



# 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  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$  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  $810 \text{ mW cm}^{-2}$  has been achieved for the DBFC employing  $\text{Na}_2\text{HPO}_4$ -based ICCSHME and operating at a cell temperature of  $70^\circ\text{C}$ .

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## 1. Introduction

A DBFC is a type of fuel cell that utilizes a borohydride species, usually sodium borohydride ( $\text{NaBH}_4$ ) 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  $\text{OH}^-$  from cathode to anode compartment, but suffer from the problem of  $\text{BH}_4^-$  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<sup>®</sup>-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  $90^\circ\text{C}$ . In DBFCs, sodium ion is transported through the Nafion<sup>®</sup> membrane instead of proton as in the case of hydrogen/oxygen polymer electrolyte fuel cells (PEFCs). Because of higher ionic conductivity of  $\text{H}^+$  as compared to that of  $\text{Na}^+$  in Nafion<sup>®</sup> membrane, ion conductivity is smaller in DBFCs as compared to that in the  $\text{H}_2/\text{O}_2$ -based PEFCs [1]. Moreover, the mechanism of proton conduction is different from that of  $\text{Na}^+$  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  $\text{CO}_2$  of air, which deactivates the cathode as well as membrane and restricts flow of  $\text{O}_2$ /air to the cathode. The problem becomes severe in extended period of operation and therefore, a way to remove  $\text{CO}_2$  from air-feed of cathode and to return  $\text{NaOH}$  from catholyte to anolyte is needed [8]. In order to reduce alkali crossover from anode to cathode of DBFC, Nafion<sup>®</sup>-961 membrane was used instead of Nafion<sup>®</sup>-117 membrane as electrolyte/separator [9,10]. Nafion<sup>®</sup>-961 membrane is a Teflon-fiber reinforced composite membrane with sulfonate ( $100 \mu\text{m}$  thick) and carboxylate ( $10 \mu\text{m}$  thick) polymer layers. The weakly-ionized carboxylate layer of Nafion<sup>®</sup>-961 membrane offers resistance to flow of  $\text{Na}^+$  and the strongly-ionized sulfonate layer

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with electrically negative polymer backbone offers resistance to flow of OH<sup>-</sup> 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<sup>®</sup>-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<sup>®</sup>-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<sub>3</sub>COOH), which converts the glucosamine unit (R-NH<sub>2</sub>) of CS into its protonated form (R-NH<sub>3</sub><sup>+</sup>). 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<sup>-2</sup> S cm<sup>-1</sup>. A H<sub>2</sub>/air PEFC using the CS-KOH as PEM delivered a current density of 30 mA cm<sup>-2</sup> [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<sub>2</sub>SO<sub>4</sub> was studied by Cui et al. [26]. CS hydrogel membrane prepared by ionic cross-linking with H<sub>2</sub>SO<sub>4</sub> 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 × 10<sup>-2</sup> S cm<sup>-1</sup> and methanol permeability of 3.9 × 10<sup>-8</sup> cm<sup>2</sup> s<sup>-1</sup> in DMFC [28]. Use of H<sub>2</sub>SO<sub>4</sub> as cross-linking agent is accompanied by health hazard. Moreover, being a corrosive liquid reagent, handling and use of H<sub>2</sub>SO<sub>4</sub> 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<sub>4</sub>Cl). 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<sub>3</sub>COONH<sub>4</sub>), NH<sub>4</sub>Cl, and ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Optimum properties were observed for CS membrane doped with CH<sub>3</sub>COONH<sub>4</sub> and worst properties were observed for CS membrane doped with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. 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<sub>4</sub><sup>2-</sup> (in the form of Na<sub>2</sub>SO<sub>4</sub>) and HPO<sub>4</sub><sup>2-</sup> (in the form of Na<sub>2</sub>HPO<sub>4</sub>) 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<sub>2</sub>SO<sub>4</sub>) and sodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>) 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<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O, Fisher Chemical) or sodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, 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<sub>4</sub><sup>2-</sup>) or hydrogen phosphate (HPO<sub>4</sub><sup>2-</sup>) ion absorbed in the wetted CS film undergoes ionic cross-linking with ammonium ion moiety (-NH<sub>3</sub><sup>+</sup>) 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

ratio of Ni:Pd was 25:1 [32]. To prepare anode catalyst ink, a certain amount of Ni powder (INCO Inc., type 210) was mixed with the required quantity of Pd/C powder (10% Pd supported on Vulcan XC-72, BASF Fuel Cell, Inc.) and adequate quantity of DI water in a glass vial. The vial containing the aforesaid suspension was agitated in an ultrasonic water bath (Branson<sup>®</sup> ultrasonic cleaner) for 2 h. Subsequently, required volume of CCH binder [33,34] solution, comprising 0.25% (w/v) solution of CS dissolved in 1% (v/v) aqueous CH<sub>3</sub>COOH solution, was added drop-wise to the aforesaid suspension with ultrasonic agitation continued for another 2 h. The loading of the anode catalyst was about 5 mg cm<sup>-2</sup>. The anode catalyst ink was pasted on a nickel foam substrate (Incofoam<sup>®</sup>) with a paint brush and the catalyst ink-coated nickel foam was dried inside an air oven at 50 °C. Finally, the dried catalyst-coated nickel foam was cooled to ambient temperature, weighed to determine catalyst loading, and then dipped in 10 mL of 6.25% (v/v) aqueous glutaraldehyde solution for 5 h to cause the cross-linking reaction between CS and glutaraldehyde to occur. After the treatment, the catalyst-coated nickel foam was washed thoroughly with DI water to remove excess impurities.

#### 2.4. Mechanical strength characterization of ICCSHMEs

The mechanical strength of ICCSHMEs prepared by ionic cross-linking of CS with Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> were characterized by Instron table mounted testing machine with a transducer capacity of 50 lb. The membrane sample size was 30 mm (length) × 20 mm (width) × 0.07 mm (thickness) and the membrane stretching speed was 1 mm min<sup>-1</sup>.

#### 2.5. Thermogravimetric analysis of CS-based membrane electrolytes

Thermogravimetric analysis (TGA) studies on uncross-linked CS membrane and ICCSHMEs prepared by ionic cross-linking of CS with Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> were carried out under nitrogen atmosphere by employing a Perkin Elmer Thermal Analysis Controller (TAC 7/DX) in the temperature range of 20–800 °C at a temperature scan rate of 10 °C min<sup>-1</sup>. Prior to heating the sample, the furnace with the membrane sample mounted inside it was purged with nitrogen gas for 1 h. The flow rate of N<sub>2</sub> during purging as well as during heating was maintained at 60 mL min<sup>-1</sup>.

#### 2.6. FTIR spectroscopic characterization of CS-based membrane electrolytes

Fourier Transform Infra Red (FTIR) spectroscopic characterizations of uncross-linked CS membrane and ICCSHMEs prepared by ionic cross-linking of CS with Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> were carried out by using a FTIR Spectrometer (Nicolet 6700, Thermo Scientific) in the wave number region of 400–4000 cm<sup>-1</sup>.

#### 2.7. Energy dispersive X-ray spectroscopic studies on CS-based membrane electrolytes

Energy dispersive X-ray spectroscopy (EDS) characterizations of the uncross-linked CS membrane and Na<sub>2</sub>SO<sub>4</sub> as well as Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHMEs were carried out using Energy dispersive X-ray spectrometer (Tracor Northern, Model No.: 5500) having Moxtek window and equipped with SiLi detector.

#### 2.8. Water uptake measurements of ICCSHMEs

For water uptake measurements, ICCSHMEs prepared by ionic cross-linking of CS with Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> were taken out of DI water bath and cut into pieces of 6 cm × 6 cm sizes. The weights

of these hydrated membranes ( $W_h$ ) were measured after wiping away the free water from the surfaces of the membrane pieces using tissue paper. After that, the ICCSHME pieces were dried inside an oven at 110 °C for 48 h to evaporate all the absorbed water. Complete evaporation of water from each of ICCSHME was ensured by weighing it at intervals of 12 h until a constant dry weight ( $W_d$ ) was reached. The percentage water uptake values of the membrane samples were then evaluated from their wet and dry weights using Eq. (1) [13].

$$\text{Water uptake (\%)} = \frac{W_h - W_d}{W_d} \times 100 \quad (1)$$

In order to ensure reproducibility in the water uptake measurements, the above procedure was repeated for five different pieces of each of Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> cross-linked ICCSHMEs.

#### 2.9. Electrochemical characterizations of ICCSHMEs

For ionic conductivity measurements, ICCSHMEs were thoroughly washed with DI water to remove any trace of impurity. Ionic conductivity ( $\sigma$ ) values for the ICCSHMEs were determined using electrochemical impedance spectroscopy recorded in the frequency range between 100 mHz and 100 kHz with a perturbation of 5 mV rms using Gamry Electrochemical system (model number: PCI4). Ionic conductivity ( $\sigma$ ) of ICCSHM electrolytes was evaluated by employing Eq. (2).

$$\sigma = \frac{L}{R_b \times A} \quad (2)$$

In Eq. (2),  $L$ ,  $A$ , and  $R_b$  are, respectively, the thickness, geometric area and bulk resistance of the ICCSHM electrolyte. Bulk resistance of the ICCSHME is obtained from the high-frequency intercept on the real impedance axis of the Nyquist plot.

For the electrochemical performance characterization of ICCSHMEs in DBFCs, membrane electrode assemblies (MEAs) were fabricated by sandwiching the anode and cathode on either side of ICCSHMEs. The cathode employed in the DBFCs was commercially procured platinum catalyst supported on high surface area carbon (Pt/C) that was coated on Teflonized-Toray paper (Electrochem Inc.). MEAs comprising ICCSHMEs prepared by ionic cross-linking of CS with Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> sodium were employed to assemble various liquid-fed DBFCs. The fuel cell set-up employed in this study was procured from Fuel Cell Technologies, Inc. The anode and cathode of each of the MEAs were contacted on their rear with fluid flow-field plates for fuel and oxidant, respectively. The fluid flow-field plates were machined from high-density graphite blocks in which channels were provided to allow supply of fuel and oxidant to the anode and cathode, respectively. The channels in the flow-field plates, thus, helped in achieving minimum mass-polarization in the DBFCs. The ridges between the channels in the flow-field plates on both sides of the MEA made electrical contact with the electrodes. The active area of each of anode and cathode was 5 cm<sup>2</sup>. The graphite flow-field plates on both sides of the MEA were provided with electrical contacts that helped in conduction of electrical current to the external circuit. The graphite block on the cathode side was provided with a tiny hole to accommodate a thermocouple that was connected to temperature controller. A constant cell temperature was maintained with the help of the thermocouple during each electrochemical measurement. All the DBFC results reported in this paper were recorded in active mode using peristaltic pumps for the fuel solution. The fuel consisted of an aqueous solution of 5 wt.% NaBH<sub>4</sub> in 10 wt.% NaOH and the oxidant consisted of gaseous oxygen (medical grade). The flow rates for fuel and oxidant were maintained constant at 5 and 150 mL min<sup>-1</sup>, respectively for all electrochemical characterizations of the DBFCs. After installing the DBFCs in the test station, performance evaluation studies were

initiated. Both cell polarization and performance durability data for the DBFCs were recorded by employing a computer-controlled fuel cell test system (Scribner Associates, Inc., Model: 890e). The computer-controlled fuel cell test system not only recorded the polarization data for various DBFCs but also controlled the flow rate of fuel solution as well as the cell temperature. The cell performance durability data for  $\text{Na}_2\text{HPO}_4$ -cross-linked ICCSHME-based DBFC has been recorded at a constant load current density of  $24 \text{ mA cm}^{-2}$  at ambient temperature.

### 3. Results and discussion

#### 3.1. Membrane characterizations

Chitosan, dissolved in aqueous  $\text{CH}_3\text{COOH}$  solution, behaves as a polycation with  $-\text{NH}_3^+$  groups attached to its backbone. Two positively charged  $-\text{NH}_3^+$  groups of one or two CS polycation chains form two ionic bonds with two negatively charged oxygen moieties of one sulfate or hydrogen phosphate anion at ambient temperature and pressure. This type of ionic bond formation takes place at multiple sites of CS chains. Due to the ionic cross-linking process, aqueous solution of CS turns into a solid mass with all water associated with the precursor solutions remaining absorbed in the polymer matrix of the solid entity. Such solid entity is termed as cross-linked CS hydrogel. Cross-linked CS hydrogel, which is insoluble in water, can be cast in the form of a thin and high surface area membrane. These characteristics of cross-linked CS hydrogel make it a suitable material for use as electrolyte-cum-separator in DBFCs.

##### 3.1.1. Mechanical property characterizations

In order to test the mechanical strengths of the ICCSHMEs, tensile strength and Young's modulus values were determined. As shown in Table 1, the tensile strength values for  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs are found to be 4.1 and 1.2 MPa, respectively. The Young's modulus values for  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs are found to be 8.3 and 6.8 MPa, respectively. The  $\text{Na}_2\text{SO}_4$ -based ICCSHME has been found to possess superior mechanical properties as compared to the  $\text{Na}_2\text{HPO}_4$ -based ICCSHME. The difference in mechanical strengths of the two membranes can be understood in terms of the behaviors of the  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  ions in aqueous medium of differing pH.  $\text{SO}_4^{2-}$  ion is the conjugate base of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) that is a strong acid ( $K_a = 1.0 \times 10^3$ ). In aqueous solution,  $\text{H}_2\text{SO}_4$  dissociates completely into  $\text{H}^+$  and  $\text{SO}_4^{2-}$  ions; the  $\text{SO}_4^{2-}$  ion is stabilized by resonance. Two negatively charged oxygen moieties of  $\text{SO}_4^{2-}$  are capable of forming ionic bonds with two  $-\text{NH}_3^+$  groups belonging to one or two CS chains.  $\text{PO}_4^{3-}$  ion is the conjugate base of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) that is a weak acid ( $K_a = 7.1 \times 10^{-3}$ ). In aqueous medium,  $\text{PO}_4^{3-}$  ion exists in four different forms depending on the pH of the medium [35]. The phosphate ion ( $\text{PO}_4^{3-}$ ) dominates in strongly alkaline medium ( $\text{pH} \approx 12.8$ ), whereas monohydrogen phosphate ion ( $\text{HPO}_4^{2-}$ ) dominates in weakly alkaline medium ( $\text{pH} \approx 8$ ). Dihydrogen phosphate ( $\text{H}_2\text{PO}_4^-$ ) dominates in weakly acidic medium ( $\text{pH} \approx 4.8$ ), whereas trihydrogen phosphate ( $\text{H}_3\text{PO}_4$ ) dominates in strongly acidic medium ( $\text{pH} \approx 1.3$ ). In ICCSHME, weakly acidic medium comprising  $\text{CH}_3\text{COOH}$  is present. This implies that the most dominant phosphate species present is  $\text{H}_2\text{PO}_4^-$ . Because of the presence of one unit of negative charge on it,  $\text{H}_2\text{PO}_4^-$  is capable of forming ionic bond with only one  $-\text{NH}_3^+$  group on a CS chain. This implies that the density of ionic bonds in  $\text{H}_2\text{PO}_4^-$  salt-based ICCSHME will be lesser as compared to that in  $\text{SO}_4^{2-}$  salt-based ICCSHME. This further implies a weaker mechanical strength for the  $\text{H}_2\text{PO}_4^-$  salt-based ICCSHME as compared to the  $\text{SO}_4^{2-}$  salt-based ICCSHME. The  $\text{Na}_2\text{SO}_4$ -based ICCSHME exhibits a tendency to shrink when removed from water. In contrast, the

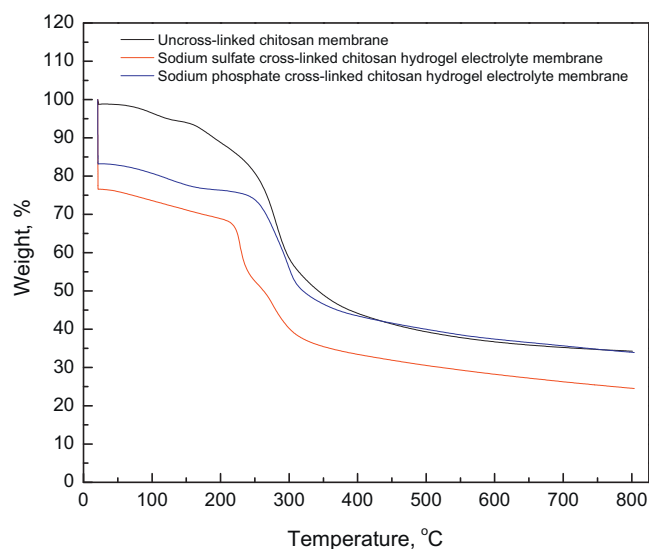


Fig. 1. Thermogravimetric analysis curves for uncross-linked CS electrolyte membrane and cross-linked CS hydrogel membrane electrolytes prepared by ionic crosslinking of CS with sulfate as well as hydrogen phosphate salts of sodium.

$\text{Na}_2\text{HPO}_4$ -based ICCSHME does not exhibit such a tendency and remains flat after its removal from water.

##### 3.1.2. Thermogravimetric analysis studies

The TGA curves for uncross-linked CS membrane and ICCSHMEs prepared by ionic cross-linking of CS with  $\text{Na}_2\text{SO}_4$  as well as  $\text{Na}_2\text{HPO}_4$  are shown in Fig. 1. From Fig. 1, it is evident that the weight loss behavior of all the three CS-based membranes is similar and each of them showed a three-stage weight loss procedure similar to reported literature [36]. The TGA curve for the uncross-linked CS membrane electrolyte sample exhibited an initial weight loss of about 5% in the temperature range of 50–150 °C. This initial weight loss is attributed to the desorption of physically absorbed water. The maximum weight loss of about 35% took place in the second stage in the temperature range of 150–300 °C. In the third stage taking place in the temperature range of 300–800 °C, a weight loss of about 20% was observed. The second and the third stages of weight losses were probably due to the decomposition of polymeric network of CS chains. The TGA curve for the  $\text{Na}_2\text{HPO}_4$ -based ICCSHME also exhibited an initial weight loss of about 5% in the temperature range of 30–175 °C. This initial weight loss is attributed to the desorption of physically absorbed water. The maximum weight loss of 25% took place in the second stage in the temperature range of 175–300 °C. In the third stage in the temperature range of 300–800 °C, a weight loss of about 20% was observed. The second and the third stages of weight losses were probably due to the decomposition of polymeric network of CS chains. The TGA curve for the  $\text{Na}_2\text{SO}_4$ -based ICCSHME sample exhibited an initial weight loss of about 7% in the temperature range of 30–200 °C. This initial weight loss is attributed to the desorption of physically absorbed water. The second weight loss of about 12% took place in the second stage in the temperature range of 200–240 °C. In the third stage in the temperature range of 240–800 °C, a weight loss of about 30% was observed. The second and the third stages of weight losses were probably due to the decomposition of polymeric network of CS chains. Thermal stability is highest for the uncross-linked CS membrane electrolyte and lowest for the  $\text{Na}_2\text{SO}_4$ -based ICCSHME. Degradation temperatures and thermal stabilities of both  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -cross-linked ICCSHMEs are lower as compared to those of uncross-linked CS membrane electrolyte. Higher degree of hydrogen bonding among CS chains is reported



**Table 1**  
Summary of physico-electrochemical data for cross-linked CS hydrogel membrane electrolytes prepared by ionic cross-linking with sulfate and hydrogen phosphate salts of sodium.

ICCSHME prepared by cross-linking with	Tensile strength (MPa)	Young's modulus (MPa)	Thicknesses ( $\mu\text{m}$ )	Water uptake (%)	Ionic conductivity ( $\text{S cm}^{-1}$ )
Sodium sulfate	4.1	8.3	70	93.5	$1.5 \times 10^{-3}$
Sodium hydrogen phosphate	1.2	6.8	80	120.7	$1.9 \times 10^{-4}$

to enhance the thermal stability of the CS-based polymer electrolytes [37]. Ionic cross-linking between polycationic CS chains and anionic cross-linking agents results in decreased flexibility and hence decreased extent of hydrogen bond formations among CS chains. The lower thermal stabilities of ICCSHMEs could be due to their increased rigidities resulting from the reduced abilities of CS chains in forming hydrogen bonds among themselves [37]. Between the two ICCSHMEs,  $\text{Na}_2\text{HPO}_4$ -cross-linked ICCSHME is thermally more stable as evident from Fig. 1. The greater thermal stability of  $\text{Na}_2\text{HPO}_4$ -cross-linked ICCSHME can be understood by taking into consideration the fact that the  $\text{Na}_2\text{HPO}_4$ -cross-linked ICCSHME possesses lesser density of ionic cross-linking sites in comparison to that of the  $\text{Na}_2\text{SO}_4$ -cross-linked ICCSHME as discussed above in the context of mechanical strengths of the two ICCSHMEs. Lesser density of ionic cross-linking sites in  $\text{Na}_2\text{HPO}_4$ -cross-linked ICCSHME enables it to form higher degree of hydrogen bonds among CS chains with the ultimate consequence of making it thermally more stable.

### 3.1.3. Fourier transform infrared spectroscopic studies

The FTIR spectra for uncross-linked CS membrane and ICCSHMEs prepared by ionic cross-linking with  $\text{Na}_2\text{SO}_4$  as well as  $\text{Na}_2\text{HPO}_4$  are shown in Fig. 2. All the three spectra show a strong band around  $3451 \text{ cm}^{-1}$  for OH stretching, two strong bands around  $3364$  and  $3313 \text{ cm}^{-1}$  for NH stretching, two weak bands around  $2910$  and  $2864 \text{ cm}^{-1}$  for CH stretching, and three bands around  $1152$ ,  $1068$ , and  $1030 \text{ cm}^{-1}$  for the saccharide structure. Assignment of these spectral bands is similar to that reported in literature [38,39]. The FTIR spectrum of pure CS membrane showed two absorption bands around  $1634$  and  $1531 \text{ cm}^{-1}$ . These two bands correspond to characteristic bending vibrations of  $\text{NH}_3^+$  group of CS membrane [26]; the  $\text{NH}_3^+$  group results from protonation of  $\text{NH}_2$  group by  $\text{CH}_3\text{COOH}$  during dissolution of CS. The absorption bands around  $1634$  and  $1531 \text{ cm}^{-1}$  merge into a single band around  $1587 \text{ cm}^{-1}$  for both  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$  cross-linked CS hydrogel membrane electrolytes. The lower absorbance of the band around  $1587 \text{ cm}^{-1}$  for both  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$  cross-linked CS hydrogel membrane electrolytes as compared to the uncross-linked CS membrane electrolyte could be due to the formation of

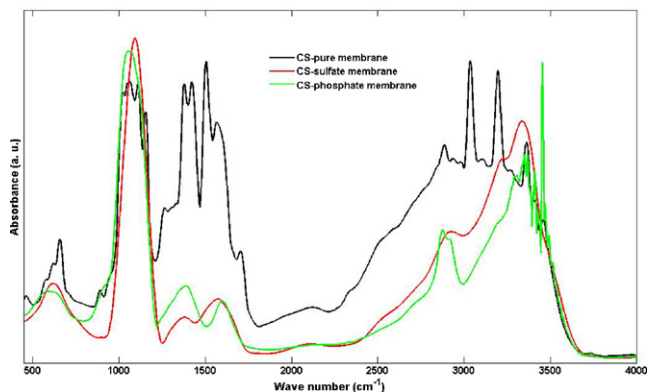
ionic bond between  $-\text{NH}_3^+$  groups of CS and  $\text{SO}_4^{2-}/\text{H}_2\text{PO}_4^-$  ion. Yuan et al. [40] assigned amide I band around  $1648 \text{ cm}^{-1}$  and amide II band around  $1565 \text{ cm}^{-1}$  to the presence of amino groups in CS molecule. It is evident from the FTIR spectra shown in Fig. 2 that the absorbances of amide I and amide II bands are far smaller for the ICCSHMEs as compared to that of uncross-linked CS membrane. The decreased absorbances could be due to the ionic bond formation between the positively charged  $-\text{NH}_3^+$  group of CS and negatively charged oxygen moieties on  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  ions. FTIR spectrum of  $\text{H}_3\text{PO}_4$  was studied by Arai et al. [35] wherein spectral bands for all the possible vibrational modes were assigned in the region of  $850$ – $1179 \text{ cm}^{-1}$ . The FTIR spectrum of  $\text{Na}_2\text{HPO}_4$ -based ICCSHME, shown in Fig. 2, exhibits a strong spectral band in the region of  $850$ – $1179 \text{ cm}^{-1}$ . This result is in conformity with the FTIR spectral study on  $\text{H}_3\text{PO}_4$  reported by Arai et al. [35], thereby confirming the presence of phosphate ion in the ICCSHME. Incidentally, the saccharide structure of CS exhibits absorption bands in the same spectral region as discussed above. The spectral band in the spectral region  $2500$ – $3000 \text{ cm}^{-1}$  and centered around  $2800 \text{ cm}^{-1}$  can be assigned to  $\text{N}^+-\text{H}$  stretching vibration in CS similar to the reported literature [41] on FTIR band assignments of protonated-polybenzimidazole. The lower absorbance of the band around  $2800 \text{ cm}^{-1}$  for both  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{HPO}_4$ -based ICCSHMEs as compared to the uncross-linked CS membrane electrolyte could be due to the ionic interaction between  $-\text{NH}_3^+$  groups of CS and  $\text{SO}_4^{2-}/\text{HPO}_4^{2-}$  ions.

### 3.1.4. Energy dispersive X-ray spectroscopic studies

In order to test the presence of ionically bound cross-linking agents in ICCSHMEs, EDS characterizations were carried out on the uncross-linked CS membrane and  $\text{Na}_2\text{SO}_4$  as well as  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs. The studies revealed the presence of carbon, oxygen, and chlorine in uncross-linked CS membrane electrolyte; carbon, oxygen, chlorine, sulfur, and sodium in  $\text{Na}_2\text{SO}_4$ -based ICCSHME; and carbon, oxygen, chlorine, phosphorous, and sodium in  $\text{Na}_2\text{HPO}_4$ -based ICCSHME. The detection of chlorine in  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs could be due to its proximity to sulfur and phosphorous in regard of atomic number. The EDS results are in conformity with the FTIR finger-printing data.

### 3.1.5. Water uptake studies

The water-uptake values of the  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs have been found to be about 93.5 and 120.7%, respectively. Because of the smaller water-uptake and retention ability, the  $\text{SO}_4^{2-}$  salt-based ICCSHME loses water rapidly in air and exhibits a tendency to shrink when removed from water. In contrast, the  $\text{HPO}_4^{2-}$  salt-based ICCSHME does not exhibit such a tendency and remains flat for a considerable period of time after its removal from water to air. The difference in the water-uptake values of the  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs can be understood by considering the structural features of the uncross-linked and cross-linked CS membranes. Because of electrostatic attraction, CS chains in ICCSHMEs will be structurally more compact as compared to the uncross-linked CS membrane. More compact structure implies less free volume available for water molecules [42,43]. Moreover, ionic cross-linking of CS with anionic cross-linking agents results in a decrease of free ionic sites in the system,



**Fig. 2.** FTIR spectra for uncross-linked CS membrane and ICCSHMEs prepared by ionic cross-linking of CS with sulfate as well as phosphate salts of sodium.

which could act as water absorption sites by virtue of ion-dipole attraction. As discussed above in relation to mechanical properties of ICCSHMEs, the density of ionic bonds will be lesser in  $\text{Na}_2\text{HPO}_4$ -based ICCSHME in comparison to  $\text{Na}_2\text{SO}_4$ -based ICCSHME. Lesser density of ionic bonds will result in lesser compact structure with greater free volume and absorption sites for water in  $\text{Na}_2\text{HPO}_4$ -based ICCSHME as compared to  $\text{Na}_2\text{SO}_4$ -based ICCSHME. This implies higher water-uptake and retention capabilities for  $\text{Na}_2\text{HPO}_4$ -based ICCSHME as compared to the  $\text{Na}_2\text{SO}_4$ -based ICCSHME.

### 3.1.6. Ionic conductivity studies

Wet thicknesses of the  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs are about 70 and 80  $\mu\text{m}$ , respectively. The room temperature ionic conductivity values for the  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{HPO}_4$ -based ICCSHMEs are found to be  $1.5 \times 10^{-3}$  and  $1.9 \times 10^{-4} \text{ S cm}^{-1}$ , respectively. The ionic conductivity of the  $\text{Na}_2\text{SO}_4$ -based ICCSHME has the same order of magnitude as that of the ICCSHME prepared by ionic cross-linking with sulfuric acid [44]. The ions responsible for ionic conductivity of ICCSHME are those associated with its preparation procedure. Hence, information about the responsible ions can be obtained by considering the preparation procedure of ICCSHME. During the dissolution of CS in  $\text{CH}_3\text{COOH}$  solution, the  $-\text{NH}_2$  group of CS gets protonated by  $\text{CH}_3\text{COOH}$  to form quaternary  $-\text{NH}_3^+$  group. The positive charge on  $-\text{NH}_3^+$  group is balanced by the negative charge of  $\text{CH}_3\text{COO}^-$  ion. When an aqueous solution of  $\text{Na}_2\text{SO}_4$  or  $\text{Na}_2\text{HPO}_4$  is added to the above system for ionic cross-linking, the negatively charged oxygen moieties of  $\text{SO}_4^{2-}$  or  $\text{H}_2\text{PO}_4^-$  ion links with the positively charged  $-\text{NH}_3^+$  groups present on adjacent CS chains. As more of such ionic cross-links form, more of CS chains come close to each other with the consequence of forming a solid water-insoluble product/membrane. It may be noted that as the ionic cross-linking density increases, steric hindrance among CS chains also increases proportionally. The increased steric hindrance may prevent some of the  $-\text{NH}_3^+$  groups from forming ionic cross-links with  $\text{SO}_4^{2-}$  or  $\text{HPO}_4^{2-}$  ions. The positive charges present on the uncross-linked  $-\text{NH}_3^+$  groups will be balanced by the negative charges present in  $\text{CH}_3\text{COO}^-$ ,  $\text{SO}_4^{2-}$  or  $\text{HPO}_4^{2-}$  ions. However, unlike the ionically bonded  $-\text{NH}_3^+$  and  $\text{SO}_4^{2-}$  or  $\text{HPO}_4^{2-}$  ions that are held together tightly, the un-bonded  $\text{CH}_3\text{COO}^-$  and  $\text{SO}_4^{2-}$  or  $\text{HPO}_4^{2-}$  ions in sterically hindered CS network are present as free hydrated ions that contribute to ionic conductivity of cross-linked CS membrane. Since only anions take part in ionic conduction process, the ionically cross-linked ICCSHME is classified as anion exchange membrane. The room temperature ionic conductivity values for the  $\text{Na}_2\text{HPO}_4$ -based ICCSHME is about one order of magnitude lower than that of  $\text{Na}_2\text{SO}_4$ -based ICCSHME. The difference in ionic conductivity of the two ICCSHMEs can be understood by considering the relative mobilities of  $\text{SO}_4^{2-}$  and  $\text{HPO}_4^{2-}$  ions through the ICCSHM network as  $\text{CH}_3\text{COO}^-$  ion is common in both the electrolytes. Both  $\text{SO}_4^{2-}$  and  $\text{HPO}_4^{2-}$  ions are almost identical in size, shape, and net amount of negative charges except for the extra H atom bonded to O atom in  $\text{HPO}_4^{2-}$  ion. The extra H atom forms hydrogen bonds with water molecules present in the hydrogel medium, thereby resulting in forming a larger hydration shell around the  $\text{HPO}_4^{2-}$  ion. The larger hydration shell results in lower mobility and hence lower ionic conductivity for  $\text{Na}_2\text{HPO}_4$ -based ICCSHME.

### 3.2. Fuel cell characterizations

Borohydride anion, dissolved in aqueous alkaline medium, undergoes electro-oxidation on the surface of a variety of electrode

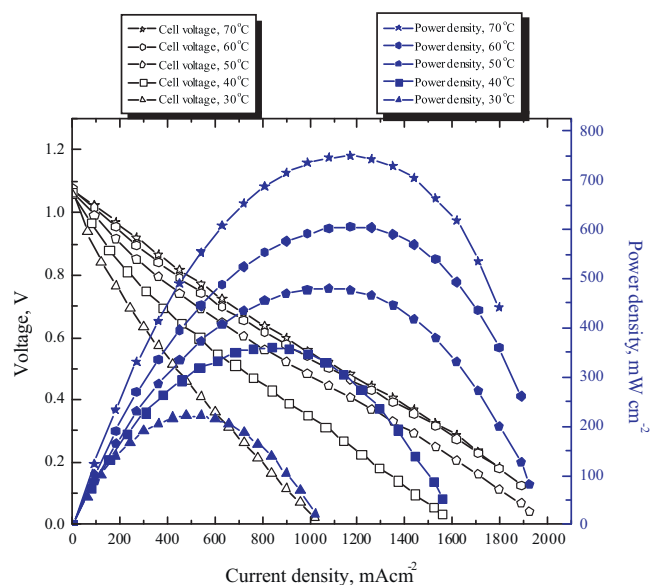
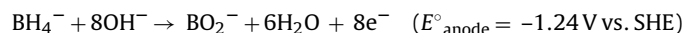
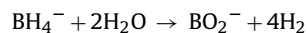


Fig. 3. Cell polarization and power density plots for DBFC employing ICCSHME prepared by ionic cross-linking of CS with sodium sulfate and operating at different cell temperatures.

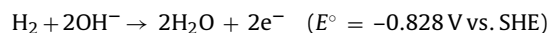
materials generating a maximum of eight electrons. The corresponding anode reaction is as follows:



Along with the electro-oxidation reaction,  $\text{BH}_4^-$  undergoes hydrolysis on almost all electrode materials liberating hydrogen gas. The chemical hydrolysis reaction of  $\text{BH}_4^-$  is as follows:



Hydrolysis of  $\text{BH}_4^-$  results in loss of fuel and hence is undesirable for DBFC performance. The loss of fuel can be minimized by oxidizing the liberated hydrogen on electrode materials that are capable of absorbing hydrogen and then oxidizing it. Palladium is capable of absorbing a large quantity of hydrogen to form palladium hydride ( $\text{PdH}_x$ , where  $x < 1$ ). When Pd is used as an anode in DBFC, it captures hydrogen and stores in its crystal lattice. The absorbed hydrogen is then oxidized in accordance with the following reaction:



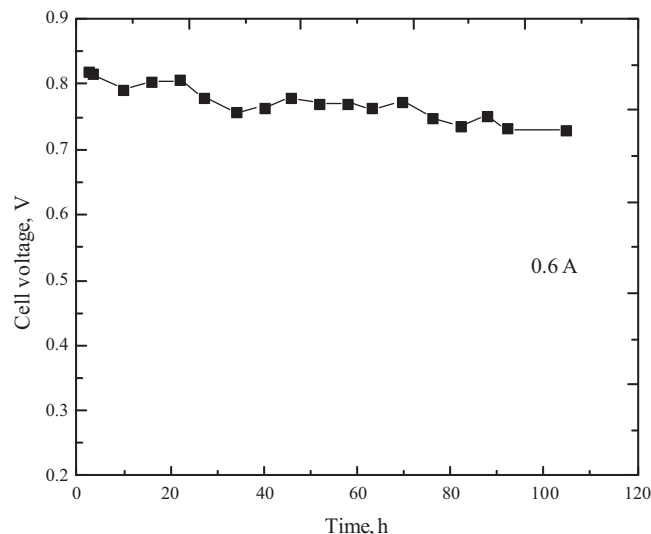
This unique property of Pd contributes positively to the electro-oxidation of  $\text{BH}_4^-$  on the electrode surface and thus helps in achieving high fuel cell performance. A detailed study on the use of Ni-Pd/C composite as anode material in DBFCs has earlier been reported by Ma et al. [32]. The detailed mechanism of electro-oxidation of  $\text{BH}_4^-$  is not yet completely understood. Possible mechanisms of electro-oxidation of  $\text{BH}_4^-$  on various electrode materials have recently been reviewed by Ma et al. [45].

The electrochemical performance data recorded at different operating cell temperatures for DBFC employing  $\text{Na}_2\text{SO}_4$ -based ICCSHME are shown in Fig. 3. The electrochemical performance data recorded at various operating cell temperatures for DBFC employing  $\text{Na}_2\text{HPO}_4$ -based ICCSHME are shown in Fig. 4. The electrochemical performance data pertaining to Figs. 3 and 4 are summarized in Table 2. It is evident from Table 2 that for DBFC employing  $\text{Na}_2\text{SO}_4$ -based ICCSHME, peak power density increased from 221 to 750  $\text{mW cm}^{-2}$  and current density corresponding to peak power increased from 480 to 1560  $\text{mA cm}^{-2}$  as the cell temperature was increased from 30 to 70 °C. It is further evident from Table 2 that for DBFC employing  $\text{Na}_2\text{HPO}_4$ -based ICCSHME, the peak power density increased from 238 to 810  $\text{mW cm}^{-2}$  and

**Table 2**  
Summary of electrochemical data for DBFCs employing CS hydrogel membrane electrolytes prepared by ionic cross-linking of CS with sulfate and hydrogen phosphate salts of sodium.

DBFC comprising	Cell temperature (°C)	Open circuit potential (V)	Peak power density (mW cm <sup>-2</sup> )	Current density (mA cm <sup>-2</sup> ) corresponding to peak power
ICCSHME prepared with Na <sub>2</sub> SO <sub>4</sub>	30	1.06	221	480
	40	1.06	360	836
	50	1.06	480	1080
	60	1.08	606	1300
	70	1.08	750	1560
ICCSHME prepared with Na <sub>2</sub> HPO <sub>4</sub>	30	1.07	238	540
	40	1.06	365	836
	50	1.06	511	1170
	60	1.06	651	1500
	70	1.07	810	1680

current density corresponding to peak power increased from 540 to 1680 mA cm<sup>-2</sup> as the cell temperature was increased from 30 to 70 °C. The Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME exhibited better power performance as compared to the Na<sub>2</sub>SO<sub>4</sub>-based ICCSHME in DBFCs at all operating cell temperatures. Although the ionic conductivity of the Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME is lower than that of the Na<sub>2</sub>SO<sub>4</sub>-based ICCSHME, the former exhibited better power performance in DBFC than the latter. The better power performance of the DBFC employing Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME as compared to the DBFC employing Na<sub>2</sub>SO<sub>4</sub>-based ICCSHME can be explained on the basis of the greater water-uptake ability of the Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME as compared to that of the Na<sub>2</sub>SO<sub>4</sub>-based ICCSHME. Greater water-uptake ability of the Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME results in its greater uptake ability of electrolyte solutions that leads to greater ionic conductivity in the DBFC operating condition. Greater ionic conductivity across the Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME in the DBFC operating condition results in greater power performance in the DBFC. Because of its greater power performance, the DBFC employing Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME was chosen for electrochemical performance durability test. The electrochemical performance durability data for the DBFC employing Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME is shown in Fig. 5. The operating cell voltage decreased from about 0.8 to 0.7 V during the 100 h period of continuous operation implying a good cell performance durability of the DBFC.



**Fig. 5.** Electrochemical performance durability data for DBFC employing ICCSHME prepared by ionic cross-linking of CS with sodium hydrogen phosphate and operating at ambient temperature.

#### 4. Conclusions

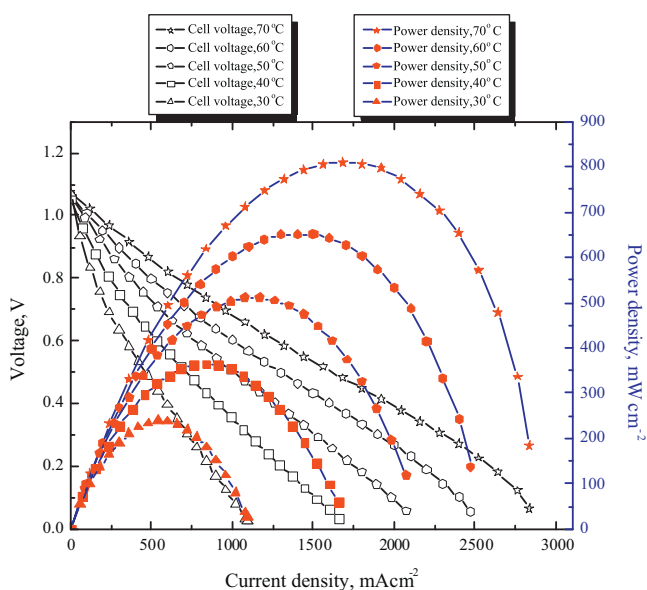
In this work, feasibility of using ICCSHMEs prepared by ionic cross-linking of CS dissolved in dilute aqueous acetic acid with aqueous solutions of sulfate and hydrogen phosphate salts of sodium as novel, cost-effective, and environmentally benign electrolytes/separators in DBFCs has been demonstrated. Preparations of ICCSHMEs and assembling of DBFCs with such membrane electrolytes are simple and time-effective. The DBFCs employing Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHMEs exhibited peak power density values of about 750 and 810 mW cm<sup>-2</sup> at corresponding current density values of about 1.560 and 1.680 A cm<sup>-2</sup>, respectively at operating cell temperatures of 70 °C. The DBFC employing Na<sub>2</sub>HPO<sub>4</sub>-based ICCSHME exhibited a stable cell performance with a cell voltage loss of only 100 mV during an operation period of 100 h.

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**Fig. 4.** Cell polarization and power density plots for DBFC employing ICCSHME prepared by ionic cross-linking of CS with sodium hydrogen phosphate and operating at different cell temperatures.

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