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Phosphoric Acid Doped Polybenzimidazole and Sulfonated Polyether Ether Ketone Composite Membrane for Hydrogen Production in High-Temperature Copper Chloride Electrolysis

M F A Kamaroddin^{1,2*}, N Sabli^{1*}, T A T Abdullah^{2,3}, L C Abdullah¹, S Izhar¹, A Ripin^{2,3} and A Ahmad^{2,3}

¹ Department of Chemical and Environmental Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

² Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

³ School of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

E-mail: mohdfadhzir@utm.my, nordin_sab@upm.edu.my

Abstract. A composite membrane of polybenzimidazole (PBI) and sulfonated polyether ether ketone (SPEEK) based electrolyzer that operates at higher working temperature above 80 °C is advantageous for faster electrochemical kinetics, higher current exchange density and more resistance to fuel impurities. A high-temperature copper chloride-based composite membrane electrolysis is proposed to overcome the issue of fuel diffusivity, membrane's thermal and mechanical stability in hydrogen production. The phosphoric acid (PA) functionalized composite PBI and SPEEK membranes were synthesized by a standard method followed with immersion in 85 wt% phosphoric acid at different temperatures for 80 minutes. The composite membranes have been characterized for water uptake, tensile strength, thermal stability by thermogravimetric (TGA) analysis, permeability by Cu diffusion cell and ionic exchange capacity (IEC). From the result, the PA doped PBI membrane (100 °C, 80 min) shows significant improvement in tensile strength (92.23 MPa) with PA doped PBI membrane (40 °C, 80 min) exhibited the lowest Cu diffusion at $5.56 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The composite PBI/ZrP has the advantage of the most thermally stable membrane and excellent ionic exchange capacity at $3.20 \times 10^{-3} \text{ mol g}^{-1}$.

1. Introduction

Fossil-based fuels like petrol and diesel are one of the most extensively used substance in energy generation especially for transportation which is the primary energy generated from the internal combustion engine [1,2]. Hydrogen is known for zero carbon dioxide contributor and a clean energy source. However, hydrogen naturally exists not in its pure form but in existence with other molecules like water for example. In fact, existing primary hydrogen production processes are synthesized by steam reforming of methane, water electrolysis, coal gasification and thermochemical method [3,4].

Polymer electrolyte membrane (PEM) is the main element of a membrane electrode assembly (MEA) that determines the performance, endurance, and efficacy of a fuel cell or an electrolyzer. Perfluorosulphonic acid (PFSA) membrane like Nafion is the most commonly used membrane for polymer electrolyte membrane fuel cell (PEMFC) and polymer electrolyte membrane electrolysis



(PEME) [5]. For instance, Balashov [6], Aghahosseini [7] and Naterer [8] conducted a study on Nafion based membrane that is utilized in the copper chloride electrolysis for hydrogen production. The results were encouraging, but the operating temperature was limited to 80 °C. Nafion performed well in the CuCl electrolysis with 0.2 – 1 M CuCl anolytes and 2 – 10 M HCl catholytes for with operating flow rate ranging between 30 to 600 ml min⁻¹. However, Nafion applications are still limited due to cost of acquiring the expensive membrane, loss of proton conductivity at high temperature due to water dehydration and high diffusivity of fuel [9].

Polybenzimidazole (PBI) membrane offers a better thermochemical and mechanical stabilities [10] for working temperature beyond 120 to 200 °C apart from being a great proton conductivity when doped with PA although at temperature above 100 °C and zero humidity [11]. The main advantages of PBI over Nafion of working at higher operating temperature includes quicker electrochemical activities, enhanced and easier water management, excellent thermal, chemical stability and better tolerance with impurities [12]. In PBI/Phosphoric Acid (PA) hybrid membrane the conductivity is greatly influenced by the level of acid doping which corresponds from the temperature and immersion time being taken for treating the membrane [13].

The sulfonated polyether ether ketone (SPEEK) is also an excellent alternative membrane due to its sulfonic acid properties that can integrate well together with the fillers and polymer backbones [14]. These PBI and SPEEK membranes cost are cheaper than Nafion with the advantage of low fuel crossover due to their lower phase separation [15].

The objective of this study is to characterize the PBI/ZrP, SPEEK/ZrP and Nafion as the reference, and to be able to select the best membrane to be fitted as the membrane electrode assembly in the CuCl electrolytic system. Extensive consideration has been dedicated in preparing the PBI and SPEEK composite membrane by introducing inorganic filler zirconia ZrO₂ and PA doping. Alteration of PBI and SPEEK membrane to improve surface morphology and structure by PA doping is hugely implemented. To the best of authors knowledge, the modification of PBI and SPEEK membrane by inorganic filler addition followed with PA doping for copper chloride electrolysis has not been reported.

2. Materials and Methods

2.1 Materials

Copper sulfate pentahydrate (CuSO₄ · 5H₂O) was purchased from System ChemAR, hydrogen peroxide (H₂O₂) 30% from QReC Grade AR, sulphuric acid (H₂SO₄) 95% and hydrochloric acid 37% (HCl) were purchased from QReC company. 3% H₂O₂ and 0.5 M H₂SO₄ were prepared from the dilution 30% H₂O₂ and pure H₂SO₄ 95%, respectively. 1 M HCl solution was acquired from the dilution of pure HCl 37%. Dimethylacetamide (DMAc) was purchased from VChem Chemicals. A commercial PBI membrane was acquired from PBI Performance Products Inc. USA. The PEEK polymer was purchased from Victrex Inc. The Cu diffusion cell and conductivity cell were customized according to the work of [16] with some modification.

2.2 Methods

2.2.1 Membrane preparation. The SPEEK membrane was prepared by sulfonation process of PEEK polymer with sulfuric acid, stirred at ambient temperature for 1 h and continued with stirring for 3 h at 60 °C. The sulfonation process was stopped by submerging the beaker containing PEEK polymer and sulfuric acid in the ice water bath. After the solution was filtered, it was rinsed with DI water until pH 7 and placed in a vacuum oven at 80 °C for 24 h for drying. The composite membrane of PBI/ZrP was prepared by dissolving a weighted PBI membrane in a beaker with DMAc solution. A 10 wt% of ZrO₂ was added into the solution and stirred for 3 h at 60 °C. Sonification was performed for 2 h and continued with membrane casting using a glass plate and desiccated for 24 h in an 80 °C vacuum oven. Next, the membrane was submerged in DI water and peeled off. The membrane was re-dried in a vacuum oven before the doping process. The PBI and SPEEK composite membrane doping was carried out at temperature of 40 °C and 80 min immersion time.

2.2.2 Membrane characterization. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TA instrument mass spectrometer complete with PC. Nitrogen air was used (20 ml min^{-1}), and the membrane samples were heated up from room temperature to $900 \text{ }^{\circ}\text{C}$ with heating rate of $30 \text{ }^{\circ}\text{C min}^{-1}$. The Cu ion presence for Cu diffusion tests were measured by using UV-Vis spectrometer (UV-Vis). The water uptake was calculated by means of weighing before and after immersion in DI water. For evaluation of proton conductivity, membranes were hydrated in DI water for 20 h before measurements. The proton conductivities of the membranes (through-plane) were quantified by using a two-point probe cell setup from Metrohm Autolab PGSTAT302N equipped with electrochemical impedance spectroscopy. Thickness of the membranes were recorded using Yuwese EC-770 ultrasonic thickness tester for coating thickness gauge. Tensile strength tests were performed using a 2.5 kN Lloyd universal tensile tester.

3. Results and discussions

3.1 Thermogravimetric analysis

TGA analyses were carried out at heating rate of $30 \text{ }^{\circ}\text{C min}^{-1}$ to examine the response of the inorganic fillers and PA doping to the thermal behavior of the tested membranes. Figure 1 illustrates the thermogram of the PBI/ZrP, PA doped PBI, undoped PBI, SPEEK/ZrP, undoped SPEEK, and Nafion 117 membranes. The addition of zirconia (ZrO_2) and PA doping step has raised the thermal stability of the membrane contributed by the molecular interaction between polymer backbone and the zirconia which functions as a cross-linker.

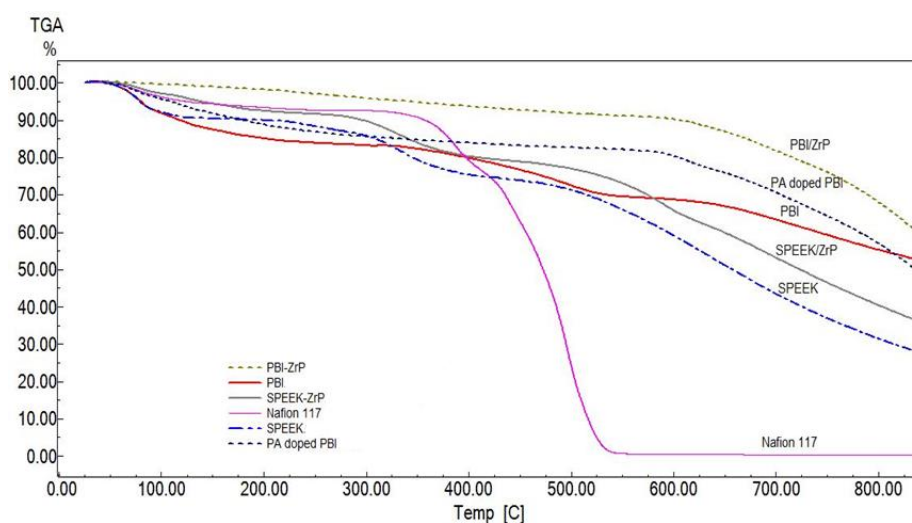


Figure 1. Thermogravimetric analyses of Nafion 117, SPEEK and PBI based membranes.

For PBI/ZrP membranes, compelling weight loss can be identified at over $600 \text{ }^{\circ}\text{C}$ while for PBI it started around $350 \text{ }^{\circ}\text{C}$. Water and remaining solvent were vaporized to the atmosphere until $150 \text{ }^{\circ}\text{C}$. There was no significant of weight reduction at temperature ranging from $150 - 500 \text{ }^{\circ}\text{C}$ which indicated that the membrane was an excellent thermally stable film. Above $200 \text{ }^{\circ}\text{C}$, the weight reduction is also contributed by the vaporization of casting solvent [17]. The existence of aromatic rings raise the thermal stability due to high intermolecular forces in the membrane [18]. The degradation of the polymer backbone occurs at temperature above $550 \text{ }^{\circ}\text{C}$ for PBI [17]. This is important as the high-temperature CuCl electrolysis process requires membrane that can withstand high temperature (thermally stable), acidic electrolytes and excellent endurance for a reliable proton electrolyte membrane.

For SPEEK based membranes the weight loss at 250 to $400 \text{ }^{\circ}\text{C}$ representing to the decomposition of sulfonic acid groups in the membrane structures while at $500 \text{ }^{\circ}\text{C}$ corresponds to the decomposition of polymeric backbone of membranes. The results indicate that the synthesized membranes are high-temperature resistance and suitable to be used in high-temperature polymer electrolyte membrane

electrolyzer applications. Nafion 117 suffered the most from TGA analysis as it degraded significantly at temperature above 350 °C. The thermal stability of the membranes is in the order of PBI/ZrP > PBI > PA doped PBI > SPEEK/ZrP > SPEEK > Nafion 117.

3.2 Mechanical and copper diffusivity analysis

Tensile strength and copper diffusivity for the tested membranes are summarized in Table 1. These tests are crucial specifically to examine the mechanical strength and anion diffusion for the membrane. The results shown can be classified to two categories; PBI and PBI based membrane has a higher band of tensile strength around 85.17 – 92.23 MPa while SPEEK, SPEEK based membrane and Nafion hold a lower tensile strength at 6.62 to 62.33 MPa. The commercial PBI tested shows 76.29 MPa of tensile strength and this is in accordance with previous findings (60 – 70 MPa) [11].

PA doping for PBI membrane has increased its tensile strength as contrast to reported by [19] that the phosphoric addition weaken the mechanical strength while inorganic filler makes the membrane stronger. However, PA doped SPEEK membrane experienced the huge reduction of almost 90% tensile strength when immersed in a 100 °C PA medium. The copper diffusion test is important to make sure the test can be conducted as long as possible without having a copper deposit on the cathode. The PBI/ZrP shows the lowest copper diffusion of 5.56×10^{-8} which is better than reported by [16] for Nafion at 6.86×10^{-7} . This makes PBI/ZrP the most suitable candidate to replace the costly Nafion in the membrane electrode assembly for an electrolyzer.

Table 1. The tensile strength and copper diffusion properties of Nafion 117, SPEEK and PBI based membranes

Membranes	Tensile strength (MPa)	Copper diffusion ($\text{cm}^2 \text{s}^{-1}$)
PBI (100°C;80 min)	92.23	2.35×10^{-7}
PBI (40°C;80 min)	90.35	5.56×10^{-8}
Pristine PBI	87.36	2.66×10^{-7}
PBI/ZrP (40°C;80 min)	85.17	7.87×10^{-7}
SPEEK (100°C;80 min)	6.62	5.46×10^{-7}
SPEEK (40°C;80 min)	12.39	1.03×10^{-6}
SPEEK/ZrP (40°C;80 min)	28.26	6.07×10^{-7}
Pristine SPEEK	62.33	1.01×10^{-6}
Nafion 117	27.30	1.67×10^{-6}

3.3 Ionic exchange capacity and water uptake analysis

Currently, the established process for copper chloride electrolysis is using Nafion as the working membrane. As for PBI, it is widely used in fuel cell application, but the application of PA doped PBI membrane as an MEA for copper chloride electrolysis is not yet reported, while for SPEEK the usage is more towards DMFC studies. Table 2 shows the water uptake and ionic exchange capacity for the tested membranes. The tests are critical to investigate the ability to hold the humidity and proton transportation across the membrane. The doping temperature used of 40 - 100°C are similar to previous research [20]. However, previous studies were only focusing on fuel cell applications that normally runs under anhydrous or partial humidification. Water uptake is needed to assist the proton transportation but if excessive, it will cause the membrane to swell and greatly reduce the mechanical strength of the membrane [21]. A water uptake of 40 – 50 wt% is good without sacrificing the mechanical robustness of the membrane. From the results, PBI/ZrP has the highest IEC ($3.2 \times 10^{-4} \text{ mol g}^{-1}$) which contributes to a higher proton conductivity due to extra effective sites that can be utilized for ion transportation.

Table 2. Water uptake and ionic exchange capacity of Nafion 117, SPEEK and PBI based membranes

Membranes	Water uptake (wt%)	Ionic exchange capacity (mol g ⁻¹)
Nafion 117	13.03	8.01 x 10 ⁻⁴
Pristine PBI (undoped)	5.49	1.33 x 10 ⁻⁴
Pristine SPEEK (undoped)	2.77	1.24 x 10 ⁻³
PBI (100°C;80 min)	46.65	1.16 x 10 ⁻³
PBI (40°C;80 min)	51.30	2.05 x 10 ⁻⁴
PBI/ZrP (40°C;80 min)	41.69	3.20 x 10 ⁻³
SPEEK (100°C, 80 min)	76.80	1.62 x 10 ⁻³
SPEEK (40 °C, 80 min)	61.94	7.82 x 10 ⁻⁴
SPEEK/ZrP (40°C;80 min)	3.46	1.74 x 10 ⁻³

4. Conclusion

Composite membranes PBI/ZrP and SPEEK/ZrP were developed by introducing of ZrO₂ followed with PA doping via immersion method at temperature of 40 and 100 °C. The Cu diffusivity was greatly improved with PA doping method due to the dihydrogen phosphate ion (H₂PO₄⁻) attached to the PBI polymer backbone. PBI/ZrP is the most thermally stable membrane with fairly high tensile strength of 85.17 Mpa. On the other hand, the ionic exchange capacity demonstrated excellent improvement of 4-fold for PBI/ZrP and 2-fold for SPEEK/ZrP, higher than the Nafion 117 membrane, contributed from the inherent characteristics of PA doped ZrO₂ based membrane. The electrolysis efficiency of the CuCl electrolysis calculated from Faraday's Law was established around 97% by dividing the experimental hydrogen flowrate with theoretical hydrogen flowrate.

5. References

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