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IJIE

Journal homepage: http://penerbit.uthm.edu.my/ojs/index.php/ijie
ISSN : 2229-838X e-ISSN : 2600-7916

The International Journal of Integrated Engineering

Effect of Temperature and Current Density on Polybenzimidazole Zirconium Phosphate Hybrid Membrane in Copper Chloride Electrolysis for Hydrogen Production

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DOI: https://doi.org/10.30880/ijie.2019.11.07.024
Received 16 July 2019; Accepted 20 October 2019; Available online 15 November 2019

Abstract: This paper presents an elevated temperature copper chloride electrolysis as a sustainable hydrogen production using a modified polybenzimidazole (PBI) based membrane. The main objective of this work was to characterize the performance of PBI Zirconium Phosphate (PBI/ZrP) hybrid membrane and evaluate its use as potential working membrane in the hydrogen production. Temperature and current density effects on hydrogen production were investigated in the range of 100 to 115 °C and 0.1 to 0.5 A/cm^2, respectively. PBI based hybrid membrane was synthesized with zirconium oxide (ZrO_2) followed by phosphoric acid (PA) doping. The membrane properties was characterized for proton conductivity, thermal stability, copper diffusivity and tensile strength. The results revealed that modification of the PBI into PBI/ZrP has significantly increased the proton conductivity by four fold, and selectivity by 30%. However, there was a slight reduction in tensile strength by 5 MPa may due to the realignment of PBI/ZrP molecule structures. Furthermore, a higher current density (0.5 A/cm^2) produced almost 40% more hydrogen (5.04 cm^3/min) compared to 0.1 A/cm^2 (3.64 cm^3/min) at 115 °C with electrolysis efficiency of 97%. PBI/ZrP exhibited superior proton conductivity, thermally stable with high tensile strength. The synergistic of the pristine PBI with ZrO_2 and PA doping has produced a hybrid PBI/ZrP membrane that can be a promising effective polymer electrolyte and budget friendly compared to Nafion.

Keywords: Hybrid membrane, zirconium oxide, phosphoric acid, hydrogen production, copper chloride electrolysis

1. Introduction

Hydrogen is a clean fuel that contributes to zero carbon footprint, but it is not readily available in nature as hydrogen gas [1]. Hydrogen is one of the promising alternative energies other than wind [2,3], solar [4] and biomass [5] due to growing concern on the greenhouse gases impact and depletion of fossil fuels [6,7]. The current primary

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hydrogen production processes are generated by steam reforming of methane, water electrolysis, coal gasification, and thermochemical method. Hydrogen production from water electrolysis is one of the promising routes to generate sustainable and clean energy [8]. The clean energy system is essential to cope with the world's energy requirement with minimum impact on the environment and dependency on fossil fuels. Nevertheless, this renewable and clean energy typically do not have a steady output due to scattered infrastructure and inconsistent supply. Therefore, hydrogen and electricity can co-exist as the storage instrument for clean, renewable energy [9]. To date, researchers have shifted their focus in proton exchange membrane (PEM) electrolyzer technology instead of alkaline electrolyzer because of non-hazardous electrolytes, lower power requirement, higher hydrogen purity and current density including more accessible hydrogen storage [10]. PEM is a vital component of a fuel cell or an electrolyzer. From PEM, the membrane electrode assembly (MEA) is assembled, which later affect the performance and the durability of the fuel cell or electrolyzer. Perfluorosulfonic acid (PFSA) membrane-like Nafion is the most commonly used membrane for polymer electrolyte membrane fuel cell (PEMFC) and polymer electrolyte membrane electrolysis (PEME) [11]. PEMFC is known as the critical component for transportation technologies for generating electrical energy from the conversion of chemical potential while PEME functions to produce the required hydrogen gas [12]. Researchers conducted a study on Nafion based membrane that was applicable in the copper chloride (CuCl) electrolysis for hydrogen production [13,14]. The results were encouraging, but the process temperature was only tested at a maximum of 80 ºC while PBI membrane offers a better thermochemical and mechanical stabilities for a higher process temperature [15].

The PBI based membranes are cheaper than Nafion with the advantage of low fuel crossover due to their lower phase separation [16]. PBI is amorphous and has aromatic components as its main molecules that translate into a polymer which has excellent thermal stability and chemical resistance, while Nafion is majorly dependent on the humidity of the membrane (water for ion H^+ movement) to have excellent conductivity properties. The main advantages of PBI over Nafion of working at higher operating temperature include quicker electrochemical activities, enhanced and more effortless water management, more efficient thermal management, and better tolerance with impurities [17]. Besides, the primary constraint for Nafion usage in the PEMFC and PEME is due to the costly membrane and high fuel diffusivity [18]. The copper chloride electrolysis process performed in a closed-loop system in which the primary electrolytes are cuprous chloride in hydrochloric acid in the anode while hydrochloric acid in the cathode. The heart of the process relies on the membrane electrode assembly where the proton and current exchange take place. Studies on the CuCl electrolysis by using a Nafion based membrane have been conducted by Edge [19], Balashov [13], Naterer [20], Abdo and Easton [21], and Schatz [22]. All of the researches used CuCl electrolytes concentration ranging from 0.02 – 2 M CuCl and 2 – 10 M HCl. The high concentration of HCl was essential to ensure complete dissolution of CuCl substrate and remain in its form for the entire experiment [23]. The membranes used include Nafion 115, Nafion 117, Nafion 117/hydrion, and composite Nafion/polyaniline with the process temperature of 22 – 80 °C. None of the researches has explored the copper chloride electrolysis at a higher temperature above 80 °C.

The objectives of this study are to characterize the physicochemical properties and evaluate the performance of the PBI/ZrP for hydrogen production. Dedication of preparing the PBI hybrid membrane by introducing inorganic filler zirconia ZrO_2 and PA doping was highlighted. The current density and temperatures on the hydrogen production were investigated in a CuCl electrolyzer system. To the best of the author's knowledge, the modification of composite PBI/ZrO_2 based membrane by phosphoric acid doping to produce PBI/ZrP membrane for copper chloride electrolysis has not been reported.

2. Materials and Methods

2.1 Materials

Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) solution was purchased from System ChemAR. Phosphoric acid 85%, zirconium oxide (ZrO_2) powder (micron), hydrogen peroxide (H_2O_2), and hydrochloric acid 37% (HCl) were acquired from QReC company. Dimethylacetamide (DMAc) and sulfuric acid (H_2SO_4) were sourced from VChem Chemicals. The membrane sheet of PBI and Nafion 117 were purchased from PBI Performance Products Inc. USA and DuPont Fuel Cells Inc, USA, respectively. PEEK membrane was acquired from Victrex Inc, USA. Carbon cloth electrode (0.5 mg/cm^2, 60% Platinum on Vulcan carbon) was obtained from Fuel Cell Store, USA.

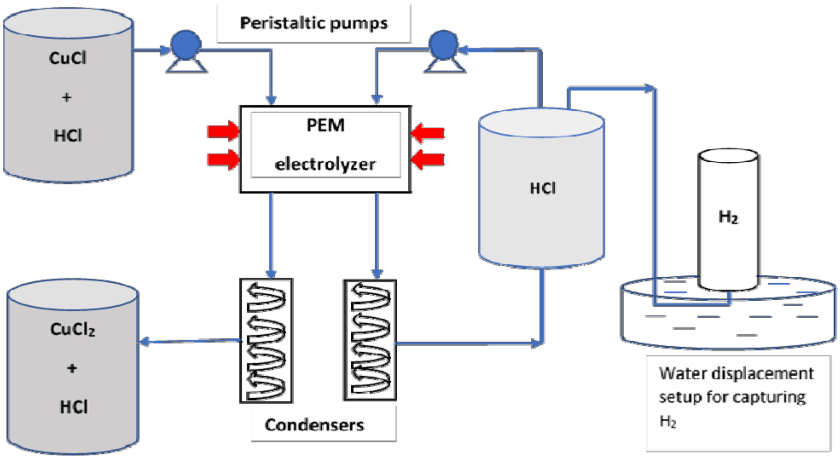
2.2 Membrane Synthesis

SPEEK membrane was prepared from sulfonation of PEEK with HCl as prepared according to a published method [24]. The functionalization of phosphoric acid (PA) on the PBI and SPEEK membrane were carried out at 40 °C with 80 min immersion time. The membranes were washed and rinsed with deionized water to remove the excess acid of PA on the surface as suggested by Parnian et al. (2017) [25]. Meanwhile, a hybrid membrane of PBI/ZrP was synthesized by dissolving a known weighted PBI membrane in a DMAc solution at 60 °C. After the solid PBI was totally dissolved in DMAc, 10 wt% of ZrO_2 was added and stirred for 3 h at a similar temperature of 60 °C. Ultrasonication was performed for 2 h to obtain a homogeneous solution, followed by membrane solvent casting on a glass plate and desiccated for 24 h in an 80 °C vacuum oven. The membrane was dried in a vacuum oven prior to PA functionalization like preparation of pristine PBI.

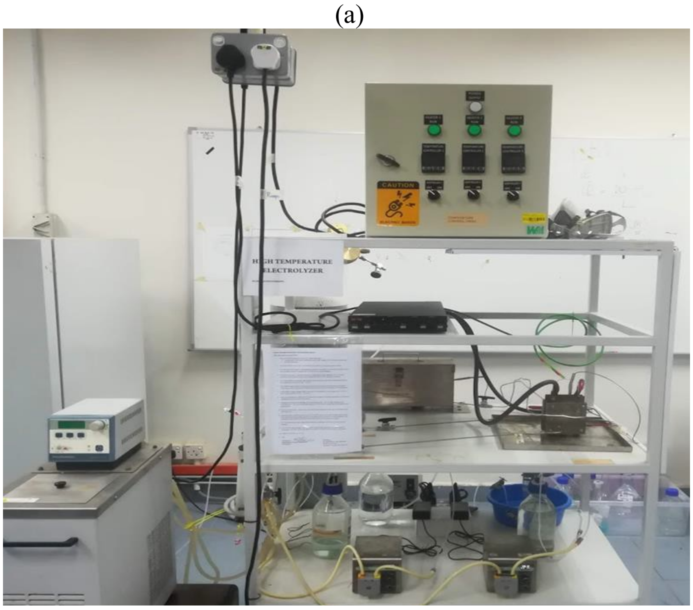
2.3 Membrane Characterization

In proton conductivity evaluation, the through-plane membrane's conductivity was measured by using electrochemical impedance spectroscopy (EIS) with a two-plate probe cell setup Metrohm Autolab PGSTAT302N under fully humidified environment at 30, 50, 70, and 90 ºC. The Cu diffusion test was carried out by placing the dissolved Cu^{2+} from $CuSO_4 \cdot 5H_2O$ in 1 M HCl as the anolyte, and 1 M HCl as the catholyte separated with a membrane in between two modified Schott bottle. Both sides were stirred by a magnetic stirrer at 100 rpm to maintain a homogenous solution during the test. The Cu ion was determined by using an Agilent 8453 UV-Vis spectrometer.

The tensile strength test of the prepared membrane was determined by using a 2.5 kN Lloyd universal tensile tester. The membrane thickness was measured using Yuwese EC-770 ultrasonic thickness tester. The thermal stability was conducted using thermogravimetric analysis (TGA) (Shimadzu TGA-50M) in a nitrogen environment with 20 mL min^{-1} purging and ramping temperature of 30 ºC min^{-1} from room temperature to 900 ºC. The copper chloride electrolysis was conducted in a planar electrolyzer with an active dimension of 2.5 cm x 2 cm for each side. The electrolyzer consists of dual electrodes, two titanium plate for the end blocks, carbon cloth electrode, membrane and two graphite plates with the serpentine channel. The schematic diagram and experimental rig set up of the CuCl electrolytic system are illustrated in Fig. 1.



(a)



(b)

Fig. 1 - The schematic diagram (a) and experimental rig set up (b) for CuCl hydrogen electrolytic system

3. Results and Discussions

3.1 Proton Conductivity

Proton conductivity of a membrane has a major influence on the efficiency of an electrolyzer. The proton conductivity was determined using the EIS method. Fig. 2 illustrates the proton conductivity at different temperatures of 30, 50, 70 and 90 ºC. The proton conductivities were 10.06 $mScm^{-1}$ for Nafion 117, 5.67 $mScm^{-1}$ for PBI/ZrP and 1.46 $mScm^{-1}$ for pristine PBI at 90 ºC. The conductivity of the tested membranes increased steadily with the rise in temperature. However, there was a dramatic surge on conductivity for PBI/ZrP (20.25 fold) compared to Nafion 117 (1.85 fold) from 70 to 90 ºC which may occur due to faster electrochemical reaction kinetics of membrane's molecules [26]. Addition of ZrO_2 and functionalized with PA significantly increased the proton conductivity of pristine PBI by allowing high ions to permit through the membrane. It can be explained by the ion transportation via vehicular movement and Grottus mechanism [27], where ion H^+ diffused through the membrane pores and hopping by the continuous formation and deformation of hydrogen bonds within and on the surface of the membrane [28]. There are limited studies for copper chloride electrolysis that used Nafion as PEM, while no previous studies were performed for high-temperature CuCl electrolysis [19,21]. In previous studies [21,29], the Nafion was not subjected to high-temperature due to its incompatibility and difficulty to retain the proton conductivity from the PEM fuel cell case studies.

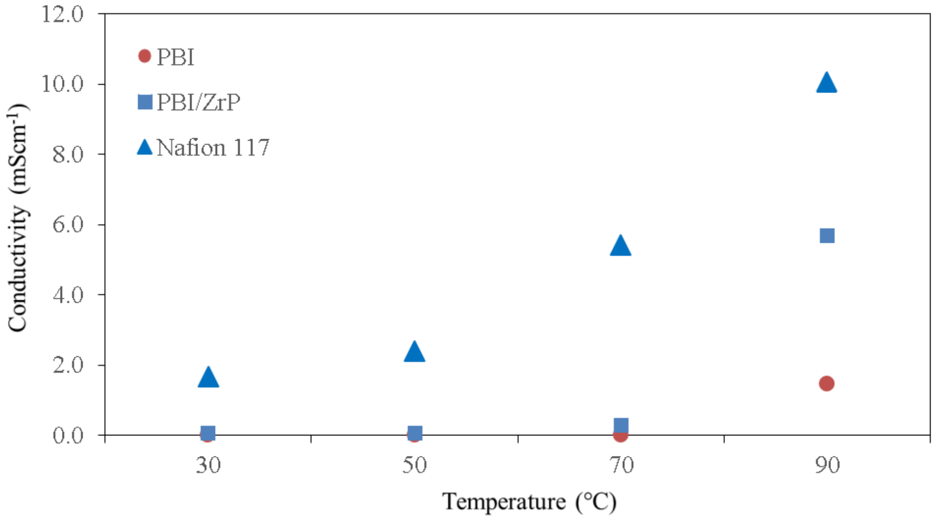


Fig. 2 - The effects of temperature on proton conductivity for Nafion 117, PBI, and PBI/ZrP hybrid membrane.

The through-plane proton conductivity of the Nafion 117 and PBI/ZrP positively affected by the changes in the process temperature under fully humidified environment. The increased in the proton conductivity was also due to the activity surge of vehicular movement and Grotthus mechanism of the membrane. As a result of higher proton conductivity with increasing temperature, more proton can be transferred for the reduction of H^+ to become hydrogen; thus increased the hydrogen production [30].

3.2 Mechanical and Thermal Analysis

The tensile strength and copper diffusivity results are summarized in Table 1. It can be categorized into two membranes of a higher band of tensile strength from 85.17 to 92.23 MPa and a membrane with a lower tensile strength from 6.62 to 62.33 MPa. The commercial PBI shows a tensile strength of 76.29 MPa as supported by a previous finding (60 – 70 MPa) [31]. The tensile strength for SPEEK and Nafion was almost similar in the 27 to 28 MPa region. PA doping on PBI membrane has increased its tensile strength, contradicted to the study reported by Di Noto et al (2010) that the phosphoric acid addition weakens the mechanical strength while inorganic filler makes the membrane stronger [32].

Table 1 - Tensile strength properties of Nafion 117, SPEEK and PBI based membranes

Membranes	PBI (100 ºC)*	PBI (40 ºC)*	Pristine PBI	SPEEK	PBI/ZrP	Nafion 117
Tensile strength (MPa)	92.23	90.35	87.36	28.26	85.17	27.30

* PA doping temperature

The gradual decrease in mass at the temperature ranging from 150 to 500 ºC indicates that PBI/ZrP hybrid membrane has excellent thermal stability, as shown in Fig. 3, as evaluated by TG analysis. From a room temperature and up to 150 ºC, the weight loss caused by the vaporization of a volatile compound of water and solvent. The weight reduction by the vaporization of casting solvent occurred at a temperature beyond 200 ºC [33]. Significant weight loss due to decomposition of polymer was monitored at over 600 ºC for hybrid PBI/ZrP membrane and PBI/ZrO_2, while for PBI, the decomposition begins as earlier at 350 ºC. The decomposition of PBI based membrane also reported in Kruger et al. (2015) and Malinowski et al. (2014) [34,35]. The aromatic structure in a polymer is identified as having high intermolecular forces within the membrane structure, which improve the thermochemical stability [36]. Hence, the presence of benzene ring in the PBI polymer backbone is recognized as a basis to have the deterioration of membrane above 550 °C [33]. Aside from a thermally stable membrane, PBI has the characteristic of having acidic tolerance, that makes it a promising proton exchange membrane at high temperature.

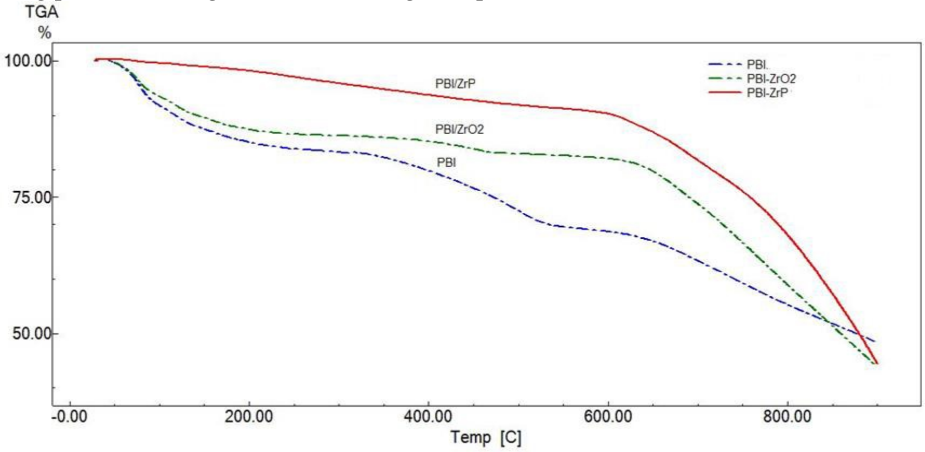


Fig. 3 - Thermogravimetric analyses of PBI based membranes.

3.3 Diffusivity and Selectivity

Table 1 shows the Cu diffusion for Nafion 117, is the highest with 1.67 x 10^{-6} $cm^2s^{-1,}$ which is relatively 2.12, 2.75, and 6.28 times fold higher compared to PBI/ZrP, SPEEK/ZrP and PBI, respectively. However, the conductivity for PBI was the lowest at 1.46 $mScm^{-}$1. Although the Cu diffusion for PBI was the lowest, it has very low conductivity. The copper diffusion in PBI, SPEEK/ZrP, PBI/ZrP, and Nafion 117 membrane can be explained according to Fick's law phenomena, which moving of ions from high to low concentration [37]. The SPEEK/ZrP and PBI/ZrP have equal potential as the candidate membrane due to excellent conductivity and selectivity. Nonetheless, the PBI/ZrP was selected due to superior durability and thermochemical stability. While the lowest diffusion value is in favour, the durability and the ability to withstand at high process temperature is the utmost importance in a high-temperature CuCl electrolysis system [38].

Table 1 – Diffusivity, conductivity, and selectivity properties of the tested membranes

Membrane	Diffusivity (x 10^{-7} cm^2s^{-1})	Conductivity (x 10^{-3} Scm^{-1})	Selectivity (x 10^7 $Scm^{-3}s^{-1}$)
PBI (2,5 – bibenzimidazole)	2.66	1.46	0.55
SPEEK/ZrP (PA doped at 40 °C & 80 min)	6.07	5.29	0.87
PBI/ZrP (PA doped at 40 °C & 80 min)	7.87	5.67	0.72
Nafion 117	16.7	10.06	0.86

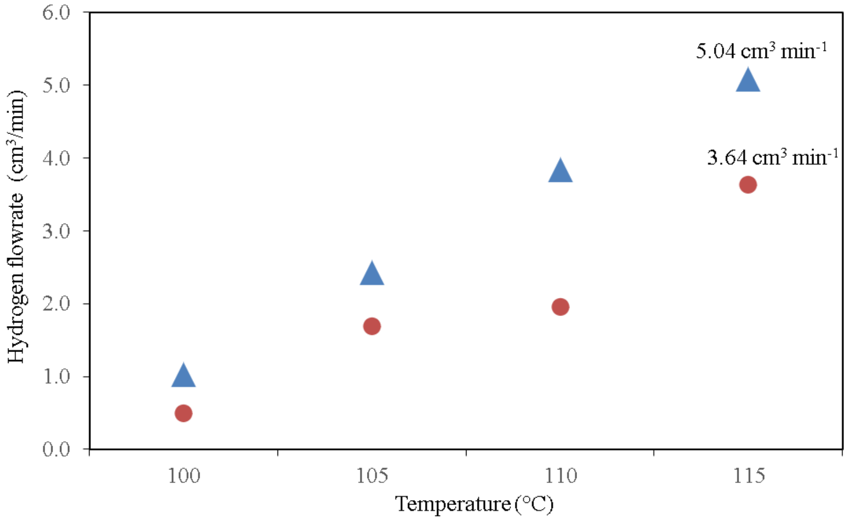


Fig. 4 - The effects of temperature and current density (Δ for 0.5 $A.cm^{-2}$ and O for 0.1 $A.cm^{-2}$) on hydrogen production for PBI/ZrP hybrid membrane

3.4 Hydrogen production

The copper chloride electrolysis was conducted using two different electrolytes. For anolyte, a known weight of CuCl was dissolved in the 1 M HCl while for catholyte an1 M HCl solution was used. The copper chloride electrolytic system was performed under an operating temperature of 100 to 115 °C to examine the effect of temperature, and current density on PBI/ZrP for hydrogen production. Hydrogen flow rate obtained from the CuCl electrolysis at 100 to 115 °C and current density of 0.5 A/cm^2 and 0.1 A/cm^2 for the prepared PBI/Zr membrane is illustrated in Fig. 4. Both current densities show a similar increasing trend at a rate of (0.27 cm^3/min and 0.21 cm^3/min) hydrogen flow rate for each 1 °C increment, respectively. A high current density applied improved the production of hydrogen. At 100 °C, the different flow rate between 0.1 A/cm^2 and 0.5 A/cm^2 is not much as at 115°C. It can be explained that by providing high dense current exchange has energized the membrane to transport more protons to the cathode, thus increased the hydrogen production flowrate [39]. At 115 °C, the hydrogen flow rate for 0.5 A/cm^2 current density was at 5.04 cm^3/min^1 which boosted around 38.5% compared to the latter.

4. Conclusion

The modification of PBI membrane by crosslinking with ZrO_2 and PA functionalization was investigated in elevated temperature CuCl electrolysis for hydrogen production. The hybrid PBI membrane (PBI/ZrP) was developed as a more durable and cheaper alternative compared to Nafion 117 which demonstrated excellent performance in CuCl electrolysis. TGA and tensile strength data demonstrated that the PBI/ZrP has high thermal stability and good mechanical strength. Furthermore, the conductivity of the PBI/ZrP has improved significantly compared to pristine PBI due to enhanced proton movement via vehicular and Grotthus mechanism. The increase in temperature and current density has contributed significant influence in boosted up the hydrogen flow rate by almost 40%. Investigation on the effect of electrolyte concentration and flow rate in CuCl electrolysis for hydrogen production can be considered in the future study.

Acknowledgement

Financial support from the Universiti Putra Malaysia project number 945200 GP-IPM and Universiti Teknologi Malaysia project number 03G10 Flagship Research University Grant under the Ministry of Education Malaysia are acknowledged.

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