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Catalyst free hydrogen generation from directly disulfonated poly (arylene ether sulfone) copolymer membranes

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ABSTRACT

In this study, catalyst free hydrogen generation for proton exchange membrane fuel cells (PEMFC) from directly disulfonated poly(arylene ether sulfone) copolymer membranes (BPSH) has been successfully achieved. A two-compartment reactor where an acid solution was separated from sodium borohydride solution via a proton exchange membrane was used to evaluate hydrogen generation capacity. Hydrogen generation rate was simply controlled by tailoring the proton conductivities of the membranes. For this purposes, BPSH membranes at various percent degrees of disulfonation (25, 35 and 45 molar percent) have been prepared. The hydrogen generation performances of both BPSH and the state of art membrane, Nafion™ have been explored. Hydrogen generation rates were observed as 124, 175, 235 and 151.3 mL min⁻¹ for BPSH 25, 35, 45 and Nafion™, respectively. The influence of temperature on hydrogen generation rates was also investigated. It was demonstrated that the hydrogen generation performance of Nafion™ was deteriorated at temperatures higher than 80 °C due to considerable loss in its proton conductivity. Last but not least, we have demonstrated that a fuel cell has been powered along 300 h with highly stable catalyst free hydrogen generation.

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1. Introduction

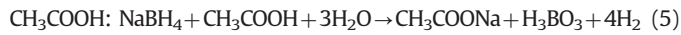
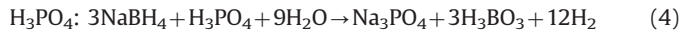
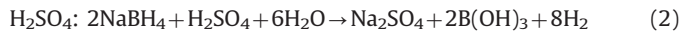
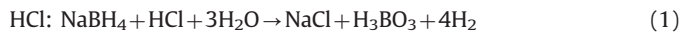
Rather since hydrogen must be produced, it is not a primary energy source. Hydrogen is actually the most promising future clean energy carrier since it provides zero-emission energy [1]. One barrier to the widespread usage of hydrogen as a transportation fuel is its safe, efficient and inexpensive on-board storage, which is a combination of currently lacking in conventional hydrogen storage technologies including cryogenic and high-pressure vessels. On the other hand chemical hydrides, which release chemically stored hydrogen such as NaBH₄, NH₃BH₃, NaAlH₄, LiH, etc. offer high volumetric hydrogen capacity and energy density [2,3]. The two major methods to produce hydrogen from a chemical hydride are hydrolysis and thermolysis. Since hydrolysis has very slow kinetics, catalytic hydrolysis can be used to achieve higher production rates. Previously reported works on hydrogen generation from chemical hydrides always used very small systems and so they produced a limited amount of hydrogen [3,4]. An effective hydrolysis reaction occurs only when chemical hydrides are in contact with a certain catalyst. Ruthenium (Ru), platinum (Pt), nickel (Ni), palladium (Pd), cobalt (Co), Ni–B, Co–B,

Co–P, Ni–Co–B, carbon nanotubes (CNT) and graphene are examples of these catalysts [4–8]. Moreover, platinum supported on carbon (Pt/C), which are extensively utilized in Proton Exchange Membrane Fuel Cells (PEMFC's), are also appropriate for hydrogen gas generation. Hydrogen generation rate depending on the surface structure of the catalysts can be varied from 1–130 L min⁻¹ g_{catalyst}⁻¹ when precious catalyst is used [1]. Precious metal catalysts are costly while metal and alloy catalysts from iron, nickel and cobalt are more inexpensive. Therefore researchers have been trying to replace precious metal catalysts with inexpensive materials to make hydrogen generation less costly. However these catalysts are generally not stable especially for long time operations. In other words, their activities usually decay over time since the catalyst involves as one of the reactants in the first step of the hydrolysis reaction [4]. Then resulted products are usually catalytically less active metal-boron compounds especially when boron related chemical hydrides are used for hydrogen generation. However, the catalytic activity of this first and fast step has been usually reported as a stable hydrogen generation rate in the literature [1,2].

On the other hand the catalyst free hydrogen generation from chemical hydrides have also been reported [9–12]. For example liquid acids reacting with chemical hydrides have been extensively studied as a self-catalyst for promoting hydrogen generation [9–12]. Typical chemical reactions including acid catalyzed hydrogen can be summarized as follows [10,13,14]:

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Although liquid acids have resulted in considerably fast hydrogen generation rates ($100\text{--}200\text{ mL min}^{-1}$), it has not been preferred because of the so-called stability issues [10,11]. Also, one of the major drawbacks of this system is that the hydrogen generation rate fluctuates a lot throughout the reaction. Moreover, there are two

unstable regimes for hydrogen generation rates reported from acid-catalyzed and self-hydrolysis reactions of NaBH_4 [9]. Therefore, these systems are vulnerable in the field of hydrogen generation area. Conversely, hydrogen generation from solid acid membranes bearing $-\text{SO}_3\text{H}$ groups have been reported [15]. However, they have suffered from very low hydrogen generation rates. This is most likely due to the fact that the hydrogen generation reaction occurs on the surface of the membrane and the proton at the bulk is not easily involve the hydrogen generation reaction because of the diffusion barrier. In this study, directly disulfonated poly(arylene ether sulfone) copolymers (BPSH) were investigated as chemically stable proton exchange membranes for application in hydrogen generation area without using any heterogeneous catalysts.

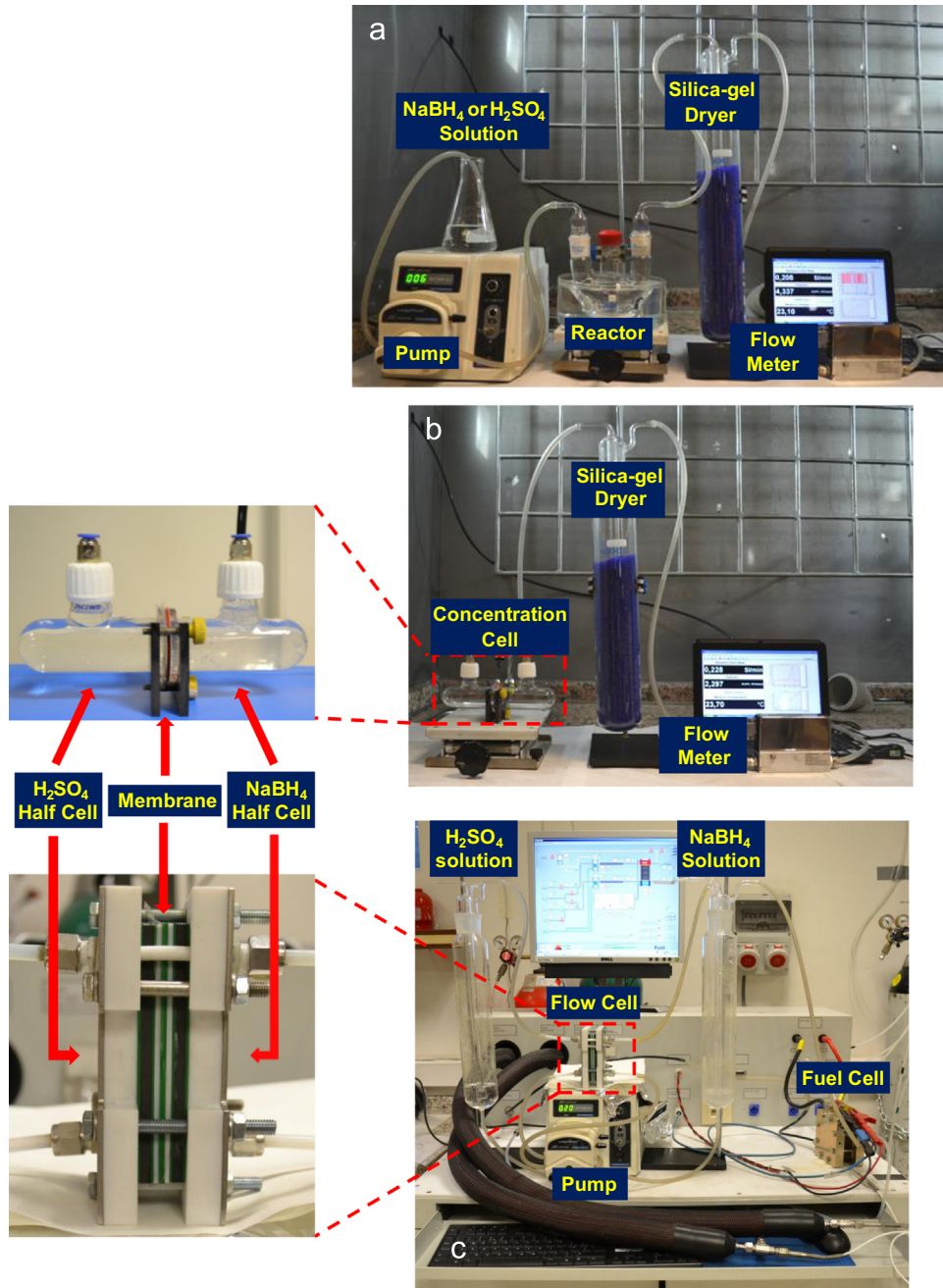


Fig. 1. Hydrogen generation systems using (a) Method 1 and 2, (b) concentration cell (Method 3) and (c) flow cell (Method 4).

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