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Analysis of polybenzimidazole and polyvinylpyrrolidone blend membranes as separating barrier in single chambered microbial fuel cells

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ABSTRACT

In present study, different blend compositions of polybenzimidazole (PBI) and polyvinylpyrrolidone (PVP) have been analyzed as polymer electrolyte membrane in single chambered MFCs. Four membranes namely, pure PBI, PBI/PVP 70:30, 50:50, and 30:70 blend ratios with increasing PVP content were casted, where the hygroscopic properties of the membranes were found enhanced with increasing PVP content. The membranes were characterized at room temperature ($22 + 2\,^\circ$C) with different ion exchange (IEC) and proton conductive capacities, where an IEC of 0.06 meq g^{-1}, 0.15 meq g^{-1}, 0.24 meq g^{-1} and 0.36 meq g^{-1} and proton conductivity of 2.5×10^{-4}, 4.8×10^{-4}, 9.36×10^{-4} and 1.2×10^{-3} S cm^{-1} were observed from pure PBI, PBI/PVP 70:30, 50:50, and 30:70 membranes respectively. As membrane electrode assemblies (MEA), the casted membranes were sandwiched in-between carbon cloths, where a maximum power and current density of 231.38 ± 12 mW m^{-2} and 1242 ± 62 mA m^{-2} were observed from 30:70 PBI/PVP fitted MFC, using mixed firmicutes as biocatalysts. A gross 84.36% COD removal from 30:70 PBI/PVP membrane indicated the added effect of PVP in blend composition with approximately 81% higher power over pure PBI membrane. The results indicate the potential efficacy of PBI/PVP blends as seperators in microbial fuel cell, for bio-energy conversion over pure PBI membrane.

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1. Introduction

In the last few decades, the advances made in microbial fuel cells have drawn much attention in the areas of membrane technology. Bennetto et al. were one of the first groups that showed microbial activity responsible for energy generation in MFCs [1,2]. Considering the parameters, choice of membrane has always been a decisive factor in MFC design, as it serves the purpose of regulating ohmic losses and thereby internal resistance of the system. Additionally, to reduce the overall fabrication cost, several studies on membrane modification and optimization have been conducted. Polymeric materials like polystyrene, polyether ether ketone (PEEK), poly (arylene ether sulfone), phenylated polysulfone, polyphosphazenes, polyimides, poly(4-phenoxybenzoyl-1,4-phenylene), polybenzimidazole(PBI), polyolefins and polypropylene (PP) have been widely studied as membrane alternatives [3–6]. In addition, different ion permeable membranes with varied molecular weights have been equated to determine its comparative effect as PEM in MFCs [7–12].

In a study, a group led by Ayyaru et al. developed a sulfonated polystyrene-ethylene-butylene-polystyrene (SPSEBS) membrane as an alternative of Nafion membrane, which showed ~106.9% higher power density with lower internal resistance in MFC [13]. In another study, using sulfonated polyether ether ketone (SPEEK) as membrane, ~55.2% higher power density over Nafion was observed [14]. The formed biofilms at anode, self mediates the electron and proton transfer in the system, where charge accumulation is generally attributed to the used membrane in the system [15–18]. Similarly, considering the low cost and availability, a group led by Gangrekar showed the efficacy of earthen pot as ion-exchanger in microbial fuel cells (MFCs) [19]. In another instance, S.Pandit et al. analyzed the performance of an anion exchange membrane (AEM) in batch mode, where a maximum voltage of 0.67 V and 0.72 V with a power density of 39.2–7.39 mW m^{-2} and 57.8–5.509 mW m^{-2} were obtained using Nafion and Ralex membranes [20]. Likewise, different methods e.g. photosulfonation, plasma treatment and radiation grafting have been shown to improve hydrophilic and adhesive properties in the membranes [21–25].

Recently, many researches on the application of polybenzimidazole (PBI) in hydrogen sensors and other high temperature fuel cells have been studied [26,27]. PBI with a glass transition temperature (Tg) of 420 °C has been found with increased proton

conductivity at higher temperatures. However, at room temperature it shows poor conductivity, which for enhancement has been studied with other N-heterocycle compounds like, polyimides (PI) and polyvinylpyrrolidone (PVP) as blends [28]. Increasing PVP contents were observed with increased weight losses in the blends, where to analyze their effect at room temperature, varying blend compositions of PBI/PVP membranes have been investigated here in MFC.

Present study highlights the suitability of PBI/PVP blends as separating barriers with their impressions on system internal resistance. The casted blends have been characterized in terms of their water uptake, ion exchange (IEC) and proton conductive capacities, where they exhibited higher miscibility with increasing in-between hydrogen interaction at room temperature. Based on their gel fraction ratio, membranes have been shown to form crosslinked networks on mild alkali treatment with increased conductivity at room temperature. Referring the above findings, the relevance of PBI/PVP blended membranes as a cost effective separating barrier with mixed *firmicutes* as biocatalysts have been presented in single chambered MFCs for bio-energy generation.

2. Materials and methods

2.1. General conditions

All chemicals used were of analytical and biochemical grade. Polyvinylpyrrolidone (PVP) (K30) was purchased from Sigma Aldrich. The solvents/chemicals e.g; DMAc, methanol, phosphoric acid, etc. were bought from Merck Millipore India. Microbial experiments and inoculations were performed strictly under sterile conditions.

2.2. Preparation of PBI/PVP blends

Polybenzimidazole (PBI) was prepared by a common solution condensation method at 190–200 °C for 24 h in presence of N_2 [29]. The monomers terephthalic acid and 3,3′,4,4′-tetraaminobiphenyl (TAB) were dissolved in a polyphosphoric acid solvent which turned into a polymerized viscous mass of dark brown colour. Later this PBI polymer was isolated, subsequently pulverized and neutralized with sodium bicarbonate solution, and finally dried in vacuum oven at 100 °C. The blend solutions were prepared by dissolving both polybenzimidazole (PBI) and polyvinylpyrrolidone (PVP) polymer in a common solvent DMAc. 2% (W/V) PBI was dissolved in refluxing condition at 160 °C for 5–6 h. Dissolved PVP was mixed with PBI solution in different 30, 50 and 70% volume ratios. This mixed blend solution was casted and vacuum dried at 100 °C in 2 M NaOH solution. PVP, being water soluble was insloublized with alkali treatment to retain intact with PBI blend composition [30–32]. Further, the prepared pure PBI, PBI/PVP (70:30), PBI/PVP (50:50) and PBI/PVP (30:70) membranes were acid doped for 48 h by immersing in phosphoric acid solution.

2.3. Membrane dissolution, water uptake and swelling ratios

Using solvent extraction method, membrane dissolution was determined. Small piece of the membranes were wrapped in filter paper and kept in DMAc and water at 60 °C. Solvents were replaced in every 15 h until no further solubility was observed in the polymer. The remaining part of the samples was dried and weighed. The gel fractions W (gel) of the membranes were calculated from Eq. (1):

$$W(gel) = W_1/W_0 \times 100 \tag{1}$$

where, W_0 is the original weight of the dried membrane, and W_1 is the mass weight of the dried membrane after complete solvent extraction.

Likewise, water uptake calculations of the casted membranes were done using the following equation:

$$Water uptake(\%) = (W_{wet} - W_{dry})(100)/W_{dry} \tag{2}$$

where, W_{wet} and W_{dry} represent the weight of respective wet and dry membranes after getting soaked for 24 h in DI water.

In addition, swelling ratios of the prepared membranes were calculated as:

$$Swelling ratio(\%) = (T_{wet} - T_{dry})(100)/T_{dry} \tag{3}$$

where, T_{wet} and T_{dry} represent the respective thicknesses of wet and dry membranes after 24 h soaking in DI water.

2.4. Ion exchange capacity (IEC)

Using the conventional titration method, ion exchange capacities (IECs) of the respective membranes were determined. Membranes were soaked overnight in 1 M H_2SO_4 solution, and thereafter rinsed with DI water to remove excess H_2SO_4 on surface. Later, the membranes were again soaked in 50 ml (1 M NaCl solution) overnight, in order to allow replacement of protons with sodium ions. The remaining solution was titrated with 0.01 N NaOH solution, using phenolphthalein as indicator. The IEC value (in meq g^{-1}) was calculated using the following equation:

$$IEC = (V_{NaOH})(S_{NaOH})/W_{dry} \tag{4}$$

where, V_{NaOH} is the volume of NaOH used in titration, and W_{dry} is the dry weight of the membrane (gm). S_{NaOH} is the strength of NaOH used in the experiment for IEC determination.

2.5. Proton conductivity

AC impedance spectroscopy at a frequency range of 1 Hz to 10^5 Hz (of 10 mV amplitude) were employed across membranes in the transverse direction (S1, Supplementary information) using a potentiostat (Gamry Reference-600). The conductivities (σ) of the casted membranes were calculated from the impedance plot employing the following equation:

$$\sigma = T/R.A \tag{5}$$

where, T and A represents the thickness and cross-sectional area of the samples, R is the lower intersect resistance on a complex nyquist plane with higher frequency semi-circle along real (Z) axis.

2.6. Anolyte preparation

Synthetic wastewater composed of nutrient broth, KH_2PO_4, and $MgSO_4$ with a COD/N/P of ratio 100/9/1.2 was used as anolyte substrate. The COD composition of the feed wastewater was 1800 ± 210 mg l^{-1} (total nitrogen: 108 ± 24 mg l^{-1}, PO$_4$–P: 27 ± 9 mg l^{-1}, MgSO$_4$:45 mg l^{-1}). The isolated microbes were found to be firmicutes class *lysinibacillus* species done by PCR amplification (EMBL accession no. HE648059, HE648060, HF548664) [33]. These when tested for viability in gas pack jar were found as facultative anaerobes. Further, these mixed strains were suspended in 50 mM phosphate buffer (50 ml volume) and subsequently transferred to 100 ml synthetic wastewater (pH ~ 6.9), making a final 150 ml volume of microbial enriched anolyte.

2.7. MEA and MFC configuration

The casted membranes (PBI, PBI/PVP (70:30), PBI/PVP (50:50), and PBI/PVP (30:70) were assembled as MEAs, where membranes