

Modification and Characterization of Bacterial Cellulose Biopolymer as Proton Conducting Membrane

C. W. Lin, S.W. Chen

Abstract—This study describes the preparation of a novel proton conducting membranes based on bacterial cellulose (BC) modified by grafting of 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) through UV-induced graft polymerization. These AMPS-g-BC membranes have been characterized by various techniques including FTIR, SEM and TGA, to find their successful grafting of AMPS on BC, surface morphology and thermal stability, respectively. Physical properties of AMPS-g-BC membranes have been assessed in terms of Lamda value (λ), ion exchange capacity (IEC) and proton conductivity. The relationship between degree of grafting and AMPS concentration used for grafting has been determined by weight gain method. An optimum proton conductivity equal to $2.89 \times 10^{-2} \text{ S cm}^{-1}$ and IEC value equal to 1.79 mmol g^{-1} have been obtained when 20 wt% AMPS concentration is used for grafting (i.e. the corresponding membrane is notated as AMPS20-g-BC).

Keywords—Bacterial cellulose, 2-acrylamido-2-methyl-1-propanesulfonic acid, Proton conducting membrane, Self diffusion coefficient, Fuel cell

I. INTRODUCTION

BACTERIAL cellulose (BC), which is synthesized by *Acetobacter xylinum*, is a natural and low-cost biopolymer [1]. It has many excellent properties such as high water holding capacity, biodegradability, and high tensile strength [2]. Ironically, BC membranes can retain its chemical and thermal stability up to 275°C with high mechanical strength [3]. The hydroxyl groups in BC can provide high hydrophilic nature, which is crucial for the operation of PEMFCs [4]. Evans et al. demonstrated the use of palladium-bacterial cellulose in manufacturing both electrical and electronic devices [5]. Moreover, bacterial cellulose has the potential to act as an adsorbent and an ion-exchange membrane (IEM) to recover heavy metals from industrial wastewater. It has been reported that a cellulose-type adsorbent, having a similar structure to that of bacterial cellulose, exhibited excellent adsorption for heavy metals [6], for binding metal ions, and for separation of trace metals [7]. Recently, Yang et al. modified BC membranes with platinum nanoparticles by *In situ* deposition and demonstrated their application in fuel cells [8]. Water-soluble 2-acrylamido-2-methylpropanesulfonic acid (AMPS), and its sodium salts are widely used as an effective flocculants and additives [9].

Some polyelectrolyte based on AMPS showed good chemical stability, high proton conductivity, and promising application in fuel cells [10-12]. The advantageous properties of BC membrane and AMPS can be utilized effectively with tailor-made modifications in order to extract favorable applications in PEMFCs. Among various modification methods, radiation graft polymerization is one of the promising methods, which enables introduction of active monomer functional group at inner polymer chains in film for the modification of the chemical and physical properties of a wide range of polymer materials. Various kinds of grafting polymerization techniques-including ion-radiation induced, photo-induced (UV and chemical initiator), and plasma-induced grafting polymerizations- have been developed in the last few decades [13-15]. However the UV-radiation technique is more available and less expensive than other techniques [16].

In PEMFC applications, it is very important for the membranes to exhibit proton conductivity and methanol/water permeability, which is largely dependent upon the properties of polymers. The surface of a polymer is important to the material performance in at least two respects: first, the microstructure and properties of surfaces are usually different from those in the bulk; second, among all parts of a polymer, the outmost surface is most prone to both physical and chemical interactions with its environment. To achieve materials with desired surface properties for specific applications, chemically tailoring the surface of polymers which has many advantages, including (1) improvement of the surface properties of a material without affecting its bulk properties; (2) elimination of the need to redesign the bulk material to achieve a target surface performance; and (3) reduction in cost, since all necessary chemistry is confined to the surface. The method is advantageous for initiating grafting in many kinds of polymers owing to its extensive penetration in the polymer matrix and its rapid and uniform formation of radicals [17]. This technique allows introducing ion conducting (electrolytes) regions directly into polymer films, which have excellent thermal and mechanical properties.

On considering these above mentioned aspects with modifications photo induced UV-graft polymerization is the best way to implement the specific properties such as, proton conductivity of AMPS in BC membranes to apply in fuel cell applications. This paper describes the preparation and characterization of AMPS-g-BC membranes, and looks at the influences of the AMPS concentrations for grafting on the physical properties such as water uptake, ion-exchange capacity (IEC), proton conductivity. Furthermore, the membrane electrode assemblies (MEAs) were fabricated using AMPS-g-BC membranes with Pt/C catalyst and gas diffusion layer.

C. W. Lin is with the National Yunlin University of Science and Technology, Yunlin, Taiwan (phone: 886-5-5342601; e-mail: lincw@yuntech.edu.tw).

S.W.Chen is with the National Yunlin University of Science and Technology, Yunlin, Taiwan (phone: 886-5-5342601; e-mail: g9815713@yuntech.edu.tw).

II. EXPERIMENTAL

A. Materials

2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was purchased from Merck, Germany. Bacterial cellulose (BC) membrane was courteously supplied by the Food Industry Research and Development Institute, Taiwan. Benzophenone, isopropanol, acetone, and methanol were purchased from Aldrich, USA.

B. Preparation of membranes

Figure 1 systematically presents the preparation procedures of grafting 2-acrylamido-2-methylpropanesulfonic acid monomers to BC biopolymer with the using of benzophenone as the photo-initiator. The radiation procedure was describes as follows: First, BC membrane was immersed in benzophenone methanol solution for 3 h. After that, the BC membrane was activated by the UV light (400 W, 110-400 nm mercury lamp) for 60 seconds in the nitrogen atmosphere environment. In this step, BP abstracts hydrogen from the membrane substrate (BC) to generate surface radicals and semipinacol radicals, which combine to form surface photoinitiators [18] (Figure 1(a)). Subsequently, a required AMPS solution (10-20 wt. %) was added into the reaction chamber and irradiated with UV light for 1 min. In this step, the introduction of monomer (AMPS) onto active membrane substrate (BC) leads to living graft polymerization process, as Figure 1(b) shows. Consequently, the resulting AMPS-g-BC membrane was then thoroughly cleaned with methanol/acetone several times to remove unreacted homopolymer and monomers.

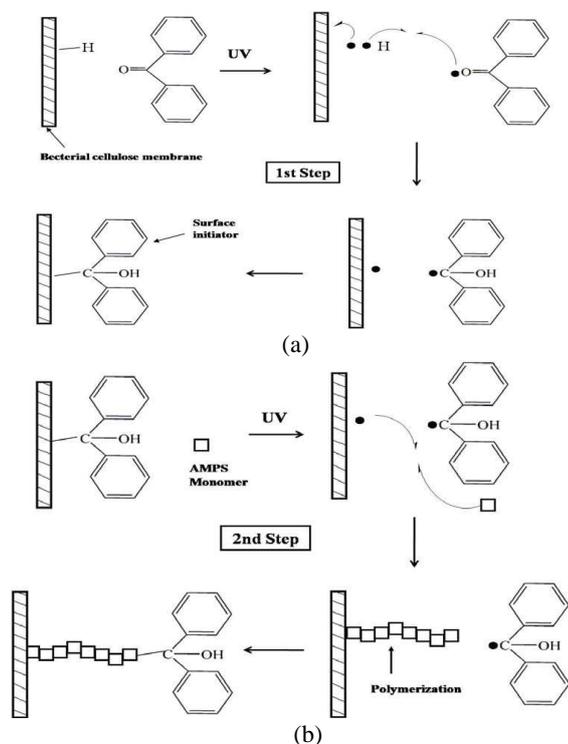


Fig. 1 Preparation procedures of grafting 2-acrylamido-2-methylpropanesulfonic acid monomers to BC biopolymer

C. Characterization of membranes

Fourier transform infrared (FT-IR) spectra were performed in the transmittance mode by a spectrophotometer (Spectrum One, Perkin Elmer, USA). The resolution and number of scans in all spectra were 4 and 32 cm^{-1} , respectively. TGA measurements of membranes were performed under nitrogen atmosphere. The weights of the testing samples were of 10 mg, and the heating rate is $10^{\circ}\text{C}/\text{min}$. Thermo-grams were obtained in the temperature range of 30 to 700°C . The water/methanol solvent uptakes of the membranes were determined by measuring the differences of membrane weights before and after immersion in the water/methanol solution overnight. The weight of the dry membrane (W_{dry}) was determined after drying the membranes at 60°C for 24h. Titration method was used to determine the ion-exchange capacity. Each membrane sample was soaked in 50 ml of 1M sodium chloride aqueous solution overnight to exchange protons with sodium ions. The ion-exchanged solution was titrated with 0.005M sodium hydroxide solution. Proton conductivity measurements were carried out at ambient temperature with a two-electrode configuration. The methanol permeability of AMPS-g-BC membrane was carried out using a side-by-side glass diffusion cell containing 2M methanol solution in one side and pure water in the other side. Gas chromatography (GC, China Chromatography 9800) was used to determine the methanol concentration in the water side. Methanol permeability was calculated from the plot slope of methanol concentration in the receptor compartment versus time. The AMPS-g-BC membrane-based MEA was fabricated using a 15% wet proof gas diffusion media as supports (HEPHAS energy, Taiwan). Carbon-supported Pt catalyst (50 % Pt on carbon black - Johnson Matthey, USA) was used to create catalyst layer of anode and cathode of H_2/O_2 FC. The catalyst loading amount in both anode and cathode is 0.5 mg cm^{-2} . Pt catalyst and iso-propanol were firstly mixed and stir unit a complete dispersion was obtained. Nafion[®] solution (5 wt.%, Sigma-Aldrich, USA) was then added in this dispersion and stirred again to create a uniform paste. The mixing ratio of Pt:IPA:Nafion[®] by weight was 1:30:1.34. The hydrogen and oxygen flow rate was used and fixed at 100 SCCM. The details of the MEA fabrication conditions and procedures were referred to our previous work [19]. A MACCOR Model 2200 fuel cell test station was used to evaluate the single cell performance.

III. RESULTS AND DISCUSSION

A. Characterization of AMPS-g-BC membranes

Figure 2 and 3 compares the FT-IR spectra and TGA curves of the BC membranes before and after the grafting of AMPS. As Figure 2 shows, the pristine BC membrane shows a characteristic absorption band of hydroxyl group at $3200\text{-}3400 \text{ cm}^{-1}$. However, after the grafting of AMPS, the characteristic bands at 1624 and 1545 cm^{-1} , corresponding to the C=O and NH group on AMPS, can be respectively observed [20]. Besides, the sharp band at 1217 cm^{-1} , reflecting to the sulfonic acid group on AMPS, can be also obtained. These results indicate the successful grafting of AMPS on the BC membranes.

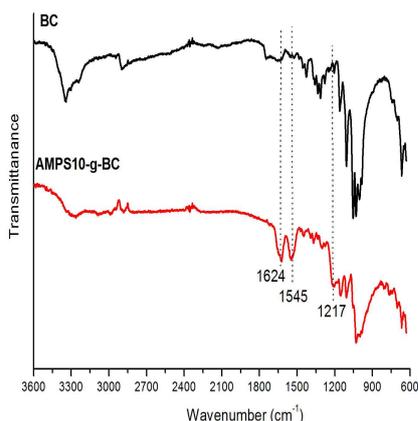


Fig. 2 FT-IR spectra of the BC membranes

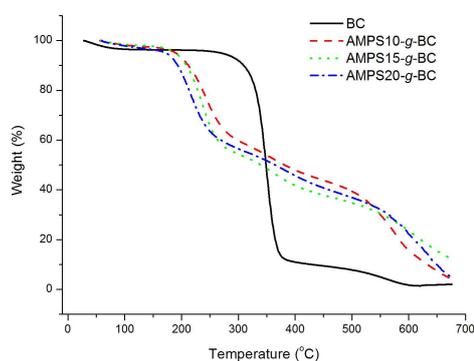


Fig. 3 TGA curves of the BC membranes

The thermal degradation curves of the membranes obtained before and after the grafting of AMPS were conducted to further identify the grafting of AMPS on BC membranes. As Figure 3 shows, the pristine BC membrane shows two major weight loss stages at 350 and 550 °C. The first one at 350 °C can be attributed to concurrent cellulose degradation processes such as depolymerization, dehydration, and decomposition of glycosyl units followed by the formation of a charred residue, and the second degradation temperature at about 550 °C can be related to the oxidation and/or breakdown of the charred residue to lower molecular weight gaseous products [21]. On the other hand, for AMPS10-g-BC membranes, observation finds the sample exhibits three weight loss stages at 216–243, 358–376 and 573–620 °C. The weight loss in the first, second and third stage can be attributed to the decomposition of sulfonic acid groups, cellulose degradation, and the breakdown of charred residue, respectively [20, 21]. These results further confirm the successful grafting of AMPS onto BC membrane and provide an efficient way to graft AMPS monomers on the BC membranes.

B. Scanning electron microscopy

Typical surface morphologies of pristine BC membrane, AMPS10-g-BC, AMPS15-g-BC and AMPS20-g-BC membranes are shown in Fig. 4. The SEM image of Fig. 4a shows a side view of the BC nanofiber membrane, with an average diameter of about 42nm and a length ranging from micrometers up to dozens of micrometers. As can be seen from Fig. 4a, the BC membrane is porous with interconnecting pores.

The pore size varies in a 10-15 μm range [15]. AMPS-g-BC membranes have shown denser structure upon increased AMPS concentration for grafting which is evident from Figs. 4c and 4d. It is understood from the surface SEM micrographs that at lower AMPS concentration of grafting, membranes show more expanded structure with pores but at higher concentration of grafting (i.e., 20 wt.% of AMPS), the membrane surface is complete dense with decrease in pore distribution.

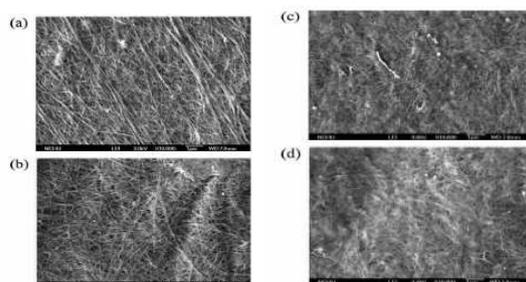


Fig. 4 Surface morphologies of pristine BC and AMPS-g-BC membranes

C. Basic properties of the AMPS-g-BC membranes

Figure 5 shows the water uptake and IEC value of the AMPS-g-BC membranes prepared in different AMPS solutions. As Figure 5 shows, both IEC value and water uptake increased with the AMPS concentration used for grafting BC membranes. The measured IEC values of the membranes increases from 1.06 to 1.79 mmol g^{-1} when the AMPS concentration increases from 0 to 20 %. This increased IEC value corresponds well with the increasing amount of sulfonic acid on the AMPS-g-BC modified with higher AMPS concentration. Moreover, this increased amount of sulfonic acid also leads to an increasing water uptake of AMPS-g-BC membranes. As Figure 5 shows, as the AMPS concentration increased from 0 to 20%, the water uptake of the AMPS-g-BC membranes increased from 100 to 264 %. Again, the increasing amount of sulfonic acid on AMPS-g-BC obtained at high AMPS concentrations can explain this trend. Accordingly, it can be deduced that a higher AMPS concentration can lead to a higher polymerization ratio of sulfonic acid on the BC membranes, and this higher polymerization ratio of AMPS on BC membrane contributes to a higher IEC value and water uptake in the BC membranes.

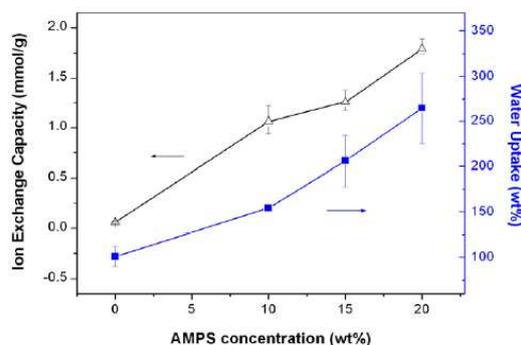


Fig. 5 Water uptake and IEC value of the AMPS-g-BC membranes

Figure 6 presents the proton conductivity of the AMPS-*g*-BC membranes as a function of AMPS concentration at room temperature. As Fig. 6 shows, the proton conductivity of AMPS-*g*-BC membranes increases as the AMPS concentration and reaches a maximum value of $2.9 \times 10^{-2} \text{ S cm}^{-1}$ when AMPS concentration up to 20% (AMPS20-*g*-BC). This increased proton conductivity relates well with the IEC and water uptake value, which can both promotes the transportation of proton in membranes. Specifically, noted this proton conductivity value is similar to that of Nafion[®] 115 measured under the same experimental conditions. The proton conductivity of Nafion[®] 115 measured here is $3.9 \times 10^{-2} \text{ S cm}^{-1}$, agreeing well with the literatures [22, 23]. This similar proton conductivity demonstrates the potential of these AMPS-*g*-BC membranes for fuel cell applications. Accordingly, to further identify the possibility of these AMPS-*g*-BC membranes in fuel cell applications, this study also tried to measure the polarization curve of these AMPS-*g*-BC membranes

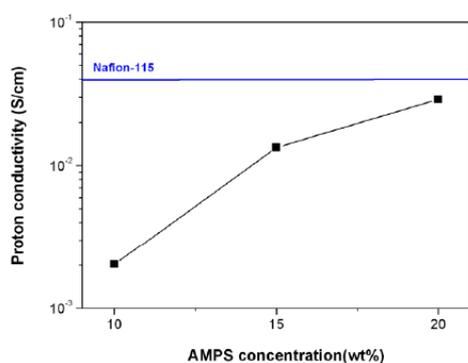


Fig. 6 Proton conductivity of the AMPS-*g*-BC membranes as a function of AMPS concentration

D. Characteristics of membrane-electrode assembly

Figures 7 compare the polarization characteristics of the membrane electrode assemblies (MEAs) consisting of AMPS15-*g*-BC and AMPS20-*g*-BC membranes at different reaction temperature. As Figures 7 shows, the fuel cell performances of the AMPS-*g*-BC membranes increased with the cell temperature. Taking AMPS20-*g*-BC membrane as examples, observation finds an improved power density from 61 to 97 mW cm^{-2} was obtained as the cell temperature increase from 30 to 50 °C. Similar trend can be also observed from the AMPS15-*g*-BC, from which an increasing power density from 41 to 62.3 mW cm^{-2} with the cell temperature was obtained. Moreover, it should be noted that the AMPS20-*g*-BC membrane shows a significantly superior power density to the AMPS15-*g*-BC membranes. This higher power density of the AMPS20-*g*-BC membranes correlates well to its higher proton conductivity. These results indicate that the grafting of AMPS on bacterial cellulose provides a promising way for the preparation of proton exchange membrane for fuel cell applications using hydrogen/oxygen as the reactant. Accordingly, this study intends to further investigate the potential of the AMPS-*g*-BC membranes in DMFC applications.

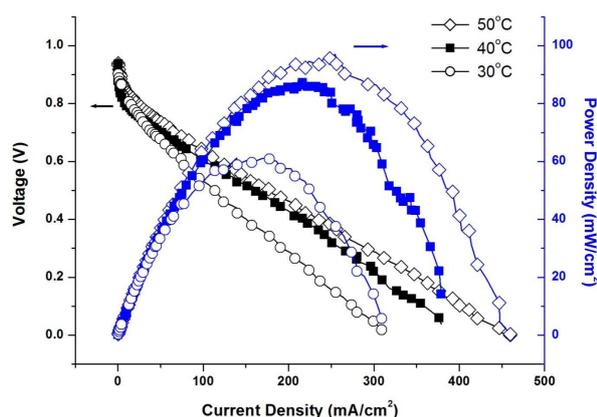


Fig. 7 Polarization characteristics of the membrane electrode assemblies (MEAs) consisting of AMPS20-*g*-BC membrane

IV. CONCLUSIONS

This work explores the preparation of novel proton conducting membranes by grafting AMPS segment on the bacterial cellulose membranes using a UV-graft polymerization process. FT-IR spectra and TGA curves confirmed the successful grafting of AMPS onto BC membrane. Experimental results indicate the higher AMPS polymerization ratio on BC membranes, determining by the concentration of AMPS solution for grafting, can lead to the increase in proton conductivity, IEC, and water uptakes of the AMPS-*g*-BC membranes. The AMPS20-*g*-BC membrane shows an optimum proton conductivity of $2.94 \times 10^{-2} \text{ S cm}^{-1}$. AMPS-*g*-BC membranes were found to be effective in single cell test under H_2/O_2 using commercialized Pt/C catalyst. The fuel cell performances of AMPS-*g*-BC membranes showed good improvement at high AMPS concentration used for grafting, and also with higher temperature (50°C). Optimum current density and power density were achieved for AMPS20-*g*-BC membrane.

REFERENCES

- [1] O. D. Klemm, D. Schumann, U. Udhardt, S. Marsch, *Prog. Polym. Sci.* 26 (2001) 1561-1603.
- [2] A. Svensson, E. Nicklasson, T. Harrah, B. Panilaitis, D. Kaplan, M. Brittberg, P. Gatenholm, *Biomaterials* 26 (2005) 419-431.
- [3] J. George, K.V. Ramana, S.N. Sabapathy, J.H. Jagannath, A.S. Bawa *Journal of Biological Macromolecules* 37 (2005) 189-194.
- [4] Y. Wan, K.A.M. Creber, B. Peppley, V.T. Bui, *J. Membr. Sci.* 280 (2006) 666-674.
- [5] B.R. Evans, H.M. O'Neill, V.P. Malyvanh, I. Lee, J. Woodward, *Biosensors and Bioelectronics*, 18 (2003) 917-923.
- [6] K. Brajter, K. Slonawska, *Anal Chim Acta* 185 (1986) 271-277.
- [7] W. Li, H. Zhao, P.R. Teasdale, R. John S. Zhang, *Anal Chim Acta* 464 (2002) 331-339.
- [8] J. Yang, D. Sun, J. Li, X. Yang, J. Yu, Q. Hao, W. Liu, J. Liu, Z. Zou, J. Gu, *Electrochimica Acta* 54 (2009) 6300-6305.
- [9] O.A. Kazantsev, A.V. Igolkin, K.V. Shirshin, N.A. Kuznetsova, A.N. Spirina, A.P. Malyshev, *Russ. J. Appl. Chem.* 75 (2002) 465-469.
- [10] C.W. Walker Jr., *J. Power Sources* 110 (2002) 144-151.
- [11] J. Qiao, T. Hamaya, T. Okada, *J. Mater. Chem.*, 15 (2005) 4414-4423
- [12] L.E. Karlsson, B. Wessle'n, P. Jannasch, *Electrochimica Acta* 47 (2002) 3269-3275.
- [13] P.A. Dworjanyn, J.L. Garnett, *J. Polym. Chem. Polym. Lett. Ed.* 26 (1988) 135-138.

- [14] J.R. Hollahan, Plasma Chemistry Industrial Application, Wiley, New York, 1974
- [15] C.A. Wilkie, C. Deacon, Graft copolymerization of acrylic acid on to acrylonitrile-butadienestyrene terpolymer and thermal analysis of the copolymers, *Eur. Polym. J.* 32 (1996) 451-455.
- [16] S. Hasegawa, Y. Suzuki, Y. Maekawa, *Radiat. Phys. Chem.* 77 (2008) 617-621.
- [17] M.M. Nasef, *J. Appl. Polym. Sci.* 77 (2000) 1003-1012.
- [18] E. O. Stejskal, J. E. Tanner, *J Chem Phys* 43 (1965) 3597-3603.
- [19] A. M. Kannan, A. Menghal, I.V. Barsukov *Electrochemistry Communications* 8 (2006) 887-891
- [20] G. Oster, O. Shibata, *J Polym Sci* 26 (1957) 233-234.
- [21] K. Watanabe, Y. Eto, S. Takano, S. Nakamori, H. Shibai, S. Yoshinaka, *Cytotechnol* 13 (1993) 107-114.
- [22] Y. Choi, Y. Ahn, M. Kang, H. Jun, I. Kim, S. Moon, *J Chem Technol Biotechnol* 79 (2004) 79-84.
- [23] M. Roman, W.T. Winter, *Biomacromolecules* 5(2004) 1671-1677