

# Set Up Improvement of Impedance Spectroscopy Characterization of Chitosan Membranes

Prajak Saeung<sup>1</sup>, Wissarut Pauypung<sup>1</sup>, Pikul Wanichapichart<sup>2,3</sup>

<sup>1</sup>Membrane Science and Technology Research Center, Department of Physics,

Faculty of Science, Prince of Songkla University, Hat-Yai, Songkla 90110, Thailand

<sup>2</sup>NANOTEC Center of Excellence at Prince of Songkla University, Prince of Songkla University,  
Hat-Yai, Songkla 90110, Thailand

<sup>3</sup>ThEP Center, CHE, 328 Si Ayutthaya Rd., Bangkok 10400, Thailand

## ABSTRACT

An Electrochemical Impedance Spectroscopy (EIS) technique was used to measure electrical properties of membranes as a function of frequency. A small signal of AC potential was applied to a charged chitosan membrane with amplitude of 2V over a frequency range of 100–300 kHz. An experimental set up was improved by adjusting two measuring electrodes from vertical to horizontal direction to the membrane plane, and being closer to the membrane surface. The test membrane was made from 400K MW chitosan with 78 % DDA. Electrical properties of the membrane were investigated by immersing the membrane in KCl solution. The results showed that the impedance obtained from vertical and horizontal direction was 17.2 kΩ and 1.3 kΩ, respectively, in 0.1 mM salt concentration. When the salt concentration was reduced by ten fold to 0.01 mM, the measured value for the former and the latter was 30.1 kΩ and 4.5 kΩ, respectively. After this improvement, the conductance and capacitance of membranes were also greater by 90 % approximately. Moreover, the membranes exhibited much greater diffusion potential and ionic permeability ratios.

**Keywords:** *Impedance spectroscopy, Diffusion potential, Chitosan membrane.*

## 1. INTRODUCTION

An electrochemical impedance spectroscopy (EIS) is the method for measuring changes in the electrical properties of synthetic membranes or investigating ion-transport characteristics of ion-exchange membrane systems (Jin-Soo Park *et al.*, 2006, Antonio Alcaraz *et al.*, 1998 and T.C. Chilcott *et al.*, 2002). Membrane ionic conductance and capacitance were revealed under electrolyte solutions. There are many work report about EIS set up with comments on the effect of EIS electrode positioning to the impedance value. Unnecessary impedance has been arisen due to electrolyte in between membrane – electrode distance. For this reason, measuring impedance is not exactly (T.C. Chilcott *et al.*, 2002, HansG .L. Coster *et al.*, 1996 and Pikul Wanichapichart and Liangdeng Yu., 2007), and there is a need to improvement the EIS measurement set up. By applying physically-sound equivalent circuit models wherein physiochemical processes occurring within the membrane in electrolyte solutions are represented by a parallel network of ionic conductance ( $G$ ) and capacitance ( $C$ ) at the membrane-electrolyte interfaces. Previously, combination terms between effective values of ionic conductance ( $G_{\text{eff}}$ ) and capacitance ( $C_{\text{eff}}$ ), in parallel, were utilized to represent a charged membrane being sandwiched by an electrolyte as shown in Figure 1 (HansG .L. Coster *et al.*, 1996). A vector sum of these two values is the impedance ( $Z_{\text{eff}}$ ),

which is frequency dependent. Recently, Wanichapichart and Yu (Pikul Wanichapichart and Liangdeng Yu., 2007) have investigated changes in these electrical properties using the four-point probe method under a frequency range between 100 Hz and 300 kHz. A pair of calomel electrodes was used to measure voltages across the test membrane, while another pair of Ag/AgCl electrodes conveyed a signal from a function generator to membrane chambers. However, the detected signals were rather weak. It is, therefore, required an improvement of the set up. To verify the achievement, membrane diffusion potentials ( $\Delta\Psi$ ) was also studied to compare the voltage and ionic selectivity with the previous set up (Pikul Wanichapichart and Liangdeng Yu., 2007 and W. Puthai *et al.*, 2005).

Chitosan is the N-deacetylated derivative of chitin which is easily dissolved in a weak acid solution. It can also act as a cationic polyelectrolyte because of its free amino groups (Ying Wan *et al.*, 2003) and be favorable for anions to diffuse through the membrane. Figure 2 illustrates the molecular structures of chitosan segment. The aim of this study is to improve our previous EIS set up. This is to minimize unnecessary impedance arising from membrane surrounding electrolyte. The effective membrane impedance,  $Z_{\text{mem}}$  (T.C. Chilcott *et al.*, 2002 and HansG .L. Coster *et al.*, 1996) could be achieved by

placing the measuring electrodes closer to the membrane surfaces.

## 2. MATERIALS AND METHODS

### 2.1 Membranes Preparation

As described before (Pikul Wanichapichart and Liangdeng Yu., 2007), chitosan membrane was prepared by the oven-dry method. In details; chitosan flakes (MW 400,000 Fluka) were dissolved in 1% acetic acid to make up a 1% (w/v) chitosan solution and degree of deacetylation (DDA) of chitosan at 78%. The solution was mixed with 0.004% glutaraldehyde in a phosphate buffer and it was oven-dried at 40 °C for 2 days. A 4% (w/v) NaOH solution was poured over the dried membranes to neutralize for 1 h and washed in distilled water several times until pH 7 was obtained. The membrane was dried at room temperature and a circular membrane of 4.5 cm was used for testing.

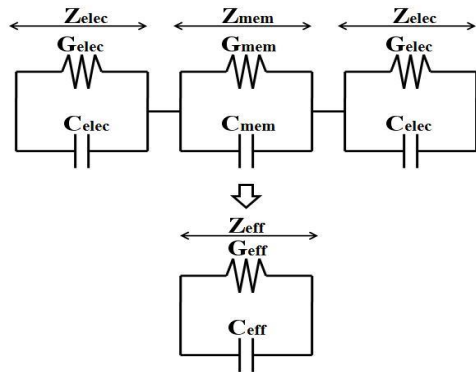


Figure 1. Equivalent circuit models (a) representing electrical units for electrolytes ( $G_{elec}$ ,  $C_{elec}$ ) and the test membrane ( $G_{mem}$ ,  $C_{mem}$ ), and (b) a combination of these parameters and named as an effective value ( $G_{eff}$ ,  $C_{eff}$ ),  $Z_{mem}$  is the combined impedance of the membrane.

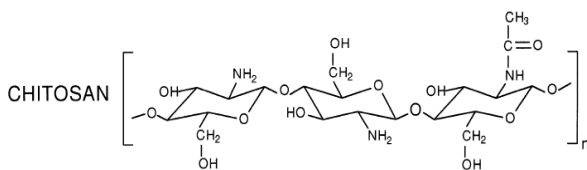


Figure 2. Chemical structure of chitosan (Ying Wan *et al.*, 2003)

### 2.2 Electrochemical Impedance Spectroscopy

A diagram showing EIS set up to measure membrane impedance in an electrolyte solution is in Figure 3. Figure 3a is the previous set up where the calomel electrodes are 1.7 cm from the membrane surfaces. Figure 3b shows the improve set up where the electrodes are next to the membrane plane. Both sides of membrane were in contact with the same KCl concentration in each chamber. The four point probe system used in this study cancelled out

any stray capacitive potential at the electrode/solution interfaces. The load R of 12 kΩ in Figure 3c was inserted in the circuit in order to estimate current  $I_m$  from the voltage drop ( $V_R$ ). The phase combination of ionic conductance ( $G_{eff}$ ) and capacitance ( $C_{eff}$ ) is the membrane impedance  $Z_{mem}$ , or Z in Figure 3d, which is functioned with  $G_{eff}$  and  $C_{eff}$ . The  $\Delta\phi$  is the phase angle between  $V_m$  and  $V_R$ . These values are related as in equation (1), where  $\omega = 2\pi f$ .

$$Z_{eff} = \frac{1}{G_{eff} + j\omega C_{eff}} \quad (1)$$

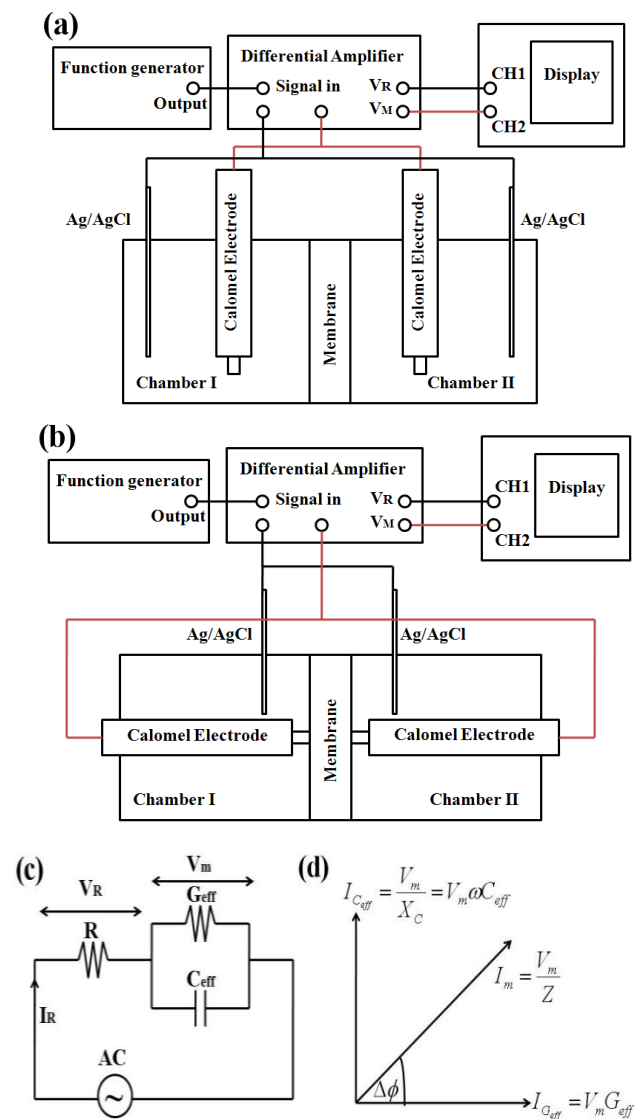


Figure 3. An EIS set up with a circuit diagram. (a) and (b) previous and the improved set up. (c) equivalent circuit of a membrane in an electrolyte and (d) phase diagram for  $G_{eff}$ ,  $C_{eff}$  and Z of the membrane. (Pikul Wanichapichart and Liangdeng Yu., 2007 and W. Puthai *et al.*, 2005)

The effective value of  $G_{eff}$  and  $C_{eff}$  were deduced from the phase diagram shown in Figure 3d. Hence, the relations obtained are:

$$|Z| = \frac{V_m}{I_m} = \frac{V_m R}{V_R} \quad (2)$$

$$G_{eff} = \frac{\cos \Delta\phi}{|Z|} \quad (3)$$

$$C_{eff} = \frac{\sin \Delta\phi}{\omega|Z|} \quad (4)$$

The impedance  $Z$  was calculated using Ohm's law. The phase angle was recorded via an oscilloscope. Nyquist plots were made to illustrate impedance spectra in form by Scilab version 5.1.

### 2.3 Membrane Diffusion Potentials ( $\Delta\Psi$ )

The diffusion potentials ( $\Delta\Psi$ ) across membrane thickness ( $\Delta x$ ) were recorded using the same two-chamber system, but only the calomel electrodes were used. The driving force for ion diffusion was controlled by varying the concentration of salt species in the chamber II (CII), while that in the chamber I (CI) was fixed at 100 mM. This study utilized uni-univalent salts,

KCl, to explore the ionic permeability ratio,  $\frac{P_{Cl}}{P_K}$ , using

the Goldman equation as in (Pikul Wanichapichart and Liangdeng Yu., 2007).

$$\Delta\Psi = -\frac{RT}{F} \left[ \ln \frac{C_K^{II} + \beta C_{Cl}^I}{C_K^I + \beta C_{Cl}^{II}} \right], \quad (5)$$

where R, T, F and  $\beta$  are molar gas constant, temperature in kelvin, Faraday constant and the permeability ratio, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1 Membrane Impedance

Impedance values of the membrane were obtained from equation (2), and displayed in Figure 4. Note that for the frequency range of 0.1–1 kHz; the membrane impedance was improved to be about 1.31 and 4.47 k $\Omega$  in 0.1 mM and 0.01 mM KCl, respectively. These values were a lot less comparing to the values measured by using the previous system, being about 17.19 and 30.10 k $\Omega$  in the

same solution above, respectively. The impedance was influenced by the electrolyte concentration such that it was greater in 0.01mM KCl than in 0.1mM KCl.

### 3.2 Membrane Conductance

Conductance studies were explained in equation (3) of chitosan membranes at before and after upgrading experimental set up of EIS and were displayed in Figure 5. Results showed frequency range of 0.1–1 kHz; conductance membranes after improvement were 0.21 and 0.74 mS, that were greater than before improvement having 0.032 and 0.056 mS at KCl 0.01 mM and 0.1 mM, respectively. In additions, higher concentration of electrolyte solutions (KCl) brings about greater conductance of membrane.

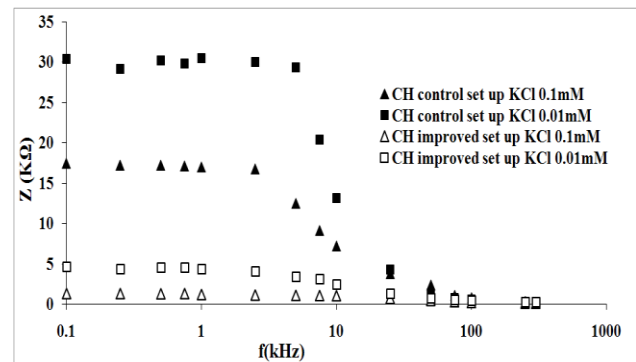


Figure 4. Impedance spectra: the control for the previous set up compared with the improved one in 0.1 mM and 0.01mM KCl

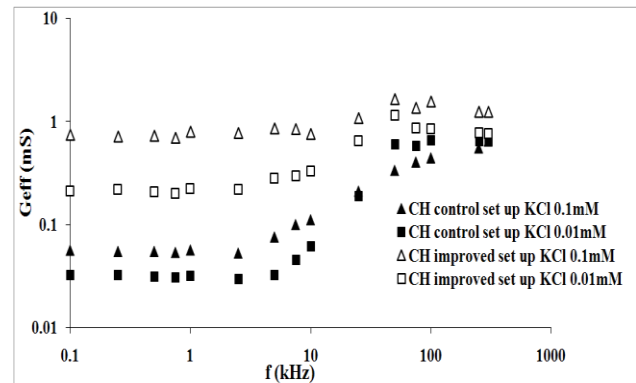


Figure 5. Conductance spectra obtained from the previous (control) and the improved set up in 0.1mM and 0.01mM KCl

### 3.3 Membrane Capacitance

The results in Figure 6, show membrane capacitance at 0.1–1 kHz frequency range, as deduced from equation (4). It was found that after the improvement, the capacitance was about  $1.68 \times 10^{-7}$  and  $4.97 \times 10^{-8}$  F in 0.1 mM and 0.01 mM, respectively. These were greater than those obtained by the previous set up,  $1.29 \times 10^{-8}$  F and

$7.46 \times 10^{-9} \text{ F}$  in 0.1mM and 0.01 mM, respectively. The greater capacitance in the higher salt solution was due to more co-ions accumulating at the membrane surfaces.

### 3.4 Nyquist Plots

Nyquist plots in Figure 7 show that the impedance spectra of real and imaginary part obtained from the previous set up were larger than that of the improved one, and that from 0.01 mM solution was greater. This is in accord with the results shown in Figure 4.

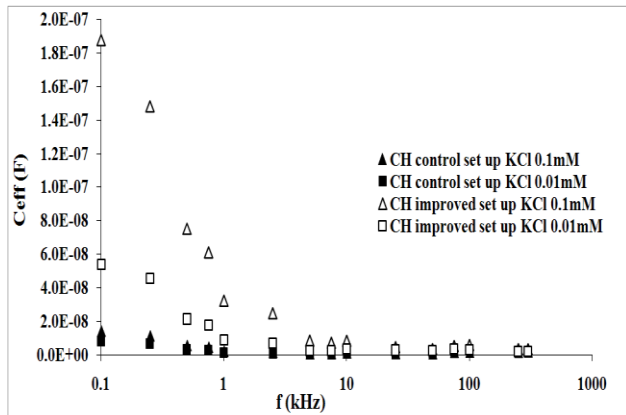


Figure 6. Capacitance spectra obtained from previous and the improved set up in 0.1 mM and 0.01 mM KCl

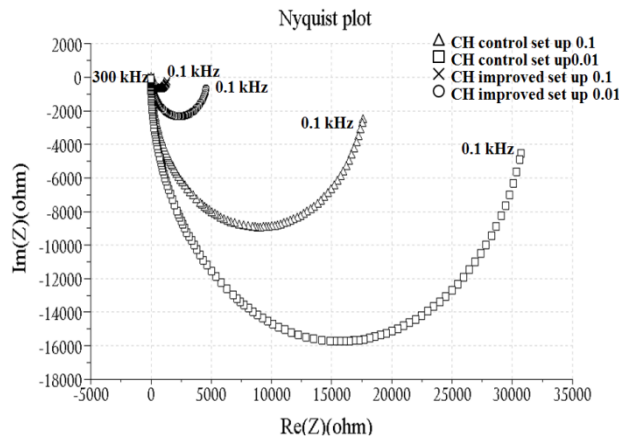


Figure 7. Nyquist plots showing a relation between real and imaginary part of membrane impedance spectrums from previous and the improved set up in 0.1 mM and 0.01 mM KCl

### 3.5 Membrane Diffusion Potential

Figure 8 shows that the potential of the chitosan membrane after the improvement is much greater for every pair of salt concentration, and the value is greater when the membrane experiences larger salt gradient. This was due to the fact that the new electrode orientation detected ionic diffusion closed to the membrane surface, where as the previous orientation would only detect some negative charges after slowly diffusing through the bulk

electrolyte. In other words, the improved set up detected ionic charges transferring from the higher concentration to the lower one were directly and soon after emerging the membrane surface. Moreover, the negative potential implied that  $\text{Cl}^-$  moves from membrane side I to membrane side II faster than  $\text{K}^+$ . This could be explained as due to the fact that chitosan membrane acts as a cationic polyelectrolyte (Figure 2). The diffusion potential, as in equations (5), depends on salt concentration and ionic permeability ratios ( $\beta = P_{\text{Cl}}/P_{\text{K}}$ ). The estimated ionic permeability ratios corresponding with the obtained potentials are showed in Table 1. Interestingly, the improved set up increased the ratios to a large extent, i.e. from 5 to 120 times greater in 100/0.01 mM salt pair and it was decreased with a smaller driving force. This proves that the new set up works more effectively, which also applied to all the above measurements.

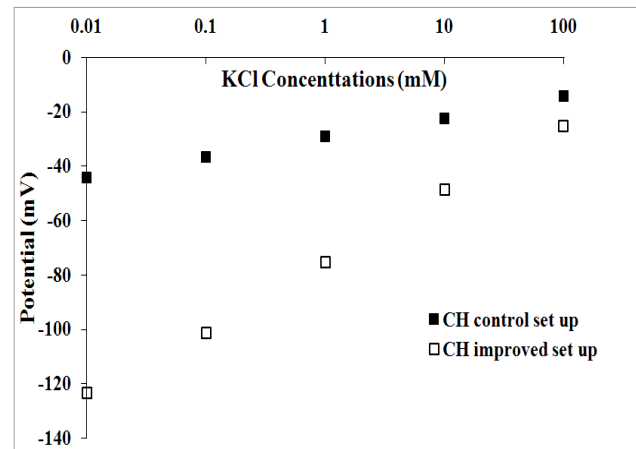


Figure 8. Membrane diffusion potential in various salt concentration gradients; 100/0.01, 100/0.1, 100/1.0, 100/10 and 100/100 mM

Table 1: Ionic permeability ratio,  $\beta = P_{\text{Cl}} / P_{\text{K}}$  obtained from the EIS set up

KCl concentration	$\beta = P_{\text{Cl}}/P_{\text{K}}$ , Previous one	$\beta = P_{\text{Cl}}/P_{\text{K}}$ , Improved one
0.01mM	5.53	120.78
0.1mM	4.15	53.46
1mM	3.17	22.78
10mM	2.98	18.95

Table 2 shows a summary of electrical parameters for chitosan membrane. As is seen, the higher salt concentration possessed a greater charges-density and, resulted in the increased conductance and capacitance values (J.-S. Park *et al.*, 2005). By doing this, the unnecessary impedance value of electrolyte solutions,  $Z_{\text{elec}}$  was eliminated to a large extent. It is, however, not the exact values of  $Z_{\text{mem}}$  since liquid is normally adhere intimately with the membrane surfaces and this always

introduces a pair of  $G_{elec}$  and  $C_{elec}$  to the measurements. In addition, distance effect was calculated and found that the impedance was decreased by  $1.0 \text{ k}\Omega/\text{mm}$  and  $1.8 \text{ k}\Omega/\text{mm}$  in  $0.1$  and  $0.01 \text{ mM}$  solution, respectively. This indicated that the improvement lead to an effectiveness of the EIS set up.

**Table 2: Electrical properties of the membranes**

Electrical properties	KCl 0.1mM	KCl 0.01mM
<b>Previous one</b>		
Impedances	17.19 k $\Omega$	30.10 k $\Omega$
Conductance	0.056 mS	0.032 mS
Capacitance	$1.29 \times 10^{-8}$ F	$7.46 \times 10^{-9}$ F
<b>Improved one</b>		
Impedances	1.31 k $\Omega$	4.47 k $\Omega$
Conductance	0.74 mS	0.21 mS
Capacitance	$1.68 \times 10^{-7}$ F	$4.97 \times 10^{-8}$ F

#### 4. CONCLUSION

This study has improved an electrochemical impedance spectroscopy (EIS) set up. Electrical properties of synthetic membranes in an electrolyte were possible to be detected more effectively. All membrane electrical parameters have been increased by about 90%. For ion-transport characteristic of ion-exchange membrane, the new system improved the ionic permeability ratios by 6 to 20 times greater, depending on the salt gradient. It is also important to mention that this improvement might help in determination of charge affinity for Donnan effect at the membrane surface in a later stage.

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