Influence of Water Transport Across Microscale Bipolar Interfaces on the Performance of Direct Borohydride Fuel Cells

Zhongyang Wang, Mrinmay Mandal, Shrihari Sankarasubramanian, Garrett Huang, Paul A. Kohl, and Vijay K. Ramani*

ABSTRACT: Direct borohydride fuel cells (DBFCs) can operate at double the voltage of proton exchange membrane fuel cells (PEMFCs) by employing an alkaline NaBH₄ fuel feed and an acidic H₂O₂ oxidant feed. The pH-gradient-enabled microscale bipolar interface (PMBI) facilitates the creation and maintenance of an alkaline environment at the anode and an acidic environment at the cathode for the borohydride oxidation and peroxide reduction reactions. However, given the need to dissociate water at the interface to ensure ionic conduction, PMBI can be efficient only when anion exchange ionomer (AEI) moieties enable fast water transport for autodissociation. Herein, a series of polynorbornene-based AEIs with a range of water uptake values are examined to unravel the optimum water uptake required to enable high performance DBFCs. The DBFC with PMBI configuration containing the optimal AEI composition delivers a current density of 302 mA cm⁻² at 1.5 V and a peak power density of 580 mW cm⁻² at 1 V. This AEI composition exhibits high hydroxide ionic conductivity of 90.7 mS cm⁻¹ at an in situ temperature of 70 °C with an IEC of 2.01 mequiv g⁻¹ and demonstrates impressive chemical stability by retaining 98.75% of its initial ionic conductivity after immersion into anolyte (3 M KOH and 1.5 M NaBH₄) at 70 °C for 36 h.

KEYWORDS: direct borohydride fuel cell, anion exchange ionomer, alkaline stability, bipolar interface, liquid fuel cell, water transport

INTRODUCTION

A key component of any future transition to a "hydrogen economy"¹ is the development of fuel cells utilizing H₂ or H₂-derived fuels such as NH₃, NaBH₄, N₂H₄, HCOOH, etc. Among these fuels, considerable attention has been drawn upon direct borohydride fuel cells (DBFCs) due to their high power density and operating voltages.² The (theoretical) energy density is calculated to be 9.3 kWh kg⁻¹ and specific capacity is calculated to be 5.67 kAh kg⁻¹ of sodium borohydride (NaBH₄), which is higher than those of most H₂-derived fuels³ even when the actual energy density is compromised upon accounting for supporting alkaline electrolyte (3 M KOH solution) required to stabilize NaBH₄. Typically, such fuel cells operate at a uniform pH environment across the cell given the difficulties associated with sustaining a disparate pH environment at the anode and the cathode. Thus, a majority of DBFCs reported in the literature utilize O₂ as the oxidant at the cathode in an alkaline environment (E° = 0.401 V vs SHE).⁴⁻¹³

Alternatively, H₂O₂ solution in an acidic supporting electrolyte (E° = 1.77 V vs SHE) can serve as a safe and energy dense oxidant for DBFCs. Such DBFCs operate with liquid fuels and face fewer issues with transportation and storage of their fuels than proton exchange membrane fuel cell (PEMFC) where compressed H₂ is used as the fuel.¹⁴ The thermodynamic cell voltage of a DBFC is 3.01 V when H₂O₂ is used as the oxidant, a significant enhancement over the 1.23 V cell voltage obtained with a traditional H₂/O₂ cell (see the Supporting Information). However, few reports exist of practical DBFCs with a cell voltage >1.5 V due to the difficulties in sustaining the disparate pH environments for the borohydride oxidation reaction (BOR) and hydrogen peroxide reduction reaction (HRR) in a given cell.¹⁵,¹⁶

Kohl and co-workers reported one of the first bipolar separator configurations by layering an anion exchange membrane (AEM) and cation exchange membrane (CEM), creating a bipolar junction for H₂/O₂ fuel cells and direct methanol fuel cells (DMFCs) operating with a pH differential between the anode and cathode.¹⁷ That H₂/O₂ fuel cell yielded few tens of mA/cm² in current density. The low current density was attributed to the fabrication procedure for the membrane electrode assembly and the thick Nafion separator (174 μm). They modified the bipolar configuration by using a highly conductive AEM binder besides the Nafion separator. This approach allowed them to reduce the resistance from the...
AEM and placed the bipolar junction closer to the electrode. This bipolar H₂/O₂ fuel cell yielded a peak power density of 62 mW/cm². These bipolar fuel cells exhibited inferior performance compared to conventional fuel cells, but provided a novel methodology for fabricating self-humidified fuel cells with water generated at the bipolar interface.¹⁷

Xiang and co-workers fabricated a composite bipolar membrane which consisted of CEM at the anode and AEM at the cathode.¹⁸ They hypothesized that water generation at the bipolar membrane junction would self-humidify the membrane during the operation of the H₂/O₂ fuel cell. This hypothesis was confirmed when a dry gas fed fuel cell exhibited a peak power density of 327 mW/cm² at 323 K, demonstrating a self-humidified, water-management-free, gas-fed fuel cell. This also provided direct evidence that water autoprotolysis occurred at the junction of their bipolar membrane. Developing this further, Ramani and co-workers fabricated a bipolar interface membrane electrode assembly using poly(phenylene oxide)-based AEM for a DBFC.¹⁴ Their device yielded a peak power density of 110 mW/cm², thereby demonstrating the device level viability of that concept.

The fundamental understanding of the operation of such interfaces and proof of the existence of sustained pH gradients across these bipolar junctions were provided by Ramani and co-workers. A pH-gradient-enabled microscale bipolar interface (PMBI) was demonstrated to enable a sharp pH gradient (0.82 pH units per nm) near catalytic sites.¹⁹ Employing this PMBI configuration in a DBFC yielded state-of-the-art performance and a record high cell voltage (1.95 V). A key requirement of this setup is that H₂O be transported to the bipolar interface. There H₂O would dissociate to protons and hydroxyl ions to enable ionic conduction inside the cell.²⁰ Sufficiently rapid water transport to the junction is required to prevent drying of the membrane and consequent rise in the ion transport resistance. Thus, anion exchange ionomers (AEIs) that can ensure rapid water transport to the PMBI are likely to result in substantial improvements of these bipolar DBFCs.

Given this background, the overarching objectives of the current work were two-fold. First, to examine the anticipated advantages of high AEI water uptake, PMBIs were experimentally prepared using polynorbornene-based AEIs (chosen for their previously demonstrated high water uptake properties).²¹,²² Fuel cell performance and stabilities of such DBFCs with PMBI configurations were tested. The resultant PMBI-based DBFC yielded a current density of 320 mA/cm² at 1.5 V and a peak power density of 580 mW/cm² at 1 V. The DBFC with PMBI configuration was able to be operated without decay for 3 h. Second, to understand the interplay between AEI water uptake, structural stability, and overall device performance, we correlated water uptake of these AEIs with peak power densities of DBFCs to reveal water transport requirement to enable high DBFC performance.

### EXPERIMENTAL METHODS

#### Materials.

The anion exchange ionomers employed as DBFC anode binders were synthesized following our previously reported procedure.²²,²³ A series of binders were synthesized and labeled as GT<sub>m</sub> (in refers to the combined mol % presence of quaternary ammonium block in the tetrablock copolymer) where, for example, GT<sub>100</sub> means the polymer with 100 mol % quaternary ammonium blocks, i.e., a homopolymer. Similarly, GT<sub>38</sub> is a polymer that contains 38 mol % quaternary ammonium blocks. These binders were characterized using a Bruker Avance 400 MHz instrument. The number-average molecular weight (M<sub>n</sub>) and dispersity (D) of binders were analyzed by Shimadzu gel permeation chromatography (GPC).
Characterization of GT Series Anion Exchange Materials. The procedures for measuring ion exchange capacity, water uptake, ion conductivity, and alkaline stability of GT-series materials are provided in the Supporting Information.

Preparation of PMBI and Direct Sodium Borohydride Fuel Cell Measurements. The procedures for fabricating GT-based PMBI and general procedures for fuel cell performance testing have been detailed by us in our previous reports and in the Supporting Information.

RESULTS AND DISCUSSION

Figure 1 depicts a DBFC incorporating a PMBI along with its associated reactions. The AEI covered catalyst surface rejects cations and provides an alkaline environment for the BOR. The Nafion 117 separator and cathode binder in turn reject anions and help maintain an acidic environment at the cathode which helps stabilize the \( \text{H}_2\text{O}_2 \) used as the oxidant. Given the lack of a common ion between electrodes, ionic conduction is maintained, and the circuit is completed, by the dissociation of water at the interface. The thermodynamic penalty for this dissociation is manifest as the junction potential. The protons move to the cathode while the hydroxide ions move to the anode. Despite the imperfect permeability (i.e., ratio of anion to cations moving through an ionomeric separator) of both the AEM and CEM, the continuous production and transport of \( \text{H}^+ \) and \( \text{OH}^- \) to the cathode and anode, respectively, helps maintain the optimal pH at both electrodes. This in turn allows for the long-term, stable operation of a DBFC with a PMBI.

The performance of a DBFC is determined by the kinetics of the electrode reaction and the ion transport across the PMBI. The choice of electrocatalyst is critical for BOR activity and efficiency in the evaluation of DBFC performance. A discussion of BOR and HRR catalysis is beyond the scope of this work and interested readers are referred to our previous reports. The focus herein is on the ion transport across the PMBI. The rate of ion transport is directly proportional to the ion-exchange capacity, and the availability of conductive ions. The water uptake by the AEI covered catalyst surface rejects the products. Thus, ideally both water uptake and ionic conductivity should be high. Both parameters are directly proportional to the ion-exchange capacity, and the availability of conductive ions. The water uptake by the AEI covered catalyst surface rejects the products. Thus, ideally both water uptake and ionic conductivity should be high.

Table 1. Properties of Anion Exchange Ionomers As Binders to form PMBI in Direct Borohydride Fuel Cells (DBFCs)

<table>
<thead>
<tr>
<th>Sample</th>
<th>IEC (mequiv/g)</th>
<th>Water Uptake (%)</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GT100</td>
<td>ND*</td>
<td>ND*</td>
<td>23.09</td>
</tr>
<tr>
<td>GT66</td>
<td>ND*</td>
<td>ND*</td>
<td>32.35</td>
</tr>
<tr>
<td>GT38</td>
<td>50.9</td>
<td>101.9</td>
<td>50.77</td>
</tr>
<tr>
<td>GT37</td>
<td>37.9</td>
<td>72.0</td>
<td>47.16</td>
</tr>
<tr>
<td>GT34</td>
<td>45.2</td>
<td>90.7</td>
<td>29.98</td>
</tr>
<tr>
<td>GT30</td>
<td>27</td>
<td>67.4</td>
<td>37.97</td>
</tr>
<tr>
<td>GT22</td>
<td>15.2</td>
<td>33.6</td>
<td>24.86</td>
</tr>
<tr>
<td>GT18</td>
<td>10.1</td>
<td>25.4</td>
<td>36.53</td>
</tr>
</tbody>
</table>

*Material was from the same batch.*

OH\(^-\) conductivity was measured by in-plane AC EIS. The samples absorbed lot of water and become gel after soaking in trimethyl amine. Hence, the ionic conductivity and water uptake were not measured. Mn was measured by GPC at RT. IEC was calculated via \(^1\)H NMR results. Water uptake was measured at RT.

D were in the range between 23.1 and 50.8 kDa and 1.3—2.3, respectively. These values were in line with our previously reported materials. Ionic conductivity is largely predicated on the formation of continuous ion conductive channels through the ionomer. GT37 exhibited a very high dispersity (D) of 2.30, indicating a poor distribution of ion conductive channels. Hence, the conductivity of GT37 was lower than that for GT34. An inverse correlation was mostly observed between D and ionic conductivity within experimental error and accounting for the fact that D is not the only parameter affecting ionic conductivity. Upon synthesis of these AEIs, a limitation of the increasing IEC approach was readily apparent as AEIs with very high IECs resulted in the formation of gels after soaking in aqueous trimethylamine solution (TMA). Nevertheless, IEC was initially expected to directly correlate with the DBFC performance until the gelation limit.

Figure 2 exhibits polarization curves of DBFCs with GT-series AEIs and performance comparison of DBFCs with the best performing GT AEI and benchmark AEI (SEBS55-TMA) reported by Wang et al. Interestingly, during the initial screening of AEIs using a 5 cm\(^2\) cell (Figure 2a), GT34 showed the best performance in a DBFC. This indicated that, contrary to our initial expectations, the best DBFC performance may occur at an optimal AEI IEC value (all other factors being the same) as opposed to exhibiting a monotonically increase with increasing IEC. The best performing DBFC with GT34 AEI exhibited an OCV of 1.93 V, a current density of 150 mA cm\(^{-2}\) at 1.5 V, and a peak power density of 326 mW cm\(^{-2}\). As discussed earlier, high-performance AEIs require high ion conductivities to allow fast transport of \( \text{BH}_4^- \) and \( \text{OH}^- \) to the catalyst surface for BOR along with reasonably good water uptake to enable autoprotolysis of water in the bipolar interface and to maintain ion conductivity. The \( \text{OH}^- \) ion conductivity of GT34 was 90.7 mS cm\(^{-1}\) at 80 °C, whereas the hydroxide ion conductivity of GT18 and GT37 at the same temperature was 25.4 and 72 mS cm\(^{-1}\), respectively. Thus, GT34 was found to be superior in this factor determining DBFC performance. The impact of water uptake is far more nuanced.

High water uptake in the AEIs will ensure that sufficient water is available to prevent separator drying and enable ionic conduction by providing mobile ions through autoprotolysis.
But once sufficient water is available at the PMBI to ensure water dissociation is no longer transport limited, further increases in the water uptake is detrimental to membrane structural integrity. Kohl and co-workers measured bound and unbound (free) water molecules/ion pair using differential scanning calorimetry and examined their impact on ionic conductivity of the membrane.\textsuperscript{23} Free water molecules aid in the transport of ions while bound water hydrates ions. Water uptake typically swells the conductive channels, easing ion transport, while greater hydration of the ions increases their radius, impeding ionic transport. Thus, a judicious optimum was sought. For example, PNB-X\textsubscript{54}Y\textsubscript{46} (water uptake = 133.6%) (GT\textsubscript{46}) exhibited $N_{\text{free}} = 10.65$ and $N_{\text{bound}} = 17.90$, while PNB-X\textsubscript{54}Y\textsubscript{46} (water uptake = 26.2%) (GT\textsubscript{26}) exhibited $N_{\text{free}} = 0.91$ and $N_{\text{bound}} = 0.85$, while PNB-X\textsubscript{54}Y\textsubscript{46} (water uptake = 26.2%) (GT\textsubscript{26}) exhibited $N_{\text{free}} = 0.91$ and $N_{\text{bound}} = 0.85$, while PNB-X\textsubscript{54}Y\textsubscript{46} (water uptake = 26.2%) (GT\textsubscript{26}) exhibited $N_{\text{free}} = 0.91$ and $N_{\text{bound}} = 0.85$. But despite the difference in water uptake, GT\textsubscript{26} exhibited OH\textsuperscript{−} ionic conductivity of 23.4 mS cm\textsuperscript{−1} while GT\textsubscript{30} exhibited an OH\textsuperscript{−} ionic conductivity of 27 mS cm\textsuperscript{−1}, illustrating the complex interplay of factors related to water uptake determining ionic conductivity. It was determined that $N_{\text{free}} = 6.74$ and $N_{\text{bound}} = 11.88$ was optimum. In the present study, an additional factor to be considered is the availability of water as a reactant at the PMBI. Thus, a series of polynorbornene-based AEIs with water uptake values around the previously reported optimum were synthesized and examined. Further, GT\textsubscript{18} and GT\textsubscript{22} which exhibit very low water uptake were also examined to substantiate our hypothesis about the impact of insufficient hydration on ion transport and autoprotolysis.

Another consideration is the possible swelling of the ionomer due to water uptake. Weber and co-workers monitored thickness change upon water uptake in thin films (film thickness < 160 nm) when studying transport limitations in confined Nafion films.\textsuperscript{34} They reported that the thickness increased by 36% for a 4 nm Nafion film at 80% RH while the increase was 16% for a 10 nm Nafion film at the same RH. They observed that films with a thickness of 4 and 10 nm absorbed more water than thicker films (57 and 160 nm), indicating greater sensitivity of polymer thickness to water uptake in the thin film regime. Analogously, we can expect significant impact of the change of water uptake on hydrated AEI film thickness, given that the thickness of AEI covering the BOR catalyst has been estimated to be 8 nm in dry state.\textsuperscript{19}

Figure 2. Polarization curves of DBFCs with pH-gradient-enabled microscale bipolar interface (PMBI) configuration. (a) Polarization curves of DBFCs with current AEI. The active cell area was 5 cm\textsuperscript{2}. The catalyst for the anode was 0.5 mg Pd/C, and the catalyst for the cathode was 0.5 mg Pt/C. The flow rate for anolyte (3 M KOH + 1.5 M NaBH\textsubscript{4}) and catholyte (1.5 M H\textsubscript{2}SO\textsubscript{4} + 15 wt % H\textsubscript{2}O\textsubscript{2}) was 0.4 mL min\textsuperscript{−1} cm\textsuperscript{−2}. (b) Polarization curves comparison between benchmark AEI (SEBS55-TMA)\textsuperscript{19} and GT\textsubscript{34} as AEI. The active cell area was 5 cm\textsuperscript{2}. The catalyst for the anode was 0.5 mg Pd/C, and the catalyst for the cathode was 0.5 mg Pt/C. The flow rate for anolyte and catholyte was 0.4 mL min\textsuperscript{−1} cm\textsuperscript{−2}. (c) Polarization curves comparison between benchmark AEI and GT\textsubscript{34} AEI. The active cell area was scaled up to 25 cm\textsuperscript{2}, The catalyst for the anode was 3 mg Pd/C, and the catalyst for the cathode was 3 mg Pt/C. Flow rates for the anolyte and catholyte were 0.8 and 4 mL min\textsuperscript{−1} cm\textsuperscript{−2}, respectively.
Given that the DBFC cell components are 25% compressed by applying a 25 psi torque during assembly, the practical (operando) increase in the AEI thickness is expected to be lower than the large ex-situ swelling values. Nevertheless, the increase in AEI thickness can result in the transport of BH$_4^-$ through AEI being more sluggish. Also, for the same type of AEI, water uptake is inversely correlated with permselectivity. This allows more protons to diffuse onto the catalyst surface, resulting in the competing hydrogen oxidation reaction (HOR). The loss in permselectivity would also lead to lower overall cell voltage, affecting the peak power produced. The performance of the DBFC with GT34 AEIs indicates that its water uptake value of 63% is the optimum to balance autoprotopolysis, BH$_4^-$ transport, and permselectivity. The higher water uptake of GT37 (70%), GT38 (71%) GT66 (gel formed), and GT100 (gel formed) resulted in lower permselectivity, sluggish BH$_4^-$ transport, and ultimately poorer performance. The inference about the impact of permselectivity on performance was borne out by the observation that the highest recorded OCV (1.93 V) among the various DBFCs tested was obtained by GT34, indicating its exceptional permselectivity.

Having identified the optimal formulation of the GTm series AEIs, the best performing AEI, GT34, was compared against the current state-of-the-art DBFC configuration in a 5 cm$^2$ and in a 25 cm$^2$ cell. The current density at 1.5 V of a GT34 DBFC with a 5 cm$^2$ active-cell-area (150 mA cm$^{-2}$) was higher than that of a DBFC with SEBS55-TMA (100 mA cm$^{-2}$) (Figure 2b). Despite the higher OH$^-$ ion conductivity of SEBS55-TMA (ca. 90 mS cm$^{-1}$ at 25 °C) compared to GT34 (45.2 mS cm$^{-1}$ at the same temperature), the higher water uptake of SEBS55-TMA (>120%) resulted in sluggish BH$_4^-$ ion transport and lower permselectivity, and, hence, led to relatively higher proportion of HOR at the anode. Consequently, the OCVs of DBFCs with SEBS55-TMA (1.8 V in a 5 cm$^2$ cell and 1.96 V in a 25 cm$^2$ cell) were lower than those of DBFC with GT34 (1.93 V in a 5 cm$^2$ cell and 2.0 V in a 25 cm$^2$ cell).

Scaling up to a 25 cm$^2$ cell, a current density of 278 mA cm$^{-2}$ was obtained by a DBFC with GT34 at a flow rate of 0.8 mL min$^{-1}$ cm$^{-2}$, which was higher than the current density obtained by a DBFC with SEBS55-TMA at the same flow rate (Figure 2c). The result agreed with DBFC performance in a 5 cm$^2$ active cell area. But at a high flow rate (4 mL min$^{-1}$ cm$^{-2}$), a DBFC with SEBS55-TMA showed slightly better performance (322 mA cm$^{-2}$ at 1.5 V) compared to the DBFC with GT34 (302 mA cm$^{-2}$ at 1.5 V). A possible explanation is the competition between the HOR and BOR reactions at the anode. At low flow rates, sufficient accumulation of H$^+$ ions may result due to lower permselectivity, leading to substantial HOR contributions, in turn lowering the overall cell voltage. As the flow rate increases, the H$^+$ ions that reach the anode, as a consequence of poor permselectivity, are rapidly flushed out of the cell, mitigating the detrimental effects of the higher water uptake. A further advantage at higher flow rates arises from the membrane formability of SEBS55-TMA which is better than GT-series AEI thanks to the aromatic component within its polymer backbone. At a high flow rate, GT34 AEIs were unable to completely bind the catalysts onto the Ni-foam substrate, resulting in loss of catalyst. Thus, having identified the need to balance water transport to the PMBI with the permselectivity of the membrane, further work on the AEI formulation is needed to improve the binding ability and to reduce the high frequency resistance (HFR) of the overall DBFC. Unlike PEMFCs, polarization curves of DBFCs with PMBI configurations exhibit a monotonic linear decrease in potential with increasing current density due to the large ohmic loss across the bipolar interface. The HFR value (ca. 1 ohm cm$^{-2}$) of a DBFC with a bipolar interface was almost 20 times higher than that of PEMFC (Figure 3), leading to polarization behavior without distinct regions with predominantly ohmic losses and mass-transport losses.

Figure 3. Polarization curve and high frequency resistance (HFR) values of a DBFC with GT34 PMBI configuration in a 25 cm$^2$ active area cell at a flow rate of 4 mL min$^{-1}$ cm$^{-2}$.

Figure 4 consolidates our previous discussion on the effect of water uptake on the peak power performance. The optimum water uptake (and resultant $N_{\text{free}}/N_{\text{bound}}$ ratio) corresponding to high ionic conductivity was also found to result in high DBFC peak power density. Notably, the optimum identified is for the GTm series of AEIs and the numerical value of the water uptake required to achieve similar peak power densities may not be directly translatable to other AEI systems. Nevertheless, given the interplay of various AEI properties...
on the performance of the DBFC, any other AEI system can also be expected to exhibit similar water uptake vs peak power behavior and similar design rules would apply.

Figure 5 shows alkaline stability tests of GT34 and in situ DBFC stability using GT34 to form the PMBI. More than 500 h of long-term alkaline stability of GT34 binder was measured in 3 M KOH and 1.5 M NaBH₄ solution at 70 °C. The drop in ionic conductivity was measured as a function of time, and only 1.25% loss in ionic conductivity was observed after 536 h of aging process (Figure 5a). This was in great agreement with previous polynorbornene membranes.²³,²⁹ There was <0.5% deviation for each ionic conductivity data point. As shown in Figure 5b, the structural characterization of the GT34 binder using FT-IR analysis showed no change in peaks after alkaline treatment. The C−N stretching frequencies at 911, 971, and 1483 cm⁻¹ remained unchanged. Thus, the chemical structure was intact after alkaline treatment. The samples were insoluble after quaternization in NMR solvents, and therefore, the scope of characterization by NMR analysis was eliminated. Cell stability tests were performed by holding the DBFC at a constant voltage (1.0 V) for 180 min. There was no performance degradation for any DBFC (Figure 5c). The steady operation of DBFC indicated that the accumulation of NaBO₂ at the bipolar interface was negligible. Also, if there was any NaBO₂ formed at the interface, it should have been flushed out of the system at the anolyte side due to the concentration gradients and high flow rates.

CONCLUSIONS

The role of water transport through the PMBI, its effect on ionic conductivity, and the overall performance of DBFCs was examined using a model AEI system. A series of polynorbornene-based AEIs were synthesized and fabricated (along with Nafion 117) into PMBIs in DBFCs. A DBFC with GT34 exhibited a higher current density at 1.5 V with extremely low catalyst loading (0.5 mg catalyst cm⁻²) than the present state-of-the-art benchmark DBFC with SEBS₅₅-TMA AEI. The DBFC with GT34 yielded a current density of 302 mA/cm² at 1.5 V and a peak power density of 580 mW/cm² at 1 V. GT34 showed excellent alkaline stability (1.25% degradation) in anolyte (3 M KOH + 1.5 M NaBH₄) at 70 °C for 536 h. This is the first report to reveal how the water transport properties of the AEI control autoprotolysis of water at the bipolar interface. Further, we demonstrate the detrimental effects of excess water availability at the PMBI in a rough analogue to the flooding phenomena in PEMFCs. This work suggests that the rational design of AEI for use in DBFCs, ionic conductivity, and water uptake of the AEI needs to be carefully optimized to ensure that the water content at the PMBI lies at the transition between kinetic and mass-transport control of the water dissociation reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.0c00145.
Half-cell and overall reactions in a DBFC; ion-exchange capacity and water uptake; conductivity and alkaline stability; preparation of PMBI; direct borohydride fuel performance tests; and direct borohydride fuel cell stability test (PDF)

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

M.M., G.H., and P.A.K. gratefully acknowledge the financial support of the ARPA-E IONICS (United States Department of Energy, grant number DE-AR0000769). Z.W., S.S., and V.R. would like to acknowledge with gratitude the Office of Naval Research (ONR grant number N00014-16-1-2833) for funding this work. V.R. acknowledges with gratitude generous support from the Roma B. and Raymond H. Witcoff Distinguished University Professorship.

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