

MODIFICATION OF PROTON PUMP MEMBRANE USING POLYVINYLPIRROLIDONE (PVP) FOR POTENTIAL TOTAL ALKALINITY SENSING

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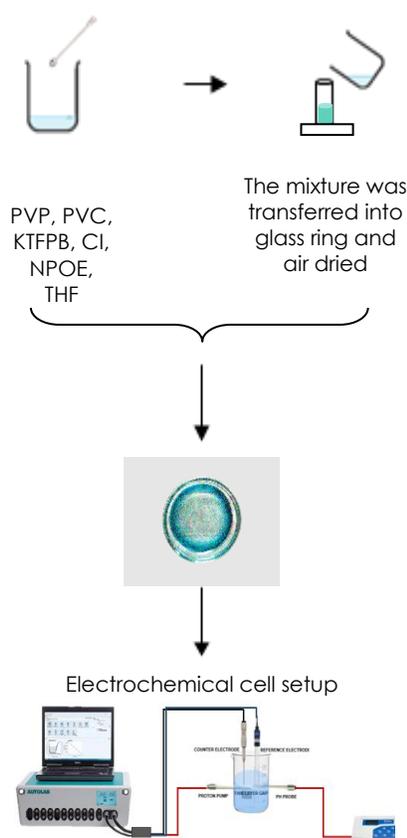
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Graphical abstract



Abstract

Total alkalinity is one of the important parameter in the regulation of seawater carbonate chemistry system to determine the capacity of water to neutralize acid. In this paper, a new proton pump membrane was successfully modified using polyvinylpyrrolidone (PVP) as a supporting material due to its excellent chemical properties. The surface morphology of the membrane was thoroughly studied using Scanning Electron Microscope (SEM), which showed the presence of pore structure, ascribed to the presence of low molecular weight of PVP. The absorption of membrane was studied using Ultraviolet-Visible (UV-Vis) spectrophotometer, where the peak appeared at 539 nm⁻¹. The functional group of the modified membrane was analyzed using Fourier Transform Infrared Spectroscopy (FTIR), and the spectra showed almost similar between modified membrane with PVP and without PVP. The electrochemical behaviour of the membrane was evaluated by cyclic voltammetry (CV) using gold (Au) electrode and the resulting voltammogram showed that the modified membrane with PVP has higher current reading compared to the membrane without PVP, indicating that there is redox reaction occurred during the immobilization. The condition and performance of modified proton pump membrane with PVP was compared and analyzed.

Keywords: Total alkalinity, proton pump membrane, polyvinylpyrrolidone, modified electrode, characterization

Abstrak

Jumlah kealkalian adalah salah satu parameter yang penting dalam peraturan sistem kimia karbonat air laut untuk menentukan kapasiti air bagi meneutralkan asid. Dalam kertas kerja ini, membran pam proton yang baharu telah berjaya diubah suai menggunakan polivinilpirolidon sebagai bahan sokongan kerana sifat kimianya yang sangat baik. Morfologi permukaan membran telah dikaji dengan teliti menggunakan mikroskopi elektron pengimbasan (SEM), yang menunjukkan kehadiran struktur liang, yang dikaitkan dengan kehadiran PVP yang mempunyai berat molekul yang rendah. Penyerapan membran dikaji menggunakan spektrofotometer ultralembayung-nampak (UV-Vis), di mana puncaknya muncul pada 539 nm⁻¹. Kumpulan berfungsi membran yang diubah suai telah dianalisis menggunakan spektr Sokopi inframerah jelmaan Fourier (FTIR), dan spektrum menunjukkan hampir serupa antara membran diubah suai dengan PVP dan tanpa

PVP. Kelakuan elektrokimia membran dinilai dengan kitaran voltametri menggunakan elektrod emas (Au) dan voltamogram yang terhasil menunjukkan membran yang diubah suai dengan PVP mempunyai bacaan arus yang lebih tinggi berbanding membran tanpa PVP, menunjukkan bahawa berlakunya tindak balas redok semasa imobilisasi. Keadaan dan prestasi membran pam proton yang diubah suai dengan PVP telah dibandingkan dan dianalisis.

Kata kunci: Jumlah kealkalian, membran proton pam, polivinilpirolidon, elektrod yang diubah suai, pencirian

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1.0 INTRODUCTION

Since industrial revolution, carbon dioxide (CO₂) has driven in increasing the global ocean's average temperature about 40%, thus the concentration of CO₂ in earth atmosphere has rapidly increased from 280 ppm to over 400 ppm today [1]. The composition of the ocean is changing dramatically as a result of increased atmospheric CO₂ dissolving in seawater, making it more acidic and known as ocean acidification [2]. Ocean acidification is a reduction in the pH of the ocean and it occurs when the CO₂ reacts with seawater and forms a weak carbonic acid [3]. This phenomenon led to a lowering pH, making the ocean more acidic as well as reducing carbonate ion concentration [4] and saturation states of other biological important minerals. The effects of seawater acidification are really threatening to marine life [5] and reduce the productivity of marine ecosystems [6].

There are four parameters to determine the ocean acidification in seawater which are pH, partial pressure carbon dioxide (pCO₂), dissolve inorganic carbon (DIC) and total alkalinity (TA) [7]. TA determination is the best among the variables to measure the sensitivity of the stream acid data [8] as it can decide the seawater's ability to neutralize the acid [9].

Confronted with this issue, researchers are aware that they need to monitor the condition environment of seawater in order to protect the marine environment as well as the marine ecosystem. Previously, TA was measured using the conventional standard titration method as it was found to achieve high precision [10]. However, this method is time-consuming and can only be applied for a single measurement at one time for a sample. Recently, Afshar in 2017 developed a new approach using polymeric functional membrane [11], as the utilization of polymers has been of interest and there are high demands for more advanced functional materials. In this approach, the proton pump membrane was synthesized using porous polypropylene (PP) membrane as a supporting material [11].

Proton pump membrane in TA measurement application acts as a hydrogen ion generator that change the concentration of hydrogen ions in the thin layer sample by generating the hydrogen ions from the proton pump to the thin layer gap. It is a hydrogen ion-

selective membrane with a rapid diffusive property that serves as a working electrode. The resulting pH is recorded at the pH probe placed directly opposite the proton pump [12].

For this reason, as one of the common polymeric materials, polyvinylpyrrolidone (PVP) has been attempted to be provided as one of the supporting materials replacing PP in the preparation of proton pump membrane in order to increase the reusability of the proton pump membrane for further application of TA measurement. As the hydrophilic polymer, the addition of PVP to the cocktail component can increase the permeability of membrane, indirectly leading to membranes less prone to fouling [13] due to the formation of well-defined pores [14, 15]. Moreover, PVP is easy to use, has no or low toxicity [16] and good environmental stability, make it suitable to be used as supporting material for producing polymeric membranes [17].

In this research, the polymeric functional membrane for proton pump was modified with PVP that was acted as supporting material together with polyvinyl chloride (PVC), ionophore, plasticizer, and additive. The membrane was characterized to study the physical, chemical and electrochemical behavior for potential measurement of total alkalinity in seawater. This proton pump membrane acts as a hydrogen ion generator [12] for further electrochemical cell setup.

Previously, we have reported the preparation and characterization of pH probe membrane for determination of total alkalinity in seawater using PVC, chromoionophore I (CI), 2-nitrophenyl octyl ether (NPOE), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB) and tetradodecylammonium tetrakis(4-chlorophenyl) borate (ETH 500) [18]. However, for the preparation and set up of electrochemical system for total alkalinity measurement requires proton pump to be coupled with pH probe to produce the effective system for the total alkalinity measurement. Hence, this study is important to obtain the optimum condition for proton pump membrane. The proton pump membrane with high porosity and high thermal degradation is required to increase the performance of total alkalinity measurement.

2.0 METHODOLOGY

2.1 Chemicals and Reagents

Polyvinyl chloride (PVC) with high molecular weight, polyvinylpyrrolidone (PVP), chromoionophore I (CI), potassium tetrakis [3,5-bis(trifluoromethyl)phenyl]-borate (KTFPB) and 2-nitrophenyl octyl ether (NPOE), were purchased from Sigma-Aldrich, Singapore. Tetrahydrofuran (THF), potassium ferricyanide $K_3Fe(CN)_6$, and potassium chloride (KCl) were purchased from Merck (Germany). All materials used were analytical grade and better.

2.2 Preparation of Proton Pump Membrane

Two different compositions of proton pump membranes were prepared which were Membrane 1 (M1) without PVP and Membrane 2 (M2) with PVP were synthesized together with PVC, chromoionophore I,

nitrophenyloxyether (NPOE), and potassium tetrakis[3,5 bis(trifluoromethyl)phenyl]borate (KTFPB) with THF as solvent to dissolve the cocktail component in order to find out the behavior of the PVP polymer in this application. The membrane was prepared, as described by modifying the method reported by [12] with the replacement of PP to PVP with different composition of the chemical components. Both of the mixtures were poured into glass ring, resting on a glass plate and being covered with aluminum foil to prevent the excessive evaporation. The solutions were aired dried at room temperature for 24 hours until completely dry. The membranes thickness were controlled by volume of the prepared solution and size of the glass ring. Table 1 shows the composition of the each prepared polymer solution for proton pump membrane.

Table 1 Different composition of proton pump membrane for M1 and M2

Membrane	PVC (%)	PVP (%)	NPOE (%)	CI (%)	KTFPB (%)	THF (mL)
M1	31	0	67.5	1	0.5	1000
M2	32.5	16	50	1	0.5	1000

2.3 Characterization of Proton Pump Membrane

The polymeric functional membranes were characterized to study the physical, chemical and electrochemical characteristics that occurred on the membranes surface. Physical characterization method used were Scanning Electron Microscope (SEM) and Thermogravimetric Analysis (TGA), chemical characterization involved are Fourier Transform InfraRed Spectroscopy (FTIR) and Ultraviolet-Visible Spectroscopy (UV-Vis) while electrochemical characterization involved is Cyclic Voltammetry (CV).

SEM analysis were employed to study the surface morphology of the membrane and to predict the surface texture, homogeneity and cracks in the prepared composite membranes [19]. The surface morphology of membrane was investigated using Scanning Electron Microscope (SEM) (JEOL JSM-6360 LA). Before the analysis, the membrane was mounted on SEM stub before coated with gold and analyze using different magnification.

The functional group of membranes were studied using Fourier Transform InfraRed Spectroscopy (FTIR) (Shimadzu/IRTRacer-100). The samples were placed on a sample holder (ATR cell) and spectrum was measured in the wavelength ranges of 600 to 3600 cm^{-1} .

TGA analysis was carried out to study the thermal stability [20] of polymeric functional membranes for degradation and decomposition temperature. This study was carried out using TGA in argon atmosphere at a heating rate of 10°C/min and the membranes were scanned from 30°C to 900°C.

Absorption of polymeric functional membranes using UV-Vis region were observed by dual beam UV-Vis Spectrophotometer (Shimadzu), equipped with UV Probe 2.43 software. Absorbance was measured in the range of 300 nm to 800 nm through 1 cm quartz cuvette.

The redox behavior of the modified proton pump membrane was studied using cyclic voltammetry [21]. The voltammetry measurement was measured using AUTOLAB PGSTAT204 (AUT51243) from Metrohm, Singapore. The membrane was deposited on gold (Au) working electrode and measured using 2.5 mM $K_3Fe(CN)_6$ in 0.1 M KCl electrolyte.

3.0 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscope

The membranes were investigated using SEM with magnification 1000x and 30x as a visual verification on how the combination of PVC and PVP polymers influences membrane morphology. Figure 1 shows the modified proton pump membrane without PVP while Figure 2 shows the proton pump membrane modified with PVP.

The homogenous mixture of PVC, plasticizer, additive, and ionophore without PVP indicates smooth surface with non-porous structure and without any visible cracks for the morphology of the M1 [22]. Based on Figure 2, the morphologies of M2 that consists of PVP showed the formation of pores on the membrane. The higher concentration of PVP resulted in increased of the pore size of the membrane [23].

Hence, the addition of PVP has been benefits of improving the membrane performance with increased permeability as agreed by Wu *et al.*, in 2021 [24].

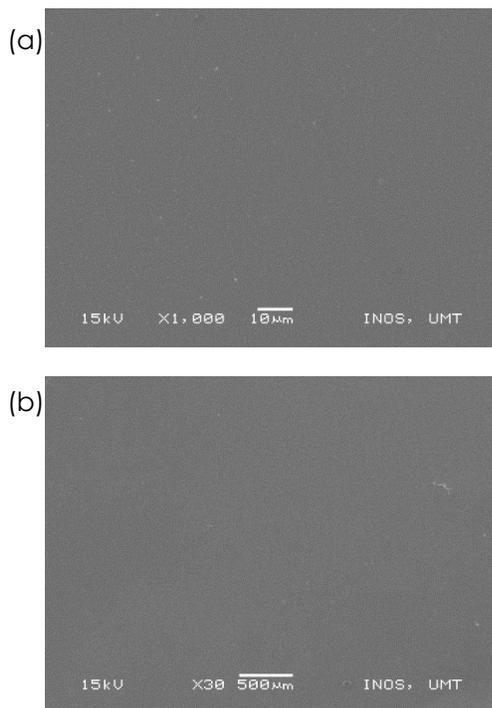


Figure 1 SEM images of M1 (a) and (b) presents surface morphology tested at 1000x and 30x magnification, respectively

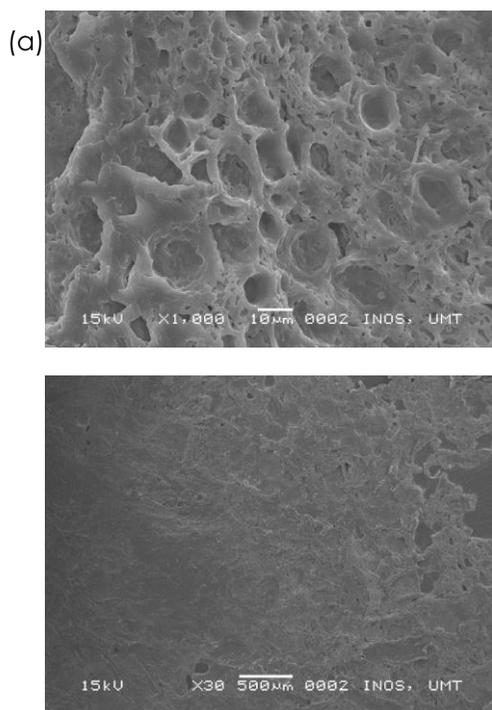


Figure 2 SEM images of M2 (a) and (b) presents surface morphology tested at 1000x and 30x magnification, respectively

3.2 Fourier Transform Infrared Spectroscopy

The Fourier Transform Infrared Spectroscopy (FTIR) spectra of the membranes are shown in Figure 3.

According to Figure 3, peak appeared at 2924 cm^{-1} were assigned to alkane (C-H) stretching, which might come from NPOE, CI, and PVC. The peaks located at 2345 cm^{-1} which signifies the existence of C-O bond which might come from NPOE, CI and the bands at 1519 cm^{-1} correspond respectively to the stretching asymmetric and symmetric modes of N=O (in NO_2) bond [25]. The aliphatic ether C-O stretching (carboxylic acid) was characterized at 1273 cm^{-1} , might came from NPOE.

M1 and M2 showed almost similar FTIR spectra, with the presence of functional groups at the same wavenumbers except at wavelength 3410 cm^{-1} . The appearance of peak at $3200\text{-}3600\text{ cm}^{-1}$ due to the stretching vibration of CH-N or O-H stretching [26], and the absorption bands at 1643 cm^{-1} correspond to C=O stretching from PVP [27] and the spectrum proving that it contains PVP compound, as reported by Behboudi *et al.*, in 2021.

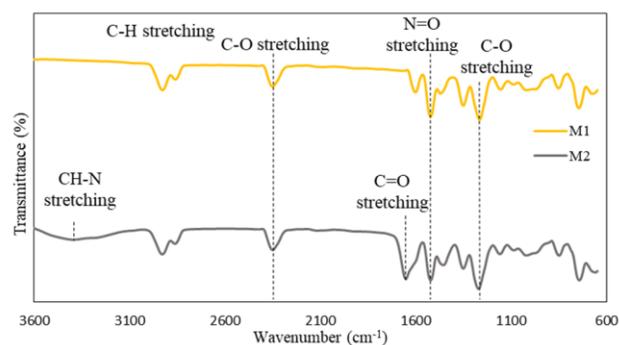


Figure 3 FTIR spectra of M1 and M2

3.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out to study the thermal stability of polymeric functional membranes for degradation and decomposition temperature. The thermograms of M1 and M2 are depicted in Figure 4. According to the graph presented, the non-single step degradation curve confirmed the presence of more than one component in the synthesized membranes. Analysis shown that both membranes thermal degradation of temperature were started at approximately 200°C . M1 has two degradation stages [28] while M2 has three degradation stages. Further analysis revealed that after heating to 900°C , addition of PVP reduced the percent weight loss in the membrane.

The first degradation temperature for M1 was between 200°C to 300°C with a weight loss of 76% due to chain stripping by elimination of HCl molecule from PVC [29]. The second degradation of M1 was occurred in range of 430°C to 800°C with the weight loss about 24%. This might due to low molecular weight

oligomers, loss of moisture and residual solvent in this range temperature [30].

The first weight loss of M2 was in the range of 200–300°C with 70% weight loss due to the elimination of HCl molecules leaving behind longer polyene chains [28]. The second decomposition of M2 occurred at approximately 414°C to 546°C, corresponding to the constituent polymers with a weight percentage loss of approximately 13%. This is probably due to the most organic materials of PVP have been disintegrated [29]. The third degradation involved the weight loss of 17% in the range of 500°C to 800°C, due to degradation of some residual solvent.

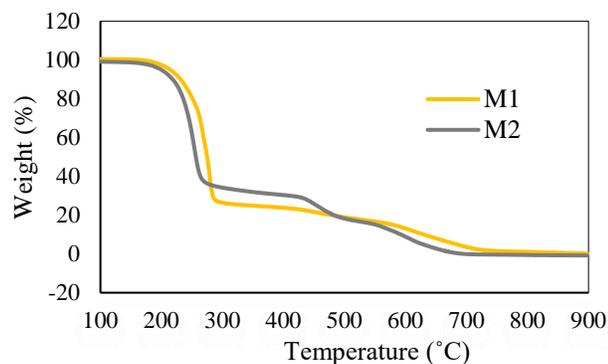


Figure 4 Thermogravimetric curve of M1 and M2

3.4 Ultraviolet Visible Spectrophotometer

Absorption of polymeric membranes were studied using UV-Vis spectrophotometer at wavelength 410 nm⁻¹ to 800 nm⁻¹. The spectrum obtained from UV-Vis spectrophotometer is shown in Figure 5.

The absorption spectrum of M1 exhibit one strong and one weak absorption peaks in the UV region, with absorption at 532 nm⁻¹ (λ_1) and 657.5 nm⁻¹ (λ_2) respectively, due to the presence of Cl [30]. The distinct characterized peaks for Cl in the visible regions has generally interpreted in term of $n - \pi^*$ excitation between bonding and antibonding molecular orbital. M2 exhibit excitation peak at 539 nm⁻¹. Thus, resulting in lower absorption peak compared to M1. The excitation band of M2 at 539 nm⁻¹ is attributed to the electronic transitions in PVP molecular orbitals. The radiation relaxation of electrons from the lowest energy unoccupied molecular orbital (LUMO) to the highest energy occupied molecular orbital (HOMO) levels in PVP [31]. Moreover, the peak on M2 was slightly shifted to the right. This might be because of the formation of charge transfer complex between the tertiary nitrogen atoms that attached to the PVP amide bond with the PVC chloro groups as stated by Radhakrishnan in 2007 [32]. In this reaction, the oxygen atom from THF attacks the carbon atom in PVP, breaking the bond between carbon atom and nitrogen atom. The PVP acts as nucleophile. The nitrogen atom consists of lone pair when break off with carbon atom in PVP, attacks the carbon atom of PVC, resulting elimination of the leaving group halogen (Cl).

Thus, the nucleophile replaces the leaving group and forms a product and byproducts. The chemical reaction of PVP and PVC are illustrated in scheme 1.

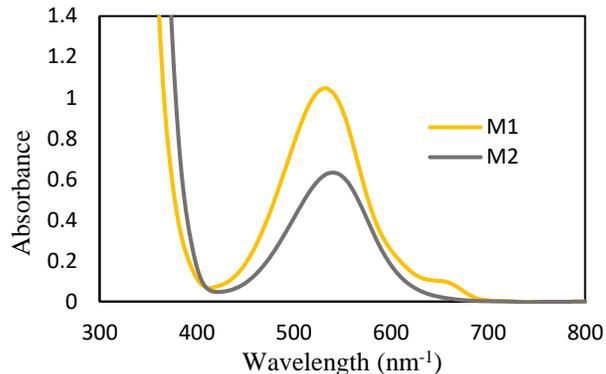
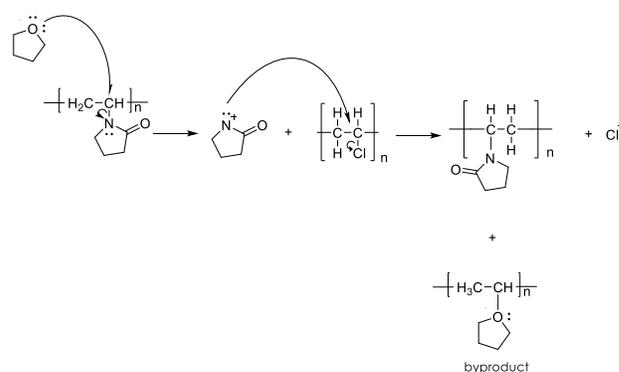


Figure 5 UV-Vis spectrum of M1 and M2



Scheme 1 Illustration of chemical reaction of PVP and PVC

3.5 Cyclic Voltammetry

The electrochemical behavior of the proton pump membrane was thoroughly studied by Cyclic Voltammetry (CV) technique with gold (Au) electrode using 2.5 mM K₃Fe(CN)₆ in 0.1 M KCl electrolyte, from potential of -0.2 V to +0.8 V. Figure 6 shows the CV of bare Au electrode and modified with M1 and M2 using 2.5 mM K₃Fe(CN)₆ in 0.1 M KCl electrolyte. The voltammogram response of bare Au, showed well-defined peaks for the redox reaction of these electrolyte [33].

M1 showed that after the modification on the electrode surface, the current reading was significantly decreased. The values were extremely small, implying that almost no current was recorded during the measurement [18]. This is in agreement with Jusoh *et al.*, (2020). In the immobilization process, the surface electrode was successfully occupied with membrane, prevent any form of electron transfer to occur [34]. Meanwhile, the M2 voltammogram showed the decreased redox peak current due to the presence of PVP molecule on the electrode surface. The electrochemical response of K₃Fe(CN)₆ in KCl electrolyte to M2 is significantly enhanced, compared to other membranes which reflects the porous structure in SEM image in Figure 2.

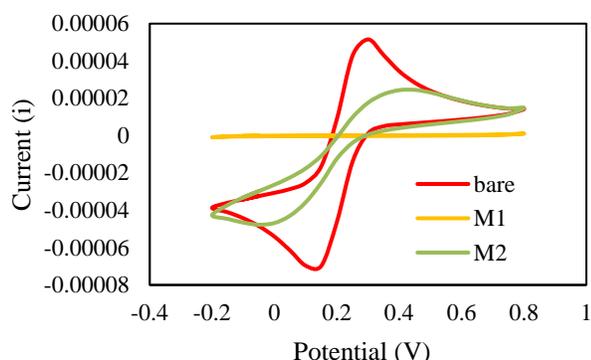


Figure 6 Cyclic Voltammogram of modified electrode with different membranes using Au electrode with 2.5 mM $K_3Fe(CN)_6$ in 0.1 M KCl

4.0 CONCLUSION

In this research, M1 and M2 were successfully prepared and compared. Owing to the high physiological compatibility, applying PVP to the membrane as the supporting material can be used for different applications not only for water monitoring. Based on the preparation of membrane M1 and M2, the physical, chemical and electrochemical characterization was carried out to study the behavior of the membranes. The SEM result showed that M1 is denser compared to M2 that consist of pores. Moreover, SEM analysis shows the compatible data to the CV analysis as the redox reaction occurred at M2 as the SEM analysis shows the porous morphology of membrane. According to FTIR spectra, M2 is composed of a blend of a PVC and PVP polymers. According to FTIR spectra, the peaks of the membranes were clearly seen. M1 and M2 has slightly difference in the peak presence due to the presence of functional group in PVP compound. TGA analysis shows that the spectrum thermograms reflects to the involved component. Both of the membranes showed the active excitation peak in the UV-Vis spectrophotometer due to the presence of Cl. Based on this findings for preparation and characterization of membranes, it showed that M2 membrane can be potentially use for the selective proton pump membrane due to its excellent properties of the membrane.

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