A high performance direct borohydride fuel cell employing cross-linked chitosan membrane

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ABSTRACT

A cross-linked chitosan (CCS) membrane has been prepared by a solution casting method using sulfuric acid as cross-linking agent. The CCS membrane was used as the polymer electrolyte and separator in a direct borohydride fuel cell (DBFC). Ionic conductivity and borohydride crossover rate have been measured for the CCS membrane. The DBFC used in this study employed nickel-based composite as anode catalyst and Nafion® as anode binder. The power performance of the CCS membrane-based DBFC was compared with a similar DBFC employing Nafion® 212 (N212) membrane as electrolyte /separator. The CCS membrane-based DBFC exhibited better power performance as compared to N212 membrane-based DBFC. Encouraged by this result, chitosan chemical hydrogel (CCH) was prepared and used as binder for anode catalysts. A DBFC comprising CCS membrane and CCH as anode binder was studied and found to exhibit even better power performance at all temperatures in this study. A maximum peak power density of 450 mW cm^{-2} was observed at 60 °C for DBFC employing CCS membrane and CCH binder-based anode. The chitosan-based DBFC was operated continuously for 100 h and its performance stability was recorded.

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1. Introduction

A direct borohydride fuel cell is an electrochemical device that converts chemical energy to electrical energy by electro-oxidation of borohydride ion (BH_4^-) at the anode and electro-reduction of an oxidant at the cathode. Usually, a DBFC employs an alkaline solution of sodium borohydride ($NaBH_4$) as the fuel and oxygen or hydrogen peroxide as the oxidant. Compared with H_2–polymer electrolyte fuel cells (PEFCs), or direct methanol fuel cells (DMFCs), a DBFC has favorable thermodynamic and energy characteristics [1].

The anode reaction of a DBFC is the direct electro-oxidation of borohydride in alkaline medium as shown in the following equation:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad E°_{anode} = -1.24\,V\ vs.\ SHE \quad (1)$$
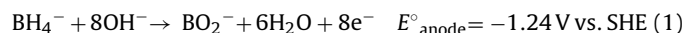
The cathode reaction with oxygen as the oxidant is written as shown in the following equation:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad E°_{cathode} = 0.40\,V\ vs.\ SHE \quad (2)$$
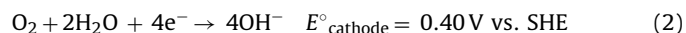
When oxygen is employed as the oxidant in the cathode, the net cell reaction is expressed as the following equation:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad E°_{cell} = 1.64\,V \quad (3)$$
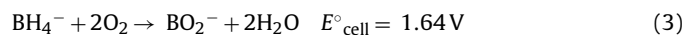
Borohydride ions readily undergo electro-oxidation even on non-precious metals, such as nickel. Alkaline nature of the anolyte solution used in DBFCs is an additional advantage because of its low corrosion activity. Both borohydride and its oxidation product, metaborate (BO_2^-), are relatively inert and non-toxic. Besides, BO_2^- can be recycled to produce borohydride [2].

Anode catalysts examined in DBFCs are primarily metallic materials including platinum (Pt), gold (Au), palladium (Pd), silver (Ag), ruthenium (Ru), and nickel (Ni) etc. and their alloys, and hydrogen storage alloys (AB_5-, AB_2-type) [1,3,4]. Bimetallic and composite catalysts could have superior activity and stability to monometallic catalysts. Amendola et al. were the first to report [5] a direct borohydride-air fuel cell which employed gold (97 wt.%)/platinum (3 wt.%) alloy as anode electro-catalyst. The DBFC reported by Amendola et al. could utilize approximately seven out of a theoretically maximum eight electrons and achieved a maximum power density of 60 mW cm^{-2} at 70 °C. In a study by Atwan et al. [6], electrochemical measurement showed that Au–Pt had higher catalytic activity for borohydride electro-oxidation than Au–Pd, and both the alloys had better activity than Au. Ni–Pt alloys demonstrated even higher catalytic activity than Au–Pt [7]. In a study by Geng et al. [8], a DBFC employing Ni–Pt/C as the anode catalyst gave much higher peak power density than that using Ni/C or Pt/C. In another study by Cao et al. [9], Ru, which mainly completes the hydrolysis of borohydride, was combined with Pt, which can oxidize hydrogen and also borohydride. It was observed that borohydride electro-oxidation underwent indirect eight electron process on Pt–Ru nanoparticles.

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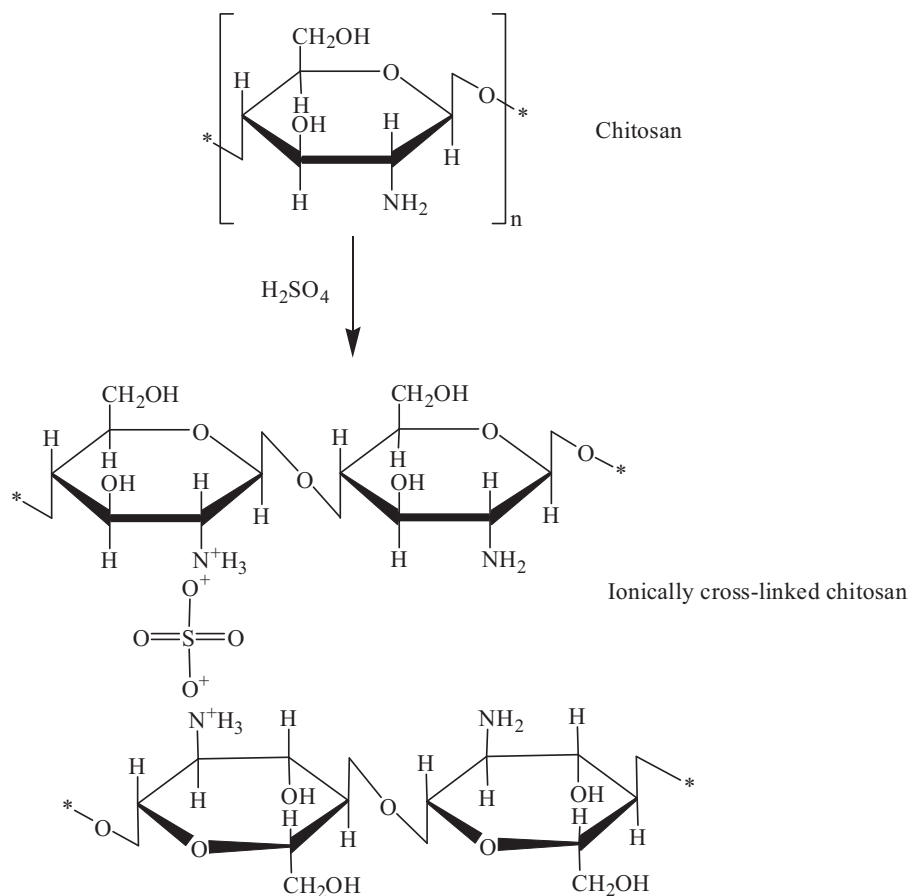*E-mail address:* sahai.1@osu.edu (Y. Sahai).

Fig. 1. Chemical structures of chitosan and sulfate ion cross-linked chitosan.

Polymer electrolyte membrane is an important constituent of fuel cells and other electrochemical energy conversion or storage devices. Nafion® membranes are a kind of cation exchange membranes (CEMs) employed in the majority of H_2-PEFCs, DMFCs, and also in DBFCs [1]. In addition to the membrane, Nafion® ionomer is also employed in the catalyst layers as an ionic conductor and catalyst binder in these fuel cells. However, Nafion® material is expensive, which is one of the major factors impeding the commercialization of polymer electrolyte fuel cells. Therefore its replacement by cost-effective polymer materials is highly desirable.

Chitosan [β-(1,4)-2-amino-2-deoxy-D-glucopyranose] shown in Fig. 1, is a hydrophilic, inexpensive, biodegradable, and non-toxic 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 biopolymer next to cellulose [10]. Chitosan is insoluble in water and most organic solvents. It is, however, soluble in some dilute aqueous solutions of weak organic acids, such as acetic, formic, and lactic acids [11,12]. The dissolution of chitosan in these organic acids allows the formation of chitosan hydrogels that can be cast into membranes, beads and other forms. It has been reported that the flexibility of chitosan films prepared by casting of chitosan dissolved in dilute aqueous lactic acid solution is higher than that dissolved in aqueous acetic acid solution [12]. Cross-linking is used as chemical modification to make chitosan insoluble in aqueous media, and to ensure good mechanical and chemical stability [13]. Typical cross-linking agents include glutaraldehyde [14], sulfuric acid [11,13], and tannic acid [15], etc. Thermal stability analysis revealed that cross-linked chitosan membranes could withstand temperature as high as 230 °C in nitrogen atmosphere, which ensures their thermal stability in the operational temperature of polymer electrolyte fuel cells [13]. Water uptake of cross-linked chitosan membrane was found to be higher than that of the Nafion® 117 membrane in the temperature range between 20 and 60 °C [11,13].

In recent research towards developing cost-effective electrode binder alternative to Nafion®, polymer chemical hydrogel binders were employed, which were found to exhibit comparable or superior performance to Nafion® [16,17]. Hydrogel is a network of polymer that absorbs and retains a significant amount of water in its polymeric matrix. Chemical hydrogels are formed by chemical reaction between a polymer and a cross-linking reagent. Due to the presence of chemical cross-links and physical entanglements, chemical hydrogels have insolubility in aqueous medium and ability to bind catalyst particles.

In this study, sulfuric acid cross-linked chitosan membrane electrolyte and chitosan chemical hydrogel binder-based electrode were prepared and employed in a DBFC. To the best of authors' knowledge, this is the first investigation on cross-linked chitosan membrane as polymer electrolyte for a direct borohydride fuel cell. Important properties of CCS membrane for DBFC application have been studied. Power performance of chitosan-based DBFC was studied in an active fuel cell system and the results were compared with Nafion®-based DBFC under identical conditions. Electrochemical performance stability of the chitosan-based DBFC was studied for a continuous duration of 100 h.

2. Experimental

2.1. Membrane preparation

Cross-linked chitosan membrane was prepared according to the following procedure: 2 g chitosan powder (Acros Organics, MW = 100,000–300,000) was added to 100 mL of 1% (v/v) aqueous solution of L(+)-Lactic acid (90%, Acros Organics) and vigorously stirred to form a solution. The solution was cast in a Petri-dish and left in ambient conditions for about 12 h for degassing. After that, the Petri-dish with the viscous chitosan solution was transferred to an air oven where it was heated at 60 °C for 24 h. Then 0.5 M H_2SO_4 aqueous solution was added to the Petri-dish for cross-linking in ambient conditions. Finally, the membrane formed was thoroughly washed by de-ionized (DI) water and stored in DI water.

2.2. Membrane characterization

For application in direct borohydride fuel cells, two important properties of membrane are ionic conductivity in alkaline medium and borohydride crossover. Therefore, ex-situ studies were carried out to investigate these two properties. As-received Nafion® 212 membrane was pretreated before measurement. Pretreatment of N212 membrane was carried out by boiling the membrane in aqueous solution of 3 wt.% H_2O_2 and 3 wt.% H_2SO_4 for 1 h and then boiling the membrane in DI water for 1 h. The pretreatment of membranes in H_2O_2 and H_2SO_4 aqueous solution served to oxidize small contaminants and converted all acidic sites to the proton form. Excess acid was washed away by rinsing with DI water. Membrane thickness was measured by a digital micrometer (Mitutoyo).

2.2.1. Ionic conductivity measurement of membrane

Ionic conductivity measurement was carried out in a two-point-probe conductivity cell at room temperature. The cell frame was machined from Teflon material and two copper electrodes were used to contact the membrane on both sides. The electrode diameter was 1 cm. Potentiostatic EIS measurement was carried out in the frequency range of 10^{-1}–10^5 Hz at open circuit potential with an AC voltage of 5 mV, by means of Gamry electrochemical system.

Before conductivity measurement, membranes were equilibrated for 24 h in DI water or 10 wt.% aqueous NaOH solution at room temperature. Prior to the assembly of cell, the membrane was surface dried by wiping it with tissue paper, and then the swollen membrane was placed quickly between the copper electrodes in the measurement cell. To ensure good membrane electrode contact, two cell frames were held tightly with bolts. The water content of the membrane was assumed to remain constant during the short period of time required for the measurement.

2.2.2. Borohydride crossover studies on membrane

Ex-situ studies were carried out to determine the extent of borohydride crossover by using passive fuel cell hardware. The chambers of the hardware are two high-density graphite blocks, each of which had a number of holes of 1 mm diameter. One chamber contained an aqueous solution of 30 wt.% $NaBH_4$ in 6 M NaOH and the other was filled with 6 M NaOH aqueous solution. The two chambers were separated by a piece of membrane and were held in tight contact with bolts. The membrane samples were equilibrated in 6 M NaOH for 24 h prior to being employed in the experiments. The set-up was kept at room temperature to allow the chemical species to crossover through the membrane. After a certain amount of time, crossovered borohydride was analyzed quantitatively.

A number of methods have been used to determine the concentration of borohydride, including titrimetric [18], polarographic [19], spectrophotometric [20], and voltammetric methods [21].

Among them, voltammetric method is a simple, rapid, and accurate analytical method that can be used directly in a reaction system [21]. In this study the concentration of borohydride was measured according to reported voltammetric method [21,22]. The detection limit of borohydride using voltammetric method is 10^{-5} M [23]. This method links the maximum oxidation current of BH_4^-, under linear sweep voltammetry, to the concentration of borohydride solution, using a three-electrode electrochemical cell. The working electrode was a 0.1 mm diameter high purity gold wire (Aldrich) of 3 cm length. The counter electrode was a piece of nickel mesh with an area of 1.1 cm × 3.3 cm. The reference electrode was a mercury/mercury oxide (MMO) reference electrode (Radiometer Analytical). As supplied, the reference electrode was filled with a 1 M KOH solution, and its potential is 0.115 V vs. SHE. The linear sweep voltammogram was recorded using a Gamry electrochemical system. The potentiostat was set to scan between −0.8 and 0.2 V (vs. MMO) at 100 mV s^{-1}.

2.3. Electrode preparation

2.3.1. Preparation of Nafion® binder-based electrode

The required amount of nickel powder (INCO Inc., type 210) and carbon-supported palladium powder (10 wt.% Pd on Vulcan XC-72, BASF Fuel Cell, Inc.) was mixed with Nafion® solution (5 wt.%, Ion Power, Inc.) and iso-propyl alcohol, and was ultrasonicated to form a slurry. The slurry was then applied to a piece of nickel foam (Inco®), and dried in an air oven at 80 °C. The loading of Nafion® ionomer electrode binder was 15 wt.% of the dry catalyst material.

2.3.2. Preparation of chitosan chemical hydrogel (CCH) binder-based electrode

First, an aqueous solution of 0.25% (w/v) chitosan was prepared by adding chitosan powder (MW: 100,000–300,000; Acros Organics) in 1% (v/v) aqueous solution of L(+)-Lactic Acid (90%, Acros Organics) in a glass beaker and stirring the contents magnetically at ambient temperature. The required amount of nickel powder (INCO Inc., type 210) and carbon-supported palladium powder (10 wt.% Pd on Vulcan XC-72, BASF Fuel Cell, Inc.) was mixed with an adequate quantity of DI water to form a suspension which was agitated in an ultrasonic water bath. Subsequently, the required volume of a 0.25% (w/v) chitosan binder solution was added drop wise to the suspension of catalyst powders in water with continued sonication. The ink was then pasted on a piece of nickel foam (Inco®) substrate and the catalyst ink-coated foam was dried inside an air oven at 60 °C. Finally, the dried catalyst-coated foam was dipped in 6.25% (v/v) aqueous solution of glutaraldehyde to cause the cross-linking reaction between chitosan and glutaraldehyde to occur. Finally, the catalyst-coated nickel foam was washed thoroughly with DI water to remove excess impurities.

2.4. Electrochemical performance tests on direct borohydride fuel cells

Both Nafion® binder-based electrode and CCH binder-based electrode were employed as anode for membrane-electrode-assembly (MEA) in DBFCs. The anode catalyst used in this study was Ni and Pd/C composite. The weight ratio of Ni:Pd was 25:1. The loading of the anode catalyst was 5 mg cm^{-2}. The weight ratio and loading were kept constant for all fuel cell tests. The cathode was commercially available platinum electrode (Electrochem, Inc.) with a Pt loading of 1 mg cm^{-2}. The active area of the fuel cell was 5 cm^2. For the electrochemical characterization of DBFCs, MEAs were prepared by sandwiching the CCS membrane or pretreated N212 membrane between anode and cathode by mechanical force. Membranes were hydrated prior to cell assembly.

The single fuel cell hardware employed in this study was procured from Fuel Cell Technologies, Inc. and was described in a previous study [24]. The fuel consisted of an aqueous solution of 5 wt.% $NaBH_4$ in 10 wt.% NaOH. The flow rate of fuel solution was 5 mL min^{-1}. The flow rate of oxygen at the cathode chamber was 0.15 L min^{-1}. Oxygen was humidified by passing through a bubbler at room temperature. The electrochemical data was recorded with a fuel cell test system (Scribner Associates, Inc.). The performance stability of the borohydride-oxygen fuel cell was evaluated by monitoring the cell voltage as a function of time at a constant load current density of 120 mA cm^{-2}.

To investigate the ion-transfer in CCS membrane, a chitosan-based DBFC was assembled and operated at a current density of 50 mA cm^{-2} for 2 h. The cathode surface was examined by scanning electron microscope (Quanta200) and EDS technique.

3. Results and discussion

3.1. Characterization of membranes

3.1.1. Ionic conductivity

In order to evaluate ionic conductivity values for N212 and CCS membranes equilibrated in DI water and aqueous NaOH solution, Nyquist plots were recorded by carrying out impedance spectroscopic measurements and are shown in Fig. 2(a) and (b). Membrane conductivity σ (S cm^{-1}) was calculated using the following equation:

$$\sigma = \frac{L}{R \times A} \qquad (4)$$

where σ (S cm^{-1}) is membrane conductivity, L (cm) is the thickness of membrane inside the conductivity cell, A (cm^2) is geometric area of the membrane, and R (Ω) is bulk resistance calculated from high-frequency intercept on the real axis of the complex impedance plot. The ionic conductivity data derived from Nyquist plots are summarized in Table 1.

After pretreatment, where membrane was boiled in 3 wt.% sulfuric acid for 1 h, N212 membrane is in H$^+$-form. The ionic conductivity of N212 membrane equilibrated with DI water was found to be 7.6×10^{-2} S cm^{-1}, which is close to the reported value [25]. After it was equilibrated in NaOH aqueous solution, N212 membrane is in Na$^+$-form. The ionic conductivity of N212 membrane in alkaline medium was 7.4×10^{-3} S cm^{-1}, which is one order of magnitude lower than that in acid form. The conduction of H$^+$ ions in the acid form of N212 membrane takes place by its transport from one anionic site ($-SO_3^-$) to another anionic site through water medium by Grotthus type mechanism which contributes to the abnormally high mobility of the proton as compared to other ions. In contrast, the conduction of Na$^+$ in NaOH-treated N212 membrane takes place by its transport from one anionic site to another through water medium by segmental motion-aided diffusion mechanism. In Grotthus type mechanism, conduction of H$^+$ through water takes place by alternation of covalent bond into hydrogen bond and vice versa [26]. Contrastingly, conduction of Na$^+$ through water medium of Na$^+$-form of N212 membrane takes place by diffusion of hydrated Na$^+$ ion. Because of the more facile conduction of H$^+$ ions as compared to Na$^+$ ions, acid form of the N212 membrane exhibits higher ionic conductivity than sodium form one. It has been found that
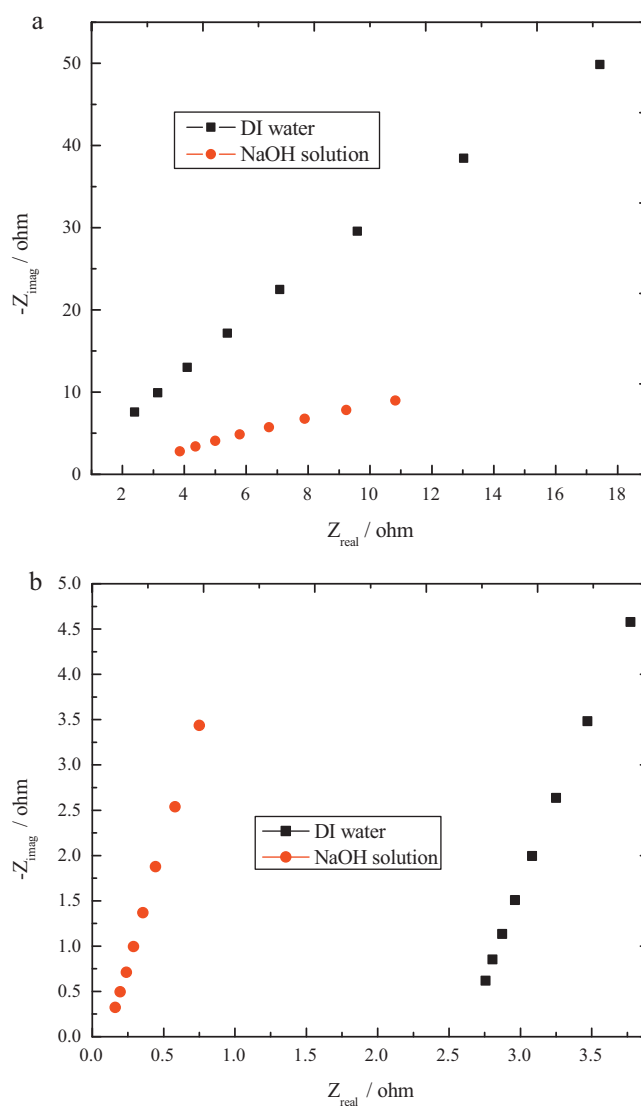
Fig. 2. Nyquist plots of (a) N212, and (b) CCS membranes recorded by electrochemical impedance spectroscopy.

the replacement of proton on the sulfonic group by cations affects the transport characteristics of polymer electrolyte, reducing ionic conductivity, and water uptake [27].

Chitosan film can be cast from dissolving chitosan powder in organic acid aqueous solution. The resulted chitosan film is in acid form ($-NH_3^+$) which can be converted to $-NH_2$ form by air drying [28] during which the organic acid is removed by evaporation. After the addition of sulfuric acid to chitosan film, the amino groups are protonated and cross-linking reaction occurs between two negatively charged oxygen moieties of sulfate ion of sulfuric acid and positively charged ammonium groups ($-NH_3^+$) of two chitosan chains (as shown in Fig. 1). This type of ionic interaction takes place at multiple points of the chitosan chains, thereby making the cross-linked chitosan hydrogel membrane insoluble in

Table 1
Properties of CCS and N212 membranes.

Membrane	Dry thickness (μm)	Wet thickness (μm)	Ionic conductivity measured after dipping in DI water (S cm^{-1})	Ionic conductivity measured after dipping in NaOH solution (S cm^{-1})	Borohydride crossover rate (mol s^{-1} cm^{-2})
N212	50	60	7.6×10^{-2}	7.4×10^{-3}	4.8×10^{-9}
CCS	45	115	6.2×10^{-3}	1.1×10^{-1}	4.6×10^{-8}

water. A molecular dynamics (MD) study of the mechanism of the ionic conductivity in sulfate ion cross-linked chitosan was done by Loĭpez-Chaĭvez et al. [29]. The ion-conducting system in their study consists of three ionic species: hydronium, hydroxide and sulfate ions. They observed that the sulfate ions anchored in the amino groups of the membrane backbone lead the mobility of the charge carrier ionic species. CCS membrane demonstrates a conductivity of 6.2×10^{-3} S cm^{-1} after washing with DI water. The ionic conductivity of CCS membrane is lower than that of N212 membrane after equilibrated with DI water. The high conductivity of Nafion® membrane is due to the linked ionic cluster structure, which enables the protons to jump from one sulfonic group to another through water medium [30,31]. In CCS membrane, ionic bonds formed between –NH$_2$ groups and –SO$_3$H groups consume some of the proton exchange sites, which is unfavorable to proton conduction. It is possible that in CCS membrane the distance between two proton receptor sites is longer and so electromosis is slower than in the Nafion® membrane [32], and as a result, the conductivity of CCS membrane is lower.

The conductivity of CCS membrane in alkaline medium is 1.1×10^{-1} S cm^{-1}, which is significantly higher than that after dipping in the DI water medium. When CCS membrane is treated with aqueous NaOH solution, Na$^+$ and OH$^-$ ions penetrate into the matrix of CCS. The hydroxide ion is capable of forming hydrogen bonding in water medium of CCS hydrogel matrix and transports through the matrix by Grotthus type mechanism. The higher ionic conductivity of NaOH-equilibrated CCS membrane is due to the contribution of OH$^-$ ion in addition to the contributions from the SO$_4{}^{2-}$ and Na$^+$ ions.

The conductivity of CCS membrane is higher than that of N212 membrane in alkaline medium. As shown in Fig. 1, chitosan contains polar functional groups, namely hydroxyl (–OH), primary amine (–NH$_2$), and ether (C–O–C) groups which have the capability of forming hydrogen bonding with water and trapping water in its polymer matrix. Nafion® polymer possesses both hydrophilic and hydrophobic properties. Since the water attracting behavior of Nafion® is restricted to its hydrophilic region only, its water retaining capability is not as good as that of chitosan. The high water uptake capability of CCS membrane is demonstrated by the difference between its wet thickness and dry thickness. It is evident from Table 1 that the wet thickness of N212 membrane (60 μm) is only slightly higher than its dry thickness (50 μm). In contrast, the wet thickness of CCS membrane (115 μm) is much higher than its dry thickness (45 μm). Greater water uptake ability of CCS membrane leads to its greater uptake ability of electrolyte solutions such as NaOH, and ultimately contributes to a higher ionic conductivity which is related to the number and mobility of conductive ions in the polymer complexes [33]. An ideal ionic conductivity of hydrated polyelectrolyte membrane should be close to 10^{-2} S cm^{-1} or higher for polymer electrolyte fuel cell application [34]. Thus, CCS membrane possesses conductivity high enough to serve as electrolyte in a DBFC.

3.1.2. Borohydride fuel crossover

The calibration plot exhibiting relation between anodic peak current and borohydride concentration is shown in Fig. 3(a). The plot is linear over a wide concentration range with a root square deviation of 0.9986. Figs. 3(b) and (c) show typical linear sweep voltammograms recorded for alkaline solution of NaBH$_4$ that crossed over during 24 h of test duration through N212 and CCS membranes, respectively. It can be seen that a lower peak current is observed for N212 membrane as compared to CCS membrane, which implies a lower rate of borohydride crossover through N212 membrane. Borohydride crossover rates through CCS and N212 membranes were calculated to be 4.6×10^{-8} and 4.8×10^{-9} mol s^{-1} cm^{-2}, respectively. Borohydride crossover rate
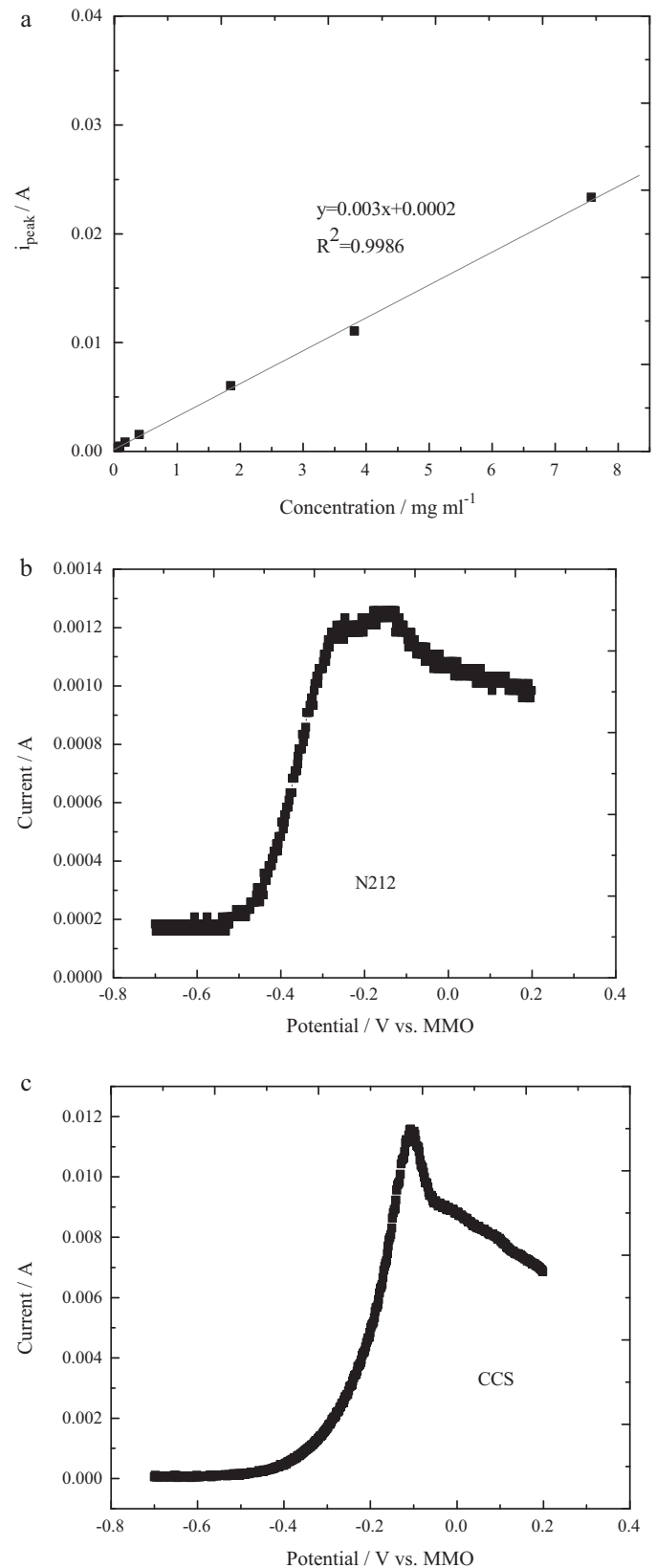
Fig. 3. (a) Dependence of peak anodic current at gold electrode on borohydride concentration, (b) a typical linear sweep voltammogram (LSV) recorded during estimation of borohydride crossover through N212 membrane, and (c) a typical LSV recorded during estimation of borohydride crossover through CCS membrane.
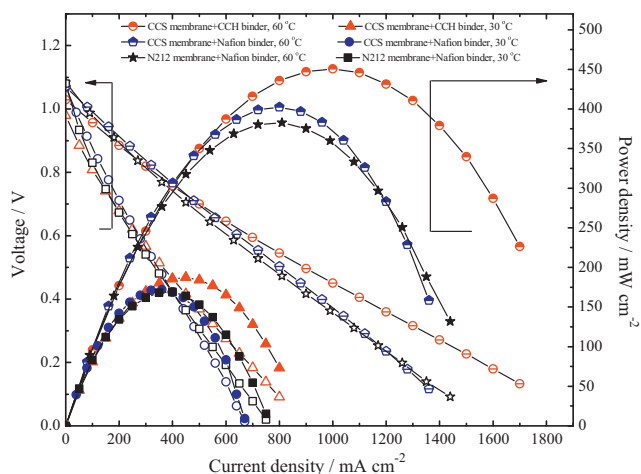
Fig. 4. Plots of cell polarization and power density vs. current density for DBFCs using CCS membrane and N212 membrane, CCH binder and Nafion® binder at 30 and 60 °C.
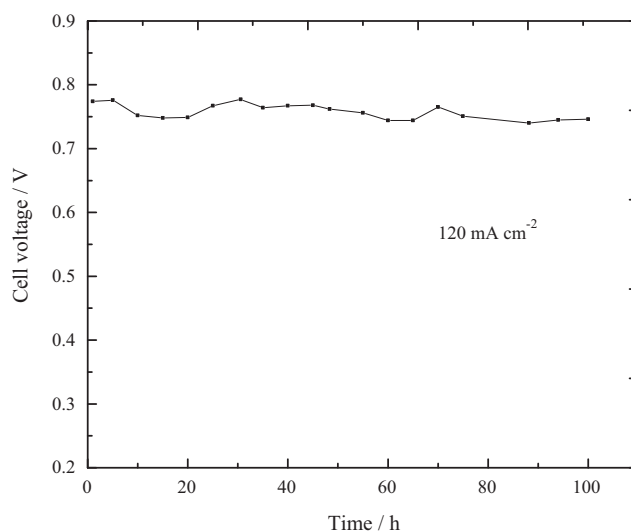

Fig. 5. Fuel cell performance stability data for a DBFC, which employs CCH as electrode binder and CCS as electrolyte/separator, recorded by operating it at a current density of 120 mA cm^{-2} and at 30 °C.

through the CCS membrane is higher than that through the N212 membrane by one order of magnitude. The difference in crossover rates of borohydride fuel through the two membranes can be understood by considering their structural features. Nafion® membrane is a cation exchange membrane with negatively charged –SO$_3^-$ groups attached to the polymer backbone. Being a negatively charged ion, BH$_4^-$ experiences a repulsive force while crossing over through the Nafion® membrane. In contrast, CCS membrane has positively charged –NH$_3^+$ groups attached to the polymer backbone. Because of the electrostatic attraction with –NH$_3^+$ group, BH$_4^-$ ion experiences a facilitated crossover through CCS membrane in contrast to N212 membrane. Therefore, Nafion® membrane is more effective in the suppression of BH$_4^-$ crossover as compared to CCS membrane.

3.2. Power performance of DBFCs

The electrochemical performance was measured in DBFCs by using either CCS or N212 membrane. The catalyst anode binder was either chitosan chemical hydrogel or Nafion® solution. The cell was operated at 30–60 °C. The anode electrocatalyst employed in this study was a composite of Ni and carbon supported Pd particles. Ni electrode was found to demonstrate smaller anode polarization and more negative open circuit potential than Pd [35]. Pd, on the other hand, has a higher coulombic efficiency, especially at a low concentration of borohydride. The addition of Nafion® ionomer to the mixture of Ni and Pd/C tends to lower the borohydride concentration on the Pd surface [36]. Thus, composites made of Ni and Pd/C can take the advantage of the merits of both metals, and as a result enhance the fuel cell performance[24]. The electrochemical performance data for DBFCs are shown in Fig. 4 and summarized in Table 2. Peak power density for DBFC employing N212 membrane and Nafion® binder increases from 169 mW cm^{-2} to 382 mW cm^{-2} as the cell temperature is enhanced from 30 °C to

60 °C. Peak power density for DBFC employing CCS membrane and Nafion® binder increases from 172 mW cm^{-2} to 402 mW cm^{-2} as the cell temperature is increased from 30 °C to 60 °C. The increase of power performance of the DBFCs with increase of cell temperature could be due to increase in electrode kinetics and ionic conductivity of the membrane electrolyte [1,24]. Under the same experimental conditions, the power performance of DBFC using CCS membrane is higher than that of DBFC using N212 membrane at both 30 and 60 °C. Higher power performance of CCS membrane-based DBFC as compared to N212 membrane-based DBFC can be understood in terms of the characteristics of the two membranes. As shown in Table 1, the wet thickness of CCS membrane is about two times that of N212 membrane whereas the ionic conductivity in alkaline medium of CCS membrane is about fifteen times that of N212 membrane. Despite the slightly higher wet thickness, significantly higher ionic conductivity leads to lower ohmic resistance and therefore a higher power density. Interestingly, the superior performance associated with the application of CCS membrane to N212 membrane is more obvious at elevated temperature. This is likely due to the high water uptake capacity of CCS membrane. Increase in temperature might result in partial dryness of membrane electrolyte. CCS membrane has higher water holding capacity compared to N212 membrane. As a result, CCS membrane is more effective in preventing partial dryness of membrane at a high fuel cell temperature.

Fig. 4 and Table 2 also give DBFC power performance with CCH binder-based anode and CCS membrane. The peak power densities of this cell were 187 mW cm^{-2} and 450 mW cm^{-2} at 30 °C and 60 °C, respectively. The DBFC with CCH as anode binder and CCS membrane yielded highest power performance among all the DBFCs studied here, and the superior performance of the said DBFC was more evident at high temperature. Chitosan chemical hydrogel was

Table 2
Summary of electrochemical data obtained from DBFCs comprising CCH binder or Nafion® binder-based electrode, CCS membrane or N212 membrane electrolyte at different operating cell temperatures.

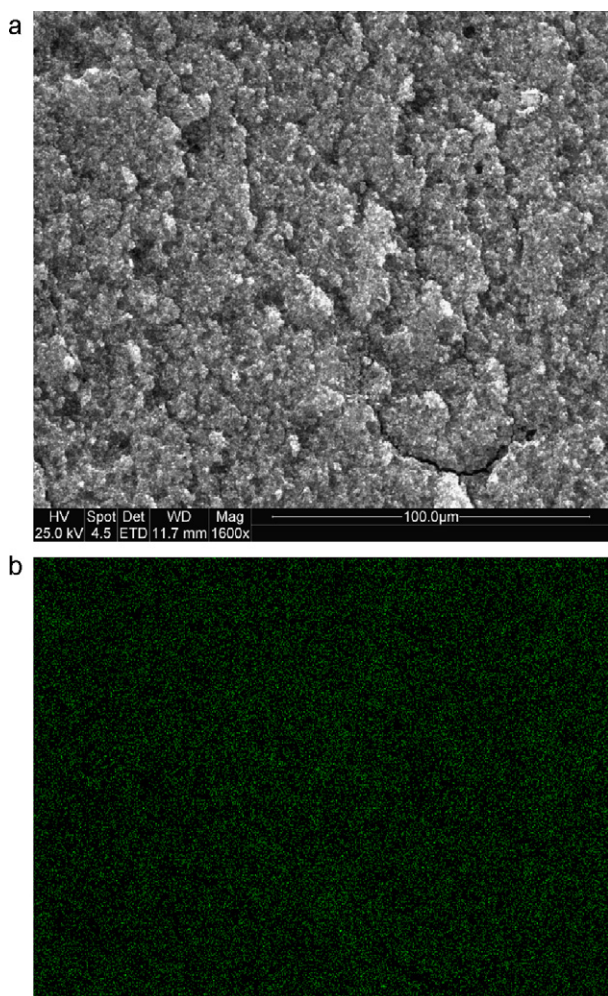| Temperature (°C)	N212 membrane, Nafion® binder		CCS membrane, Nafion® binder		CCS membrane, CCH binder	
	Peak power density (mW cm^{-2})	Corresponding current density (mA cm^{-2})	Peak power density (mW cm^{-2})	Corresponding current density (mA cm^{-2})	Peak power density (mW cm^{-2})	Corresponding current density (mA cm^{-2})
30	169	400	172	360	187	450
60	382	809	402	800	450	900

Fig. 6. (a) Scanning electron micrograph of cathode surface, and (b) Na-mapping EDS image of cathode surface after used in a DBFC at a current density of 50 mA cm^{-2} for 2 h.

formed by dissolving chitosan powders in dilute aqueous solution of lactic acid and cross-linked with aqueous glutaraldehyde. The cross-linking reaction between chitosan and glutaraldehyde takes place by Schiff base mechanism [37]. Chitosan chemical hydrogel is able to absorb and retain a significant amount of water in its polymeric matrices. The large water retention capacity of CCH helps in attaining high mobility of ions and fuel within the hydrogel-bonded electrode matrix. Therefore, the performance of CCS membrane-based DBFC has been further improved by using CCH as anode binder as compared to Nafion® binder.

3.3. Performance stability of DBFCs

Performance stability of a borohydride-oxygen fuel cell using CCS membrane and CCH anode binder was tested continuously for more than 100 h at 30 °C. As shown in Fig. 5, the DBFC exhibited a stable performance over the test period. The operating cell voltage was fairly constant at 0.75 V with slight fluctuations over the test period. CCS membrane and CCH binder are not only able to achieve high power but also good performance stability in DBFC application. Voltage efficiency of a fuel cell can be expressed as $\varepsilon = E(i)/E_r$, where $E(i)$ is the cell potential at a given applied current density and E_r is the reversible potential. The observed open circuit potential of the present DBFC is about 1 V as seen from Fig. 4. The observed OCP is lower than the theoretical value of 1.64 V due to fuel crossover, mixed potential at electrode, and sluggish elec-

trode kinetics. The single fuel cell potential during operation of a fuel cell is diminished by the losses in over-potential at anode, cathode, and electrolyte. The over-potential losses encountered in a fuel cell include activation loss due to slow kinetics of electrochemical reactions at the electrodes, ohmic loss due to resistance of electrolyte membrane, cell components and inter-connects, mass transport loss due to insufficient concentrations of reactants at the electrode/electrolyte interface at high load current condition, and fuel crossover loss due to crossover of fuel through membrane electrolyte. Due to these losses, the operating efficiency of fuel cells is lower than the theoretical value. It is noteworthy that in the present study, the potential vs. time plot was recorded at a constant load current density of 120 mA cm^{-2}. If the applied load current density is lowered, the observed voltage will be higher than 0.75 V with the ultimate consequence of increased voltage efficiency of the same DBFC.

3.4. SEM analysis of DBFC cathode

In a DBFC with Nafion® membrane, it has been proved that sodium ions are charge carriers in it [38]. In CCS membranes, it is expected that Na$^+$ is also responsible for the ionic charge transfer. To verify that Na$^+$ is the ion conducting through the CCS membrane during DBFC operation, the cathode was analyzed by SEM after the fuel cell was operated for 2 h at a current density of 50 mA cm^{-2}. Fig. 6(a) shows a scanning electron micrograph of the cathode surface. Fig. 6(b) is a SEM mapping image which shows the presence of Na (green spot) in the cathode (For interpretation of the references to color in this sentence, the reader is referred to the web version of the article.). This result proved that Na$^+$ ions migrated from the anode compartment to the cathode compartment through the CCS membrane.

4. Conclusions

Ionically cross-linked chitosan hydrogel membranes were prepared by a simple solution casting method. Cross-linked chitosan membrane demonstrated higher ionic conductivity in alkaline medium and higher borohydride crossover rate than Nafion® 212 membrane. Under identical conditions, cross-linked chitosan membrane exhibited better power performance as compared to Nafion® 212 membrane in a DBFC at both 30 and 60 °C. The performance of chitosan membrane-based DBFC was further improved by using chitosan chemical hydrogel as anode binder as compared to Nafion® binder. The chitosan-based DBFC exhibited a stable fuel cell performance for a continuous duration of more than 100 h. Various studies reported in this paper show that chitosan is a cost-effective alternative material to Nafion® for application in direct borohydride fuel cells. Use of chitosan in DBFC would significantly reduce its cost and may help in its commercialization.

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