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Bipolar polymer electrolyte interfaces for hydrogen–oxygen and direct borohydride fuel cells

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ABSTRACT

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Direct borohydride fuel cells (DBFCs) using liquid hydrogen peroxide as the oxidant are safe and attractive low temperature power sources for unmanned underwater vehicles (UUVs) as they have excellent energy and power density and do not feature compressed gases or a flammable fuel stream. One challenge to this system is the disparate pH environment between the anolyte fuel and catholyte oxidant streams. Herein, a bipolar interface membrane electrode assembly (BIMEA) is demonstrated for maintaining pH control of the anolyte and catholyte compartments of the fuel cell. The prepared DBFC with the BIMEA yielded a promising peak power density of 110 mW cm^{-2} . This study also investigated the same BIMEA for a hydrogen–oxygen fuel cell ($\text{H}_2\text{--O}_2$ FC). The type of gas diffusion layer used and the gas feed relative humidity were found to impact fuel cell performance. Finally, a BIMEA featuring a silver electrocatalyst at the cathode in a $\text{H}_2\text{--O}_2$ FC was successfully demonstrated.

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Introduction

Direct borohydride fuel cells (DBFCs) are an attractive type of polymer electrolyte fuel cell (PEFC) because: a) the oxidation half-cell potential of sodium borohydride (NaBH_4) is -1.24 V versus the standard hydrogen electrode (SHE), b) the NaBH_4 alkaline solution has a very high flash point, and c) this fuel has an energy density of 9.3 kWh kg^{-1} [1]. Because hydrogen storage remains a challenge (i.e., high pressure and/or extremely low temperatures are required to store enough hydrogen to power a device for a prolonged period of time),

fuel cell researchers have investigated liquid fuels that can be electrochemically oxidized at favorable potentials. Liquid fuels are advantageous because their transportation, storage and delivery to the fuel cell are relatively simple. Direct methanol fuel cells are the most popular PEFC using a liquid fuel, but there are several key problems hindering their commercialization including sluggish methanol electro-oxidation kinetics and the mixed potential and chemical short-circuit arising from methanol crossover from the anode to the cathode, all of which impact performance [2]. Some other type of liquid fuels investigated for use in PEFCs include ethanol, propylene glycol, and hydrazine. [3,4] Of the liquid

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fuels mentioned, NaBH_4 dissolved in alkaline solutions is the only fuel with a high flash point and high energy density. While most terrestrial consumer products can be engineered with safety controls that can handle lower flash point fuels, certain military applications, such as unmanned underwater vehicles (UUVs), will preferably require non-flammable fuels.

Several reviews detail the development of DBFCs [1,5]. In these reviews, most of the literature surveyed discusses DBFCs that use oxygen as the oxidant. However, the reviews only detail a few reports of DBFCs that use H_2O_2 as the oxidant. DBFC operation has mainly been demonstrated with a cation exchange membrane (CEM) or an anion exchange membrane (AEM) electrolyte configuration [6,7]. Each configuration offers unique advantages and disadvantages. A CEM configuration transfers sodium ions from the anode to the cathode to complete the circuit. But this configuration results in the precipitation of sodium hydroxide at the cathode. The alternative configuration using an AEM transfers hydroxide ions from the cathode to the anode, but the AEM is readily permeable to BH_4^- resulting in fuel crossover and mixed-potentials. Furthermore, the alkaline stability of AEMs is a serious problem still being addressed by many researchers [8–12].

Switching the oxidant from oxygen to H_2O_2 changes the species transported across the membranes in the DBFC [6]. Because optimal electrochemical reduction of H_2O_2 takes place in acidic environments, the oxidant stream mainly consists of hydrogen peroxide dissolved in either sulfuric acid [13] or hydrochloric acid [14,15]. The acidic catholyte and basic anolyte stream in a DBFC using H_2O_2 as the oxidant creates a disparate pH environment separated by the membrane. Using a CEM configuration will result in the unwanted transport of acid from the catholyte to the anolyte, resulting in a lower pH at the anolyte versus time and, subsequently, the hydrolysis of BH_4^- (which is unstable at low pH). Similarly, an AEM configuration is undesired because it can transfer hydroxide ions from the anolyte to the catholyte, raising the pH of the catholyte stream. This will reduce the half-cell potential of the cathode because H_2O_2 electrochemical reduction is more favorable at low pH [13]. The pH dependence of the half-cell potential of the H_2O_2 reduction reaction is given in equation (1) [5].

$$E_{\text{o},\text{H}_2\text{O}_2}(\text{V}) = 1.78 - 0.059 \cdot \text{pH} \quad (1)$$

A possible approach to mitigating the transport of undesired species across a monopolar electrolyte configuration for a DBFC using H_2O_2 as the oxidant may reside in the use of a bipolar membrane or a bipolar membrane-electrode interface configuration. Fig. S1a and b in the supplementary information (SI) illustrate a bipolar membrane and bipolar membrane-electrode interface for a DBFC using H_2O_2 as the oxidant, and list the reactions and electrode potentials. The bipolar membrane is composed of an AEM in direct contact with a CEM to create a bipolar (solid) junction at the interface of the two membranes. The AEM segment of the bipolar membrane interfaces with the anode, while the CEM segment interfaces with the cathode. In this configuration, the pH at the catholyte remains acidic, while the anolyte remains basic. Water is dissociated at the bipolar junction and the protons are transported across the CEM segment to the cathode to

facilitate electrochemical H_2O_2 reduction, while the hydroxide ions are transported across the AEM segment to the anode to facilitate BH_4^- oxidation. In the bipolar membrane setup, BH_4^- cannot migrate from the anolyte to the catholyte due to the Donnan exclusion effect provided by the CEM [16]. Another advantage of this setup is the regeneration of ions. With a monopolar configuration, 8 mol of hydroxide are consumed per mole of BH_4^- oxidized. Recirculating the fuel stream in a DBFC requires the addition of metal hydroxide salts to facilitate pH control. With the bipolar configuration, the splitting of water at the bipolar junction replenishes the ions consumed at the electrodes. One detrimental consequence of using a bipolar configuration is the minimum cell voltage drop of 0.83 V required to dissociate water at the bipolar junction [17]. However, this bipolar junction potential is an acceptable loss as the overall cell voltage with this configuration is still high (2.18 V) even after accounting for the bipolar junction potential.

Kohl and co-workers recently described the use of bipolar membranes in hydrogen–oxygen and DMFC fuel cell devices [17–23]. In their seminal papers, they showed that an AEM and CEM laminated together yielded modest hydrogen–oxygen fuel cell (H_2/O_2 FC) performance (e.g., a current density of only a few mA cm^{-2} could be drawn). They improved the performance of the bipolar membrane H_2/O_2 FC by moving away from a bipolar membrane (i.e., laminated membranes) to a bipolar membrane-electrode interface, and through better material selection [19,20,22]. Their work also established that forming water at the bipolar membrane electrode interface yielded better FC performance compared to splitting water at the bipolar junction [17]. This configuration also created a self-humidifying membrane, allowing for inlet gases with no moisture or small relative humidity to be used for fuel cell operation. Fig. S2c in the SI section illustrates the CEM–AEM bipolar membrane electrode interface configuration wherein water is formed at the bipolar junction. Splitting water at the bipolar junction yields poor fuel cell performance because the water dissociation kinetics are sluggish at the bipolar junction and the reaction operates under a high overpotential.

Another potentially attractive feature of the alkaline cathode-acidic anode bipolar interface design is the possibility of eliminating the use of platinum-group metal catalysts at the cathode. The oxygen reduction reaction (ORR) is more facile in alkaline environments than in acidic environments and several non-platinum group metal (PGM) catalysts are available for the ORR [24]. The hydrogen oxidation reaction (HOR), on the other hand, is extremely facile in acid media and requires only small amounts of platinum electrocatalyst as long as high purity hydrogen is fed to the cell. However, the HOR in alkaline environment is relatively sluggish even on platinum [25]. A bipolar membrane-electrode interface design can foster a disparate pH environment wherein the HOR takes place in acidic environments, while the ORR is conducted in alkaline environments. It is envisaged that a hydrogen–oxygen bipolar interface fuel cell could have a low platinum loading at the anode and a non-PGM metal at the cathode. This design, which eliminates most of the PGM in the fuel cell and possibly the humidifiers for the gas feeds, could drastically reduce the cost of PEFCs.

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