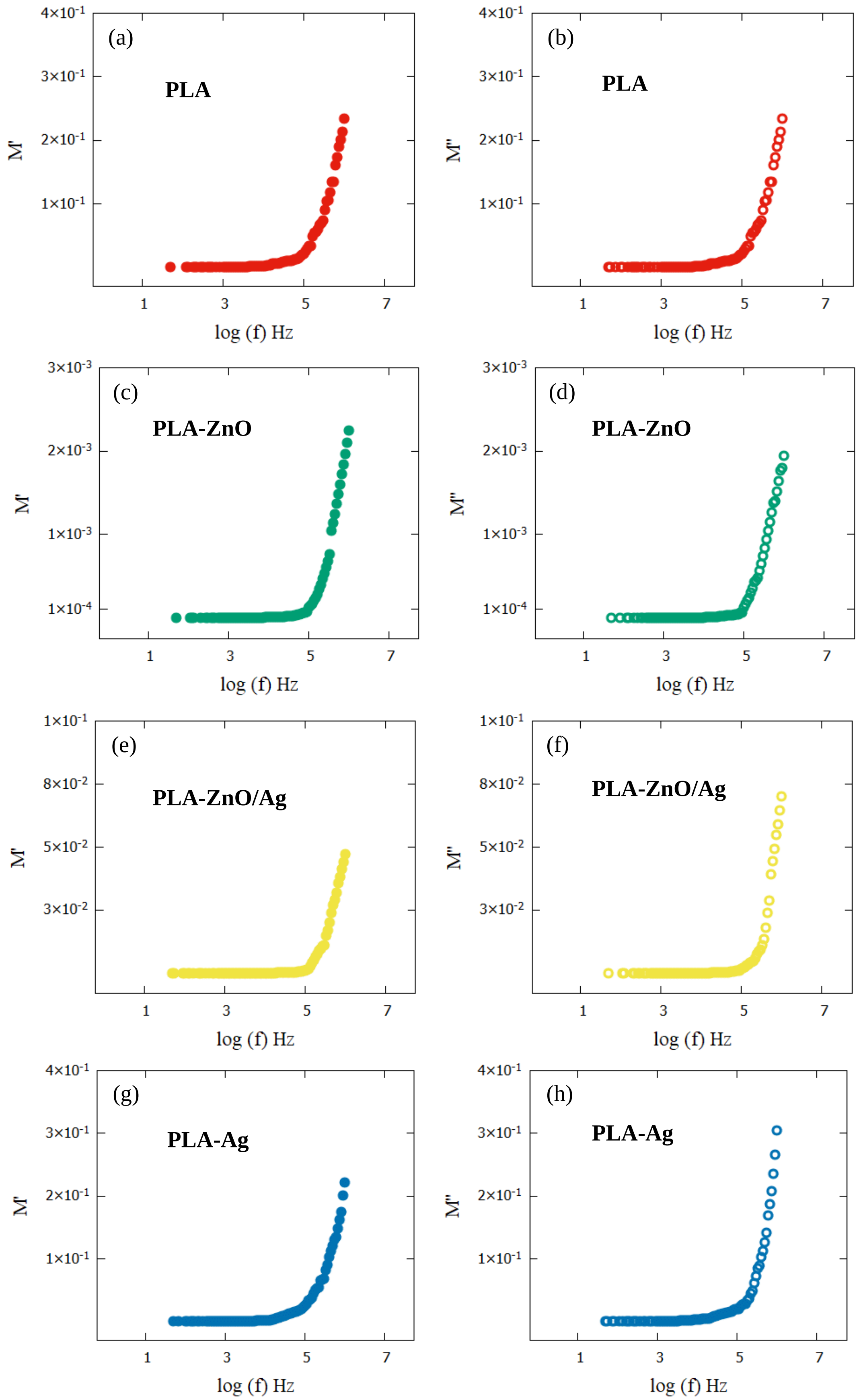

FIG. 5: Real (M') and imaginary (M'') modulus electric of PLA, PLA-Ag, PLA-ZnO/Ag, and PLA-ZnO as a function of logarithmic frequency.

ZnO would have the tendency to attract Zn^{2+} cations from the electrolyte regions; hence there is a possibility of the reversible reaction shown in Eq. (4).

$$ZnO + Zn^{2+} \longleftrightarrow ZnO : Zn^{2+} \tag{4}$$

These ZnO:Zn^{2+} species form charge regions space that induces local electric field and is responsible to the enhancement of Zn^{2+} ion mobility.

As shown in Fig. 4(e) and (f), the ϵ' and ϵ'' spectra of PLA-ZnO/Ag show a similar pattern as that in PLA and PLA-ZnO. The highest value are found at low frequency, indicating the magnitude of polarization and dipole accumulation. Meanwhile, the fast saturation at high frequency signifies ion diffusions and pairing effects that are accelerated by the presence of Ag [14, 25, 26]. We found that the ϵ' and ϵ'' of PLA-Ag have a short-term saturation at low frequency, as shown in Fig. 4(g) and (h). This phenomenon indicates that Ag addition in PLA helps the ionic transport on PLA membrane to become faster. We found a similar case in previous study by Shukur *et al.* [26]. At higher frequencies, the periodic reversal of the electric field occurs so fast that there is no ion diffusion in the applied field [26, 27]. Then, the accumulation of ions at the electrodeelectrolyte interface will decrease following a progressive decrease in its magnitude in the high frequency at ϵ'' spectra [26, 28].

Electric Modulus Study

The formalism that is helpful for study the conductivity relaxation occurring in polymer electrolytes is electrical modulus [29]. In electric modulus representation, the contributions of electrode polarization are ignored [12, 30]. The electric modulus has been calculated by Eqs. (5) and (6) [23].

$$M' = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} = j\omega C_0 z'' \tag{5}$$

$$M'' = \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} = j\omega C_0 z' \tag{6}$$

where ω is the angular frequency, and C_0 is the capacitance of dielectric cell without SPEs.

Fig. 5 (a) and (b) exhibit both the frequency dependence of real (M') and imaginary (M'') parts of electric modulus of PLA at room temperature, respectively. The M' values at lower frequencies are quite small, implying the removal of electrode polarization contribution [31]. The increase of M' with increasing frequency is expected due to the bulk effect [12]. Whereas in the imaginary part, the small value of M'' at low frequencies might be caused by the larger value of capacitance associated with the electrode, resulted from the large charge carriers accumulation at the electrodeelectrolyte interface [30]. Thus, we can say that the busies condition is caused by charge accumulation and diffusion [20]. At high frequencies, welldefined peaks are obtained, signifying that the relaxation process is induced by ions dispersion process [12, 14, 20, 30]. We also confirm that ZnO is playing a key role in the enhancement of the electrical activity. The electric modulus of PLA with ZnO addition reduces significantly. These results have linearity with their dielectric results, as shown in Fig. 5(c) and (d).

ZnO activities on PLA membrane give a large amount of polarization on electrodeelectrolyte interface, thus will reduce the relaxation at low frequency. It also yields a fast ion diffusion and dispersion process on the M' and M'' spectra due to Zn^{2+} mobility [24]. Furthermore, electrical modulus activity on PLA with ZnO/Ag addition can be seen in Fig. 5 (e) and (f). A similar pattern on its spectra is shown by lower values in low frequencies and high values in higher frequencies against real (M') and imaginary (M'') parts. A slight enhancement of electrical modulus occurs in this sample, therefore the conductivity relaxation and polarization as well as the ionic diffusion become slower than that of the samples with ZnO addition. We conclude that Ag decreases the conductivity of PLA based electrolytes. It indicates that the busies situation at low frequencies are slightly decreased. However, the ionic conductivity remains high and shows a low conductivity relaxation [12, 14, 20, 32].

In Fig. 5(g) and (h), we found the high electric modulus in PLA with Ag nanoparticles addition, yet still has a similar spectra. The M' of PLA-Ag shows a higher bulk effect compare with PLA. It is expected that PLA-Ag has a higher polarization than PLA at low frequencies or known as the busies region. It is also confirmed by M'', which has a lower value in low frequencies. This result is similar with the previous studies [16, 21] in which Ag is embedded in chitosan-based electrolyte. Referring to the studies on the properties of Ag as filler of polymer electrolytes, we may say that Ag could give more free charge ions within polymer chain and thus increase the ionic conductivity [16]. Moreover, the peaks at high frequencies are related by conductivity relaxation [32]. Despite it can increase the conductivity, PLA with Ag addition remains to have a lower dielectric properties than that of the PLA with ZnO or ZnO/Ag addition.

IV. SUMMARY

PLA with Ag, ZnO/Ag, and ZnO addition has been successfully synthesized by laser ablation. The EIS data point out differences in ionic conductivity, complex dielectric, and electric modulus among those three systems. The analyses confirm that the electrical feature can be used to determine a potential candidate for SPEs. Among the samples, PLA-ZnO has the highest ionic conductivity. However, PLA-ZnO/Ag has more potential as SPEs because the presence of Ag stabilizes the system.

Acknowledgment

This work was supported by Research Center for Physics-Indonesian Institute of Sciences and Ministry of Research and Technology and Higher Education Indonesia through Insentif Riset Sinas (INSINAS) grant on Active Packaging Based on ZnO nanoparticle at budget year 2019 No. 15INS1/PPK/E4/2019.

[1] R. Guo *et al.*, "Electrical and thermal conductivity of polylactic acid (PLA)-based biocomposites by incorporation of nanographite fabricated with fused deposition modeling", Polymers, vol. 11, pp. 549, 2019.
[2] A. Kim *et al.*, "Highly transparent low resistance ZnO/Ag nanowire/ZnO composite electrode for thin film solar cells", ACS Nano, vol. 7, pp. 1081-1091, 2013.
[3] R. Kotsilkova *et al.*, "Exploring thermal annealing and graphene-carbon nanotube additives to enhance crystallinity, thermal, electrical and tensile properties of aged poly(lactic) acid-based filament for 3D printing", Compos. Sci. Technol., vol. 181, pp. 107712, 2019.
[4] C. Dichtl, P. Sippel, S. Krohns, "Dielectric properties of 3D printed polylactic acid", Adv. Mater. Sci. Eng., vol. 10, pp. 659, 2017.
[5] Z. Chu *et al.*, "Characterization of antimicrobial poly (lactic acid)/nano-composite films with silver and zinc oxide nanoparticles", Materials, vol. 10, pp. 659, 2017.
[6] K. Shinyama, "Mechanical and electrical properties of polylactic acid with aliphatic-aromatic polyester", J. Eng., vol. 2018, pp. 7, 2018.
[7] Q. Zhang *et al.*, "High stable transparent and conductive ZnO/Ag/ZnO nanofilm electrodes on rigid/flexible substrates", Energies, vol. 9, pp. 443, 2016.
[8] S. Seong *et al.*, "Synthesis of Ag-ZnO core-shell nanoparticles with enhanced photocatalytic activity through atomic layer deposition", Mater. Des., vol. 177, pp. 107831, 2019.
[9] Y. Zhao, S. Li, Y. Zeng, Y. Jiang, "Synthesis and properties of Ag/ZnO core/shell nanostructures prepared by excimer laser ablation in liquid", APL Mater., vol. 3, pp. 086103, 2015.
[10] G. Al-Dahash *et al.*, "Preparation and characterization of ZnO nanoparticles by laser ablation in NaOH aqueous solution", Iranian Journal of Chemistry and Chemical Engineering., vol. 37, pp. 11-16, 2018.
[11] R. Anugrahwidya *et al.*, "Optical and structural investigation of synthesis ZnO/Ag nanoparticles prepared by laser ablation in liquid", Mater. Sci. Semicond. Process., vol. 105, pp. 104712, 2020.
[12] S. B. Aziz, O. G. Abdullah, S. R. Saeed, H. M. Ahmed, "Electrical and dielectric properties of copper ion conducting solid polymer electrolytes based on chitosan: CBH model for ion transport mechanism", Int. J. Electrochem. Sci., vol. 13, pp. 3812-3826, 2018.
[13] S. B. Aziz, "Role of dielectric constant on ion transport: Reformulated arrhenius equation", Adv. Mater. Sci. Eng., vol. 2016, pp. 11, 2016.
[14] A. Arya, M. Sadiq, A. L. Sharma, "Salt concentration and temperature dependent dielectric properties of blend solid polymer electrolyte complexed with NaPF6", Mater. Today Proc., vol. 12, pp. 554-564, 2019.
[15] I. Osada, S. M. Hosseini, S. Jeong, S. Passerini, "Novel ternary polymer electrolytes based on poly(lactic acid) from sustainable sources", ChemElectroChem., vol. 4, pp. 463-467, 2017.
[16] S. B. Aziz, Z. H. Z. Abidin, A. K. Arof, "Influence of silver ion reduction on electrical modulus parameters of solid polymer electrolyte based on chitosan-silver triflate electrolyte membrane", eXPRESS Polym. Lett., vol. 4, pp. 300-310, 2010.
[17] S. Choudhary and R. J. Sengwa, "Structural and dielectric studies of amorphous and semicrystalline polymers blend-based nanocomposite electrolytes", J. Appl. Polym. Sci., vol. 132, pp. 41311, 2015.
[18] N. Shukla, A. K. Thakur, A. Shukla, D. T. Marx, "Ion conduction mechanism in solid polymer electrolyte: An applicability of almond-west formalism", Int. J. Electrochem. Sci., vol. 9, pp. 7644-7659, 2014.
[19] S. B. Aziz *et al.*, "Ion transport study in CS: POZ based polymer membrane electrolytes using Trukhan model", Int. J. Mol. Sci., vol. 20, pp. 5265, 2019.
[20] N. Tripathi, A. Shukla, A. K. Thakur, D. T. Marx, "Electric modulus and conductivity scaling approach to the analysis of ion transport in solid polymer electrolytes", Polym. Eng. Sci., vol. 60, pp. 297-305, 2020.
[21] S. B. Aziz *et al.*, "Increase of metallic silver nanoparticles in chitosan:AgNt based polymer electrolytes incorporated with alumina filler", Results Phys., vol. 13, pp. 102326, 2019.
[22] C. H. Chan and H. Kammer, "Impedance spectra of polymer electrolytes", Ionics, vol. 23, pp. 2327-2337, 2017.
[23] S. B. Aziz *et al.*, "Employing of Trukhan model to estimate ion transport parameters in PVA based solid polymer electrolyte", Polymers, vol. 11, pp. 1694, 2019.
[24] Sellam and S. A. Hashmi, "Enhanced zinc ion transport in gel polymer electrolyte: Effect of nano-sized ZnO dispersion". J. Solid State Electrochem., vol. 16, pp. 3105-3114, 2012.
[25] V. Alzari *et al.*, "Study of polymeric nanocomposites prepared by inserting graphene and / or Ag, Au and ZnO nanoparticles in a TEGDA polymer matrix, by means of the use of dielectric spectroscopy", AIP Adv., vol. 6, pp. 035005, 2016.
[26] M. F. Shukur *et al.*, "Conduction mechanism and dielectric properties of solid biopolymer electrolyte incorporated with silver nitrate", Adv. Mater. Res., vol. 701, pp. 115-119, 2013.
[27] K. Ramly, M. I. N. Isa, A. S. A. Khiar, "Conductivity and dielectric behaviour studies of starch/PEO+x wt% NH_4NO_3 polymer electrolyte", Mater. Res. Innov., vol. 15, pp. s82-s85, 2011.
[28] S. Ramesh, T. F. Yuen, C. J. Shen, "Conductivity and FTIR studies on PEO-LiX [X: CF_3SO^{3-}, SO_4^{2-}] polymer electrolytes", Spectrochim. Acta - Part A Mol. Biomol. Spectrosc., vol. 69, pp. 670-675, 2008.
[29] S. B. Aziz, R. M. Abdullah, M. F. Z. Kadir, H. M. Ahmed, "Non suitability of silver ion conducting polymer electrolytes based on chitosan mediated by barium titanate (BaTiO3) for electrochemical device applications", Electrochim. Acta., vol. 296, pp. 494-507, 2019.
[30] L. N. Patro and K. Hariharan, "Frequency dependent conduction characteristics of mechanochemically synthesized $NaSn_2F_5$", Mater. Sci. Eng. B., vol. 162, pp. 173-178, 2009.
[31] S. Ramesh and O. P. Ling, "Effect of ethylene carbonate on the ionic conduction in poly(vinylidenefluoride-hexafluoropropylene) based solid polymer electrolytes", Polym. Chem., vol. 1, pp. 702-707, 2010.
[32] S. B Aziz, W. O. Karim, H. O. Ghareeb, "The deficiency of chitosan:$AgNO_3$ polymer electrolyte incorporated with titanium dioxide filler for device fabrication and membrane separation technology". J. Mater. Res. Technol., vol. 9, pp. 3, 2020.