The Ion Transport Characteristics of Chitosan Composite Membranes ‘Ch-AgNP’ with Emphasis on the Amount of Filler

Ni Nyoman Rupiasih*, W. G. Suharta, Made Sumadiyasa, I Ketut Putra and Ni Made Ayu Mega Trisnayani Putri

Department of Physics, Faculty of Mathematics and Natural Sciences, Udayana University, Kampus Bukit Jimbaran, Bali 80362, Indonesia

*Corresponding author: rupiasih@unud.ac.id

Abstract. In this study, we report about the characteristics of ion transport of chitosan composite membranes “chitosan-silver nanoparticle”. The chitosan composite membranes were prepared by a casting method using chitosan as a matrix, silver nanoparticle (AgNP) as filler, and acetic acid 1% as a solvent. The various amount of filler added e.g. 10, 100, 250, 500, 750, and 1000 μg. These membranes called chitosan composite membrane Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, Ch-AgNP500, Ch-AgNP750, and Ch-AgNP1000. A membrane without AgNP has also been prepared named chitosan membrane (Ch membrane) as a comparison. The ion transport experiments conducted by using a cell model consisting of two chambers, chamber 1 and 2, and the area of the membrane was 9.616 cm². The driving force used is a gradient concentration (dC/dx). The electrolyte solutions used were KCl and CaCl₂ with concentrations of 0.1, 1, 10, 100, 250, 500, 750, and 1000 mM. The voltage difference (V) is measured using Ag/AgCl electrodes which connected to a voltmeter. All measurements were done at room temperature, 28.1°C. The result showed that the obtained $J_{\text{diff}}-V$ curves of chitosan composite membranes are similar to $J_{\text{diff}}-V$ curves of Ch membrane, where the diffusion current densities of chitosan composite membranes increased with increasing the concentration gradient of solution. It also depends on the electrolyte solutions. The diffusion current density of chitosan composite membranes had affected by the amount of AgNP added that is increased as increasing the mass of AgNP added.

Keywords: chitosan membrane, chitosan composite membranes, silver nanoparticles, electrolyte solution, ion transport, diffusion current density

1. Introduction

Membrane technology is widely used in the field of industry, biology, and health so that more research on membrane phenomenon both biological membrane and artificial membrane. Membrane characterization is one of the many research subjects to learn more about membrane phenomena.

Chitosan is a natural polymer composed of glucosamine and N-acetyl glucosamine units linked by 1-4 glucosidic bonds. It is obtained by alkaline deacetylation of chitin which extracted from the exoskeleton of crustaceans such as shrimps and crabs, as well from the cell walls of some fungi [1].
Chitosan can be processed into several products including fine powders, membranes, sponges, fibers, and gels [2]. Some applications of chitosan membranes involve for active transport of chloride ions in aqueous solution [3], as a chelating agent of heavy metal ions [4], as a carrier and/or a selective barrier controlling the transport rate of the substances involved. Chitosan membrane has also been used to recover silver from X-ray film processing wastes [5], and as an anion-exchange membrane directly [6]. Also it has been reported, chitosan-polytetrafluoroethylene composite membrane applied for separation of methanol/toluene mixture by pervaporation [7], and the polyvinylidene fluoride (PVDF)/chitosan (CS) membranes is a potential solution on the low flux and fouling of common PVDF microfiltration membranes [8]. These characteristics make chitosan has considerable application in various industrial areas such as pharmaceutical and biomedical engineering, food industry, agriculture and wastewater treatment [9-12].

Many studies with various methods used by researchers, in particular, to improve the application of technology for industrial purposes. In various fields, membrane is an option in filtering, separating, and purifying chemically sensitive substances and environment.

In this research the focus is physical membrane characterization through ion transport properties which can be seen from the diffusion current density value of the membrane. By measuring this parameter, it will be able to explain the mechanism of external ion transport through the membrane especially on chitosan composite membranes so that through this research is expected to obtain important information in the progress of membrane technology.

2. Experimental methods

2.1. Materials

The chitosan composite membranes were prepared by a casting method using chitosan as a matrix, silver nanoparticle (AgNP) as filler, and acetic acid 1% as a solvent. The chitosan powder used has a degree of deacetylation (DD) of 87.4%, average molecular weight of 900,000, and the solubility in acetic acid 1% is 99.4%. The sodium hydroxide and acetic acid were analytical grade. Demineralized water was used in preparing solutions. Silver nanoparticles used has characteristics of particles size about 10-30 nm, Surface Plasmon Resonance (SPR) wavelength of 423 nm and crystal structure of face center cubic (FCC) with lattice parameter, a, of 4.03 Å [13]. The various amount of AgNP added e.g. 10, 100, 250, 500, 750, and 1000 μg. These membranes called chitosan composite membrane Ch-AgNP10, Ch-AgNP100, Ch-AgNP250, Ch-AgNP500, Ch-AgNP750, and Ch-AgNP1000. A membrane without AgNP has also been prepared named Ch membrane as a comparison.

2.2. The ion transport measurement

The ion transport measurements were done using a cell membrane model which composed of two compartments, compartment 1 and 2, and the area of the membrane was 9.616 cm². The driving force used is a gradient concentration of the solution (dC/dx) between the two chambers. The electrolyte solutions used were KCl and CaCl₂ with concentrations of 0.1, 1, 10, 100, 250, 500, 750 and 1000 mM. The potential difference through the membrane was measured using Ag/AgCl electrodes which connected to a voltmeter. All measurements were conducted at room temperature of 28.1 °C.

3. Results and discussion

3.1. The characteristics of the voltage difference of chitosan composite membranes (Ch-AgNP)

The average voltage differences (further it calls as the voltage differences (V)) of the membranes measured are shown in Tables 1 and 2, for KCl and CaCl₂ solutions respectively. In accordance with the Nernst equation (1), if the concentrations in the two chambers are equal then the voltage difference equals to zero. But experimentally at the same concentrations, there is a voltage difference measured.
This can be described as the voltage difference generated by the membrane itself, in this case the chitosan membrane is a positive membrane, so it formed polarization of charges on both sides of the membrane surfaces e.g. Cl⁻ ion at the both sides membrane surfaces [14].

\[ V = 2.303 \frac{k_B T}{z e} \log \left( \frac{C_1}{C_2} \right) \]  

(1)

Where \( k_B \) is Boltzmann constant (1.38 \times 10^{-23} \text{ JK}^{-1}), \( T \) is absolute temperature, \( e \) is electron charges (1.602 \times 10^{-19} \text{ C}), \( z \) is ion valence, \( C_1 \) and \( C_2 \) are concentration of the solution in chamber 1 and 2.

**Table 1.** The voltage difference data of Ch membrane and chitosan composite membranes (Ch-AgNP) measured in KCl solution.

| Concentration of solution (mM) | \( V \pm \text{sd} \) (x 10³ V) |
|-------------------------------|---------------------------------|
| Chamber 1 Chamber 2           | Ch membrane                      |
|                               | Ch-AgNP10 membrane               |
| 0.1                           | 0.50 ± 0.10                      |
| 1                             | 0.80 ± 0.04                      |
| 10                            | 1.20 ± 0.06                      |
| 100                           | 1.33 ± 0.06                      |
| 250                           | 1.67 ± 0.06                      |
| 500                           | 1.93 ± 0.06                      |
| 750                           | 2.23 ± 0.06                      |
| 1000                          | 2.53 ± 0.06                      |

| Chamber 1 Chamber 2           | Ch membrane                      |
|                               | Ch-AgNP100 membrane              |
| 0.1                           | 0.87 ± 0.06                      |
| 1                             | 1.30 ± 0.10                      |
| 10                            | 1.67 ± 0.06                      |
| 100                           | 1.93 ± 0.06                      |
| 250                           | 2.27 ± 0.06                      |
| 500                           | 2.53 ± 0.06                      |
| 750                           | 2.83 ± 0.06                      |
| 1000                          | 3.10 ± 0.10                      |

| Chamber 1 Chamber 2           | Ch membrane                      |
|                               | Ch-AgNP250 membrane              |
| 0.1                           | 1.30 ± 0.10                      |
| 1                             | 1.77 ± 0.06                      |
| 10                            | 2.10 ± 0.10                      |
| 100                           | 2.33 ± 0.06                      |
| 250                           | 2.77 ± 0.06                      |
| 500                           | 3.13 ± 0.06                      |
| 750                           | 3.47 ± 0.06                      |
| 1000                          | 3.83 ± 0.10                      |

| Chamber 1 Chamber 2           | Ch membrane                      |
|                               | Ch-AgNP500 membrane              |
| 0.1                           | 1.57 ± 0.06                      |
| 1                             | 1.87 ± 0.06                      |
| 10                            | 2.17 ± 0.06                      |
| 100                           | 2.33 ± 0.06                      |
| 250                           | 2.67 ± 0.06                      |
| 500                           | 2.93 ± 0.06                      |
| 750                           | 3.23 ± 0.06                      |
| 1000                          | 3.57 ± 0.10                      |

| Chamber 1 Chamber 2           | Ch membrane                      |
|                               | Ch-AgNP750 membrane              |
| 0.1                           | 1.77 ± 0.06                      |
| 1                             | 2.07 ± 0.06                      |
| 10                            | 2.33 ± 0.06                      |
| 100                           | 2.67 ± 0.06                      |
| 250                           | 3.00 ± 0.10                      |
| 500                           | 3.37 ± 0.06                      |
| 750                           | 3.73 ± 0.06                      |
| 1000                          | 4.03 ± 0.06                      |

| Chamber 1 Chamber 2           | Ch membrane                      |
|                               | Ch-AgNP1000 membrane             |
| 0.1                           | 1.90 ± 0.10                      |
| 1                             | 2.37 ± 0.06                      |
| 10                            | 2.63 ± 0.06                      |
| 100                           | 3.00 ± 0.10                      |
| 250                           | 3.47 ± 0.06                      |
| 500                           | 3.80 ± 0.10                      |
| 750                           | 4.27 ± 0.06                      |
| 1000                          | 4.80 ± 0.10                      |

The graphs of the voltage differences (V) vs. \( \log(C_1/C_2) \) are presented in Figure 1 and 2. Figures 1 and 2 show graph of the voltage differences vs. \( \log(C_1/C_2) \). It shows that the voltage difference increased as increasing the concentration ratio (\( C_1/C_2 \)). At low concentration ratios, 0.1: 0.1, 0.1: 0.1, 10: 0.1, and 100: 0.1, the voltage differences increase linearly, but at high concentration ratios, 250: 0.1, 500: 0.1, 750: 0.1, and 1000: 0.1, the increase in voltage difference is exponential relation. These results are in accordance with Nernst equation (1) that in aqueous solution (solution with low concentration), the membrane voltage difference is directly proportional to logarithmically with the ion concentration ratio (\( \log(C_1/C_2) \)). This is observed both on chitosan membrane (Ch) and chitosan composite membranes and is observed in both types of electrolyte solutions (KCl and CaCl₂). Figures 1 and 2 also show that the addition of AgNP with various masses affect the voltage difference characteristics of the chitosan.
composite membranes, that is, by increasing the mass of AgNP added, the greater the membrane voltage difference obtained.

**Figure 1.** Graph of voltage difference (V) vs. log(C₁/C₂) of chitosan membrane and chitosan composite membranes (Ch-AgNP) in KCl electrolyte solution.

**Figure 2.** Graph of voltage difference (V) vs. log(C₁/C₂) of chitosan membrane and chitosan composite membranes (Ch-AgNP) in CaCl₂ electrolyte solution.

At low concentration regions, by doing linear regression obtained gradients of each curve as shown in Table 3. Table 3 shows that the gradient of the Ch membrane is smaller than that of the chitosan composite membranes. While the variation of AgNP added from 10 - 1000 μg affect the gradients around 1%-7% in KCl solution and around 1.2%-7.6% in CaCl₂ solution randomly. These results show that the solutions affect the ion transport process (gradient) of the membranes.

**Table 3.** The gradient of each curve of ‘membrane voltage difference vs. log(C₁/C₂)’ at concentration ratios (C₁/C₂) is 0.1: 0.1, 1: 0.1, 10: 0.1, and 100: 0.1.

| Membranes    | Gradient in KCl solution | Gradient in CaCl₂ solution |
|--------------|--------------------------|----------------------------|
| Ch           | 0.293                    | 0.317                      |
| Ch-AgNP10    | 0.357                    | 0.393                      |
| Ch-AgNP100   | 0.333                    | 0.393                      |
| Ch-AgNP250   | 0.333                    | 0.373                      |
| Ch-AgNP500   | 0.303                    | 0.330                      |
| Ch-AgNP750   | 0.32                     | 0.329                      |
| Ch-AgNP1000  | 0.363                    | 0.357                      |

3.2. The characteristic of the diffusion current density of chitosan composite membranes (Ch-AgNP)

The diffusion current density (J_{diff}) of each membrane can be calculated using equation (2) and the results are presented in Figure 3 and 4.

\[
J_{\text{diff}} = V \frac{x^2 \cdot z \cdot e}{k_B \cdot T \cdot t \cdot \left( \log \left( \frac{C_1}{C_2} \right) \right)^2} \frac{\Delta C}{\Delta x}
\]

(2)

Where x is the distance of the voltage difference measured and t is time.
Figures 4 and 5 show that the diffusion current densities increase linearly as increased concentration gradient on two chambers. This condition is observed both, in the Ch membrane and in chitosan composite membranes. The similar study of Ch membrane also has been reported in the ref. [15]. This is in accordance with first Fick’s Law (equation (3)) [14].

\[
J_{\text{diff}} = -D \frac{dC}{dx}
\]  

(3)

Where \(D\) is diffusion coefficient and \(\frac{dC}{dx}\) is concentration gradient. So, by taking the gradient of each curve, the properties of diffusion current densities of both membranes can be explained as shown in Table 4.

**Figure 3.** Graph of the diffusion current density \((J_{\text{diff}})\) with concentration gradient \((\Delta C/\Delta x)\) of Ch membrane and chitosan composite membranes \((\text{Ch-AgNP})\) in KCl solution.

**Figure 4.** Graph of the diffusion current density \((J_{\text{diff}})\) with concentration gradient \((\Delta C/\Delta x)\) of Ch membrane and chitosan composite membranes \((\text{Ch-AgNP})\) in CaCl\(_2\) solution.

Table 4 shows the gradients of each curve (which according to Fick I law is called diffusion coefficient (D)) of Ch membrane is smaller than the chitosan composite membranes which occurs on both solutions. This means that the number of ions diffusing per unit area on Ch membrane is smaller than that of the chitosan composite membranes. It also appears that the gradient increases with increasing AgNP content. From the gradients ratio (the last column on Table 4), it showed that the diffusion current density in aqueous CaCl\(_2\) solution (low concentration solution) on the Ch membrane and the chitosan composite membranes with AgNP of 10 to 250 μg were more than 2-fold compared with KCl solution. While on the composite membranes with AgNP of 500 - 1000 μg, the diffusion current density on CaCl\(_2\) solution slightly larger about 5% - 13% compared with KCl solution. These results indicate that the addition of AgNP has affected the characteristics of the diffusion current density of the chitosan composite membranes. It is also observed that the solutions greatly affect the ion transport characteristics, both on Ch membrane and chitosan composite membranes. The similar study also has been reported in the ref. [16, 17].
Table 4. Gradient of the $J_{\text{diff}} - (\Delta C/\Delta x)$ graph of each membrane and the gradient ratio.

| Membranes | Gradient (Am$^2$M$^{-4}$) KCl solution | CaCl$_2$ solution | gradient in CaCl$_2$ : gradient in KCl |
|-----------|-----------------------------------------|--------------------|----------------------------------------|
| Ch        | $0.99 \times 10^{-6}$                  | $2.44 \times 10^{-6}$ | 2.26                                   |
| Ch-AgNP10 | $1.22 \times 10^{-6}$                  | $2.54 \times 10^{-6}$ | 2.08                                   |
| Ch-AgNP00 | $1.33 \times 10^{-6}$                  | $3.61 \times 10^{-6}$ | 2.21                                   |
| Ch-AgNP25 | $1.45 \times 10^{-6}$                  | $3.11 \times 10^{-6}$ | 2.14                                   |
| Ch-AgNP50 | $2.97 \times 10^{-6}$                  | $3.16 \times 10^{-6}$ | 1.06                                   |
| Ch-AgNP50 | $3.11 \times 10^{-6}$                  | $3.31 \times 10^{-6}$ | 1.05                                   |
| Ch-AgNP100| $3.37 \times 10^{-6}$                  | $3.40 \times 10^{-6}$ | 1.13                                   |

From the voltage differences (V) data in Tables 1 and 2, and the diffusion current densities ($J_{\text{diff}}$) on Figure 3 and 4, graph made to represent the relation between $J_{\text{diff}}$ and V as shown in Figure 5 and 6. Figures 5 and 6 showed that the diffusion current density increases exponentially with an increase in the potential differences. These are in accordance with the potential difference which is a function of $\log(C1/C2)$, Figure 1 and 2 so that the diffusion current densities are also very dependent on a $\log(C1/C2)$. At initial, the diffusion current density increases very slowly (image insert), then at a certain potential difference the diffusion current density increases very sharply. The similar result also has reported in the previous study in the ref. [15]. Where for the composite membranes, the curve begins to rise sharply it shifts toward a larger potential difference and a larger the diffusion current density the curve begins to parallel to each other. It shows that the diffusion current density in CaCl$_2$ solution shifts to the right side, toward a larger potential difference when compared to the diffusion current density in KCl solution. These results indicated that the AgNP addition and the use of different types of solutions have an effect on the Jdiff - V characteristics on both membranes, Ch membrane, and chitosan composite membranes.

Figure 5. Graph of the diffusion current density ($J_{\text{diff}}$) with concentration gradient ($\Delta C/\Delta x$) of Ch membrane and chitosan composite membranes (Ch-AgNP) in KCl solution.

Figure 6. Graph of the diffusion current density ($J_{\text{diff}}$) with concentration gradient ($\Delta C/\Delta x$) of Ch membrane and chitosan composite membranes (Ch-AgNP) in CaCl$_2$ solution.

4. Conclusion
This study described the characteristics of ion transport of chitosan composite membranes “chitosan-silver nanoparticle (Ch-AgNP)”. The $J_{\text{diff}}$ - V curves were determined in KCl and CaCl$_2$ solutions. The obtained $J_{\text{diff}}$ - V curves of chitosan composite membranes are similar to $J_{\text{diff}}$ - V curves of Ch membrane, where the diffusion current densities of chitosan composite membranes increased with increasing the concentration gradient of the solution. It also depends on the electrolyte solutions. The diffusion current
density of chitosan composite membranes had affected by the amount of AgNP added that is increased as increasing the mass of AgNP content.

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