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Ferrocene-Modified Polybenzimidazole Membrane with Enhanced Proton Conductivity

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Polymer electrolyte membranes with high proton conductivity continue to pose a challenge especially in the fields of biomaterial, semiconductor, membrane separation, and ion conductive membrane. Here, an alternative of a new class of highly conductive ferrocene-modified polybenzimidazole (PBI/Fc) membranes was prepared by the solvent casting method after the amidation reaction of ferrocene carboxylic acid (FCA) with imidazole groups in PBI solution. The properties of the as-prepared membranes were characterized by varied spectroscopic measurements. For instance, in the attenuated total reflectance-Fourier transform infrared (ATR-FTIR) measurements the characteristic vibrational bands of ferrocenyl moieties, and amide bond formation were identified. Interestingly, in the electrochemical studies, membrane PBI/Fc-5 was found to exhibit low absolute impedance and high proton conductivity of $537 \times 10^3\ \Omega$ and 0.0249×10^{-8} S/cm, respectively.

Key words: Polybenzimidazole; ferrocene carboxylic acid; ferrocene; amide; proton conductivity

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Proton conducting polymers have been widely used in energy storage systems, particularly in powering electronic machines and devices [1]. With energy storage, renewable energy can be made more reliable and less expensive. So far, Nafion membranes, which are highly hydrated, remain one of the most powerful man-made proton conductors [2]. Nevertheless, the water management system related to Nafion membranes is complex and expensive [3]. Thus, membrane-inspired polybenzimidazole (PBI) and its derivatives, with exceptional physicochemical properties have attracted significant interest in many applications, including in chemical and biological applications [4,5]. PBI exhibits high proton conductivity at low water content, excellent thermal stability up to 200ºC, and has good mechanical properties. Problems for further enhancement may include improved proton conductivity, durability, stability, and mechanical strength. Different methods are being used to boost the proton conductivity of the PBI membrane without affecting its mechanical strength, for instance, with the addition of inorganic fillers, acids, and structural modifications via the formation of ionic cross-linking [2].

Herein, in this report, we focus our efforts on studying the preparation, characterization, and proton conductivity study of PBI membranes modified with ferrocene carboxylic acid (FCA). Primarily, FCA was covalently cross-linked to PBI by amide bond linkages through the imidazole groups of the polymer at room temperature, thus leading to the formation of ferrocene-modified PBI. The efficiency of these modified PBI membranes was examined in the proton conductivity test by using electrochemical impedance spectroscopy (EIS) at room temperature.

MATERIALS AND METHODS

Materials

Celazole® polybenzimidazole (PBI) solution (26%, MW = 27000 g/mol, PBI Performance Products Inc (USA)) and ferrocene carboxylic acid, FCA (1 g, Merck) were all used as the precursor materials of PBI/Fc membrane. The PBI solution contained 26 wt% polymer solids and 1.5 wt% lithium chloride (stabilizer) dissolved in DMAc. Dimethylacetamide (DMAc) (2.5 L, Merck) was used without any further purification. Distilled water was used throughout the experiment.

Preparation of 15 wt% PBI Solution

The PBI solution preparation processes were carried out according to the previously reported procedure [6].

Celazole® S26 was diluted to 15 wt% polymer concentration with 21 mL of DMAc and stirred continuously at room temperature for 24 hours until a homogeneous solution was gained. Then, the polymer solution was left overnight for the removal of air bubbles.

Preparation of 1 wt% FCA Solution

Firstly, 0.1 g of FCA was dissolved in 10 mL of DMAc in a glass vial to form 5 wt% FCA solution. Then, the solution was stirred overnight at room temperature and a brown solution formed. The same procedure was followed by adding 0.5 g of FCA, for the preparation of 5 wt% FCA solution.

Membrane Preparation

To 10 mL of PBI solution, 10 mL of 1 wt% FCA solution was added dropwise at 25°C. After the mixture was stirred vigorously for 3 hours at that temperature, the solution was left at room temperature overnight. Next, the solution was poured onto an 8 × 8 cm glass plate and casted with a stainless steel scraper. Then, the casted membrane was dried in an oven at 80°C for one day, during which DMAc slowly evaporated, and a light brown membrane was formed. Afterward, for easy peeling, and LiCl elimination, the membrane was immersed in 80°C water bath for 1 hour and dried at 110°C for 1 hour for water removal. This membrane was named as PBI/Fc-1. For comparison, a similar membrane was fabricated using the same procedure but with replacing 1 wt% FCA solution with 5 wt% FCA solution, which the membrane was noted as PBI/Fc-5. All the membranes were stored in a zip lock bag and placed in a desiccator.

Spectroscopies

ATR-FTIR spectroscopic studies were performed with Thermo Scientific Model Nicolet iS10 FT-IR spectrophotometer with 32 numbers of scans in the wavenumber range of 500–4000 cm^{-1} at 4 cm^{-1} resolution. The FTIR spectrophotometer was well-equipped with a platinum ATR single reflection diamond-sampling module. Before the analysis, the ATR platform was cleaned using ethanol. Then, the sample was placed onto the platform until the crystal surface was covered entirely. Before sample analysis, a background spectrum was carried out first. The FTIR spectra were recorded as the percentage of transmittance (% T) versus wavenumber. The optical properties of the samples were characterized by Perkin Elmer ultraviolet-visible (UV-Vis) diffuse reflectance spectrophotometer Lambda 900, employing barium sulfate ($BaSO_4$) as the internal reflectance standard. The scan range was from 200 to 800 nm, with the scan parameter set with a slit size of 1 nm. The spectra were recorded as absorbance versus wavelength. X-ray diffraction (XRD) patterns of the samples were collected by using Bruker Advanced D8 Siemens 500 diffractometer (CuKα radiation, λ=1.5418 nm). For obtaining the morphological properties of the membranes in the form of scanning electron microscopy (SEM) images, as well as the thickness of the membranes, the as-prepared membranes were examined using JEOL JSM-6390LV instrument with an accelerating voltage of the electron gun at 10 kV.

Proton Conductivity

Proton conductivity of the prepared membranes was measured by electrochemical impedance spectroscopy. The measurements were conducted at room temperature. The fabricated membranes were used as the anode, while the counter electrode (cathode) was graphite, and Ag/AgCl was used as the reference electrode. The three electrodes were placed in water, as the source of protons (H^+). The proton conductivity value was measured by using Equation (1):

$$\sigma = l / (RA) \qquad (1)$$

Where σ is the proton conductivity (S/cm), l is the thickness of the membrane (cm), A is the area of the membrane, and R is the resistance value of the membrane (Ω) obtained from the absolute impedance plot.

RESULTS AND DISCUSSIONS

In this contribution, ferrocene-modified polybenzimidazole membranes were prepared via the solvent casting method by the addition of FCA solutions to 15 wt% PBI solution at a volume ratio of FCA : PBI = 1 : 1 (Figure 1). Figure 2 shows the photographic images of membranes PBI/Fc-1 and PBI/Fc-5. The membranes were transparent, and this indicated the homogeneity of the ferrocene-modified membranes. The obtained membranes were characterized by ATR-FTIR, DR UV-vis, XRD, and SEM.

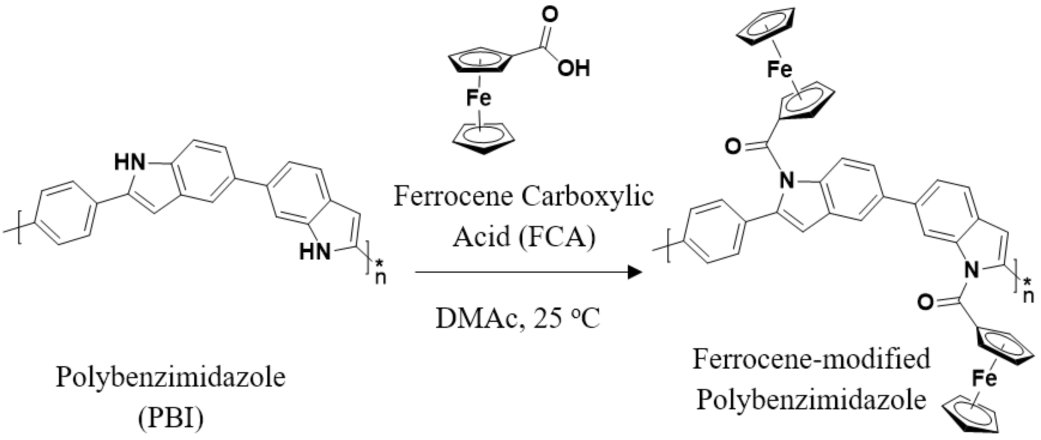


Figure 1. Synthesis of ferrocene-modified polybenzimidazole

(a) (b)

Figure 2. Photographic images of membranes (a) PBI/Fc-1 and (b) PBI/Fc-5

Figure 3 displays the FTIR spectra of membranes PBI/Fc-1 and PBI/Fc-5. FTIR analysis was carried out to examine the type of chemical bonding present on the surface of the casted PBI-based membranes. Both spectra were similar except that some of the peaks of PBI/Fc-5 were much sharper compared with PBI/Fc-1. This confirmed that the difference in weight percent of FCA added influenced the chemical structures of the membranes. Also, the characteristic peaks of PBI and FCA were confirmed with the spectra of PBI and FCA published in the literature [6-8].

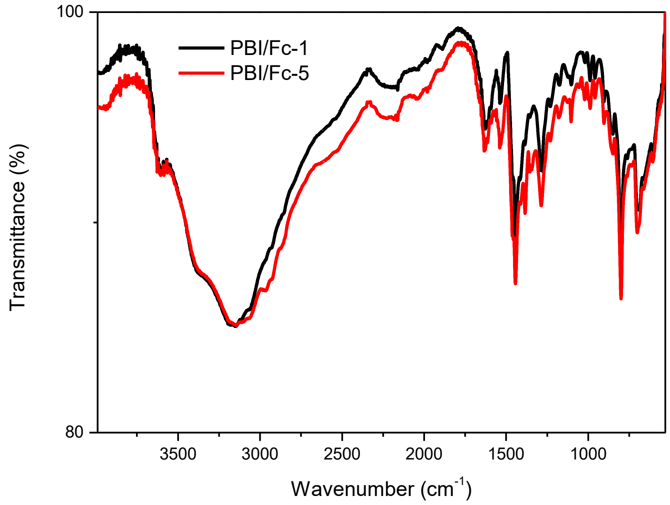


Figure 3. Infrared spectra of membranes PBI/Fc-1 and PBI/Fc-5

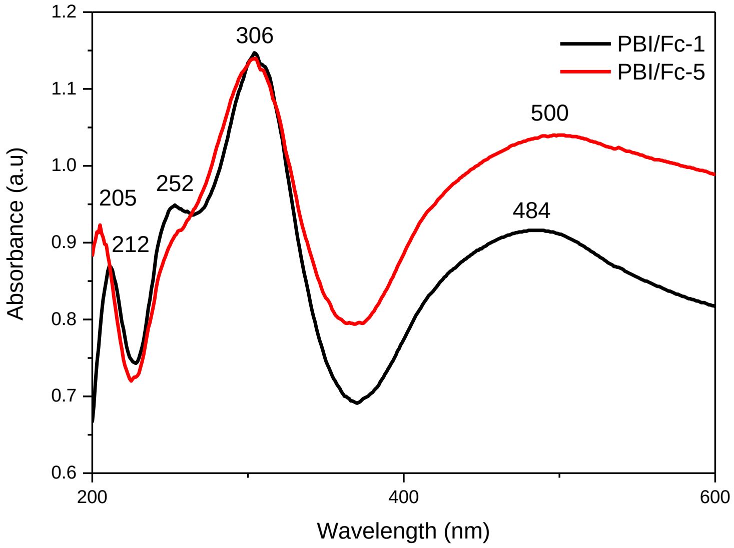


Figure 4. Absorption spectra of membranes PBI/Fc-1 and PBI/Fc-5

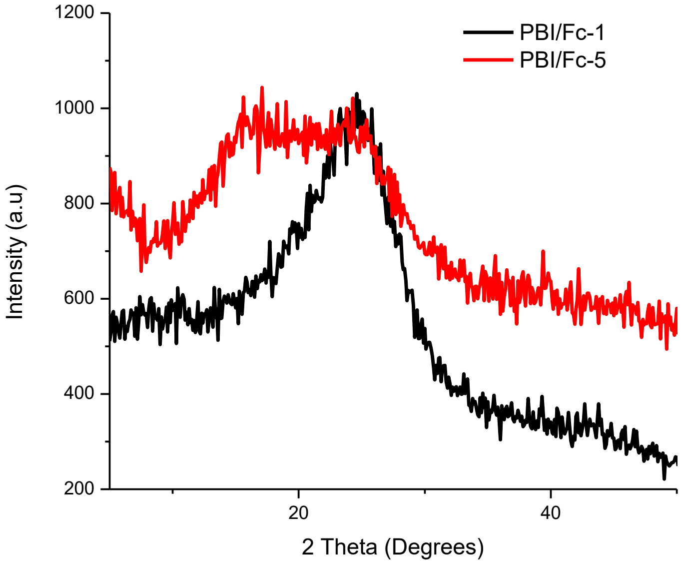


Figure 5. XRD patterns of PBI/Fc-1 and PBI/Fc-5

The absorption bands for the O-H and N-H functional groups appeared around 3168 cm^{-1} for both samples. The peaks showed broad bands, and these were due to the hydrogen bonds formed between imidazole N and NH [9]. Another absorption band was observed at 1632 cm^{-1}, which was attributed to the C=O of the amide bond, indicating that FCA had been functionalized with PBI. However, in the case of PBI/Fc-5, it could be observed that the peak intensity was significantly high, and this was due to the interactions between the high weight percent of FCA with the polymer matrix that led to the formation of the high amount of the C=O functional group. Meanwhile, the vibration at 1535 cm^{-1} was due to the C=N. A strong band around 1443 cm^{-1} was assigned to the C=C aromatic in both FCA and PBI. Also, two bands observed at 798 cm^{-1} and 701 cm^{-1} were attributed to the C-H bend. Furthermore, C-O bands could be seen at 1286 cm^{-1}. This observation indicated a good interaction between FCA and the polymer matrix.

The electronic absorption spectra of PBI/Fc-1 and PBI/Fc-5 are shown in Figure 4. The $\pi \rightarrow \pi^*$ transition of the aromatic ring and imidazole moiety of PBI/Fc-1 and PBI/Fc-5 appeared at 205 and 212 nm, respectively. The spectrum of PBI/Fc-5 demonstrated a hypsochromic shift around 200 nm.

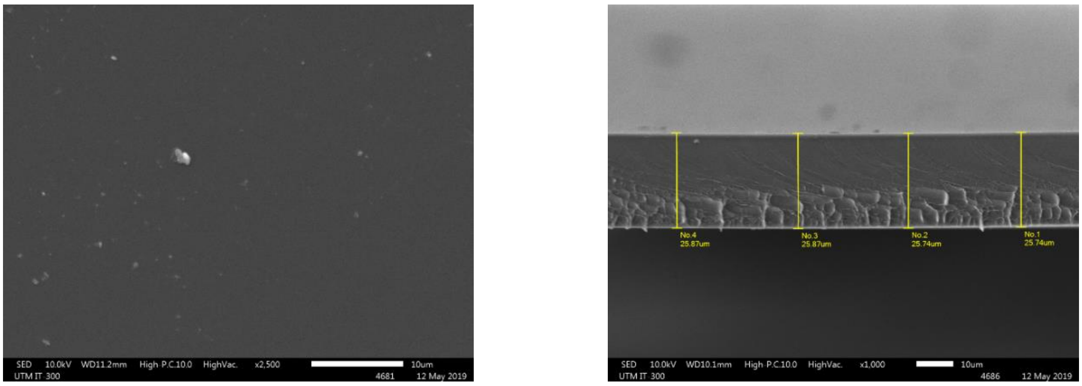
This suggested that with the addition of an excess amount of FCA to the PBI solution, a minor blue shift of the DR UV-Vis spectrum was induced. Moreover, the observed broad maximum at 252 and 306 nm for both membranes may be attributed to the $n \rightarrow \pi^*$ transition of the azomethine group [10-12]. Two other absorption bands appeared at 484 and 500 nm for PBI/Fc-1 and PBI/Fc-2, respectively. This was due to the $d \rightarrow d$ (assigned to the $^1A_{1g} \rightarrow {}^1E_{1g}$) transition. However, in comparison with PBI/Fc-1, the absorption band of PBI/Fc-5 got red-shifted. This was because the amount of FCA reacted with PBI was higher compared to PBI/Fc-1. Thus, this increased the number of π-conjugation system of the polymer matrix and ferrocenyl moiety, that led to the strong electronic communication in the compound [13,14].

Figure 5 shows the XRD spectra of membranes PBI/Fc-1 and PBI/Fc-5. No sharp peaks but broad absorption bands were observed for both membranes, indicating that these samples were amorphous. PBI/Fc-1 showed an absorption band at 25^{o} which corresponded to the benzimidazole chains forming a π-π stacked structure of PBI [15]. For PBI/Fc-5, there appeared a broad amorphous peak which composed of two convoluted peaks with peak maxima of 17^{o} and 25^{o}. According to Kumbharkar and his colleagues, this may be due to the bulky side chains present in the PBI structure which cause different chain packing arrangements [16]. The high amount of FCA added in this study could contribute to the increase in the side chain formation with PBI through the amide bond, thus producing two convoluted peaks in the XRD spectrum.

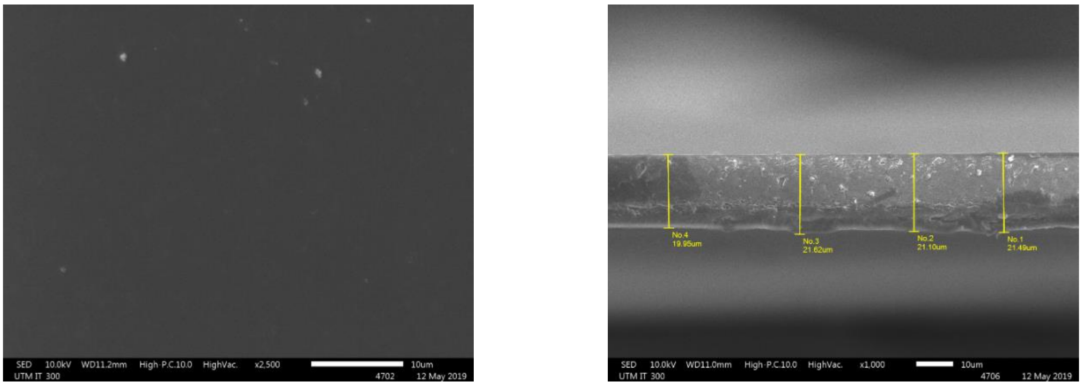
The SEM images of the membranes are shown in Figure 6. The surfaces of membranes PBI/Fc-1 and PBI/Fc-5 were generally flat, continuous, free of holes, and dense. Roughly, the cross-sectional images were also free of holes and dense. However, for PBI/Fc-1, it was obvious that the membrane displayed some cracks at the bottom of the cross-sectional image. Since the membranes were too tough to fracture easily, brittle fracture of the liquid nitrogen method was used in preparing the samples for the analysis. Thus, the cracks present were the effect of fracturing the membrane using this technique [17]. Besides, when the percent content of FCA was upped to 5%, the cross-section view was not smooth, which may be due to the aggregation of FCA in the PBI matrix.

Surface Morphology

Cross-section



PBI/Fc-1



PBI/Fc-5

Figure 6. Surface and cross-sectional images of membranes PBI/Fc-1 and PBI/Fc-5

Proton Conductivity

To find out the effect of adding FCA into the PBI matrix, proton conductivity test was conducted by employing the electrochemical impedance spectroscopy (EIS). The absolute impedance (|Z|) as well as the proton conductivity, σ of the PBI samples were evaluated from the EIS study. The impedance measurements were carried out at $25^{o}C$. Figure 7 shows the plots of absolute impedance versus frequency and proton conductivity of the samples. The resistance value is the impedance value in the low-frequency region (1 Hz) obtained from Figure 7a. The resistance for PBI/Fc-1 and PBI/Fc-5 was 767×10^{5} Ω and 537×10^{3} Ω, respectively. Table 1 shows the parameters used to calculate the proton conductivity of the membranes. The proton conductivity increased from 0.0002×10^{-8} S/cm to 0.0249×10^{-8} S/cm as FCA increased from 1 wt% to 5 wt%. This could be explained by the presence of more ferrocenyl moiety in the polymer matrix through the amide bond (N-C=O) formation. The carbonyl (-C=O) groups could serve as proton carriers for proton transfer, which led to high-efficiency enhancement of proton transportation [18]. Besides, the presence of nitrogen-containing heterocycles of PBI also would enhance the proton conductivity of the material. Thus, the results suggested that the introduction of ferrocenyl moiety into the polymer matrix promises good proton-conducting properties.

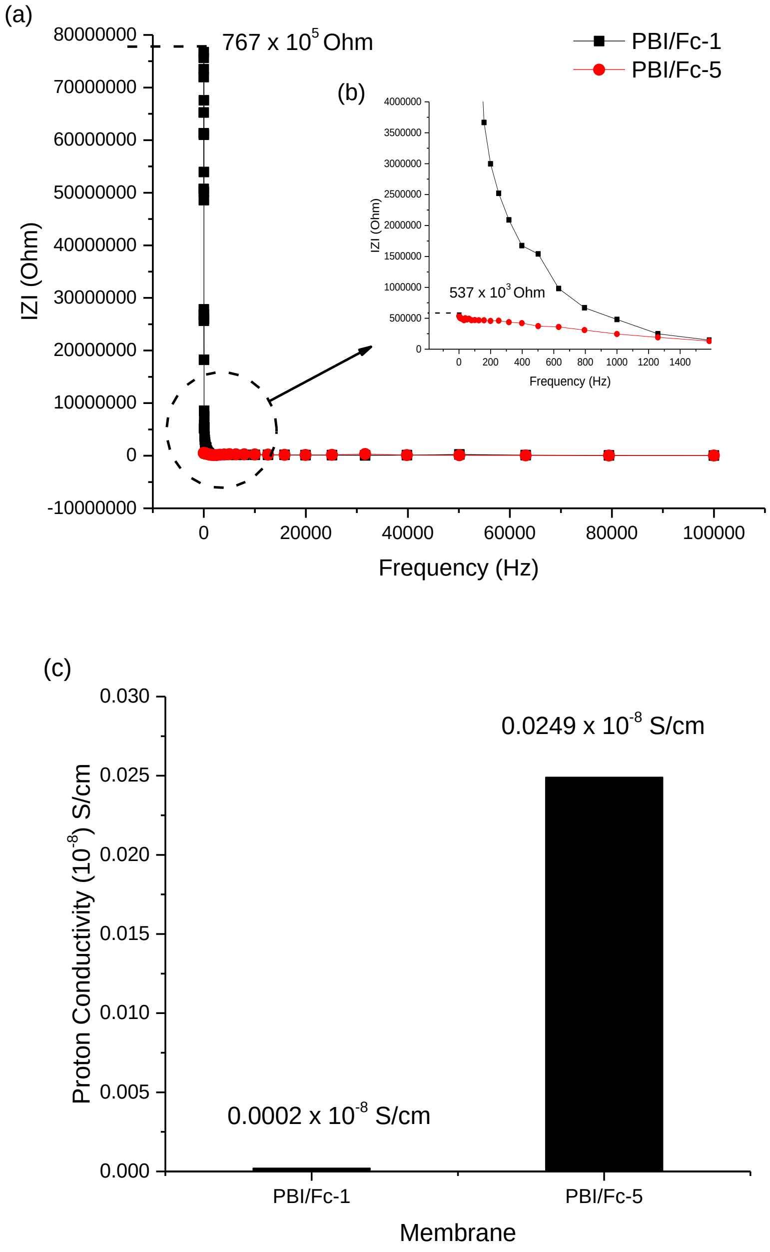


Figure 7. Plots of (a and b) absolute impedance and (c) proton conductivity of membranes PBI/Fc-1 and PBI/Fc-5

Table 1. Resistance, area, thickness, and proton conductivity values of membranes PBI/Fc-1 and PBI/Fc-5

Membrane	Resistance, R (Ω)	Area, A (cm^2)	Thickness, *l* (cm)	Proton Conductivity (10^{-8} S/cm)
PBI/Fc-1	767×10^5	16	0.002583	0.0002
PBI/Fc-5	537×10^3	16	0.002140	0.0249

CONCLUSION

Ferrocene-modified polybenzimidazole membranes have been successfully prepared by the solvent casting technique. The attachment of ferrocenyl moiety with the PBI polymer was confirmed by FTIR studies. Covalent cross-linking of polybenzimidazole with FCA occurred via amide bond formation through the imidazole group. The amount of FCA added to the PBI solution has been found to affect the proton conduction, where PBI/Fc-5 showed higher proton conductivity compared with PBI/Fc-1. Indirectly, it is worth to conclude that covalent cross-linking of ferrocenyl moiety enhances the proton conductivity of the membrane.

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