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High performance and eco-friendly chitosan hydrogel membrane electrolytes for direct borohydride fuel cells

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ABSTRACT

Novel, cost-effective, and environmentally benign polymer electrolyte membranes (PEMs) consisting of ionically cross-linked chitosan (CS) hydrogel is reported for direct borohydride fuel cells (DBFCs). The membranes have been prepared by ionic cross-linking of CS with sulfate and hydrogen phosphate salts of sodium. Use of Na_2SO_4 and Na_2HPO_4 as cross-linking agents in the preparation of ionically cross-linked CS hydrogel membrane electrolytes (ICCSHMEs) not only enhances cost-effectiveness but also environmental friendliness of fuel cell technologies. The DBFCs have been assembled with a composite of nickel and carbon-supported palladium as anode catalyst, carbon-supported platinum as cathode catalyst and ICCSHMEs as electrolytes-cum-separators. The DBFCs have been studied by using an aqueous alkaline solution of sodium borohydride as fuel in flowing mode using a peristaltic pump and oxygen as oxidant. A maximum peak power density of about $810\,mW\,cm^{-2}$ has been achieved for the DBFC employing Na_2HPO_4-based ICCSHME and operating at a cell temperature of 70 °C.

1. Introduction

A DBFC is a type of fuel cell that utilizes a borohydride species, usually sodium borohydride ($NaBH_4$) in aqueous alkaline medium, directly as a fuel. DBFCs have the advantages of exhibiting high open circuit potential, power density, and current density values at ambient temperature. In DBFCs, cathode catalysts employed are generally metals or metallic alloys that are reactive towards electro-oxidation of borohydride fuel and hence, it is necessary to prevent the fuel from coming in contact with cathode catalyst while allowing transport of ions [1]. This purpose can be served by separating the electrode chambers with a PEM. Both anion exchange membrane (AEM) and cation exchange membrane (CEM) serve this purpose to a great extent. AEMs allow efficient transport of OH^- from cathode to anode compartment, but suffer from the problem of BH_4^- crossover. In contrast, use of CEM greatly alleviates the effect of borohydride crossover. Besides, CEMs are commercially available and among them, the perfluorinated sulfonic acid membranes show good ionic conductivity, chemical and mechanical stability [1,2]. Nafion®-117 membrane is a kind of CEM that was first employed in DBFC by Li et al. [3] and is still employed in a majority of DBFCs [4–6]. These membranes rely on water for high ionic conductivity and therefore, are preferably operated at temperatures below 90 °C. In DBFCs, sodium ion is transported through the Nafion® membrane instead of proton as in the case of hydrogen/oxygen polymer electrolyte fuel cells (PEFCs). Because of higher ionic conductivity of H^+ as compared to that of Na^+ in Nafion® membrane, ion conductivity is smaller in DBFCs as compared to that in the H_2/O_2-based PEFCs [1]. Moreover, the mechanism of proton conduction is different from that of Na^+ ion conduction in water-containing PEMs [7]. Thickness is a major factor in determining the performance of PEMs in DBFCs. DBFCs with thin PEMs possess low ohmic resistance and hence, exhibit high power performance. The problem with the usage of CEMs in DBFCs is that it would reduce alkali concentration in the anolyte, which causes instability and inefficient use of the borohydride fuel. Moreover, the buildup of alkali in the cathode associated with the use of CEMs as well as oxygen reduction reaction results in the formation of carbonates in the presence of CO_2 of air, which deactivates the cathode as well as membrane and restricts flow of O_2/air to the cathode. The problem becomes severe in extended period of operation and therefore, a way to remove CO_2 from air-feed of cathode and to return NaOH from catholyte to anolyte is needed [8]. In order to reduce alkali crossover from anode to cathode of DBFC, Nafion®-961 membrane was used instead of Nafion®-117 membrane as electrolyte/separator [9,10]. Nafion®-961 membrane is a Teflon-fiber reinforced composite membrane with sulfonate (100 μm thick) and carboxylate (10 μm thick) polymer layers. The weakly-ionized carboxylate layer of Nafion®-961 membrane offers resistance to flow of Na^+ and the strongly-ionized sulfonate layer

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with electrically negative polymer backbone offers resistance to flow of OH^- from anode to cathode, thereby improving cathode polarization behavior of DBFC.

In DBFCs with gaseous oxidants, it is necessary to balance water content of the PEM. This is because hydration is essential to maintain high ionic conductivity of the PEM whereas excess water leads to flooding of cathode [11]. It is also worthwhile to consider the effect of cell temperature on the performance of PEM. Increase in cell temperature increases the ionic conductivity of PEM and therefore, enhances the power density of DBFC [4]. However, increased cell temperature also leads to dehydration of the PEM and poor water balance inside the cell, which results in higher resistance and lowered cell performance [12]. Stability of PEM under fuel cell operating conditions exerts a large impact on the lifetime and cost of MEAs. Efforts are being made to develop PEMs that are cost-effective and high performance alternative to Nafion®-membranes for use in DBFCs [11,13,14].

The limitation of PEMs arising from their easy dehydration can be overcome by using cross-linked polymer hydrogels as PEMs in fuel cells. Hydrogels are 3-dimensional solid polymeric networks that absorb and retain in their polymeric matrices many times of water than their actual dry weight. A cross-linked polymer hydrogel is formed either by a chemical cross-linking reaction between a polymer and a cross-linking reagent or by ionic cross-linking of an ionomeric polymer with a suitable ion [15]. Polymer hydrogels have been used as solid electrolytes in electrochemical energy devices [7,16–19]. Polymer hydrogel electrolytes with focus on application to electrochemical supercapacitors were reviewed by Choudhury et al. [20]. Choudhury et al. [21] have reported a comparative study on the use of polyvinyl alcohol chemical hydrogel and Nafion®-117 membranes as electrolytes/separators for DBFCs and have observed that both the PEMs yield comparable performances at ambient temperature.

CS is a natural polymer that is derived by deacetylation of chitin [poly(N-acetyl-d-glucosamine)]. Chitin, which is present in the exoskeleton of arthropods, is the second most abundant natural polymer next only to cellulose [22]. CS is weakly alkaline and is soluble in dilute aqueous solution of acetic acid (CH_3COOH), which converts the glucosamine unit ($R–NH_2$) of CS into its protonated form ($R–NH_3^+$). Being inexpensive, biodegradable and nontoxic, CS finds use as an additive in food industry, as a hydrating agent in cosmetics, and as a pharmaceutical agent in biomedicine [23]. The chemical cross-linking reaction between CS and glutaraldehyde takes place by Schiff base mechanism [24]. A PEM comprising CS as matrix and KOH as dopant showed ionic conductivity in the order of $10^{-2}\,S\,cm^{-1}$. A H_2/air PEFC using the CS–KOH as PEM delivered a current density of $30\,mA\,cm^{-2}$ [25]. CS hydrogel can be prepared by either chemical cross-linking with aldehydes such as glutaraldehyde or ionic cross-linking with polyatomic multivalent anions such as sulfate ion, phosphate ion etc. Ionic interaction between CS and H_2SO_4 was studied by Cui et al. [26]. CS hydrogel membrane prepared by ionic cross-linking with H_2SO_4 was employed as electrolyte-cum-separator in DMFC by Osifo et al. [27]. A polyelectrolyte complex membrane prepared by ionic cross-linking of CS with polyacrylate ion exhibited proton conductivity of $3.8 \times 10^{-2}\,S\,cm^{-1}$ and methanol permeability of $3.9 \times 10^{-8}\,cm^2\,s^{-1}$ in DMFC [28]. Use of H_2SO_4 as cross-linking agent is accompanied by health hazard. Moreover, being a corrosive liquid reagent, handling and use of H_2SO_4 as cross-linking agent is cost-intensive. Use of salts such as sodium sulfate and sodium phosphate overcomes both of the limitations. Sodium sulfate was employed as cross-linking agent to prepare CS hydrogel microspheres for application as drug delivery agent by Hejazi et al. [29]. Du et al. have reported [30] synthesis and proton-conductivity characterizations of CS membrane doped with ammonium chloride (NH_4Cl). Du et al. have further reported [31] studies on the structural and electrical properties of proton-conducting CS membranes doped with three different ammonium salts, namely, ammonium acetate (CH_3COONH_4), NH_4Cl, and ammonium sulfate ($(NH_4)_2SO_4$). Optimum properties were observed for CS membrane doped with CH_3COONH_4 and worst properties were observed for CS membrane doped with $(NH_4)_2SO_4$. It is noteworthy that in both of the studies reported by Du et al. [30,31], the salt doped-CS membranes have not been tested for their stabilities and performances in any electrochemical energy device. During our present study, however, it was observed that CS hydrogel membrane prepared by ionic cross-linking (doping) with divalent anion such as SO_4^{2-} (in the form of Na_2SO_4) and HPO_4^{2-} (in the form of Na_2HPO_4) was stable in aqueous medium for the entire duration of our study spanning over a few months whereas CS hydrogel membrane prepared by ionic cross-linking with monovalent anion such as chloride (in the form of NaCl) dissolved in aqueous medium within about three days time. In this paper, we report our studies on various characterizations of ICCSHMEs prepared by ionic cross-linking of CS with sodium sulfate (Na_2SO_4) and sodium hydrogen phosphate (Na_2HPO_4) as well as their performance evaluations as electrolyte-cum-separators in DBFCs.

2. Experimental details

2.1. Preparation of CS solution

A 2% (w/v) aqueous solution of CS was prepared by adding the required amount of CS powder (MW: 100,000–300,000; Acros Organics) to a given volume of 2% (v/v) aqueous solution of glacial acetic acid (Certified ACS reagent, Fisher Scientific) in a glass beaker. The beaker was covered with Para film so as to prevent evaporation of water and the contents were stirred magnetically at ambient temperature for ∼12 h to obtain a pale yellow solution.

2.2. Preparation of ICCSHMEs

ICCSHMEs were prepared by a solution casting technique in which the required volume of 2% (w/v) solution of CS, as prepared by a procedure described in Section 2.1, was cast on a glass Petri dish and left at ambient conditions of temperature and pressure for ∼36 h to allow the water to evaporate. The solid layer of CS, which was left on the Petri dish after evaporation of water, was further dried in an air-convection oven at 55 °C for 24 h. The dried layer of CS in the Petri dish was cooled to room temperature (25 °C). A sufficient volume of 0.5 M solution of sodium sulfate ($Na_2SO_4{\cdot}10H_2O$, Fisher Chemical) or sodium hydrogen phosphate ($Na_2HPO_4{\cdot}12H_2O$, Acros Organics) was then added to the Petri dish so as to completely dip the dried CS film inside the salt solution. The Petri dish was covered with a piece of Para film so as to prevent evaporation of water from salt solution and left at ambient temperature for about 24 h to allow absorption of salt solution by the dried CS film. The sulfate (SO_4^{2-}) or hydrogen phosphate (HPO_4^{2-}) ion absorbed in the wetted CS film undergoes ionic cross-linking with ammonium ion moiety ($-NH_3^+$) of CS. Due to the absorption of salt solution and subsequent ionic cross-linking, the CS mass turns into a solid hydrogel film that was subsequently peeled off the surface of the Petri dish with the help of a stainless steel spatula. The ICCSHME was then taken out of the salt solution bath, washed thoroughly with DI water and stored in de-ionized water (DI) water bath for use in DBFCs.

2.3. Preparation of CCH binder-based anode

The anode catalyst employed in this study was a composite of nickel and carbon-supported palladium (Pd/C) wherein the weight