

# V.P.17 Transport Phenomena and Interfacial Kinetics in Planar Microfluidic Membraneless Fuel Cells

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## Abstract

Unconventional fuel cell technologies are combined to create a system that not only avoids most typical fuel cell drawbacks, but also achieves the highest power density yet recorded for a non-H<sub>2</sub> fuel cell. Rigorous electrochemistry is used to characterize the high-energy-density fuel BH<sub>4</sub><sup>-</sup>, providing important mechanistic insight for anode catalyst choice and avoiding deleterious side reactions. All major fuel cell oxidants used in place of O<sub>2</sub> are compared in a detailed, uniform manner, and a powerful new oxidant, cerium ammonium nitrate (CAN), is described. The high-voltage BH<sub>4</sub><sup>-</sup>/CAN fuel/oxidant combination is employed in a membraneless, room temperature, laminar-flow fuel cell, with herringbone micromixers which provide chaotic-convective flow which, in turn, enhances both the power output and efficiency of the device.

## Progress Report

Previous research centered around a membraneless, laminar-flow fuel cell described earlier, with the goal of creating a high power density device for portable power applications. A transport-enhancing, chaotic-convective flow design was employed to boost power and efficiency. The fuel cell system was studied from both analytical and practical standpoints, with electroanalytical studies of fuel and oxidant accompanying performance testing in this microfluidic fuel cell device.

As a potential fuel, BH<sub>4</sub><sup>-</sup> has been the subject of intense investigation, as its energy density is superior to that of MeOH, yet its kinetics are much faster, its onset potential is much lower, and it does not poison the anode or any known cathode material. However, BH<sub>4</sub><sup>-</sup> does suffer from a deleterious, acid-catalyzed conversion to H<sub>2</sub> in aqueous media. This decreases its effective concentration in solution, in turn decreasing its power output.

Our rigorous study of BH<sub>4</sub><sup>-</sup> oxidation at Pt and Au revealed a number of misconceptions in the literature about BH<sub>4</sub><sup>-</sup>'s reaction mechanism. We found that, unexpectedly and most surprisingly, BH<sub>4</sub><sup>-</sup> has more problems with hydrolysis to H<sub>2</sub> at Au than at Pt surfaces, and that low-potential current at Pt stems from direct BH<sub>4</sub><sup>-</sup> oxidation, rather than H<sub>2</sub> produced via BH<sub>4</sub><sup>-</sup> hydrolysis (Figure 1). Though Au is the literature preferred BH<sub>4</sub><sup>-</sup> anode, we found that Pt is the superior catalyst, capable of delivering just as much current as Au, but at potentials nearly 0.5V lower. This difference translates to a 0.5V gain in *operating* voltage for direct BH<sub>4</sub><sup>-</sup> fuel cells that use Pt rather than Au anodes.

## Objectives

Our research aims to achieve a fundamental understanding of the transport behavior in planar microfluidic membraneless fuel cells and to take advantage of their unique properties, including the lack of a physical membrane and the ability to utilize different pH solutions in fuel and oxidant streams to optimize power output and efficiency. We have identified the borohydride/cerium ammonium nitrate fuel/oxidant combination as one capable of delivering over 0.25W/cm<sup>2</sup>. This was only enabled by detailed fundamental studies of the redox reactions of sodium borohydride as fuel and numerous potential oxidants.

## Technical Barriers

While membraneless fuel cells have numerous attractive features, their performance has been limited by a low utilization efficiency of fuel and oxidant as well as relatively low energy density. In our investigations we have been able to overcome these limitations through the use of "structured" electrodes (herringbone micromixers) and the identification of high-energy (and high solubility) fuel and oxidant couples. While the scale-up of these devices to deliver 2-10 watts remains a challenge, we have begun studies that we feel will overcome this limitation.

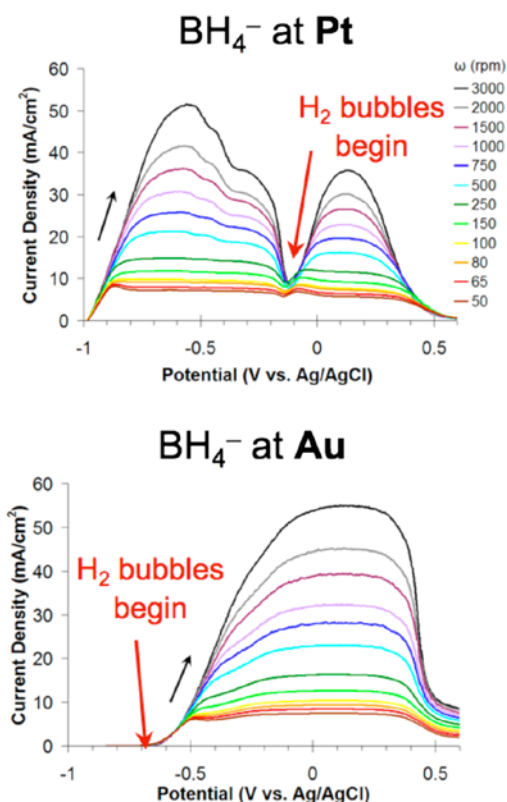


FIGURE 1.

Our fuel cell studies with our new oxidant cerium ammonium nitrate (CAN), showed that BH<sub>4</sub><sup>-</sup> was actually the limiting reagent, largely due to its limited stable solubility. BH<sub>4</sub><sup>-</sup>'s hydrolysis to H<sub>2</sub> is first order with respect to BH<sub>4</sub><sup>-</sup> and must be stabilized with highly concentrated base, and above 3M NaOH, various fuel cell components were degraded. Since 3M NaOH can hold only 0.15M BH<sub>4</sub><sup>-</sup>, we studied BH<sub>4</sub><sup>-</sup> oxidation in nonaqueous solvents to improve its maximum *stable* solubility and, therefore, its maximum current/power.

We found that BH<sub>4</sub><sup>-</sup> had a solubility higher than 0.4M in DMSO, DMF, diglyme, and EtOH, and higher than 0.3M in MeOH. As literature suggested, BH<sub>4</sub><sup>-</sup> will undergo a conversion to H<sub>2</sub> in MeOH and, to a lesser extent, in EtOH, similar to its hydrolysis to H<sub>2</sub> in water, and it did not appear to be stable in diglyme, either. Thus, DMSO, DMF, and EtOH appeared to be the most promising solvents, but BH<sub>4</sub><sup>-</sup> was found to have a disappointing onset potential of around -0.1V vs. NHE in these solvents, which is 0.7V more positive than its onset in alkaline solution. We continue studying these solvent systems to determine if 0.4M BH<sub>4</sub><sup>-</sup> in organic solvents has superior performance as compared to 0.15M BH<sub>4</sub><sup>-</sup> in 3M NaOH, and whether specific additives can enhance BH<sub>4</sub><sup>-</sup> oxidation.

Laminar-flow fuel cells provide the tremendous advantage of fuel cell operation without a membrane,

but usually require that the oxidant be dissolved in solution, so as to have fluid fuel and oxidant streams with which to establish laminar flow. Since O<sub>2</sub>'s solubility in water and other solvents is minimal, highly soluble oxidants with high onset potential and fast kinetics are needed to generate high power density. All fuel cell oxidants with literature precedent were characterized in detail, in a uniform manner, at the common catalysts Pt, Au, and GC, and all oxidants were compared using their best respective catalysts (Tables 1 and 2).

Almost every oxidant was found to have a critical weakness. H<sub>2</sub>O<sub>2</sub> established high current density but catalytically decomposed to form laminae-disrupting O<sub>2</sub> bubbles. MnO<sub>4</sub><sup>-</sup> produced tremendous voltage and current, but quickly precipitated at its electrodes. VO<sub>2</sub><sup>+</sup>, used in “vanadium redox battery” fuel cells, has fundamentally low current. ClO<sup>-</sup> poisons Pt, Au, and even GC. Only our new oxidant, CAN, performed in a trouble-free manner, exhibiting the highest onset potential of +1.6V vs. NHE, with reasonable current. It was the only practical alternative oxidant found, although its low solubility limits its max current, and higher-power fuel cells will need a better oxidant.

TABLE 1. Oxidant Reactions

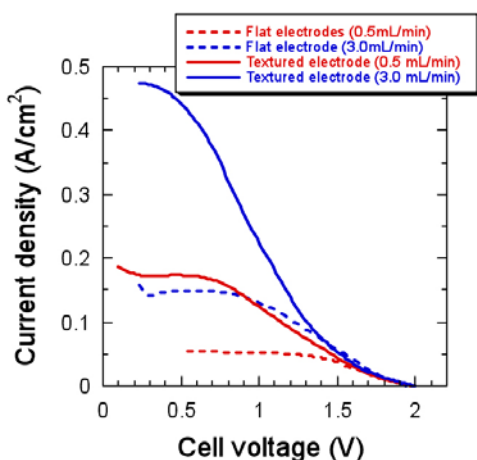
| Oxidant   | Possible Reactions:  | E <sup>0</sup> (V vs. Ag/AgCl) |
|---|--|--------------------------------|
| O <sub>2</sub>  | O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> ⇌ H <sub>2</sub> O <sub>2</sub>                       | 0.498                          |
|   | O <sub>2</sub> + 4H <sup>+</sup> + 4e <sup>-</sup> ⇌ H <sub>2</sub> O                                    | 1.032                          |
| H <sub>2</sub> O <sub>2</sub>                                     | H <sub>2</sub> O <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> ⇌ 2H <sub>2</sub> O                    | 1.579                          |
| MnO <sub>4</sub> <sup>-</sup>                                     | MnO <sub>4</sub> <sup>-</sup> + e <sup>-</sup> ⇌ MnO <sub>4</sub> <sup>2-</sup>                          | 0.361                          |
|   | MnO <sub>4</sub> <sup>-</sup> + 4H <sup>+</sup> + 3e <sup>-</sup> ⇌ MnO <sub>2</sub> + 2H <sub>2</sub> O | 1.482                          |
|   | MnO <sub>4</sub> <sup>-</sup> + 8H <sup>+</sup> + 5e <sup>-</sup> ⇌ Mn <sup>2+</sup> + 4H <sub>2</sub> O | 1.310                          |
| Ce(NH <sub>4</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>6</sub> | Ce <sup>4+</sup> + e <sup>-</sup> ⇌ Ce <sup>3+</sup>   | 1.523                          |
| VO <sub>2</sub> <sup>+</sup>                                      | VO <sub>2</sub> <sup>+</sup> + 2H <sup>+</sup> + e <sup>-</sup> ⇌ VO <sup>2+</sup> + H <sub>2</sub> O    | 0.794                          |
|   | VO <sup>2+</sup> + 2H <sup>+</sup> + e <sup>-</sup> ⇌ V <sup>3+</sup> + H <sub>2</sub> O                 | 0.140                          |
|   | V <sup>3+</sup> + e <sup>-</sup> ⇌ V <sup>2+</sup>   | -0.452                         |
| ClO <sup>-</sup>  | HClO + H <sup>+</sup> + 2e <sup>-</sup> ⇌ Cl <sup>-</sup> + H <sub>2</sub> O                             | 1.285                          |
|   | HClO + H <sup>+</sup> + e <sup>-</sup> ⇌ ½Cl <sub>2</sub> + H <sub>2</sub> O                             | 1.414                          |

TABLE 2. Oxidants Performance Parameters Determined or Confirmed by RDE Analysis

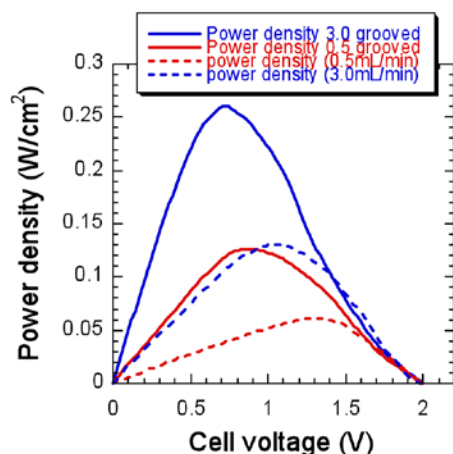
| Compound                      | n   | D <sub>O</sub> (x10 <sup>-5</sup> cm <sup>2</sup> /s) | max C <sub>O</sub> <sup>*</sup> (M) | E <sub>onset</sub> (V) |       |       | i <sub>t</sub> at 3000rpm (mA/cm <sup>2</sup> ) |       |
|-------------------------------|-----|---|-------------------------------------|------------------------|-------|-------|---|-------|
|                               |     |   |                                     | Pt                     | Au    | GC    | 5mM   | 100mM |
| O <sub>2</sub>                | 2.6 | 2.4 <sup>2</sup>                                      | 0.001 <sup>2</sup>                  | 0.600                  | -     | -     | 6.2 <sup>1</sup>                                | -     |
| H <sub>2</sub> O <sub>2</sub> | 2   | 1.5 <sup>15</sup>                                     | 42.4 <sup>2</sup>                   | 0.640                  | 0.100 | -     | 12.5  | 217   |
| MnO <sub>4</sub> <sup>-</sup> | 5   | 1.2 <sup>23</sup>                                     | 7.3 <sup>2</sup>                    | 1.270                  | 1.120 | 1.110 | 30.0  | 593   |
| CAN                           | 1   | 0.36 <sup>44</sup>                                    | 2.6 <sup>50</sup>                   | 1.470                  | 1.309 | 1.309 | 3.0   | 57    |
| VO <sub>2</sub> <sup>+</sup>  | 1   | 0.25 <sup>1</sup>                                     | < 3 <sup>56</sup>                   | 0.800                  | 0.880 | 0.350 | 2.3   | 43.4  |
| ClO <sup>-</sup>              | -   | 1.1 <sup>57</sup>                                     | 10.7 <sup>2</sup>                   | 1.200                  | 1.010 | 1.010 | -   | >50   |

<sup>1</sup>Determined from RDE of VO<sub>2</sub><sup>+</sup> at Pt and Au assuming n = 1. See Results and Discussion for details. <sup>2</sup>Calculated from the density of pure H<sub>2</sub>O<sub>2</sub> liquid. <sup>3</sup>O<sub>2</sub> was studied at its maximum aqueous solubility of -1.27 mM<sup>2</sup> rather than 5mM.

Both  $\text{BH}_4^-$  and CAN were employed in a membraneless, room-temperature, laminar-flow fuel cell. Electrodes with microfabricated, staggered-herringbone micromixers were employed to separately convect the fuel and oxidant streams, disrupting laminae enough to bring unreacted fuel and oxidant to the anode and cathode, respectively, without allowing the fuel and oxidant streams to mix. We were able to achieve current densities of  $0.4 \text{ A/cm}^2$  (Figure 2) and power densities of  $0.27 \text{ W/cm}^2$  (Figure 3).



**FIGURE 2.** Load curves for flat and textured Pt electrodes for a planar membraneless fuel cell with  $0.15 \text{ M NaBH}_4$  in  $3 \text{ M NaOH}$  as fuel and  $0.5 \text{ M CAN}$  in  $1 \text{ M HNO}_3$  as oxidant and at flow rates of  $0.5$  and  $3.0 \text{ mL/min}$ .



**FIGURE 3.** Power curves for flat and textured/grooved Pt electrodes for a planar membraneless fuel cell with  $0.15 \text{ M NaBH}_4$  in  $3 \text{ M NaOH}$  as fuel and  $0.5 \text{ M CAN}$  in  $1 \text{ M HNO}_3$  as oxidant.

Comparison with literature values are difficult, as other groups use high-surface area electrodes but normalize to geometric area. By normalizing outputs to catalyst loading, our system achieved the highest power density yet recorded for a non- $\text{H}_2$  fuel cell. Whereas  $\text{MeOH}$  and  $\text{BH}_4^-$  fuel cells use  $1.5\text{--}3 \text{ M}$  fuel at  $60^\circ\text{C}$  and provide up to  $30$  and  $220 \text{ mW/mg}$  catalyst, our system used  $0.15 \text{ M}$  fuel at room temperature and produced  $1,230 \text{ mW/mg Pt}$ .

## Future Directions

We are continuing to use innovative experimentation to develop fundamentally new fuel cell chemistries and transport. New oxidants are being analyzed to find a replacement for  $\text{CAN}$  with higher maximum current density. We are testing  $\text{BH}_4^-$  at less expensive catalysts and in new solvent systems to improve its current output as well. A fuel cell 60 times larger than described above has been built and is undergoing testing to demonstrate that laminar flow fuel cells are scalable. New fuel cell fluid flows and geometries are being investigated to improve the overall device efficiency.

## Publications (including patents) acknowledging the grant or contract

1. Finkelstein D.A., J.D. Kirtland, Da Mota N., Stroock A.D., Abruña H.D. (2010) Alternative oxidants for high-power fuel cells. Submitted.
2. Da Mota N., Kirtland J.D., Finkelstein D.A., Rodriguez C., Stroock A.D., Abruña H.D. (2010) Membraneless, room-temperature, direct borohydride fuel cell with power density over  $0.25 \text{ W/cm}^2$ . Submitted.
1. Finkelstein D.A., Da Mota N., Cohen J.L., Abruña H.D. (2009) Rotating disk electrode investigation of  $\text{BH}_4^-$  and  $\text{BH}_3\text{OH}^-$  Electro-oxidation at Pt and Au: Implications for  $\text{BH}_4^-$  Fuel Cells. *J. Phys. Chem. C.*, *113*, 19700-19712.