

Effect Concentration of Citric Acid Solution on Properties Double Layer Electrodes in Impedance Spectroscopy Measurements

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ABSTRAK

Penelitian mengenai bahan biologi dengan menggunakan bahan dielektrik telah banyak dilakukan, namun saat ini belum banyak penelitian yang menggunakan bahan/larutan elektrolit. Tujuan penelitian ini adalah untuk mengetahui hubungan antara konsentrasi larutan dengan nilai impedansi larutan, serta hubungan antara frekuensi dengan nilai impedansi larutan. Penelitian ini menggunakan teknik spektroskopi impedansi elektrokimia (SIE) dalam larutan Asam Sitrat ($C_6H_8O_7$). Hasil penelitian yang diperoleh menunjukkan bahwa nilai impedansi merupakan bilangan kompleks dengan bagian real (Z') dan bagian imajiner (Z''). Nilai impedansi (Z') dapat dibedakan dengan baik pada rentang frekuensi 100 Hz – 1 kHz dengan variasi konsentrasi $17.10^{(-5)}$ M – $85.10^{(-5)}$ M frekuensi rendah pengaruh konsentrasi terhadap nilai impedansi (Z') tidak dapat dibedakan dengan baik, namun pada frekuensi tinggi pengaruh konsentrasi larutan terhadap nilai impedansi dapat dibedakan dengan baik. Pada rentang frekuensi >100 kHz nilai impedansi tidak dapat dibedakan dengan baik karena perangkat menjadi kurang sensitif terhadap perubahan frekuensi. Penelitian ini menunjukkan bahwa spektroskopi impedansi elektrokimia dapat digunakan untuk mempelajari pengaruh konsentrasi dan frekuensi terhadap sifat lapisan ganda dalam larutan asam sitrat.

Research on biological materials using dielectric materials has been widely conducted, but currently there are not many studies using electrolyte materials/solutions. The purpose of this study is to determine the relationship between solution concentration and solution impedance value, as well as the relationship between frequency and solution impedance value. This study uses the electrochemical impedance spectroscopy (EIS) technique in Citric Acid ($C_6H_8O_7$) solution. The results of the study obtained indicate that the impedance value is a complex number with a real part (Z') and an imaginary part (Z''). The impedance value (Z') can be distinguished well in the frequency range of 100 Hz - 1 kHz with a concentration variation of $17.10^{(-5)}$ M - $85.10^{(-5)}$ M. At low frequencies, the effect of concentration on the impedance value (Z') cannot be distinguished well, but at high frequencies, the effect of solution concentration on the impedance value can be distinguished well. In the frequency range >100 kHz, the impedance value cannot be distinguished well because the device becomes less sensitive to changes in frequency. This study shows that electrochemical impedance spectroscopy can be used to study the effects of concentration and frequency on the properties of double layers in citric acid solutions.

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I. INTRODUCTION

Currently, several studies have been conducted on biological materials using dielectric materials such as impedance measurements on tilapia (Putri et al., 2017) and milk (Gabriel Durante et al., 2016) with the addition water and aquades. Electrical impedance is an electrical quantity that can be used to determine the bioelectrical characteristics of biological materials (Khalil et al., 2014). From these studies, the biological material that is measured is a dielectric material, while electrolyte solutions have been rarely researched.

Impedance spectroscopy is a useful technique for investigating the electrical properties of condensed materials (Zhao et al., 2017). Measurements using the electrochemical impedance spectroscopy technique (Gunawan et al., 2018) can be divided into three frequency domains, namely the high-frequency range associated with the transfer of charge to the counter electrode, the medium frequency region associated with the transfer of electrons in the sample and in the region with two low frequency usually reflects surface effects due to the dynamics of the electrolyte particles (Lima et al., 2017). Electrochemical impedance spectroscopy (EIS) is a measurement method that can be used to determine the electrical properties of a material (Liu et al., 2018). This method can be used to study intrinsic properties related to the conductivity of electrochemical cells. These intrinsic properties can be divided into two, namely properties related to the material itself such as charge mobility, equilibrium concentration, conductivity, and dielectric constant, and properties related to electrodes and materials such as intersurface capacitance, diffusion coefficient, and adsorption reaction rate. Bioelectricity is an electrical characteristic of cells that exist in living things (Schofield et al., 2020). Bioelectric characteristics that can be observed including impedance, capacitance, inductance, electrical conductivity, and dielectric constant (Kustyanto et al., 2019).

The EIS method is carried out by injecting an electrical or input stimulus, either in the form of a potential or an electric current, then measuring the output value in the form of a signal (potential or current) (Liu et al., 2018). Citric Acid ($C_6H_8O_7$) is part of the electrolyte solution, which has electrical conductivity (Ciriminna et al., 2017). Electrolyte solutions can be divided into several types, namely, acids, bases, and salts (Dewi et al., 2016). The three types of electrolyte solutions can conduct different electric currents. In this measurement, alternating current (AC) is used. If direct current (DC) is used, electrolysis and polarization will occur, namely modification of the composition of the charge layer in contact with the electrode. The electrical conductivity of a material can be related to the conductivity of the material, the impedance of the material. Thus a solution of citric acid ($C_6H_8O_7$) can be used in measuring electrical characteristics using the EIS method (Abraha, 2017).

The phenomenon of the appearance of a surface layer on an electrode is very important in electrochemical and electrostatic studies. When a metal electrode is immersed in an electrolyte solution, an electrical double layer will form between the metal surface and the electrolyte (Jurado & Espinosa-Marzal, 2017). This double electric layer (EDL) plays a very important role in the phenomenon of the electrode/electrolyte interface (Bohra et al., 2019). When ions have a charge that is opposite to the charge on the surface of the electrode, these ions will accumulate on the surface of the electrode, otherwise ions that have a charge similar to the charge on the electrode will be repelled. As a result, a potential difference will appear between the electrode and the electrolyte solution. Several studies have been made to understand the effect of EDL on physical and chemical systems (Velikonja et al., 2015). This study aims to determine relationship between solution concentration and solution impedance value, and between frequency and solution impedance value.

II. METHOD

In the impedance measurement, the sample citric acid is inserted into the chamber using a syringe so that no airwaves arise in the chamber. Measurements were made at a frequency range of 1 Hz to 1 MHz which was set via the picoscope software on the computer, and the current used was 100 μ A which was set on the V to I converter. Measurements were carried out on each sample solution with seven different concentration variations, after finishing the first solution then the next solution in the was carried out on same way. Channel 1 is the input voltage (V input) in the form of a blue sinusoidal wave, and channel 2 is the output voltage (V output) in the form of a red sinusoidal wave. The measured input and output values will be read in the picoscope table at the bottom, in the form of peak-to-peak

(V_{pp}) voltage values. Measurement of the conductivity of the $C_6H_8O_7$ solution was carried out in parallel with 3 repetitions of the experiment. Conductivity was measured using a conductive meter.

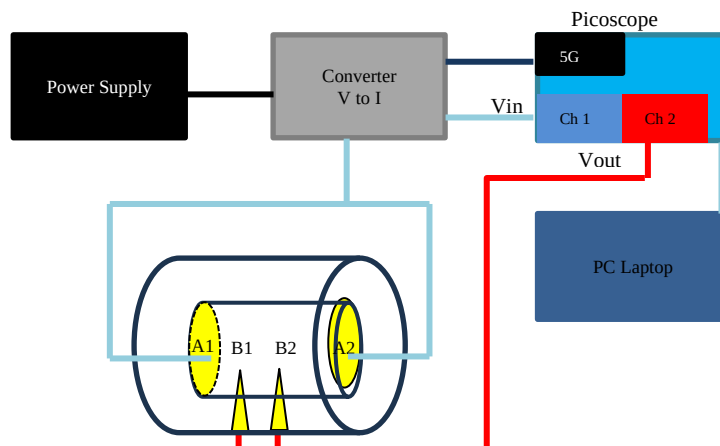


Figure 1 Design of a 4-electrode measurement circuit

III. RESULT AND DISCUSSION

Measurement of the impedance value was carried out three times for citric acid solutions with different concentrations. The results obtained are in the form of a graph plot of impedance as a function of frequency between solutions with each of the 7 different concentrations. The use of a logarithmic scale on the graph of impedance as a function of frequency since the impedance value depends on the components of resistance and capacitance. The use of a logarithmic scale on the impedance graph as a function of frequency makes it possible to display the data more clearly, identify relevant trends, and understand the relationships between the various experimental parameters. The graph of the citric acid solution depicts the impedance portion of the complex which consists of real (Z') and imaginary (Z'') parts. Impedance values (Z') can be distinguished well in the frequency range of 100 Hz - 1 kHz, this frequency range is influenced by the resistance and double-layer capacitance on the electrode which is quite large. The effect of this double layer can inhibit the movement of ions so that currents are unable to penetrate the electrode.

The impedance drop in the frequency range of 1 kHz – 100 kHz is affected by the double layer capacitance which decreases with increasing frequency, in which case there is a large enough migration of ions which causes the current to be able to pass through the double layer and penetrate the electrode. The values measured in citric acid solutions with various concentrations have a range of impedance values of 8000 Ω to 424 Ω in testing with a fixed concentration and an increase in frequency, the double layer properties will remain (permanent). At low frequencies the effect of concentration on the impedance (Z') cannot be well distinguished, but at high frequencies the effect of the concentration of the solution on the impedance can be well distinguished.

The higher the concentration of the solution, the smaller the impedance (Z'), conversely the lower the value of the concentration of the solution, the greater the value of the impedance (Z'). In the frequency range >100 kHz the impedance values cannot be distinguished properly because the instrument is increasingly insensitive to changes in frequency. In essence, the higher the frequency, the harder it is for the measuring instrument to give accurate results. This is because at high frequencies, small components in the circuit (such as cables, connectors) that are usually ignored at low frequencies, start to have a significant effect. This interferes with the actual impedance measurement and at high frequencies, electronic noise becomes stronger and can mask the signal you are trying to measure. $C_6H_8O_7$ is a resistive electrolyte solution. The impedance value measurement results based on the above data appear capacitive properties caused by the double-layer effect.

Currents can arise due to oxidation and reduction reactions on the surface. The electrode, like the Helmholtz surface theory in Figure 5, is an electrical double layer. The surface of the electrode will be electrically charged when connected to a voltage source. Ions that have a charge opposite to the charge on the electrode in the citric acid solution will be attracted to the surface of the electrode to form a Helmholtz surface. The charge on the Helmholtz surface and the electrode surface will form an electrical double layer. If the metal electrode is negatively charged, the positively charged ions in the

solution are attracted to the metal surface and the negatively charged ions are repelled. The process of adsorption of electrons from metal to electrolyte occurs in the Inner Helmholtz Plane (IHP) so that this layer experiences a linear potential decrease, the Outer Helmholtz Plane (OHP) is the boundary between the Stern layer and the diffusion layer, the Diffusion layer is where the potential decreases exponentially.

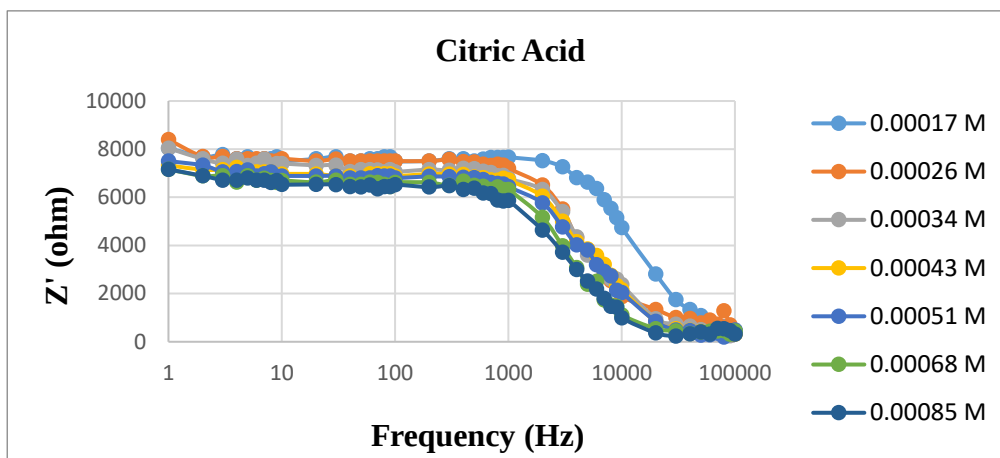


Figure 2 Graph of real parts (Z') of electrical impedance against frequency at seven variations of concentration of citric acid solution ($C_6H_8O_7$)

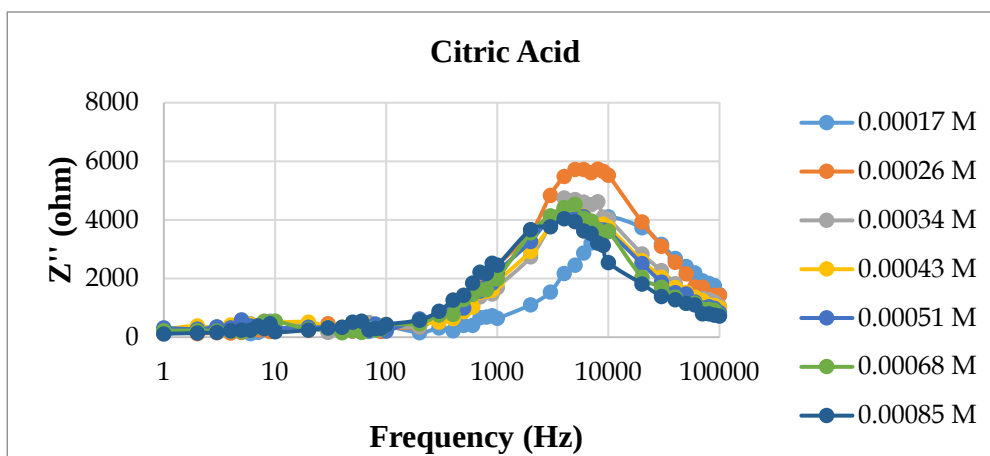


Figure 3 Graph of the imaginary parts (Z'') of electrical impedance against frequency at seven variations of concentration of citric acid solution ($C_6H_8O_7$)

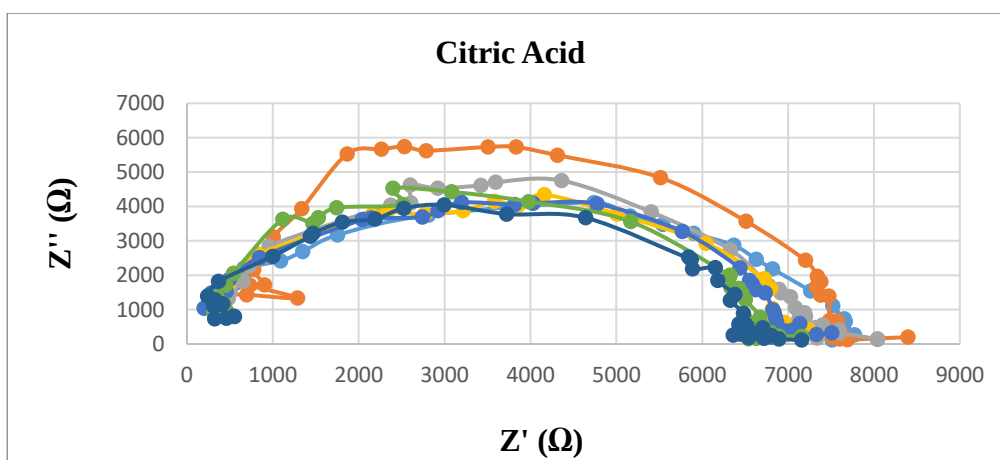


Figure 4 Graph of the nyquist plot at seven variations of citric acid solution concentration ($C_6H_8O_7$)

Increasing the concentration of citric acid solution causes a decrease in the movement of ions because the distance between the ions becomes closer. When the concentration of citric acid solution increases, the number of ions present also increases. The presence of more and more ions makes the

potential greater and gives a greater driving force for the ions to move towards the electrode so that it will easily penetrate the double layer. This will cause the impedance value to decrease. The imaginary graph (Z'') in Figure 3 shows anionic relaxation at frequencies > 100 kHz which has the same tendency at low frequencies. This is in accordance with the Nyquist modeling analogy that has been made (Figure 4). Citric acid solution ($C_6H_8O_7$) is an electrolyte solution that is weak acid, with increasing electrolyte concentration, the characteristic frequency will shift to a higher value, in other words if the concentration of the electrolyte solution is high enough, the characteristic frequency will be very high. The frequency of this characteristic is influenced by the value of resistance and capacitance. So, in the Nyquist plot above we can observe that the arc is half the circle will get smaller with increasing concentration.

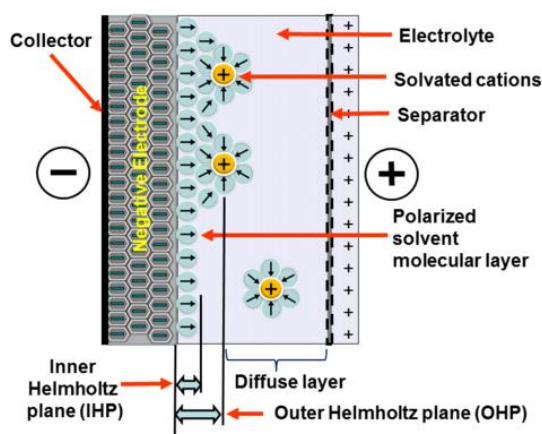


Figure 5 Helmholtz surface theory double-layer of negative ions in the electrode and solvated positive ions in the liquid electrolyte, separated by a layer of polarized solvent molecules

IV. CONCLUSION

The results of the study are in accordance with the theory that the concentration of citric acid affects the value of the electrical impedance of the citric acid solution, the impedance value of citric acid decreases as the concentration of the citric acid solution increases. Impedance measurement of citric acid solution for current injection of $100 \mu A$ could not differentiate between citric acid concentration variations with a frequency of more than 100 kHz.

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