



Enhancement of current density using effective membranes electrode assemblies for water electrolyser system

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ABSTRACT

The goal of this study was to develop and design a composite proton exchange membrane (PEM) and membrane electrode assembly (MEA) that are suitable for the PEM based water electrolysis system. In particular, it focuses on the development of sulphonated polyether ether ketone (SPEEK) based membranes and calcium salt of silico-tungstic acid (CsSiWA) matrix compared with one of the transition metal oxides such as titanium dioxide (TiO₂), silicon dioxide (SiO₂) and zirconium dioxide (ZrO₂). The resultant membranes have been characterized by Fourier transform infrared spectroscopy, scanning electron microscopy, ion exchange capacity (IEC), water uptake and atomic force microscopy. Comparative studies on the performance of MEAs were also conducted utilizing impregnation-reduction and conventional brush coating methods. The PEM electrolysis performance of SPEEK-CsSiWA-ZrO₂ composite membrane was more superior than that of other membranes involved in this study. Electrochemical characterization shows that a maximum current density of 1.4 A/cm² was achieved at 60 °C, explained by an increased concentration of protonic sites available at the interface.

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1. Introduction

Hydrogen energy is considered as the solution to world's increasing energy demand and due to concerns regarding pollution and contamination [1,2]. Moreover, the increased requirement for high efficiency energy supplies has contributed to active research on alternative approaches for hydrogen energy production that are environmentally friendly and are both subject to high cost and a limited supply. The development of renewable, efficient and economical hydrogen production technologies is a key element towards a sustainable 'hydrogen energy resource' [3]. Water electrolysis is the best technology for producing hydrogen and oxygen with no resulting greenhouse gas emissions [4,5]. This water electrolysis may be carried out using aqueous alkaline electrolytes or with solid polymer electrolyte membrane (PEM) as electrolytes [6]. Whereas PEM water electrolysis is an attractive method for producing high pure hydrogen. This way is more environmentally friendly and enabling continued compatibility with the use of renewable energy sources. Recently, a number of studies were related to water electrolysis—the development of novel solid polymer electrolyte (SPE) based water electrolyser as an efficient method for large-scale renewable high-purity hydrogen production with minimal environmental impact. Water elec-

trolysis is a process that takes place by passing electricity through water to break apart the water molecule into hydrogen (H⁺) and oxygen (O⁻) ions (so called water splitting). These hydrogen and oxygen ions migrate towards their respective opposite electrodes leading to formation of diatomic H₂ and O₂ molecules due to electron transfer. Typical membranes used in SPE are fabricated by conventional Nafion[®] membranes but challenges of the conventional Nafion[®] membranes are high cost and fluorinated polymer. Hence the researchers have focused on the development of low cost and more non-fluorinated polymers such as sulphonated Polyether ether ketone (SPEEK) [7], Poly (benzimidazole) (PBI), Poly (Ether sulphone) (PES), Sulphonated Poly sulphone (SPSF), poly(arylene ethers), polyphosphazene and polyimides [8,9]. These polymers have excellent chemical, mechanical, thermal properties and low cost. Among these polymers, the SPEEK polymer based membranes have shown superior properties for water electrolysis. Since they possess higher mechanical stability, which is sustainable over a wide range of degree of sulphonation (DS), thereby increasing the proton conductivity. The mechanical stability allows the time and temperature of the sulphonation reaction to be changed in order to achieve the optimum DS as a main factor that effectively controls the water splitting efficiency. In addition, the –SO₃H group improves the chemical properties of the polymer such as selectivity, water uptake and increased solubility. Their lifetime goes up to 3000 h as a proton conducting membrane material [10]. More importantly, the DS has a strong influence

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on both proton conductivity and stability of SPEEK. So, we have selected SPEEK as aromatic material for fabrication of membranes.

In order to improve the efficient process of water electrolysis system, the energy loss has to be reduced and the overall cost has to be lowered. Consequently, a large number of recent reports are to make the electrolysis production of hydrogen more efficient. It is achieved by one among them there are recent proposals pertaining about zero-gap electrolysis cell. An attractive approach is established on the design of zero-gap water electrolyzers with ion conducting membranes [11,12]. In such a cell, the gap between the electrodes is the distance that the ions have to travel in the electrolyte. A smaller gap has the advantage of lower resistance for ionic transportation. As such, the use of membranes in zero gap electrolyser will increase in direct proportion to the advancement on their synthesis and developmental applications.

The significant attempts have been made to synthesize efficient electrode materials to achieve high catalytic activity for electrolyser's applications. Platinum (Pt) and Iridium oxide (IrO₂) were employed as the most active cathode and anode catalyst for hydrogen and oxygen evolutions, respectively. Since IrO₂ [13] catalyst exhibits higher corrosion resistant properties but slightly lower electro catalytic activity than Ruthenium oxide [14]. Since there are many different kinds of catalytic formulations have also been evaluated to achieve optimum zero gap water electrolyser over a wide range of current densities. Two types of catalyst coating were employed for the membrane electrode assembly (MEA) system, which were the Pt–IrO₂ by non-equilibrium Impregnation-Reduction (I-R) method and Pt–IrO₂ by conventional brush coating method.

On the other hand, in order to address the limitations of these sulphonated polymers, invented composite proton-conducting additives and fillers have been incorporated to the polymer moiety. In the past few years, this approach has been concentrated on a kind of composites; these composite membranes possess relatively high ionic conductivity and exhibit reasonable stabilities. Among this, heteropolyacid (HPA), titanium dioxide (TiO₂), silicon dioxide (SiO₂) and zirconium dioxide (ZrO₂) [15], have been utilized as proton conducting materials. The choice of these filler is selected on the assumption that these filler materials could possibly furnish extra mobile protons as charge carrier site and serve as 'proton conducting materials' [16]. Since HPA have the dual role of being both proton conduction and hydrophilic in nature. In general, pure HPAs are normally water-soluble in nature. Whereas the degree of solubility is reduced in composite HPAs [7], while maintaining their high proton conductivity. Consequently, broad research has been dedicated to fix the HPAs in its stable form by forming composites [17], which can preserve their high proton conductivity. Thus, the composite matrix reduces the leaching of HPAs. In order to limit the HPAs solubility and leaching of the HPAs filler, ion exchange protons of HPAs with large moiety cations is used, which are insoluble in water such as Cs⁺, NH₄⁺, Rb⁺ [18] and by forming in situ M–O linkage between HPAs and clusters of the SPEEK matrix. This manuscript presents the results of an improved scheme directed exclusively at resolving the previous [7] leaching problem.

In this study, we have developed a new type of composite membrane by incorporating caesium salts of silico-tungstic acid (CsSiWA) and inorganic fillers [19] such as TiO₂/SiO₂/ZrO₂ into the SPEEK polymer matrices via sol gel process. Further, the zero gap water electrolyser system is designed using two different catalyst coating methods—impregnation-reduction (I-R) method and conventional brush coating method.

2. Experimental

2.1. Raw material

Poly(ether ether ketone) (PEEK) was obtained from Victrex® USA, Inc. (450 PF); 1-methyl-2-pyrrolidinone (NMP) was obtained

from Merck; titanium dioxide, silicon dioxide, zirconium dioxide, silico-tungstic acid and caesium carbonate were obtained from Sigma–Aldrich; and were used as received without further purification.

2.2. Synthesis of SPEEK membrane

PEEK was first dried at 100 °C in a vacuum oven for 8 h. Then 10 g of the polymer was dissolved in 500 mL of concentrated sulphuric acid and stirred at room temperature for 8 h [20]. Then, the resultant polymer solution was precipitated over cold water under continuous mechanical agitation, and left to settle overnight. The DS for the studied samples are identical throughout the experiment. The resulting precipitate was filtered and washed with distilled water. It was then dried under vacuum at 100 °C for 7 h. The final product was the sulphonic acid form of PEEK, i.e., SPEEK.

2.3. Preparation of SPEEK composite membranes

Salts of silico-tungstic acid were prepared by neutralizing with caesium carbonate and then were dried at room temperature for few hours to attain the constant mass.

SPEEK composite membranes were prepared by dissolving the SPEEK sample in NMP solvent under vigorous stirring to obtain a homogeneous solution at 70 °C, to which 20 wt% of CsSiWA was added identical among the three solutions and 10 wt% TiO₂/SiO₂/ZrO₂ were added respectively, and then refluxed for 6 h at 80 °C to obtain a clear viscous liquid. Previously, we demonstrated that the optimum loading of 10 wt% TiO₂/SiO₂/ZrO₂ in polymer was sufficient for high conductivity. While higher loading levels of HPAs have some retreats [21], i.e., the loss of the mechanical strength as well as leaching out of unbound acid. In order to address this problem, the membranes were hot pressed between two Teflon sheets at 80 °C for 3 min. This approach has certainly improved the mechanical properties. The membranes were casted on a clean glass plate with the desired thickness and dried at 60 °C for 12 h. The thickness of the wet composite polymer membrane was between 0.20 mm and 0.30 mm. Then, the composite membranes were detached from the glass plate by adding distilled water. The resultant membranes were further purified by heating at 70 °C in 3% H₂O₂, 15% H₂SO₄ and distilled water for 1 h, respectively.

2.4. Ionic conductivity and transport property measurements

Conductivity measurements were made for the composite membrane by two-probe impedance technique, under potentiostatic conditions at a sweep rate of 5 mV/s from 1-Hz to 1-MHz excitation signal. During the measurement each membrane was sandwiched between stainless steel and ion blocking electrodes, and the cross-sectional area of the surface was 0.50 cm². The ionic conductivity (σ) of the samples in the transverse direction was calculated from the impedance data using the relationship of $\sigma = L/RA$, where A is the area of the electrodes, and L and R are the thickness and bulk resistance of the films, respectively. R was derived from the high frequency x-axis intercept of the complex impedance plot. All the samples were soaked in deionized water prior to the test.

2.5. Water uptake

Water uptake (W_{wd}) after 2 h of immersion was determined as the difference in weight (W) between the dried and the swollen membranes.

$$W_{wd}(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where, W_{dry} is the mass of the dry membrane. W_{wet} is the mass of the wet membranes.

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