



Chitosan chemical hydrogel electrode binder for direct borohydride fuel cells

Nurul A. Choudhury, Yogeshwar Sahai*, Rudolph G. Buchheit

Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210, USA

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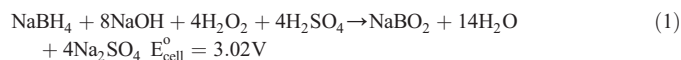
ABSTRACT

A novel and cost-effective electrode binder consisting of chitosan chemical hydrogel (CCH) is reported for direct borohydride fuel cells (DBFCs). The DBFCs have been assembled with Misch-metal-based AB₅ alloy as anode, carbon-supported palladium (Pd/C) as cathode and polyvinyl alcohol (PVA) hydrogel membrane electrolyte (PHME) as well as Nafion[®]-117 membrane electrolyte (NME) as separators. Operating in passive mode without using peristaltic pump and under ambient conditions of temperature as well as pressure, the DBFC exhibited a maximum peak power density of about 81 mW cm⁻².

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1. Introduction

A fuel cell that utilizes a borohydride compound, usually sodium borohydride (NaBH₄) in aqueous alkaline medium, directly as a fuel is termed as direct borohydride fuel cell. DBFCs have the advantages of exhibiting high open circuit potential, power density, and current density values at ambient temperature. The oxidation product metaborate (BO₂⁻) can be recycled to produce BH₄⁻ [1]. Although the concept of DBFC was first demonstrated by Indig and Snyder [2], Amendola et al. [3] were the first to report an air-breathing DBFC that employed an anion exchange membrane (AEM) as electrolyte. The DBFC [3] would suffer from borohydride crossover as BH₄⁻ can easily pass through AEM. To mitigate borohydride-crossover in DBFCs, Li et al. [4] employed Nafion[®] membrane as electrolyte. In DBFCs [3,4], it would be mandatory to scrub CO₂ from air to avoid carbonate fouling and to prevent alkali deposition in cathode pores to facilitate oxidant flux. To prevent carbonate fouling and alkali deposition at the cathode, Choudhury et al. [5] reported a DBFC using hydrogen peroxide (H₂O₂) as oxidant. Being a liquid oxidant, H₂O₂ yield higher energy density in DBFCs as compared to gaseous oxygen. It may be noted that H₂O₂ is a suitable oxidant in DBFCs in contrast to direct methanol fuel cells (DMFCs) [6]. Raman et al. [7] reported a DBFC that employs acidified H₂O₂ as oxidant and delivers high electrochemical performance. The net cell reaction of such a DBFC is expressed as Eq. (1).



Perfluorosulfonic acid (Nafion[®]) and poly (tetrafluoroethylene) (PTFE) are widely employed as electrode binders in fuel cells. Krishnan et al. [8] reported polymer electrolyte fuel cells (PEFCs) that use sulfonated poly (ether sulfone)-based catalyst binder in conjunction with membrane made of same polymers. Lee et al. [9] reported a hydrocarbon binder in sulfonated polyimide triethyl ammonium salt-form for DMFCs. Wilson [10] reported PVA as electrode binder for fuel cells. Since PVA is soluble in water, it is expected to dissolve gradually in aqueous solutions of fuel and/or oxidant, thereby adversely affecting fuel cell performance.

Hydrogels are 3-dimensional solid polymeric networks that absorb and retain in their polymeric matrices many times of water than their actual dry weight. Chemical hydrogels are formed by chemical reaction between a polymer and a cross-linking reagent [11]. Polymer hydrogels have been used as solid electrolytes in electrochemical devices [12–14]. PVA and gelatin chemical hydrogels have been reported as solid electrolytes in supercapacitors [13,15]. Choudhury et al. reviewed various polymer hydrogel electrolytes for application in supercapacitors [16].

Chitosan (CS) is a weakly alkaline natural polymer that is soluble in dilute aqueous acetic acid (CH₃COOH), which converts glucosamine unit (R-NH₂) of CS into its protonated form (R-NH₃⁺). 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 [17]. The cross-linking reaction between CS and glutaraldehyde takes place by Schiff base mechanism [18]. Rohindra et al. [19] reported that equilibrium swelling ratio (E_{sr}) of CCH, which is inversely related to its mechanical strength, decreased with increase in the extent of chemical cross-linking and pH of the aqueous media but increased with increase in both time and temperature. A polymer electrolyte membrane (PEM) comprising CS as matrix and KOH as dopant showed ionic conductivity in order of

* Corresponding author. Tel.: +1 6142921968; fax: +1 6142921537.
E-mail address: sahai.1@osu.edu (Y. Sahai).

$10^{-2} \text{ S cm}^{-1}$. A PEFC using the CS-KOH as PEM, platinum as electro-catalysts, hydrogen as fuel and air as oxidant delivered a current density of 30 mA cm^{-2} [20]. A polyelectrolyte complex membrane prepared by ionic cross-linking between CS and poly (acrylic acid) exhibited proton conductivity of $3.8 \times 10^{-2} \text{ S cm}^{-1}$ and methanol permeability of $3.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ in DMFC [21]. There are a few more reports in literature on the use of CS as PEM for PEFCs and DMFCs. However, to the best of authors' knowledge, CCH has not been employed as electrode binder in fuel cells. In this paper, we report our studies on the use of CCH as electrode binder in DBFCs. It may be noted that CCH binder can also be used in other electrochemical energy devices [22].

2. Experimental details

2.1. Preparation of CCH binder-based electrodes

To prepare anode catalyst ink, required amount of an AB_5 alloy ($\text{La}_{10.5}\text{Ce}_{4.3}\text{Pr}_{0.5}\text{Nd}_{1.4}\text{Ni}_{60.0}\text{Co}_{12.7}\text{Mn}_{5.9}\text{Al}_{4.7}$) powder (Ovonic Battery Company) was mixed with 10 wt.% Vulcan XC 72 carbon powder and adequate quantity of water in a glass vial. The vial containing the aforesaid suspension was agitated in an ultrasonic water bath (Bransonic[®] ultrasonic cleaner) for 2 h. Subsequently, required volume of a 2% (w/v) solution of CS dissolved in 1% (v/v) aqueous CH_3COOH solution was added drop-wise to the aforesaid suspension with ultrasonic agitation continued for another 2 h. The ink for cathode catalyst, 10 wt.% Pd/C (Aldrich), was prepared in a similar way. The loadings of AB_5 in anode, palladium in cathode and CCH binder in both anode as well as cathode were 30 mg cm^{-2} , 1 mg cm^{-2} , 0.5 wt.%, and 2 wt.%, respectively. The anode or cathode ink was pasted on a carbon cloth (Zorflex[®] Activated Carbon Cloth, FM 10, Chemvicon Carbon) substrate with a paint brush and the catalyst ink-coated carbon cloth was dried inside a forced air-convection oven at room temperature. Finally, each of the dried catalyst-coated carbon cloth was separately 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 carbon cloth was washed with de-ionized water.

2.2. Electrochemical characterization of CCH binder-based DBFCs

For electrochemical characterization of DBFCs, membrane electrode assemblies (MEAs) were prepared by sandwiching PHME or NME between anode and cathode. PHME was prepared by a solution casting technique [23]. Prior to its use in a DBFC, NME was cleaned by a pre-treatment [24]. MEAs comprising CCH binder-based electrodes and PHME as well as NME were employed to assemble various liquid-

feed DBFCs. The anode and cathode of each of the MEAs were contacted on their rear with graphite storage tanks for fuel and oxidant, respectively. The DBFC assembly employed in this study was similar to that used by Raman et al. [25]. The fuel comprised an aqueous solution of 1.7 M NaBH_4 in 7.0 M NaOH and the oxidant comprised an aqueous solution of 2.5 M H_2O_2 in 1.5 M H_2SO_4 . All DBFC results reported in this communication were recorded in passive mode employing a Keithley sourcemeter at ambient conditions of temperature and pressure.

3. Results and discussion

Chitosan, dissolved in aqueous CH_3COOH solution, undergoes a chemical cross-linking reaction with aqueous glutaraldehyde at ambient temperature and pressure. Due to the reaction, 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 a solid entity is termed as chitosan chemical hydrogel. During solidification of aqueous solutions of chitosan and glutaraldehyde in the presence of electrode materials, the electrode materials get bonded to the electrode substrate. Water absorbed in the CS hydrogel matrix during electrode fabrication helps in establishing and maintaining three-point contact among reactant (fuel/oxidant), electro-catalyst and PEM. CCH is insoluble in water and does not disintegrate on heating. These characteristics of CCH make it a suitable electrode binder for DBFCs. The CCH in an inverted glass beaker is shown in Fig. 1, where a Teflon-coated magnetic stirring bar that was used to mix solutions of CS and glutaraldehyde is seen stuck within the hydrogel at the bottom of the beaker. This figure clearly shows the solid nature of CCH. Fig. 1 also makes it easier to understand how the electrode materials are held within the hydrogel and bound to the carbon cloth substrate in the actual electrode while allowing transport of any water-soluble species such as ion, fuel or oxidant to the catalyst. It is evident from Fig. 1 that CCH is transparent and brown in color.

The electrochemical performance data for DBFCs employing CCH as electrode binder and PHME as well as NME as electrolytes-cum-separators are shown in Fig. 2. As evident from Fig. 2, open circuit voltages (OCVs) of about 1.8 V are observed for both the DBFCs. Peak power densities of about 81 and 72 mW cm^{-2} have been observed at corresponding current density values of about 85 and 73 mA cm^{-2} for DBFCs employing PHME and NME, respectively. Total current densities achieved from DBFCs with PHME and NME are about 148 and 160 mA cm^{-2} , respectively. The higher power density of PHME-based DBFC as compared to NME-based DBFC can be explained in terms of thickness and density of the membrane electrolytes. Thicknesses of PHME and NME are about 100 and 178 μm ,

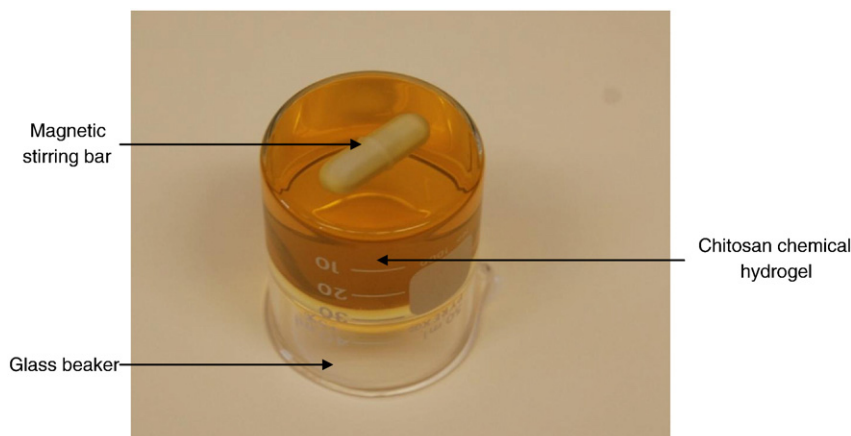


Fig. 1. Chitosan chemical hydrogel along with a Teflon-coated magnetic stirring bar in an inverted glass beaker.

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