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Investigation of SPES as PEM for hydrogen production through electrochemical reforming of aqueous methanol

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ABSTRACT

A polymer electrolyte membrane for hydrogen production through methanol electrolysis was prepared by converting poly ether sulfone (PES) into ionomer via sulfonation and fashioned into membrane. The physical and electrochemical properties of the prepared membrane and a single cell using the fabricated membrane are examined using various characterization techniques, such as, FTIR spectrometry, scanning electron microscopy, thermogravimetric analysis, tensile strength measurement, ion exchange capacity, electrochemical impedance spectroscopy and polarization studies. A current density of 0.802 A/cm^2 was obtained at a cell voltage of 1.2 V at 80 °C with the sulfonated polyethersulfone (SPES) based membrane electrode assembly (MEA) under suitable fabrication conditions. The energy requirements for hydrogen production are also compared with conventional water electrolysis. The observational results suggest that SPES membrane could be an option to costly perfluorosulfonate membranes in methanol electrolysis for hydrogen production.

1. Introduction

Hydrogen has been seen as an option to conventional fossil fuels as an energy source with less environmental change, greater conversion efficiency and an acceptable cost [1,2]. There are four major hydrogen production categories: Chemical, electrochemical (water electrolysis; photo electrochemical; halide electrolysis; H_2S electrolysis), biological, and thermal technologies [3]. Presently, most hydrogen production methods in the world consume fossil fuel and leads to carbon emissions. Nevertheless, carbon free hydrogen can be developed by using water electrolysis, which is in fact, the most mature method of renewable hydrogen production and thus seen as a key technique in hydrogen energy.

The electrolysis based on a proton exchange membrane (PEM) is suitable for portable power applications because it can start up and shut down quickly and can produce hydrogen at a low temperature. It was realized that electrolysis systems based on PEM had a number of advantages in comparison with traditional alkaline water electrolysers, such as ecological cleanliness, a high purity gas and an increased level of safety, much higher volume specific hydrogen capacity and higher efficiency [4]. Nevertheless, water electrolysis has not experienced a substantial commercial impact because it consumes much electricity, which fixes the process economically unattractive [5] and the most employed solid polymer electrolyte is a perfluorinated polymer [6–8] such as nafion which are highly expensive and their disposal when disused can also be expensive because of the presence of fluorine. Moreover, the practical engineering issues of hydrogen production, distribution, compression, safety and public acceptance, limit the large scale adoption of a hydrogen economy.

Liquid alcohols could serve as a bridge between gasoline and gaseous hydrogen. They have high energy densities and can be easily stored and passed out through the existing gas infrastructure. It has also been debated that alcohols are the next liquid fuels to use after the depletion of petroleum resources [9]. Methanol is a readily available electro active alcohol, which can be economically mass produced from non-renewable resources such as natural gas, coal, or from renewable resources such as biomass. Generally, both methanol and ethanol are liquid hydrocarbons and ethanol is twice as expensive as methanol [10]. Moreover, most of the biomass processes for bio-ethanol production using food products which have attracted criticism given the increasing food prices and the global food shortage [11]. Alcohols can be used directly in fuel cells

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to produce electricity or mechanical energy in internal combustion engines. Nevertheless, an alcohol electrochemical reformer or electrolysis can be utilized to create clean hydrogen, which can be applied in other schemes, resulting in an improvement in the overall system functioning. The problems associated with using ethanol, n-propanol, isopropanol, ethylene glycol as a fuel in PEM electrolyser include the difficulty in C–C bond breakage and also the intermediate generation, which increases the energy consumption for hydrogen production and the CO_2 emission also increased (Table 1). Hydrogen production from methanol electrolysis has lower power consumption than hydrogen production from water electrolysis since the standard voltage for the oxidation of methanol in the liquid phase is only 0.016 V versus the standard hydrogen electrode (SHE) compared to 1.23 V versus SHE for the oxidation of water. It has been estimated that hydrogen production from the electrolysis of methanol costs about 50% less compared to that of water, even when the cost of methanol is taken into account [10]. Contempt of the aforesaid advantages of this process, but only a few groups is active in this area and limited work has been reported [12–16].

The polymer electrolyte membrane methanol electrolyser cells are based on perfluorocarbon sulfonate ionomers which operate in the 80 °C range, and are likely limited to 125–150 °C. The perfluorinated polymers have three major drawbacks: very high cost; loss of conductivity at high temperature (>80 °C) and high methanol permeability, which hinder their further application [20,21]. In prospect of this, there is a widespread effort being expended to develop alternative more economical non-perfluorinated polymer based PEMs. Many promising polymers are based on aromatic thermoplastics [20,22–24], such as PES, poly (ether ether ketone) (PEEK), polybenzimidazole (PBI), and so forth, which have excellent chemical resistance, high thermo-oxidative stability, good mechanical properties and low cost. By the attachment of sulfonic groups to the polymer chains of PEEK [20,22–27], PES [28,29], polyimides [30,31] and PBI [32,33] were applied as PEM materials. The interest in the ontogeny of this form of membranes as PEM is based along its high oxidative and thermal stability [34], while their role in direct methanol fuel cells relies on their low methanol crossover [35]. Hydrogen production by methanol electrolysis is also a field of potential interest for these membranes. Among the potential alternatives, SPES is apparently the best material to be used as a PEM for methanol electrolyser because of their advantages of low cost, easy preparation, controllable composition, good mechanical strength and high chemical and thermal stabilities. Sulfonation of PES can also be performed by the chemical modification method and negatively charged sulfonic groups can be chemically introduced into PES backbone using chlorosulfonic acid or sulfuric acid as a sulfonating agent [36]. Moreover, to the best of our understanding, no work has been reported on the performance of a SPES based membrane for methanol electrolyser applications.

Thus, the present work is focussed to synthesize the SPES membrane and the fabricated membranes were characterized for its morphological, thermal and electrochemical properties. The effects of various factors which influence the membrane and electrode fabrication were also studied. The membrane performance in producing clean hydrogen at a higher rate through aqueous methanol electrolysis and the various parameters which influence it, has been demonstrated.

Table 1
Energy consumption for hydrogen production.

Electrolyzer	On board energy consumption (kWh/kg)
Methanol	16.20 [17]
Ethanol	29.17 [18]
Water	50.00 [19]

2. Experimental

2.1. Membrane fabrication

Polyethersulfone (PES) (Gafone 3200P, M_w 123 kDa), procured from Gharda Chemicals Limited (India) was subjected to sulfonation reaction using concentrated sulfuric acid and chlorosulfonic acid to obtain SPES as described in our previous study [37]. A predetermined quantity of SPES was weighed and dissolved as such in N-methyl-2-pyrrolidone (NMP) to prepare a 20 wt% membrane dope solution. The prepared solution was then ultrasonicated before being decanted onto a petri dish and held on in an oven at 110 °C for 24 h and further treated at 80 °C in a vacuum oven until complete evaporation of the residual solvent. The fabricated membrane was then cooled to room temperature and took-off from the glass plate with deionised water. Further usage of the membrane was carried out by immersing it in 1 M sulfuric acid and rinsing with deionised water, ahead it was stored in deionised water for later experiments.

2.2. Membrane characterization

Fourier transform infrared (FTIR) spectrometry (Perkin–Elmer Spectrum one) was employed to distinguish the presence of the sulfonic acid group in polymer samples. It was also used to observe the interactions between SPES polymer and solvent in the membrane. Spectra were obtained in the range of 4000–500 cm^{-1} in absorbance mode.

The morphological characteristics of the fabricated membrane were examined with the use of scanning electron microscope (JEOL-6340F).

The tensile strength of the membranes was evaluated with the help of Universal Testing Machine (UTM) possessing a load cell of 5 kN, at ambient temperature. The gauge length and breadth of all membranes were 50 mm and 5 mm, respectively. Trials were conducted with a constant strain rate of 10 mm/min and up to failure of the sample.

The thermal stability of the membrane was studied by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under nitrogen atmosphere.

The ion exchange capacity (IEC) of the membrane was determined by an acid-base titration method [38] from which the extent of sulfonation of membrane was also calculated using the relation

$$\text{Degree of sulfonation (DS)} = \frac{0.244\,[\text{M (NaOH)} \times \text{V(NaOH)}]}{\text{W}-0.081[\text{M (NaOH)} \times \text{V(NaOH)}]} \times 100$$

The proton conductivity of the membrane was determined by an AC impedance technique using an Autolab Potentiostat/Galvanostat electrochemical analyser over a frequency range of 1–10^7 Hz to 50–500 mV oscillating voltage. The membranes were previously hydrated by immersion for 24 h at room temperature. The conductivity, σ, was calculated from the impedance data, using the relation

$$\sigma = \frac{l}{RS}$$

where l and S are the thickness and cross-section area of the membrane, respectively, and R was derived from the intersection of the characteristic spike on a complex impedance plane