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Aerobic and anaerobic operation of an active membraneless direct methanol fuel cell

Alfred Lam ^{a,b}, Mohammad S. Dara ^a, David P. Wilkinson ^{a,b,*}, Khalid Fatih ^{a,b}^a Department of Chemical & Biological Engineering and Clean Energy Research Centre, University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1Z3^b National Research Council, Institute for Fuel Cell Innovation, 4250 Wesbrook, Vancouver, BC, Canada V6T 1W5

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ABSTRACT

In this paper the operational and architectural flexibilities of a membraneless direct liquid fuel cell were demonstrated under aerobic and anaerobic configurations at 60 °C and 1 atm. The aerobic membraneless direct methanol fuel cell (DMFC) was fed an anolyte solution of 1 M CH₃OH/0.5 M H₂SO₄ and an air oxidant. The anaerobic membraneless direct methanol redox fuel cell (DMRFC) was fed an anolyte solution of 1 M CH₃OH/0.1 M HClO₄ and a catholyte solution of 2 M Fe(ClO₄)₃ and 0.22 M Fe(ClO₄)₂ oxidant. For both cases the membraneless architecture performed significantly better than for the conventional PEM architecture with Nafion® 117. The maximum power density for the membraneless and Nafion® 117 based DMFC was 52 mW·cm⁻² and 41 mW·cm⁻² respectively. The maximum power density for the membraneless and Nafion® 117 based DMRFC was 46 mW·cm⁻² and 34 mW·cm⁻² respectively. In addition, anaerobic operation using a Fe²⁺/Fe³⁺ catholyte gave similar performance to that for air as an oxidant. Both membraneless and anaerobic operation can result in significant cost reduction with improved operational flexibility.

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1. Introduction

A direct methanol fuel cell (DMFC) offers the advantage of extended and continuous operation through the replacement of a fuel cartridge. A conventional DMFC membrane electrode assembly (MEA) consists of a polymer electrolyte membrane (PEM) compressed between an anode and cathode. To simplify this design, the removal, replacement or integration of the membrane electrode assembly (MEA) components has been studied by various research groups [1–7].

Previous work by the authors has focused on a novel passive air-breathing membraneless DMFC operating under ambient conditions (25 °C, 1 atm) [6,7]. In the novel architecture, the conventional PEM was eliminated and replaced with an open spacer and a liquid electrolyte for proton conduction, and a 3D electrode structure to address fuel crossover. A significant advantage to this design is the operational flexibility. It can be operated under conditions with different fuels, electrolytes and oxidants. In this preliminary study, PEM based (Figs. 1a, 2a) and membraneless (Fig. 1b) configurations of a DMFC and direct methanol redox fuel cell (DMRFC) (Fig. 2b) are demonstrated under active conditions. Both membraneless and

anaerobic operation can result in significant cost reduction and use in a wider number of applications without sacrificing performance.

The aerobic membraneless DMFC utilizes a 3D anode structure and a fuel electrolyte (1 M CH₃OH + 0.5 M H₂SO₄) to extend the reaction zone and mitigate/eliminate the effects of methanol crossover [6]. The proton conduction within the open spacer is provided by a liquid electrolyte and air is used as an oxidant. The half cell reactions and overall reaction (25 °C, 1 atm) for this system are shown in Eqs. (1)–(3) [6].

The anaerobic membraneless DMRFC is a hybrid of a redox flow battery and a membraneless DMFC. It operates in much the same way as the previous system, except that the fuel electrolyte and the air oxidant are replaced with a 1 M CH₃OH + 0.1 M HClO₄ and a 2 M Fe(ClO₄)₃ + 0.22 M Fe(ClO₄)₂ metal ion redox catholyte respectively. The total iron concentration was kept at 2.22 M (9:1 ratio of the ferric to ferrous) to simulate a redox regeneration process with an efficiency of 90% [8]. In addition a 3D cathode structure is implemented to extend the reaction zone and mitigate/eliminate the effect of liquid oxidant crossover. The half cell reactions and overall

* Corresponding author at: Department of Chemical & Biological Engineering and Clean Energy Research Centre, University of British Columbia, 2360 East Mall, Vancouver, BC, Canada V6T 1Z3. Tel.: +1 604 822 4888; fax: +1 604 822 6003.

E-mail address: dwilkinson@chbe.ubc.ca (D.P. Wilkinson).

Fig. 1. a) Aerobic PEM based DMFC; b) Aerobic membraneless DMFC.

reaction at (25 °C, 1 atm) for this system are shown in Eqs. (4)–(6) [9].

There are several advantages to the anaerobic DMRFC. Since the activity of the Fe^{3+} is comparable on Pt and C, precious group metal (PGM) catalysts on the cathode are not required [9]. This significantly

Fig. 2. a) Anaerobic PEM based DMRFC; b) anaerobic membraneless DMRFC.

reduces the cost and eliminates fuel crossover since methanol is not active on carbon. Additionally, the regeneration of the catholyte from Fe^{3+} to Fe^{2+} requires no power and can be done in an in-situ power producing process [10].

2. Material and methods

2.1. Electrode preparation

An ink spray deposition method was used to fabricate the electrodes. The 3D anode structure was made by stacking a BASF TGP-60 carbon fiber paper (CFP) with 20% wet proofing with a catalyst loading of 3.0 mg cm^{-2} Pt–Ru black and 5.0 mg cm^{-2} Pt–Ru black catalyst + Nafion® loading of 15 wt.% on opposing sides and a SIGRACET 25BC diffusion layer with 5% polytetrafluoroethylene (PTFE) microporous layer (MPL). The cathode of the DMFC was made by depositing a loading of 6.1 mg cm^{-2} Pt black catalyst with a Nafion® loading of 10 wt.% and a 1.00 mg cm^{-2} Cabot carbon sublayer with 20 wt.% PTFE onto a BASF TGP-60 CFP with 20% wet proofing.

The anode structure for the DMRFC was similar to the DMFC but without the SIGRACET 25BC layer. A 3-D cathode was fabricated by stacking a layer of BASF TGP-120 (no wet proofing), a layer of 2.5 mg cm^{-2} C (Vulcan XC-72) with 10% Nafion loading and a SIGRACET 25BC diffusion layer with 5% PTFE MPL.

2.2. Solution preparation

The anolyte was prepared with methanol, sulfuric acid or perchloric acid and 18.2 MΩ deionized (DI) water. The anolyte compositions consisted of 1 M $\text{CH}_3\text{OH}/0.5 \text{ M H}_2\text{SO}_4$ and 1 M $\text{CH}_3\text{OH}/0.1 \text{ M HClO}_4$ for the respective aerobic and anaerobic systems. The catholyte for the DMRFC was prepared with ferric perchlorate and ferrous perchlorate from GFS Chemicals and 18.2 MΩ deionized (DI) water to a concentration of 2 M $\text{Fe}(\text{ClO}_4)_3$ and 0.22 M $\text{Fe}(\text{ClO}_4)_2$.

2.3. Spacer and membrane preparation

The spacer was cut from a silicone sheet with a thickness of 0.410 mm and an open area of 3.24 cm^2 . Nafion® 117 was prepared by boiling in the following: 3% H_2O_2 , 18.2 MΩ DI water and 0.5 M H_2SO_4 for 30 min with a DI water rinse between each step.

2.4. Fuel cell configuration and testing

The electrode assembly was incorporated into single cell under a compression pressure of 10 psi and was operated at 60 °C and 1 atm. Two serpentine graphite plates with channel dimensions of 1 mm

Fig. 3. Polarization and power density curve for an aerobic membraneless and PEM based DMFC.

Fig. 4. Polarization and power density curve for an anaerobic membraneless and PEM based DMRFC.

(width) $\times$ 1 mm (depth) for the anode and 0.58 mm (width) $\times$ 0.30 mm (depth) for the cathode were used. The performance curves were developed using a Solartron 1420E Multistat. The overall resistance was recorded using an Instek LCR meter.

3. Results and discussion

3.1. Aerobic DMFC

Shown in Fig. 3 is a comparison in performance of an active DMFC with a membraneless and PEM architecture at 60 °C, 1 atm and a fuel and oxidant flow rate of 2 mL·min⁻¹ and 36 mL·min⁻¹ respectively. The polarization curves for the two configurations exhibited similar kinetic performances in the activation region (i.e., 0–15 mA·cm⁻²) and divergent results in the ohmic region (i.e., 15–180 mA·cm⁻²). The difference in performance can be attributed to the improved conductivity and lower resistance of the liquid electrolyte (0.5 M H₂SO₄) and open spacer. The overall fuel cell resistance of the membraneless and Nafion® 117 cases was determined to be 0.121 Ω and 0.215 Ω respectively.

Prior studies of a passive air-breathing DMFC with a similar membraneless configuration could only achieve power densities in the range of 6–10 mW·cm⁻² [6,7]. For higher power applications, active systems are advantageous as operating parameters can be controlled with balance of plant components. The maximum power density for the active membraneless configuration was 52 mW·cm⁻², which is ~27% higher than the Nafion® 117 case at 41 mW·cm⁻².

3.2. Anaerobic DMFC

The anaerobic design allows for the implementation of systems in environments where the availability and the quality of air is low or non-existent (e.g., underwater, subterranean). Shown in Fig. 4 are the performance curves for an active DMRFC having a membraneless and PEM based architecture at 60 °C, 1 atm and a fuel and oxidant flow rate of 10 mL·min⁻¹ and 9 mL·min⁻¹ respectively. Because a non-PGM carbon cathode is selectively active to only the catholyte, methanol crossover is not an issue. However, anode depolarization can be an issue as the ferric ions from the catholyte can crossover. To mitigate the effects of catholyte crossover under an applied current, a 3D cathode structure can be implemented to control the diffusion and increase the rate of consumption at the cathode. This mitigation method is analogous to the one used for methanol in the aerobic DMFC structure.

As shown in the aerobic DMFC, the benefit of improved conductivity and lower resistance is also observed when using a liquid electrolyte and open spacer. The overall resistance for the membraneless and Nafion® 117 based configurations was determined to be 0.170 Ω and 0.210 Ω respectively. This results in a slight divergence in the ohmic region (i.e., 25–200 mA·cm⁻²) of the polarization curves leading to an increase in maximum power density from 34 mW·cm⁻² for the Nafion® 117 case to 46 mW·cm⁻² for the membraneless configuration or ~35% improvement.

3.3. Durability

The aerobic and anaerobic membraneless systems were shown to operate for 4 h at a current density of 100 mA·cm⁻² (Fig. 5). The aerobic configuration had an anode and cathode flow rate of 3 mL·min⁻¹ and

Fig. 5. 4h durability of an aerobic DMFC and anaerobic DMRFC.

36 mL·min^{−1} respectively with a re-circulating fuel solution. The anaerobic configuration had an anode and cathode flow rate of 11 mL·min^{−1} and was operated in a single pass configuration (i.e., no recirculation).

The initial drop in voltage was as a result of the fuel cell reaching an equilibrium for the selected current density. The variability in the anaerobic configuration is caused by the formation and transport of product gas in the electrode structure. The performance decreases when the product gas blocks the access of liquid reactants to the catalyst sites and recovers when it is removed. Better voltage stability is observed in the aerobic DMFC case.

4. Conclusions

The operational and architectural flexibilities of a membraneless direct liquid fuel cell were demonstrated under aerobic and anaerobic configurations. The maximum power density for the membraneless DMFC was 52 mW·cm^{−2} and was shown to be ~27% higher than the Nafion® 117 based DMFC case at 41 mW·cm^{−2}. The maximum power density for the membraneless

DMRFC configuration was 46 mW·cm^{−2} and was shown to be ~35% higher than the Nafion® 117 based DMRFC case at 34 mW·cm^{−2}. Similar performances were achieved for both aerobic (air) and anaerobic (Fe²⁺/Fe³⁺) systems and both were shown to operate for 4 h. Significant opportunities exist for membraneless and anaerobic operation using different fuels.

References

- [1] E. Kjeang, N. Djilali, D. Sinton, *Journal of Power Sources* 186 (2009) 6890.
- [2] M. Priestnall, V.P. Kotzeva, D.J. Fish, E.M. Nilsson, *Journal of Power Sources* 106 (2002) 21.
- [3] S. Barton, T. Patterson, E. Wang, T.F. Fuller, A.C. West, *Journal of Power Sources* 96 (2001) 329.
- [4] J.P. Meyers, H.L. Maynard, *Journal of Power Sources* 109 (2002) 76.
- [5] S. Motokawa, M. Mohamedi, T. Momma, S. Shoji, T. Osaka, *Electrochemistry Communications* 6 (2004) 562.
- [6] A. Lam, D.P. Wilkinson, J.J. Zhang, *Electrochimica Acta* 53 (2008) 6890.
- [7] A. Lam, D.P. Wilkinson, J.J. Zhang, *Electrochemistry Communications* 11 (2009) 1530.
- [8] K. Fatih, D.P. Wilkinson, F. Moraw, A. Ilcic, F. Girard, *Electrochemical and Solid-State Letters* 11 (2) (2008) B11–B15.
- [9] A.B. Ilcic, M.S. Dara, D.P. Wilkinson, K. Fatih, *Journal of Applied Electrochemistry* 40 (2010) 2125.
- [10] A.B. Ilcic, D.P. Wilkinson, K. Fatih, *Journal of the Electrochemical Society* 157 (2010) B529.