



Evaluation of multivalent phosphate cross-linked chitosan biopolymer membrane for direct borohydride fuel cells

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ABSTRACT

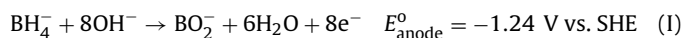
The direct borohydride fuel cell (DBFC) is a promising power supply for stationary and mobile devices. A high performance and low cost membrane electrolyte would reduce fuel cell stack cost and may help in its commercialization. In the work presented here, a cost-effective and eco-friendly chitosan membrane has been prepared and modified by phosphate or triphosphate salt. The paper describes the membrane preparation method, and various studies performed on it, which includes thermal analysis, water uptake, mechanical strength, ionic conductivity, and fuel cross-over measurements. These studies show that the triphosphate chitosan membrane has slightly higher figure of merit than phosphate chitosan membrane for application in a DBFC. A chitosan chemical hydrogel has been synthesized and used as the electrode binder. A borohydride-oxygen fuel cell employing triphosphate chitosan membrane and chitosan binder has achieved a peak power density of 685 mW cm^{-2} at 60°C , which is over 50% higher than the power performance of a DBFC using commercial Nafion® materials. In addition to the far superior power density, this chitosan-based DBFC has exhibited comparable stability and efficiency as Nafion®-based DBFC.

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1. Introduction

A direct borohydride fuel cell utilizes a borohydride compound, usually sodium borohydride (NaBH_4) in aqueous alkaline medium, directly as a fuel. The DBFC is a promising new type of fuel cell with intense investigation only in the past few years [1–3]. Compared to H_2 -polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs), DBFCs have several advantageous thermodynamic and energy characteristics, including high theoretical cell potential, and high number of electron transferred [4]. Alkaline medium of a DBFC opens up the possibility of using non-noble electro-catalysts and also features low corrosion activity.

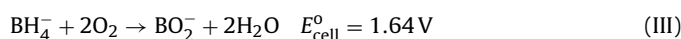
The anode reaction of a DBFC is the direct electro-oxidation of borohydride in alkaline medium as shown in Eq. (I).



The cathode reaction with oxygen as the oxidant is written as shown in Eq. (II).



When oxygen is employed as the oxidant in the cathode, the net cell reaction is expressed as Eq. (III).



Both cation exchange membrane (CEM) and anion exchange membrane (AEM) have been employed as electrolyte and separator between two electrodes in a DBFC. When AEM is used, hydroxide ions transfer from cathode to anode. Whereas in the case of CEM, sodium ions transfer through membrane and combine with hydroxide ions formed in the cathode.

A great deal of research has focused on anode electro-catalysts including various supported and unsupported metals, such as Pd, Pt, Au, Os, Ag, Ru, and Ni, and their binary alloys, and hydrogen storage alloys (AB_5 - and AB_2 -type) [5]. Less attention has been paid to polymer membrane materials for DBFCs. Commercial Nafion® perfluorinated membranes are widely employed as polymer electrolyte in DBFCs. Nafion® material is also used as electrode binder which facilitates ion conduction, provides mechanical support for catalyst particles, and enhances dispersion of catalyst particles in the catalyst layer. A major disadvantage of Nafion® material is its high cost. Thus researchers have been focusing on the use of low-cost materials as possible replacement for Nafion® [6,7].

Chitosan, a biodegradable, biocompatible, natural polymer, has been extensively examined in the pharmaceutical industry for its potential use in drug delivery systems [8,9]. Chitosan is derived from chitin by deacetylation. Chitin is largely found in the exoskeletons of crustaceans, and fungi, and is the most abundant natural

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biopolymer next to cellulose [10]. In weak organic acids, chitosan dissolves into gel solution that allows for physical modifications to form gel beads, membranes and other forms. Cross-linking is used as a chemical modification to ensure good mechanical and chemical stability [11]. Both phosphate and triphosphate can interact with cationic chitosan by electrostatic forces and form ionically cross-linked chitosan membrane [12].

In this study, phosphate chitosan (CsP) and triphosphate chitosan (CsTP) hydrogel membranes have been prepared, characterized, and fabricated into a membrane-electrode-assembly (MEA) for use in a DBFC. The properties of these cross-linked chitosan membranes were compared with a commercial Nafion® membrane.

2. Experimental

2.1. Materials

Chitosan powder (MW = 100,000–300,000) and sodium borohydride powder ($\geq 98.0\%$) were purchased from Acros Organics USA. Nickel powder (type 210) and Ni foam (IPASO-0050679-0001) were obtained from INCO Inc. Carbon-supported palladium powder (10 wt.% Pd on Vulcan XC-72) was purchased from BASF Fuel Cell, Inc. Nafion® 212 membrane and Nafion® solution (5 wt.%) were purchased from Ion Power, Inc. Sodium triphosphate (purum p.a., $\geq 98.0\%$) and sodium phosphate tribasic dodecahydrate ($\geq 98.0\%$) were obtained from Sigma-Aldrich USA. Glacial acetic acid, iso-propyl alcohol, and sodium hydroxide (reagent grade) were purchased from Fisher Scientific. Pt electrode (1 mg cm⁻² Pt loading, 20 wt.% Pt/Vulcan XC-72) was purchased from Electrochem, Inc.

2.2. Membrane preparation

2 g chitosan powder was added to 100 mL of 2% aqueous solution of glacial acetic acid and vigorously stirred to form a solution. The solution was cast in a Petri-dish and left under ambient conditions for 12 h for degassing. After that, the Petri-dish with the viscous chitosan solution was dried in an air oven at 60 °C for 24 h to form pristine chitosan membrane. Then a sufficient volume of 0.013 M sodium triphosphate or sodium phosphate tribasic dodecahydrate aqueous solution was added to the Petri-dish at ambient condition for 24 h. Due to the absorption of salt solution and subsequent ionic interaction as shown in Fig. 1, the chitosan mass turned into a solid chitosan hydrogel membrane which was then washed with DI water and stored in DI water bath.

2.3. Membrane characterization

Characteristics of chitosan membrane were studied and compared with commercial Nafion® 212 membrane. Nafion® membrane was pretreated before use. Pretreatment of Nafion® membrane was carried out by boiling the membrane in aqueous solution of 3% H₂O₂ and 3% H₂SO₄ for 1 h and then boiling the membrane in DI water for 1 h. After pretreatment, Nafion® membrane was stored in DI water.

2.3.1. Thermal analysis

Membrane samples were dried at 25 °C for 24 h before thermal analysis measurement. The thermogravimetric analysis (TGA) was studied by a Perkin Elmer Thermal Analysis Controller (TAC 7/DX) in nitrogen atmosphere from room temperature to 600 °C at a temperature scanning rate of 10 °C min⁻¹.

2.3.2. Water uptake study

Membrane samples were stored in DI water at room temperature for several days to ensure sufficient water uptake. To determine the water uptake at hydration, the membranes were removed from water, blotted dry with filter paper to remove surface water, and quickly weighed to give the initial wet weight. Then the wet membranes were dried at atmospheric conditions for 24 h (step I), and then further dried in an air convection oven (carbolite) at 100 °C for 3 h (step II) until the weight of membranes were constant. The percentage water uptake of the membranes was calculated by using the equation below:

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

where W_w is the weight of wet membrane, and W_d is the weight of dry membrane.

2.3.3. Mechanical test

The mechanical strength of membranes was characterized in a water tank at ambient temperature by Instron table mounted testing machine with a transducer capacity of 50 lb. The membrane size was 25 mm (length) × 15 mm (width) and stretching speed was 10 mm min⁻¹.

2.3.4. Ionic conductivity measurement

The ionic conductivity of membranes in the through-plane direction was measured in a two-point-probe conductivity cell, as shown in Fig. 2, at room temperature by the electrochemical impedance spectroscopy (EIS). Nyquist plots were recorded with Gamry electrochemical system over a frequency range of 10⁻¹–10⁵ Hz at open circuit potential with an AC voltage of 5 mV. Before conductivity measurement, membranes were equilibrated for 24 h in 10% aqueous NaOH solution. Prior to the assembly of cell, the swollen membrane was surfaced dried by tissue paper and placed between the copper electrodes in the measurement cell. Membrane conductivity σ (S cm⁻¹) was calculated using the following equation:

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

where σ (S cm⁻¹) is membrane conductivity, L (cm) is the thickness of membrane inside the conductivity cell, A (cm²) 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. Membrane thickness was measured by a digital micrometer (Mitutoyo).

2.3.5. Borohydride crossover measurement

Ex-situ studies were carried out to determine the extent of borohydride crossover by using passive fuel cell hardware as shown in Fig. 3. Chamber A and chamber B are two high-density graphite blocks, each of which had a number of holes with 1 mm diameter. Chamber A contained an aqueous solution of 30 wt.% NaBH₄ in 6 M NaOH and chamber B 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 employing in the experiments. The set-up was then kept at room temperature to allow the chemical species to crossover across the membrane. After a certain amount of time, 50 mL solution from chamber B was analyzed quantitatively in a three-electrode electrochemical cell by a reported voltammetric method [13]. A gold wire was used as the working electrode and a piece of nickel mesh as the counter electrode. The reference electrode was a mercury/mercury oxide (MMO) reference electrode (Radiometer Analytical). As supplied, the reference electrode is filled with 1 M KOH solution, and its potential is 0.115 V

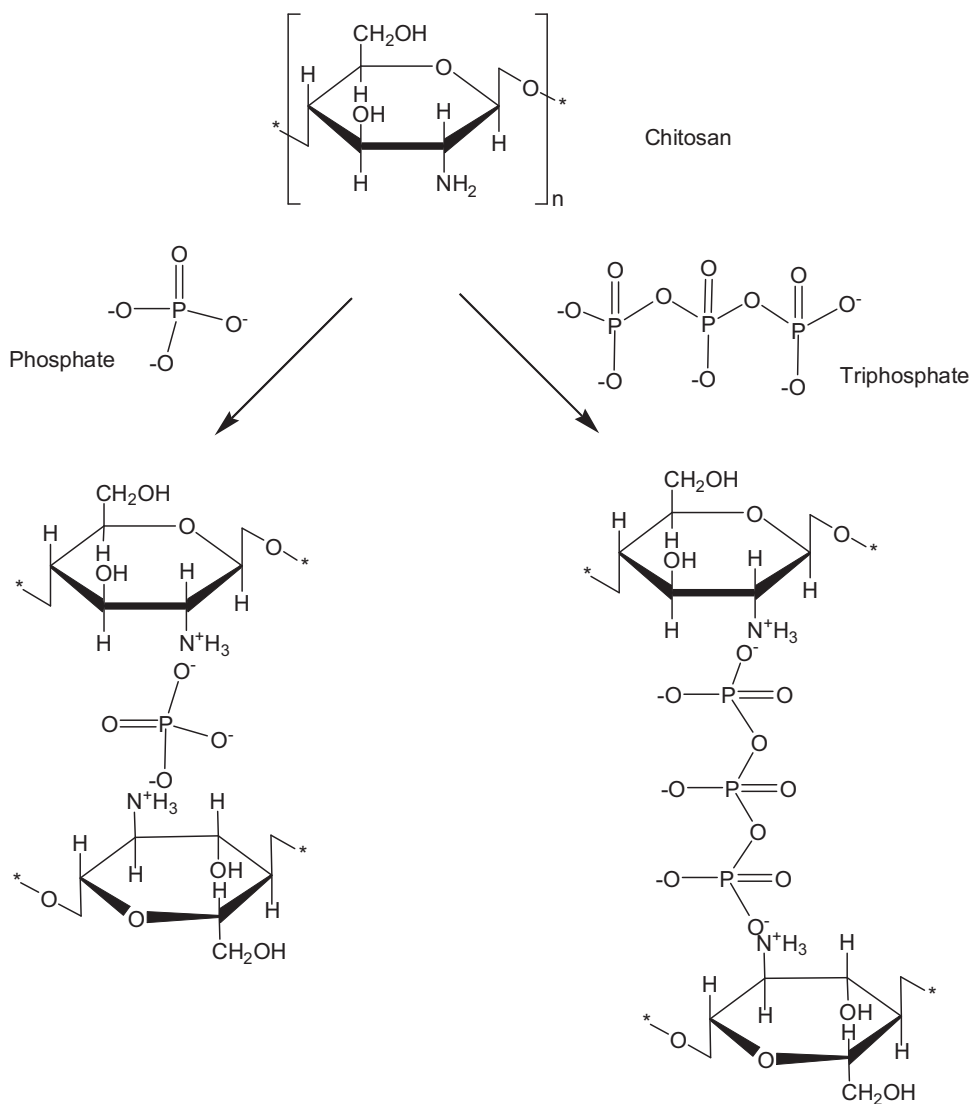


Fig. 1. Chemical structures of chitosan and ionic interaction between chitosan and multivalent phosphate.

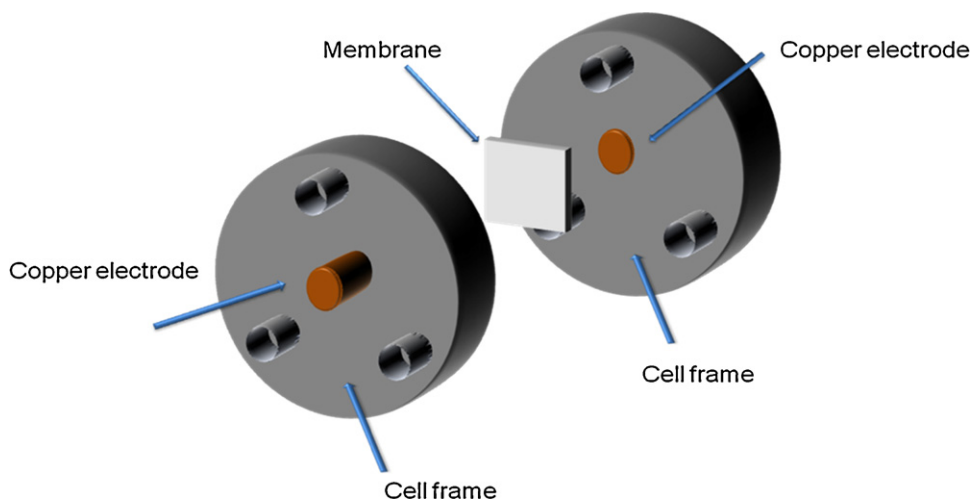


Fig. 2. A schematic diagram of a two-probe conductivity measurement cell for recording Nyquist plots by electrochemical impedance spectroscopy.

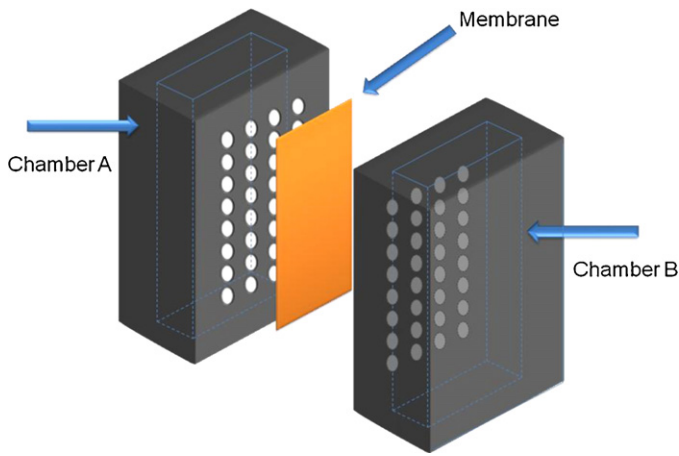


Fig. 3. A schematic diagram of a set-up for crossover measurement of borohydride fuel across chitosan membranes.

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} .

2.4. Electrode preparation

2.4.1. Preparation of Nafion® binder-based electrode

A piece of Ni foam was used as electrode substrate. The as-received Ni foam has a density of 500 g m^{-2} and a pore size of $590 \mu\text{m}$. It was roller pressed to a thickness of 0.5 mm . The required amounts of nickel powder and carbon-supported palladium powder were mixed with Nafion® solution and iso-propyl alcohol, and the mixture was ultrasonicated to form slurry. The slurry was then applied to a piece of nickel foam, and catalyst-coated foam was

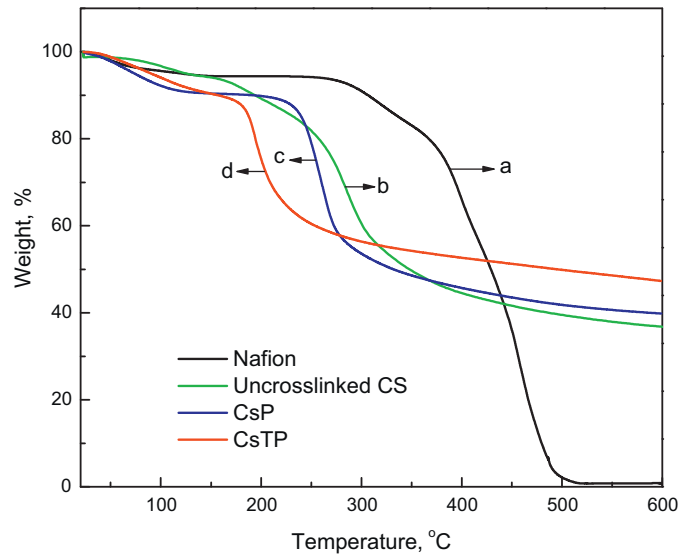


Fig. 5. TGA thermograms of (a) Nafion®, (b) pristine chitosan, (c) CsP, and (d) CsTP membranes.

dried in an air oven at $80 \text{ }^\circ\text{C}$. The loading of Nafion® ionomer electrode binder was 12.5% of the dry catalyst material.

2.4.2. Preparation of chitosan chemical hydrogel binder-based electrode

0.25% chitosan solution was prepared by adding chitosan powder in 2% aqueous solution of glacial acetic acid in a glass beaker and stirring the contents magnetically at ambient temperature. The required amounts of nickel powder and carbon-supported palladium powder were mixed with chitosan solution and DI water

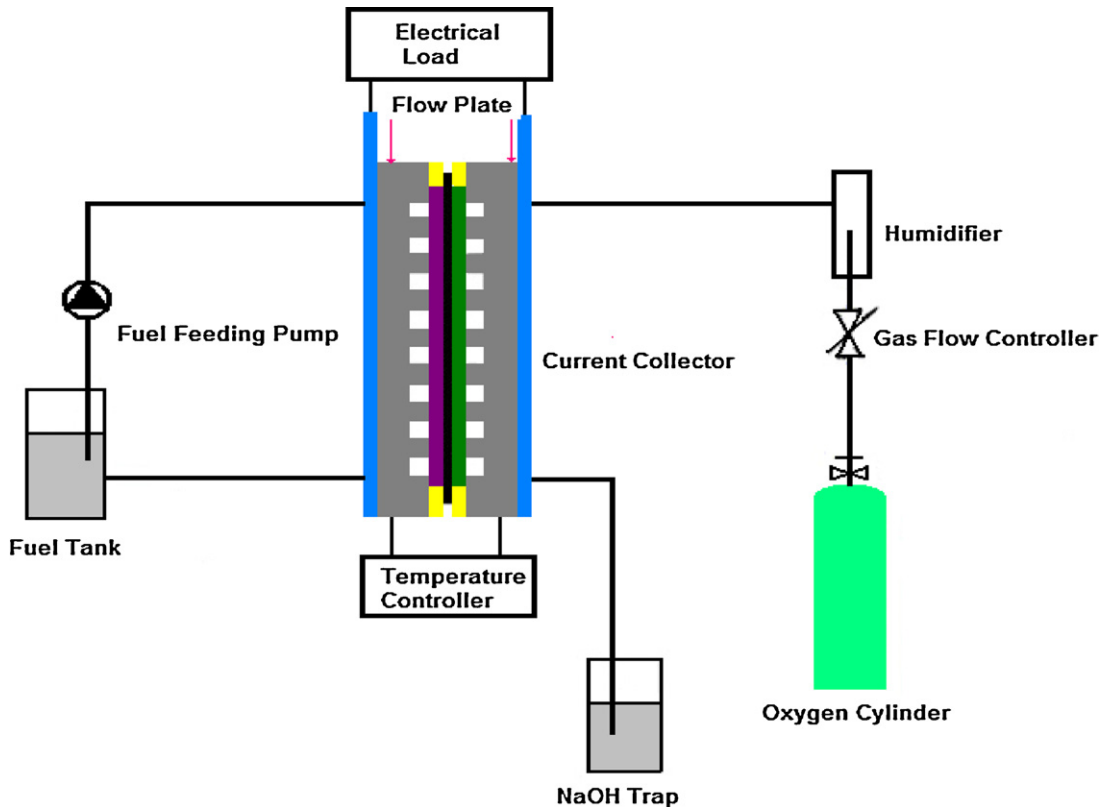


Fig. 4. A schematic diagram of a DBFC test system.

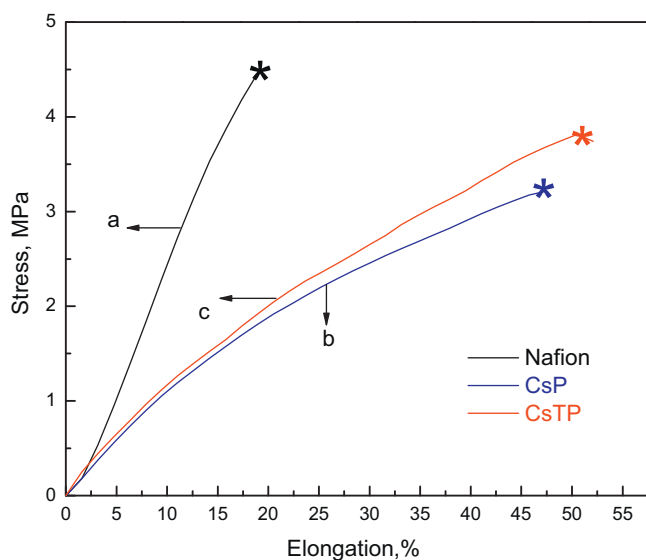


Fig. 6. Stress–strain curves of (a) Nafion®, (b) CsP, and (c) CsTP membranes.

Table 1

Water uptake values of Nafion®, CsP, and CsTP membranes.

Membrane	Water uptake (%)	
	25 °C (step I)	100 °C (steps I and II)
Nafion®	34	36
CsP	150	199
CsTP	102	144

to form a suspension which was agitated in an ultrasonic water bath. The ink was then pasted on a piece of nickel foam 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% 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 chemicals and any impurities.

2.5. Fuel cell test

Both Nafion® binder-based electrode and chitosan binder-based electrode were employed as anode for MEA in a DBFC. 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 commercial Pt electrode (1 mg cm⁻² Pt loading, 20 wt.% Pt/Vulcan XC-72). The active area of the fuel cell was 5 cm². For the electrochemical characterization of DBFCs, MEAs were prepared by sandwiching the cross-linked chitosan membrane or pretreated Nafion® membrane between anode and cathode by mechanical force. The single fuel cell hardware employed in this study was procured from Fuel Cell Technologies, Inc. The fuel consisted of an aqueous solution of 5% NaBH₄ in 10% NaOH. The flow rate of fuel solution was 5 mL min⁻¹. Dry oxygen

Table 2

Ionic conductivity and borohydride crossover values of cross-linked chitosan membranes.

Membrane	Ionic conductivity measured after dipping in NaOH solution (S cm ⁻¹)	Borohydride crossover rate (mol s ⁻¹ cm ⁻²)
CsP	0.089	4.57 × 10 ⁻⁸
CsTP	0.114	1.32 × 10 ⁻⁸

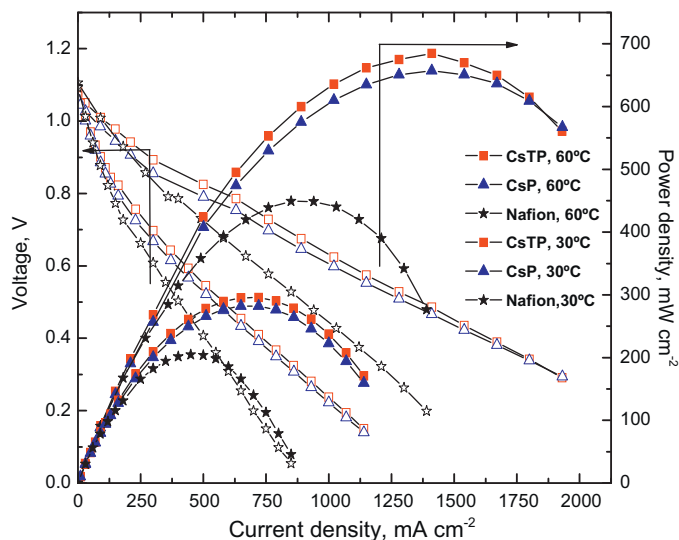


Fig. 7. Plots of cell polarization and power density vs. current density for DBFCs using Nafion®, CsP, and CsTP membranes at 30 and 60 °C.

was supplied from a high-pressure oxygen cylinder and its pressure was reduced by a pressure regulator to 3 psi. The flow rate of oxygen was controlled by a mass controller. The dry oxygen was humidified while it passed through a bubbler with a spiral heating tape at 25 °C. After passing through the bubbler, the wet oxygen reached the single cell and reacted in the cathode, and then was fed to ambient environment. Fig. 4 shows a schematic diagram of the DBFC test system. The flow rate of oxygen at the cathode chamber was 0.15 L min⁻¹. The electrochemical data was recorded with a fuel cell test system (Scribner Associates, Inc.). The performance stability of the fuel cell was evaluated by monitoring cell voltage as a function of time at a constant load current density. Coulombic efficiency was analyzed under a constant current discharge with a start from the cell to be fueled with a certain amount of fuel solution at 30 °C. Different current densities (60, 120, and 180 mA cm⁻²) were applied to the fuel cell and the cell voltages were recorded. Coulombic efficiency, which indicates the ratio of the actual discharging capacity to the theoretical discharging capacity, is defined as:

$$\eta = \frac{\text{Discharging capacity}}{\text{Theoretical discharging capacity}} = \frac{it}{8NFV} \quad (3)$$

where i (A) is the discharging current, t (s) the time of the discharging process, N (M) is the concentration of the fuel solution, V (L) is volume of the fuel solution, F (96,485 C mol⁻¹) is Faraday constant.

3. Results and discussion

3.1. Thermal analysis

The weight loss (%) against temperature curves for Nafion®, pristine chitosan, CsP, and CsTP membranes in the presence of nitrogen are given in Fig. 5. Pristine chitosan membrane shows a gradual weight loss starting from 25 °C and a major weight loss occurs from 213 to 416 °C. The maximum decomposition rate occurs at 280 °C with a weight loss of 32%. CsP membrane has two major different stages of weight loss. The first stage ranges between 25 and 126 °C, during which there is a 10% weight loss corresponding to the loss of adsorbed and bound water. A 38% weight loss has been observed for CsP membrane from 220 to 330 °C due to chitosan decomposition. Similar to CsP, TGA of CsTP membrane mainly shows two stages of weight loss. The first stage has a 10% weight loss in the temperature range between 25 and 144 °C, during which CsTP membrane

Table 3

A list of membrane–electrode-assembly materials employed in literature and related DBFC performance.

Anode	Cathode	Membrane	DBFC performance	Ref.
Ni+Pd/C (Ni:Pd mass ratio 25:1) and 15% Nafion® loaded on Toray carbon paper, 1 mg metal cm ⁻²	Pt/C loaded on PTFE treated carbon paper, 1 mg metal cm ⁻²	Polyvinyl alcohol hydrogel membrane	Peak power density of 242 mW cm ⁻² at 60 °C	[7]
Pt–Ru black and 30% PTFE loaded on Ni foam, 1 mg metal cm ⁻²	15% of PTFE and mixed powders consisting of MnO ₂ catalyst + BP2000 carbon black loaded on Ni foam	Poly (vinyl alcohol)/hydroxyapatite (Ca ₁₀ (PO ₄) ₆ (OH) ₂) composite membrane	Peak power density of 45 mW cm ⁻² at ambient condition	[26]
Pt–Ru/C and 10% Nafion® loaded on gas diffusion electrode, 1 mg metal cm ⁻²	Pt/C and 10% Nafion® loaded on gas diffusion electrode, 1 mg metal cm ⁻²	ADP–morgane anion exchange membrane	Peak power density of 200 mW cm ⁻² at 60 °C	[27]
Au/C and 10% Nafion® loaded on gas diffusion electrode, with 1 mg cm ⁻² Nafion® solution spread on surface of electrode, 2 mg metal cm ⁻²	Pt/C and 10% Nafion® loaded on gas diffusion electrode with 1 mg cm ⁻² Nafion® solution spread on surface of electrode, 2 mg metal cm ⁻²	ETFE-g-PSSA polymer membrane	Peak power density of 112 mW cm ⁻² at 85 °C	[6]

gradually loses water. After 144 °C, CsTP membrane continues to lose weight up to 320 °C. In this range there is a 45% weight loss due to the degradation of chitosan polymer. Compared with pristine chitosan membrane, both CsP and CsTP membranes have lower degradation temperatures, which indicate a lower thermal stability. The decrease in thermal stability of cross-linked chitosan membranes is associated with reduced hydrogen bonding. Generally speaking, hydrogen bonds between polymer chains contribute to raising the degradation temperature. Cross-linking results in a loss of hydrogen bonding, and hence a lower degradation temperature for cross-linked membranes as compared to uncross-linked membranes [14]. The TGA results have also demonstrated that CsTP membrane has less thermal stability than CsP membrane. This is possibly because CsTP has a higher degree of cross-linking and thus a larger extent of hydrogen bonding loss. The larger cross-linking density associated with CsTP membrane might be because triphosphate salt (P₃O₁₀⁵⁻) with more negative charges has a higher ability to ionically cross-link with chitosan than phosphate salt (PO₄³⁻) with a lower charge number.

Studies on the thermal behavior of Nafion® membrane have shown that this membrane is thermally stable up to 260 °C. Below this temperature, there is a gradual weight loss of 4% which is mainly attributable to water evaporation. A decomposition stage with a weight loss of 12% has been observed at range between 260 and 352 °C, and is associated with the desulfonation process (i.e. the loss of –SO₃H groups) [15]. At temperatures above 352 °C, Nafion® membrane continues to decompose until about 99.9% was lost at 520 °C. This weight loss is attributed to the decomposition of the perfluoropolyalkylether side chains and the polytetrafluoroethylene chains on its backbone [16]. TGA analysis shows that Nafion® membrane has better thermal properties than chitosan membrane, primarily because its main chain decomposes at 352 °C and its initial decomposition occurs at 260 °C, which is a higher decomposition temperature than that of chitosan membranes. However, DBFCs are operated in temperatures below 100 °C, and thus both cross-linked chitosan membranes are stable at desired operating temperatures of DBFCs.

3.2. Water uptake

Table 1 shows the results of water uptake for Nafion®, CsP, and CsTP membranes. The membrane water uptake has been determined at two different temperatures. When drying at room temperature for 24 h, the water uptake values of CsP and CsTP membranes are 150% and 102%, respectively, remarkably higher than that of Nafion® membrane (34%). Weight losses of 36%, 199% and 144% have been observed for Nafion®, CsP, and CsTP membranes, respectively, after the membranes were further dried at 100 °C for 3 h. Nafion® membrane demonstrates about the same

weight loss after drying at two different temperatures. In the case of cross-linked chitosan membranes, an approximately 40% increase in water uptake values has been found after the membranes were dried at an elevated temperature. From the above discussion, it can be surmised that chitosan membranes possess higher hydrophilic characteristics as compared to Nafion® membrane. The high water uptake capacity of chitosan is due to its distinct hydrophilicity. Chitosan contains three different polar functional groups, namely, hydroxyl (–OH), primary amine (–NH₂), and ether (C–O–C) groups, and due to the presence of these functional groups, chitosan is highly capable of forming hydrogen bond with water and trapping water in its ring structures [17]. Nafion®, however, contains polar hydrophobic C–F bonds in its backbone, polar C–O–C linkages, and highly dissociable as well as hydrophilic sulfonic acid (–SO₃H) group in its structure. Because of the presence of its contrasting properties, Nafion® possesses both hydrophilic and hydrophobic zones separated by an intermediate region [18]. Since the water-attracting behavior of Nafion® is restricted to its hydrophilic region only, its water retaining capability is not as high as that of chitosan. Water uptake results show that CsTP membrane has a lower water uptake capacity than CsP membrane. This might be explained by the difference in cross-linking density of these two membranes. As membranes are cross-linked, the membranes would be more rigid and structurally compact, and thus free volume available for water molecules would be decreased. Besides, the number of available water absorption sites might be reduced as a result of cross-linking between amino groups of chitosan chain and phosphate or triphosphate salt. As indicated by TGA results, CsTP membrane might have a higher cross-linking density and thus it can be expected that CsTP membrane would have less free volume and absorption sites for water as compared to CsP membrane.

3.3. Mechanical properties

Since membranes for a DBFC are operated in aqueous environment, mechanical properties of membranes were tested in a water tank. Stress–strain curves of Nafion®, CsP, and CsTP membranes are shown in Fig. 6. Nafion® membrane demonstrates higher tensile strength at break (4.5 MPa), and lower elongation at break (18.7%) than CsP or CsTP chitosan membranes. Tensile strength and elongation at break of CsP membrane are 3.2 MPa and 46.7% respectively. In the case of CsTP membrane, tensile strength and elongation at break are 3.8 MPa and 50.7% respectively. From the results, it can be observed that CsTP membrane exhibits higher strength and larger elongation at break than CsP membrane. When a certain degree of cross-linking is achieved, enough bridges and even a cross-linked network may be set up between the chitosan molecules, and as a result the tensile strength of the chitosan membrane is enhanced

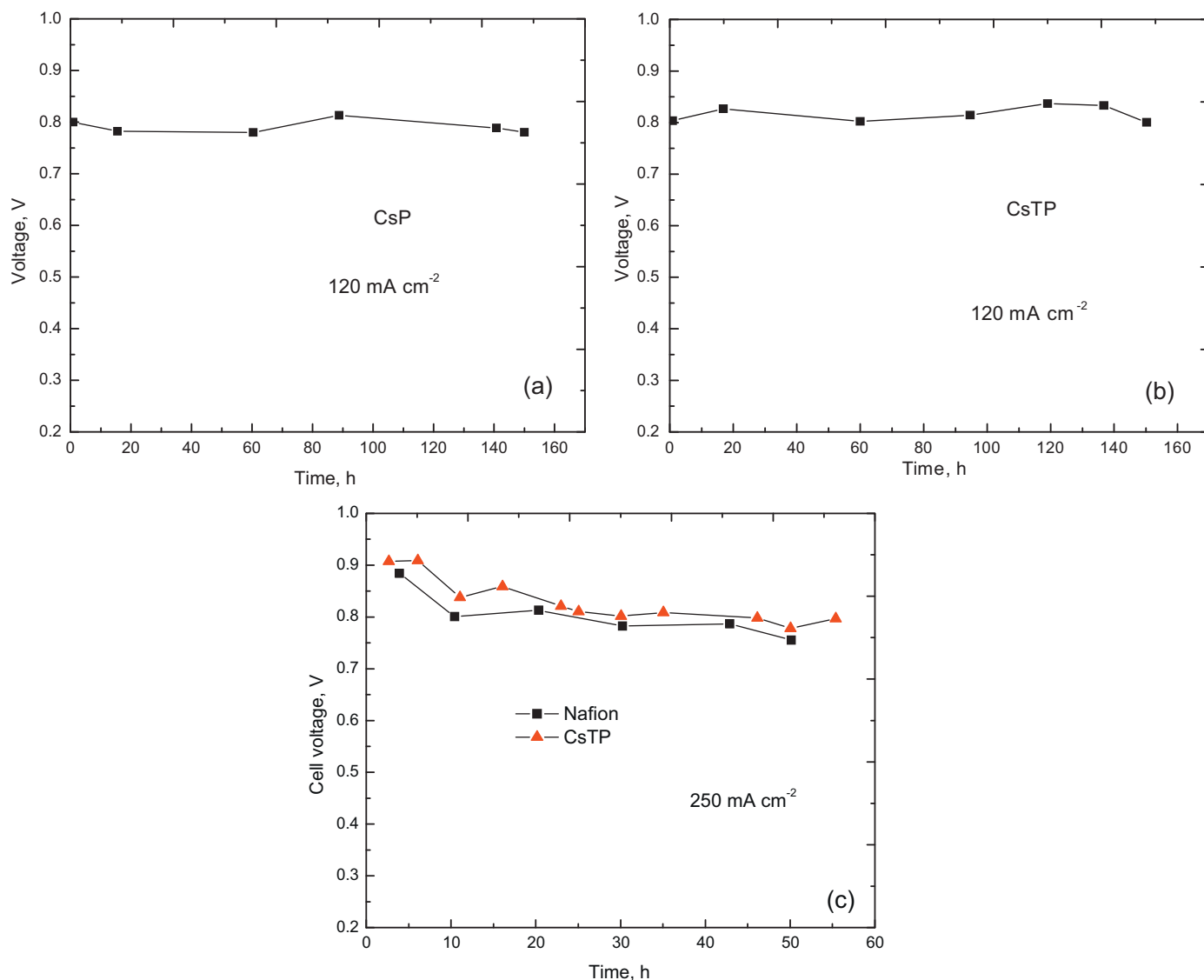


Fig. 8. (a) Performance stability of a DBFC using CsP membrane at 30 °C, (b) performance stability of a DBFC using CsTP membrane at 30 °C, and (c) comparative performance stability of chitosan-based DBFC and Nafion[®]-based DBFC at 60 °C.

[19]. Thus, the higher mechanical strength of CsTP membrane is possible because CsTP membrane has a higher cross-linking density than CsP membrane, which is also indicated by TGA and water uptake studies. Besides, water uptake studies have shown that CsP has a higher degree of water content than CsTP membrane. Excessive high levels of water uptake can result in the dimensional change of the membranes, which leads to loss of mechanical properties [19].

3.4. Ionic conductivity

As shown in Table 2, the conductivities of CsP and CsTP membranes after being equilibrated in alkaline medium are 0.089 and 0.114 S cm⁻¹, respectively. These values are higher than the ionic conductivity of Nafion[®] membrane (7×10^{-3} S cm⁻¹) [20]. The higher ionic conductivity of chitosan membranes than Nafion[®] membranes in alkaline medium may be attributed to higher water uptake capacity of chitosan. As shown in water uptake studies, chitosan membranes have significantly higher water holding capacity than Nafion[®] membrane. Greater water uptake ability of chitosan

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 ions in the polymer complexes [21].

Considering the water uptake property, it is interesting to note that CsTP membrane with a lower water uptake value exhibits a higher ionic conductivity than CsP membrane. This is possibly because increased amount of water uptake dilutes ion concentration and extends the distance of ion migration due to membrane swelling [22]. The higher ionic conductivity associated with CsTP membrane might be also due to its larger number of anionic sites for sodium ion conduction, which is the result of its higher degree of cross-linking and larger number of negative charges of triphosphate than phosphate.

3.5. Borohydride crossover

Borohydride crossover rates through CsP and CsTP membranes are calculated to be 4.57×10^{-8} and 1.32×10^{-8} mol s⁻¹ cm⁻², respectively. CsTP membrane demonstrates lower BH₄⁻ crossover

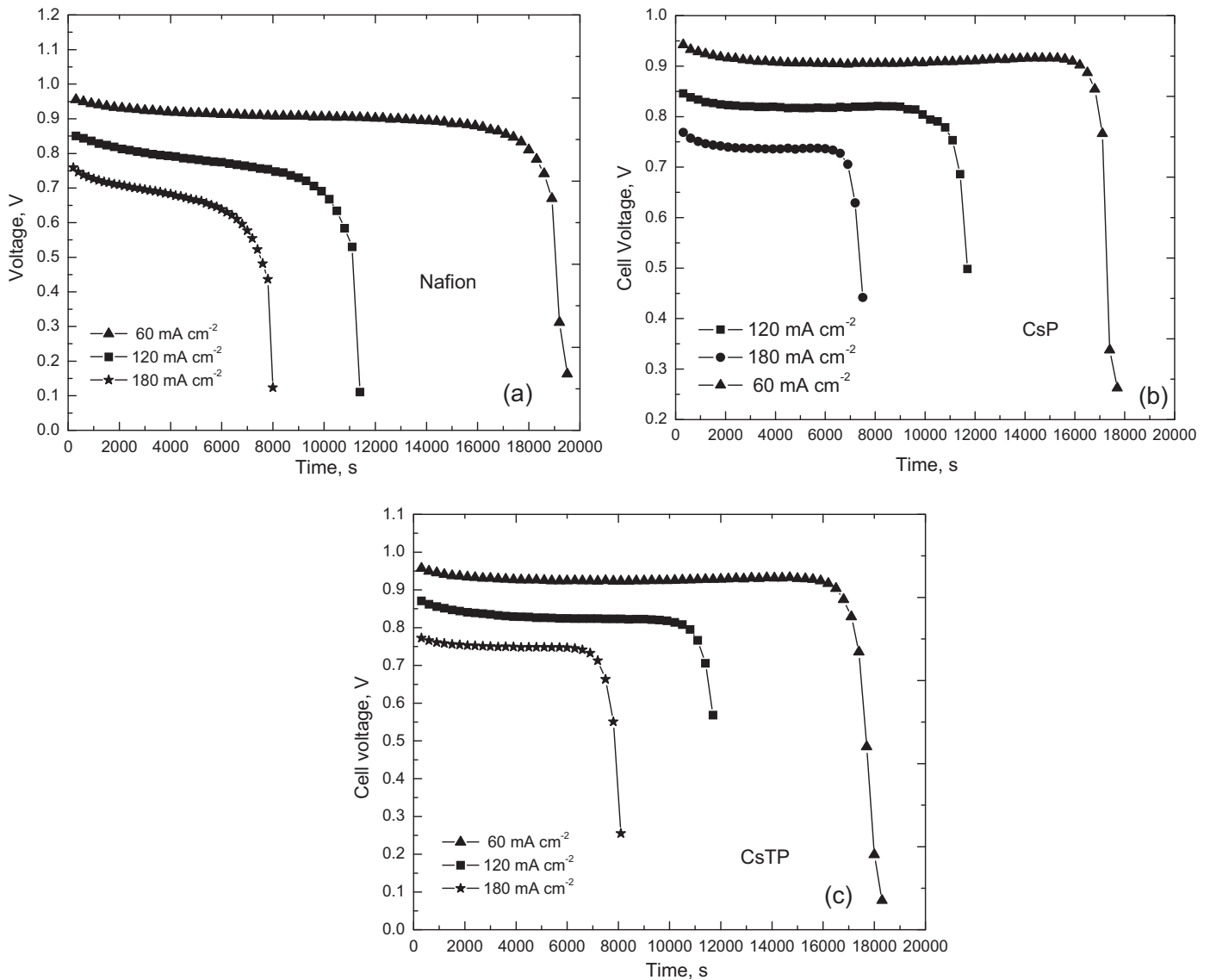


Fig. 9. Fuel efficiency of a DBFC using (a) Nafion[®] membrane and Nafion[®] binder, (b) CsP membrane and chitosan hydrogel binder, and (c) CsTP membrane and chitosan hydrogel binder at 30 °C.

rate than CsP membrane. This is possibly because, compared with CsP membrane, CsTP membrane has a larger number of anionic sites of negatively charged oxygen moieties, due to its higher degree of cross-linking and large number of negative charges of triphosphate salt, and these anionic sites repel BH_4^- of the same charge.

The borohydride crossover rate of Nafion[®] membrane is in the order of magnitude of $10^{-9} \text{ mol s}^{-1} \text{ cm}^{-2}$ [20], which is much lower than the values of the cross-linked chitosan membranes in this study. This is because Nafion[®] membrane is a cation exchange membrane with negatively charged $-\text{SO}_3^-$ groups attached to the polymer backbone. Being a negatively charged ion, BH_4^- experiences a repulsive force while crossing over through the Nafion[®] membrane. Therefore, Nafion[®] membrane is more effective in the suppression of BH_4^- crossover as compared to cross-linked chitosan membrane.

3.6. Performance of DBFCs

3.6.1. Power performance

A DBFC has been assembled with Nafion[®] membrane and Nafion[®] ionomer as anode binder and its electrochemical

performance has been recorded. A similar DBFC has also been assembled with cross-linked chitosan membranes. For a chitosan membrane-based DBFC, chitosan chemical hydrogel binder has been used as anode catalyst binder. Hydrogel is a network of polymer that absorbs and retains a significant amount of water in its polymeric matrix. Chitosan chemical hydrogels are formed by covalent cross-linking reaction between chitosan polymer and glutaraldehyde by Schiff base mechanism. Due to the presence of chemical cross-links and physical entanglements, chitosan chemical hydrogels have insolubility in aqueous medium and ability to bind catalyst particles.

The performance data for DBFCs are shown in Fig. 7. The peak power densities of Nafion[®]-based DBFC are 204 and 448 mW cm^{-2} at 30 and 60 °C, respectively. DBFC employing CsP membrane achieves peak power densities of 282 and 657 mW cm^{-2} at 30 and 60 °C, respectively. DBFC employing CsTP membrane achieves peak power densities of 295 and 685 mW cm^{-2} at 30 and 60 °C, respectively. As the cell temperature is enhanced from 30 to 60 °C, power performance is also increased due to improved electrode kinetics and ionic conductivity of the membrane electrolyte [23]. Significantly higher power performance is achieved

by chitosan-based DBFC as compared with Nafion[®]-based one as shown in Fig. 7. This can be attributed to the higher ionic conductivity of chitosan membrane in alkaline medium than Nafion[®] membrane as demonstrated by the EIS study. Besides, chitosan-based DBFC employs chitosan chemical hydrogel as anode binder which has a larger water retention capacity and thus is more effective in attaining high mobility of ions, fuel within the hydrogel-bonded electrode matrix. CsTP membrane gives slightly superior power performance than CsP membrane, and this result is consistent with that of EIS study which shows that the ionic conductivity of CsTP membrane is higher than that of CsP membrane in alkaline medium. Table 3 shows some alternative membrane materials to Nafion[®] employed in literature and related DBFC performance. Comparing with the data shown in the table, it can be concluded that with cost-effective Ni-based composite anode and chitosan membrane and binder, a high power performance can be achieved.

3.6.2. Stability

Fuel cell stability is another important aspect that should be examined. Performance stability of a borohydride-oxygen fuel cell using CsP or CsTP membrane and chitosan chemical hydrogel anode binder has been tested by monitoring the cell voltage change during the galvanostatic discharge of 120 mA cm⁻² in a period of more than 100 h at 30 °C. As shown in Fig. 8(a) and (b), the DBFC exhibits a stable performance over the test period. The operating cell voltage is fairly constant at 0.8 V with slight fluctuations over the test period. In order to evaluate the stability of cross-linked chitosan membrane at an elevated temperature, stability of a DBFC using CsTP membrane has been recorded at 60 °C and compared with a Nafion[®]-based DBFC under the same condition. As shown in Fig. 8(c), chitosan-based DBFC shows comparable stability as Nafion[®]-based one. Thus chitosan-based DBFC demonstrates not only high power performance but also reasonable stability at both low and elevated temperatures.

3.6.3. Coulombic efficiency

To investigate the fuel utilization, coulombic efficiencies of the chitosan-based and Nafion[®]-based DBFCs have been analyzed under a constant current discharge. As shown in Fig. 9, the cell voltage under these currents stays almost stable, with slow drop caused by the gradual decrease of NaBH₄ concentration. The final rapid drop of cell voltage is due to the exhaustion of NaBH₄. Based on the chronopotentiometric curves, coulombic efficiencies for DBFCs employing Nafion[®], CsP, and CsTP membrane are estimated to be in the range of 31–42%, 31–38%, 31–41%, respectively. Borohydride undergoes hydrolysis both chemically and electrochemically on various electrode materials of DBFCs. This leads to the evolution of hydrogen at the anode, which limits the coulombic efficiency. The actual number of electron transferred of the anodic reaction depends on the anodic materials, and current. The anode catalyst employed in this study is Ni and Pd/C composite. It has been found that the borohydride electro-oxidation on Ni is generally a four-electron process even with changing currents and borohydride concentrations, while in the case of Pd and Pt, the coulombic number is higher than four electrons at high anode currents and low borohydride concentrations [24]. At certain anode current and borohydride concentration (less than 1 M), the coulombic number of Pd anode is between six and eight electrons, and a quasi-eight-electron reaction occurs at Pt anode. The coulombic efficiency loss is also attributed to borohydride crossover from the anodic side to the cathodic one through membrane, and remaining borohydride in the anode chamber which cannot be used due to mass transfer limitations. It can also be seen from Fig. 9 that the voltage of chitosan-based DBFC is more stable than that with Nafion[®] materials. This is possible because the use of chitosan hydrogel binder

facilitates mass transport of fuel from the anode diffusion layer to anode catalyst layer [25].

4. Conclusions

Chitosan membranes were prepared and modified by sodium tribasic phosphate and sodium triphosphate. Chitosan membranes were characterized in terms of thermal properties, mechanical properties, water uptake, ionic conductivity, and borohydride crossover rate, and these characteristics were compared with commercial Nafion[®] 212 membrane. Thermal stability analysis revealed that chitosan membranes could withstand temperature higher than 200 °C in nitrogen atmosphere, which ensures their thermal stability in the operational temperature of DBFCs. Tensile test showed that multivalent phosphate modified chitosan membranes had higher elongation and lower tensile strength at break in aqueous medium than Nafion[®] membrane. These chitosan membranes also demonstrated higher water uptake, higher ionic conductivity in alkaline medium and higher borohydride crossover rate than Nafion[®] membrane. Characterization results indicated that triphosphate chitosan membrane might have higher cross-linking density than tribasic phosphate chitosan membrane.

Chitosan membranes were employed as the polymer electrolyte in a direct borohydride fuel cell. This DBFC employed nickel-based composite as anode catalyst and chitosan chemical hydrogel as anode binder. The power performance, stability, and coulombic efficiency of the chitosan-based DBFC were examined and compared with a similar DBFC employing Nafion[®] membrane and Nafion[®] anode binder. The chitosan-based DBFC exhibited significantly higher power performance, and comparable stability and coulombic efficiency as compared to Nafion[®]-based DBFC. 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 a DBFC would significantly reduce its cost and may help in its commercialization.

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