



## Preparation and characterization of poly (vinyl alcohol)/Carboxymethyl Cellulose/ Acrylamide - based membranes for DMFC applications

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### Abstract

Blending polyvinyl alcohol (PVA) -Carboxy methyl cellulose (CMC) - Acrylamide (AA) membranes are prepared and crosslinked using succinic acid and investigated as a polymer electrolyte membrane (PEM) in direct methanol fuel cell (DMFC). The membranes were prepared through the solution casting technique. The effect of different blend addition on physicochemical properties was studied. Scanning electron microscopy (SEM) was used to study the morphological structure, which indicated that no phase separation or cracks and good component compatibility. Chemical interaction between PVA, CMC, and AA was confirmed using Fourier transform infrared (FT-IR) in which the four characteristic absorption bands at 572, 1414, 3302 and 3411  $\text{cm}^{-1}$  which confirm the presence of -NCO-, -COO-, -OH and -NH<sub>2</sub>, respectively. Furthermore, the membrane mechanical strength, water uptake, gel fraction, and ion exchange capacity (IEC) were evaluated as functions of assorted membrane components. The results revealed that the addition of CMC and AA improves mechanical strength, IEC and protonic conductivity that reached 23.41 MPa, 0.11 mmol/g and  $1 \times 10^{-3}$  S/cm, respectively. These findings increase the viability of PVA/CMC/AA polyelectrolytic membranes for PEMFC application.

Keywords: polyvinyl alcohol; carboxymethyl cellulose; acrylamide; direct methanol fuel cell; polyelectrolyte membrane;

### 1. Introduction

Nowadays, fuel cells are a major player in clean energy production due to their carbon neutrality [1]. Direct methanol fuel cells (DMFC) are electrochemical devices that use methanol as an oxidant to produce electricity. DMFC operates at low temperatures with high power density. Methanol is one of the attractive fuels since it's economical in production, and has high hydrogen enrichment, and the reactions not involving the C-C bond broken may lower the fuel cell response [2, 3]. The reactions take place, and the working principles are illustrated in Scheme 1.

The operating heart of DMFC is the polymeric

membrane that allowed the transfer of protons ( $\text{H}^+$ ) to the cathode from the anode part. The membrane must have possessed low methanol permeability, quietwater retention, withstand operating conditions, thermal stable, ionic conductor and electrically insulator.

PVA and CMC are good membrane-forming materials and have great potential in DMFC membranes. They are low in cost, excellent film-forming materials, nontoxic, biodegradable and have different ways for modification [4, 5]. PVA is a water-soluble polymer so it must be crosslinked using one of the traditional crosslinkers as succinic acid, formic acid, epichlorohydrin [6], or sodium sulfite [7] to avoid deterioration during cell operation conditions. Also, PVA and CMC membranes have

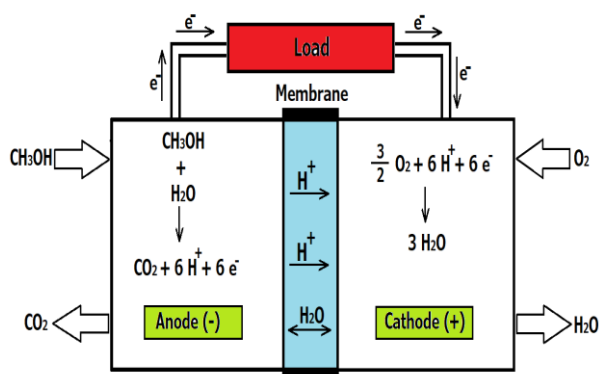
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poor ionic conductivity to use in DMFC so they must be modified to improve their conductivity. Blending with other polymers is the one of modification process as Acrylamide, hyaluronic acid [6], polyacrylic acid [8] or alginic acid [9]. Chemical treatment is also used to modify polymeric membranes to improve conductivity, mechanical and thermal stability rather than switching barriers to fuel crossover and managing swelled water in the membrane. The incorporation of one ammonium complexes system ( $\text{NH}_4^+$ ) can enhance the proton conductivity [10, 11]. Leena et al. [12] stated that the  $\text{NH}_4\text{SCN}$  can be used to improve membrane ion transportation through the formation of ionic channels that contain positively charged ammonium ions ( $\text{NH}_4^+$ ) which act as proton ( $\text{H}^+$ ) holders. Yang et al. [13] studying the relation between the ionic conductivity and the chemical composition of PVA-KOH- $\text{H}_2\text{O}$  system and indicating that the protonic conductivity is strongly depends on the KOH and swelled water content in PVA membranes. Terbish et al. [14] reported that the CMC blended chitosan membranes exhibit good mechanical strength and cationic conductivity properties. Thus, in this work we tried to find an alternate polymeric membrane that meets the standard requirements for DMFC. PVA, CMC and AA-based membranes were prepared and characterized for this purpose.



Scheme. 1: Direct methanol fuel cell reactions and working principles.

## 2. Experimental

### 2.1 Materials

CMC (DS= 0.7, AMw = 90000 g/mol) and PVA (typically average Mw = 124,000 g/mol, 95-96.5 %hydrolyzed) were acquired from Fisher Scientific,

UK. Acrylamide (purity 99%, Mw = 71.08 g/mol) was obtained from Merck, Germany.

### 2.2. Procedure of membrane preparation

Weighed quantity of PVA was dissolved in de-ionized water with continuous stirring at room temperature (RT) for 8h to prepare a 10%wt solution. 10wt% solutions of AA and CMC were prepared through following the previous method with stirring for 2h. The calculated amount of succinic acid was dissolved in deionized water with stirring for 30 min at RT to prepare 2wt%. All solutions were stored at room temperature.

Three membrane samples were prepared through the direct blending technique of PVA, PVA-CMC and PVA-CMC-AA in a molar ratio (of 4:3:2), respectively (according to previous experiments [6]). Succinic acid was added to all samples in fixed amounts (1 mL v/v). All mixtures were stirred for 4h at 40°C then cast to plate of polypropylene. All samples were placed at RT for 12 h to allow solvent to evaporate subsequently, exposed to 70°C for 6h to completely remove the solvent. Eventually, the obtained dried samples were stored in polypropylene containers at RT before being exposed to characterization techniques.

### 2.3. Characterizations

#### 2.3.1. Structure analysis

Japanese Shimadzu FTIR-8400 S (wavenumber range of 400–4000  $\text{cm}^{-1}$  and resolution of 4  $\text{cm}^{-1}$ ) was used to evaluate the functional groups and chemical bonds with in prepared PVA, PVA/CMC and PVA/CMC/AA membranes [2].

#### 2.3.2. Morphological analysis

Japanese SEM (JSM-6360LA, JEOL) with 500 to 5000 magnification power and 15 Kv acceleration voltage was utilized to investigate microstructure and morphological features of prepared PVA, PVA/CMC and PVA/CMC/AA membranes [15, 16].

#### 2.3.3. Mechanical properties

Japanese Shimadzu UTM universal testing Machine was employed to evaluate Tensile strength and the elongation at break of prepared membrane specimens (30 × 10 mm) with cross heads movement at a constant speed of 3 mm/min [16].

#### 2.3.4. Water uptake

The prepared membrane samples were cut off into 3 × 3 cm and dried at 90°C for 6h. The weight of dried samples is determined as ( $W_d$ ). Consecutively, all dried membranes were drenched in distilled water for 0.5, 1, 3 and 6 hours at RT.

Then, the swelled samples were leached and weighted again ( $W_w$ ). The water uptake was estimated through following equation (1) [12, 13].

$$\text{Water uptake (\%)} = \frac{W_w - W_d}{W_d} \times 100 \quad (1)$$

Where, ( $W_d$ ) and ( $W_w$ ) are the weights before and after membrane drenching, respectively in distilled water.

### 2.3.5. Determination of Gel fraction

The obtained PVA, PVA/CMC and PVA/CMC/AA membranes are dried at RT for 12h and weighed ( $W_1$ ), then dipped in distilled water for 24h to remove the leachable or non-crosslinked components. Then the samples were dried and weighed again ( $W_2$ ). The GF percentage was done according to the procedure mentioned by Fahmy et al. [17] and estimated by equation (2).

$$\text{Gel Fraction (GF\%)} = \frac{W_2}{W_1} \times 100 \quad (2)$$

Where, ( $W_1$ ) and ( $W_2$ ) are the weights before and after membrane dipping, respectively.

### 2.3.6. Determination of ion exchange capacity (IEC)

Acid-base titration technique is used to estimate IEC. The obtained membrane samples were weighted ( $W$ ) and soaked in 20 cm<sup>3</sup> of NaCl solution with concentration of (2 M) at RT for 12 h. Then, the obtained soaking solution was titrated against NaOH solution to determine the amount of hydrogen ion ( $H^+$ ) released as result of ion exchange process. The IEC was calculated through the equation (3) [18, 19]:

$$\text{IEC (mmol/g)} = \frac{N(\text{mmol/cm}^3) \times V(\text{cm}^3)}{W(\text{gm})} \quad (3)$$

Where  $W$ ,  $N$  and  $V$  are the sample weight, the NaOH concentration and titrate volume of NaOH, respectively.

### 2.3.7. Determination of protonic conductivity

Solartron 1260 with 1480 multistate impedance spectroscopy used to determine the obtained PVA, PVA/CMC and PVA/CMC/AA membranes protonic conductivity at 60°C. The protonic conductivity ( $\sigma$ ) was estimated through equation (4) from impedance data [20, 21].

$$\sigma (\text{s/cm}) = \frac{L}{RWD} \quad (4)$$

where,

- (W) Membrane thickness
- (A) Width of membrane
- (R) resistance of membrane

- (L) electrodes distance

## 3. Results and discussion

### 3.1. Chemical structural analysis

Fig. 1 illustrates the FT-IR spectra analysis of PVA, PVA/CMC and PVA/CMC/AA membranes. The IR spectra of the PVA membrane (Fig 1a) that crosslinked using succinic acid demonstrate common peaks at 2917 and 3302 cm<sup>-1</sup> related to C-H and -OH, respectively [22]. Typical recorded band at 1414 cm<sup>-1</sup> is relevant to symmetrical stretching of -COO<sup>-</sup> which displays the forming of ester covalent bonds as result of crosslinking reactions between succinic acid and polymer blend [23]. Moreover, the intensity of -COO<sup>-</sup> spectra is decreased (Fig1 B and C) with the addition of CMC and AA indicating network formation reactions between polymeric blends. (Fig1-C) exhibits new peaks at 572 and 3411cm<sup>-1</sup> were observed and can be assigned to carbonyl of amide groups (-N-C=O) and -NH<sub>2</sub> groups, respectively. The obtained results validate the existence of -OH, -COO<sup>-</sup>, -NH<sub>2</sub> and -NCO- groups within the PVA/CMC/ AA polymeric blend matrix [23, 24].

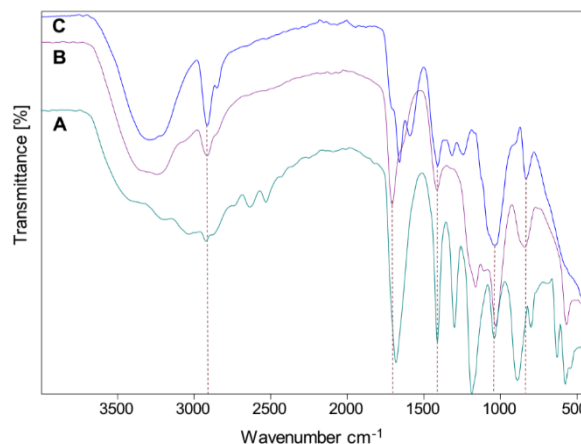


Fig. 1. FT-IR spectra of (A) PVA (B)PVA/CMC (C) PVA/CMC/AA based membranes.

PVA/CMC/AA membranes was shown in Fig. 2 for surface and cross section. In general, the PVA membrane exhibit no phase separation or cracks passed across the membrane due to good chemical compatibility blend and using succinic acid as a cross-linker [25]. The embedding of CMC into the PVA membrane leads to the formation of different-sized globules which grow larger with the addition of AA to the PVA/CMC membrane. This behaviour may be attributed to decreasing the adhesive between polymer blends as result to the hygroscopic properties of AA

[26]. The presence of these globules decreases the crystallinity, which can improve the protons conducting [27].

### 3.3. Mechanical strength measurements

The mechanical stability of PVA, PVA-CMC and PVA-CMC-AA membranes were evaluated through the determination of tensile strength and ultimate elongation summarized in Table 1 which illustrates that the tensile strength and elongation are affected by the blended membranes. At pristine PVA membrane the tensile strength displays a lower amount due to low molecular interaction forces between PVA polymer chains confined to hydrogen bonds and cross-linked bridges by succinic acid.

Table 1

The influence of polymer blend in mechanical strength and elongation at break.

| Sample     | Tensile Strength (MPa) | Elongation at Break (%) |
|------------|------------------------|-------------------------|
| PVA        | 18.62                  | 254.31                  |
| CMC/PVA    | 22.35                  | 276.37                  |
| PVA/CMC/AA | 23.41                  | 283.22                  |

With the addition of CMC and AA the tensile strength and elongation increased as result to increasing intermolecular and intramolecular molecular forces as a result of the attendance of more ionic groups (-COO-, -OH and -NH<sub>2</sub>) leading to more polymeric chains interaction [28].

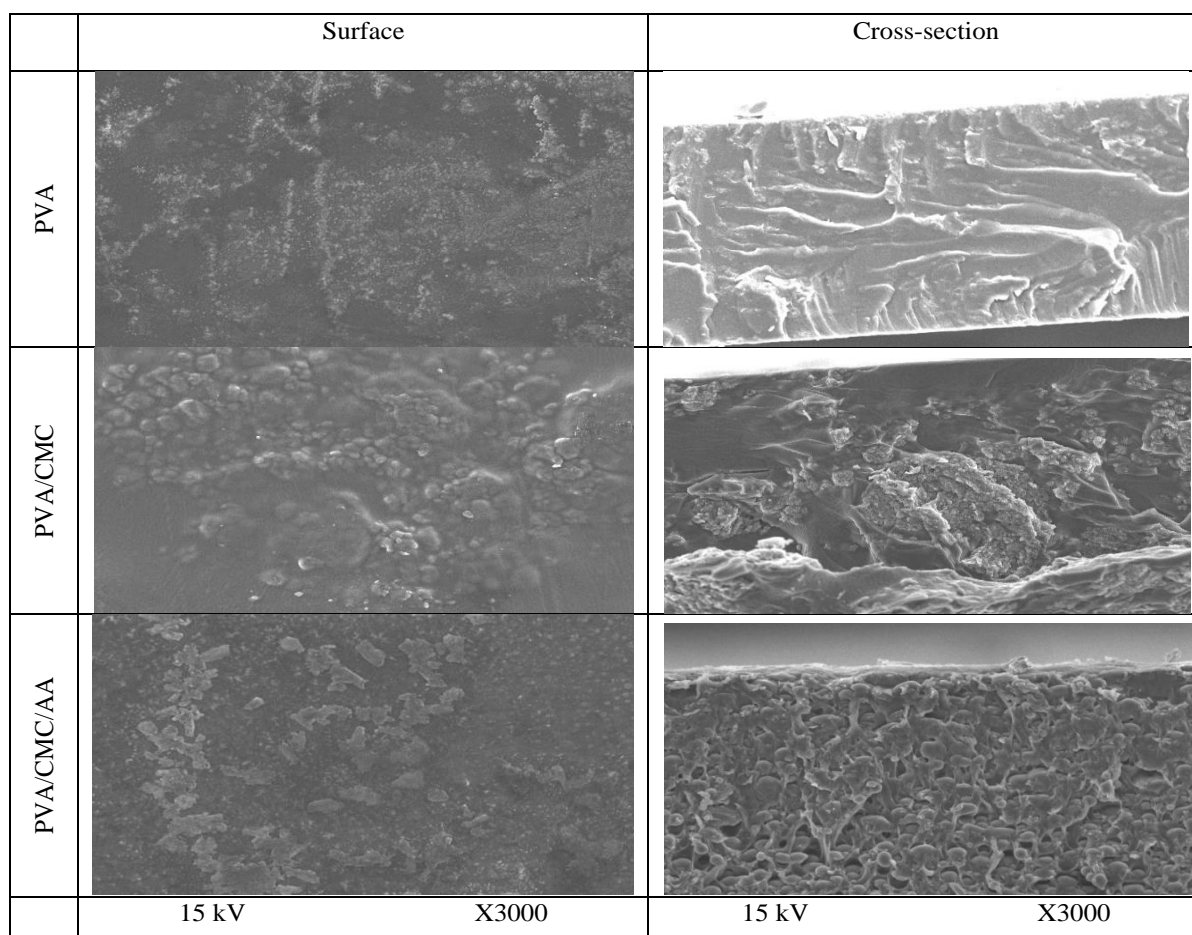


Fig. 2. photograph of SEM for obtained PVA, PVA/CMC and PVA/CMC/AA membranes (surface and cross-section).

### 3.4. Water uptake

Polymeric fuel cell membrane should be embedded in an amount of water to facilitate proton transportation across two cell parts [29]. As shown in Fig. 3 the amount of water taken by all membranes increased with growing swelling time. At pristine PVA the amount of water uptake exhibited a lower ratio (550%) compared to PVA-CMC and PVA-CMC-AA which possess 571.8 and 615.3%, respectively. This behaviour can be illustrated according to that, only -OH functional groups found in the membrane of pure PVA which bonded water molecules through a hydrogen bond. At PVA-CMC and PVA-CMC-AA the additional function groups were founded to attract further water molecules [6].

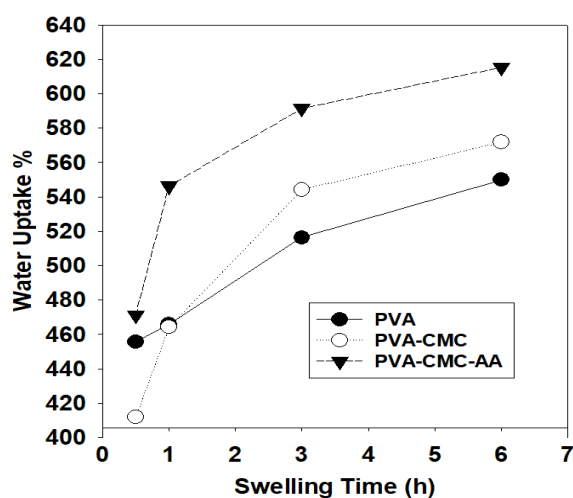


Fig. 3. Water Uptake of PVA, PVA-CMC and PVA-CMC-AA.

### 3.5. Gel Fraction

Gel fraction analysis was determined to define uncross-linked components and crosslinking density [30]. Fig. 4 reveals the amount of gel fraction of PVA, PVA-CMC and PVA-CMC-AA membranes. The crosslinking density increased with the addition of a polymer blend because of increasing interactions between membrane components. The obtained results inherent to that obtained from tensile strength measurements [31].

### 3.6. Ion exchange capacity (IEC) and protonic conductivity (PC)

IEC gives an impression of an ionic group that can hold and exchanges protons ( $H^+$ ) till delivered to the cathode [32, 33] thus, polymeric membranes must possess good IEC to enhance excellent protonic conductivity (PC) [34]. Fig. 5 shows the IEC and PC values of PVA, PVA-CMC and PVA-CMC-AA membranes. As shown, the PC is strongly dependent on IEC and exhibits similar behaviour by increasing of

polymer blend. With pristine PVA, the values of IEC and PC were  $9.12 \times 10^{-3}$  mmol/g and  $5.43 \times 10^{-4}$  S/cm, respectively as a result of poor strong ionic groups. At the PVA/CMC/AA membrane the amount of IEC and PC reached a higher value of 0.11 mmol/g and  $1 \times 10^{-3}$  S/cm, respectively owing to introducing of more ionic groups ( $-NH_2$  and  $-COO^-$ ) [26, 35].

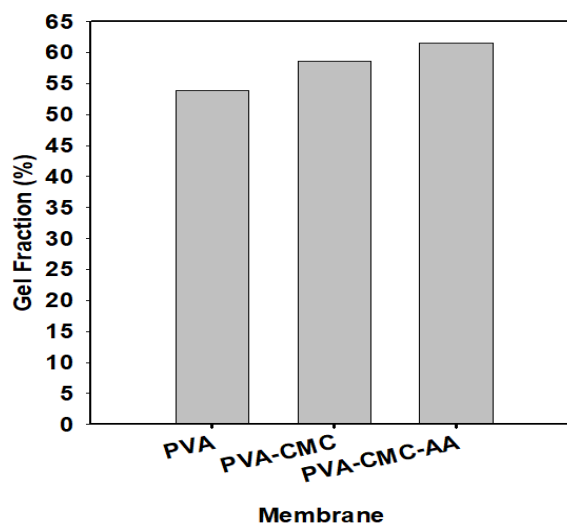


Fig. 4. Gel fraction of PVA, PVA-CMC and PVA-CMC-AA.

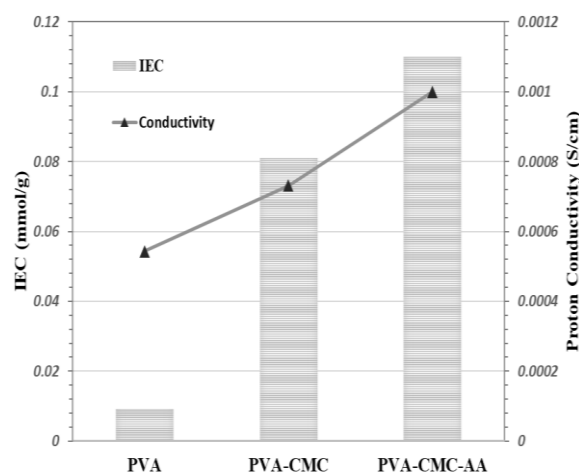


Fig. 5. IEC and PC of PVA, PVA/CMC and PVA/CMC/AA.

## 4. Conclusion

Blend CMC/PVA/AA polymeric membranes with the addition of succinic acid as crosslinker were successfully prepared through a solution casting technique and investigated as a polyelectrolyte membrane. The functional and morphological



properties of prepared membranes were approved by FT-IR and SEM, respectively. Other physicochemical analyses as ion exchange capacity, gel fraction, water uptake, tensile strength, and hydrogen ions ( $H^+$ ) conductivity. The work outcomes revealed that the addition of polymer blends CMC and AA as well as succinic acid has been achieving the purpose of addition that improves mechanical strength to afford DMFC operating conditions and enhance good proton conductors and capacitors. Ion exchange capacity and protonic conductivity reached maximum values of 0.11mmol/g and  $1 \times 10^{-3}$  S/cm, respectively with PVA/CMC/AA membranes. In addition, the prepared membranes exhibit an acceptable water uptake ratio that can improve the transportation of  $H^+$  across membrane. Finally, the CMC/PVA/AA membranes acquire acceptable electrochemical properties for further improvements to use as low-cost DMFC membranes.

## 5. Conflicts of interest

“There are no conflicts to declare”.

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