

Short communication

Mass transfer layer for liquid fuel cells

M.S. Yazici*

GrafTech International Ltd., 12900 Snow Road, Cleveland, OH 44130, United States

Received 28 October 2006; received in revised form 18 December 2006; accepted 19 December 2006

Available online 12 January 2007

Abstract

Performance of a new type of mass transfer layer (MTL) compared to a commercial material has been shown in single fuel cell testing. GRAFCELL® natural graphite MTL is used as a cathode diffusion media along with carbon cloth. Its chemically modified permeable structure is diffusion limited at high current densities, independent of temperature, while perforated structure provides temperature dependent performance increases. The impact of open area variation in perforated mass transfer layer (PMTL) is demonstrated at high current densities and shows advantages over commercial material at room temperature operation. Performance reaches about 25 mW cm^{-2} at room temperature testing with maximum current density around 250 mA cm^{-2} . Better performance is attributed to large openings for liquid transfer with PMTL compare to ELAT. Being able to design perforations on expanded graphite material may also play role in developing passive fuel supply systems for future liquid fuel power sources.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Mass transfer layer; Diffusion; DMFC; Expanded graphite; Perforation

1. Introduction

Commercial micro-fuel cells for portable electronics, i.e. cellular phones, laptop computers, are expected to be available in the near future. Interest in portable power sources continues to exceed all expectations, spurred by the demand for longer running and more reliable portable electronic devices. The ability of methanol to react electrochemically at low temperatures as a liquid fuel makes DMFC systems attractive as a power source for portable electronic devices with no need for humidification and thermal management [1–3].

The interfaces (cathode side mass transfer layer-carbon-catalyst layer-membrane, and anode carbon-catalyst layer-anode mass transfer layer) are simultaneously involved in electrochemical reactions, current distribution, hydrodynamics, multi-component transport, and heat transfer. The dominant factors are the catalyst that drives the electrochemical reaction with liquid fuel and the mass transfer layer (MTL) that makes a path for gas and liquid solutions to enter or leave the system [4,5]. The two-phase counter flow of reactants and products involves

air diffusion, methanol supply, removal of N_2 , CO_2 and management of water. The gas diffusion layer (GDL) in the literature is referred to as a “mass transfer layer” in this paper due to the multi-phase flow nature of the DMFC operation. These complicated transport processes can be managed by passive and active engineering designs. It is possible to alter the structure of the mass transfer layer to have substantial improvements in the performance of the cell.

Mass transfer layer properties that are relevant to optimized system performance are thickness of the material, hydrophilic–hydrophobic nature of the material, permeability of structure, porosity and pore-size distribution within the structure, electrical conductivity and corrosion resistance. The effect of mass transfer layer thickness can be attributed to a decrease in the electrical resistance of the mass transfer electrode as the mass transfer layer thickness increases. A thinner layer will improve diffusion properties by providing a shorter path for diffusion, but the contact area between the catalyst and mass transfer layer becomes too small lowering cell performance due to high electronic resistance.

Transport of multi-phase components through a macro-porous mass transfer-backing layer treated with a hydrophobic polymer is important as the cell current reaches a level where the electrochemical reaction rate is limited by the removal of water. In a methanol system, the impact will be more severe

* Present address: UNIDO-ICHET, Sabri Ulker Sk. 38/4, Cevizlibag, Istanbul Turkey. Tel.: +90 212 416 4848; fax: +90 212 416 8947.

E-mail address: yazicims@yahoo.com.

due to the removal of gases and liquids from both anode and cathode. The balance of hydrophobicity and hydrophilicity should enhance preferential cross-transport of gases and liquids within large and small pores at the diffusion layer. Mass transfer layers for commercial applications have been obtained by deposition of an aqueous solution of carbon black mixed with polytetrafluoroethylene (PTFE) onto the support by different methods such as screen printing, filtration and spraying. The presence of PTFE helps bind the high surface carbon particles into a cohesive layer, forming a structure of micro- and macro-pores and hydrophobic networks.

Permeability, porosity and varying pore-size distribution are needed for uniform distribution of reactant and product across the interfaces. Low permeability mass transfer layers are useful for non-humidified operating conditions. Highly humidified operating conditions require higher permeability through the mass transfer layer. Saturated streams with high pressure require faster reaction product removal to eliminate mass transfer limitations on the same pathway. High electrical and thermal conductivity material may help eliminate energy losses associated with contact resistance and heat generated by the fuel cell.

Common mass transfer media used in polymer electrolyte fuel cell, whether hydrogen or alcohol based, is not different even though the mass transfer aspect of the fuel cells are somehow different. DMFC prototype systems currently use carbon paper, cloth or fiber as media for both the gas and liquid mass transfer [6]. The fibers are typically manufactured from polyacrylonitrile (PAN) (other options include pitch or rayon) by spinning the polymer into a tow and carbonizing (and possibly graphitizing), which requires a specific environment and temperature cycle [7]. The resulting paper is typically 200–500 μm in thickness with a void volume greater than 70% to ensure high mass transfer rates throughout the paper. Improvements in mass transfer are typically achieved by rendering the paper hydrophobic. Additionally, a micro-porous sub-layer is typically applied to at least the one side towards the catalyst to improve water management. The engineering aspects of the mass transfer layer and interfaces have been getting little attention due to increased focus on membrane and catalyst development. New developments in the area require system evaluation with proper understanding of physical and chemical requirements for gas–liquid operation.

Natural graphite based material used in this research is a monolithic, binderless graphite structure that is flexible, conformable and highly electrically and thermally conductive. Natural graphite products are manufactured from crystalline flake natural graphite, intercalated with acid under oxidizing

conditions, and then thermally shocked to generate exfoliated graphite with a vermiform structure. The exfoliated graphite is then pressed without binder, resulting in a continuous expanded graphite sheet. Expanded graphite can rapidly be formed as a flow field plate or as a mass transfer layer and can be easily attached to a variety of substrates. Graphite sheets that are manufactured by the continuous sheet-forming processes can be mechanically (perforations) and chemically (pore formers) modified to form, in addition to natural porosity of the material, an artificial porosity that allows directional flow of gases and liquids in the fuel cell [8,9]. Processing tools allow preferred perforated areas so that internal sealing with a picture frame structure (middle is permeable while sealing areas not) is possible. The resulting structure will not only provide greater control over packaging flexibility, weight reduction and control over flow rate for each particular application, but also, due to continuity in the structure, excellent heat transfer properties will be achieved at high current demand applications. GRAFCELL[®] mass transfer layer has about $200 \text{ W m}^{-1} \text{ K}^{-1}$ in-plane thermal conductivity. Such a high thermal conductivity facilitates quick spread of local heat in the plane eliminating hot spots in the cell for more uniform temperature distribution.

Expanded graphite based mass transfer layer, shown in Fig. 1a, was made by perforation process ($2500 \text{ tips in.}^{-2}$) from 250- μm thick flexible graphite sheet. The surface was very smooth and did not contain any structural cracks or variations. Open area can be varied from 1% to 30% based on the compression level during the perforation process. Other approaches, in addition to perforation, are possible to give porous expanded graphite structure more diffusional functionality. In one case, expanded graphite was mixed with graphite fibers to provide random path for permeability. Fig. 1b shows that structure following perforation. Samples with modified structures were significantly more absorbent to the methanol than conventional material. As a result of its uniform open structure, the material was more permeable and had mass transport properties in every direction. The final structure in Fig. 1c is intrinsically hydrophobic and carbon/graphite forms a network of structure on the surface and within. This was achieved by blending hydrophobic carbon structure with expanded graphite during manufacturing and turning it into continuous sheet form before perforation. This approach eliminates several steps in making hydrophobic structures. Attempted variations gave expanded graphite sheet a three-dimensional diffusion structure and reduced surface tension to provide better attachment of the additional carbon-PTFE coating on the graphite surface.

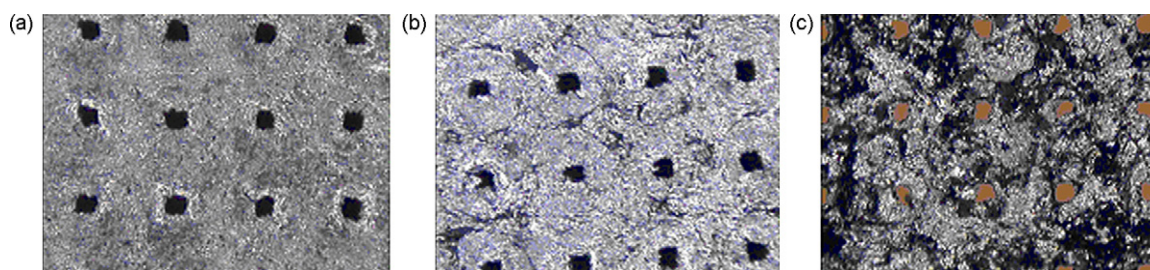


Fig. 1. Perforated, fluid permeable flexible sheets made from (a) expanded graphite, (b) fiber added expanded graphite, and (c) 20% C/PTFE added expanded graphite.

This paper attempts to compare some of the commercial material with newly developed expanded graphite based mass transfer layers in direct methanol fuel cell environment.

2. Experimental

Commercial and in-house made cathode mass transfer layers (MTL) were assembled with catalyst-coated membranes (CCM) of 5-cm² active area in commercial test hardware with graphite flow field plates. The catalyst-coated membranes included Nafion 117 with 4 mg cm⁻² Pt catalyst on cathode and 4 mg cm⁻² Pt/Ru (1:1) catalyst on anode. On the anode side, a carbon cloth mass transfer layer was used for all cell tests. This hydrophobic MTL had about 200- μ m thickness with no MPL on it. On the cathode side, three different types of MTL were used as shown in Fig. 2. Commercial control was 450 μ m thick cloth based ELAT MTL with 50 μ m thick C/PTFE MPL on one surface. Two GRAFCELL[®] variations were tested. First one is called Intrinsic Mass Transfer Layer (IMTL), which was obtained by mixing 80% expanded graphite with 20% PTFE coated carbon to form a 150- μ m thick porous sheet. Carbon and PTFE were added to expanded graphite since 100% expanded graphite structure was not permeable enough for mass transfer functionality. Carbon/PTFE mixture provided necessary hydrophobicity for water management while giving permeability to the structure. Perforated Mass Transfer Layer (PMTL) was obtained after IMTL, mentioned above, was perforated with a 2500 tips in.⁻² tool for more permeability. Thickness of PMTL grew to 200 μ m due to flow of graphite during densification.

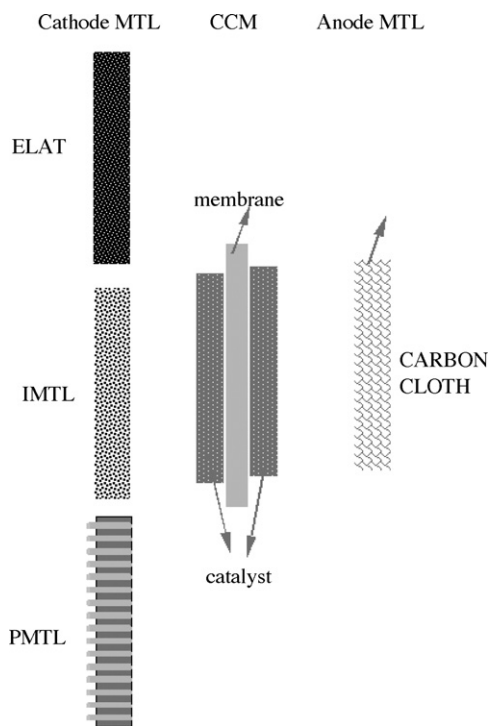


Fig. 2. Schematic of variations in cathode mass transfer layer testing: ELAT (450 μ m thick cloth with single surface coated with C/PTFE MPL); IMTL (150 μ m thick sheet with 80% expanded graphite and 20% C/PTFE); PMTL (200 μ m thick perforated intrinsic mass transfer layer).

Fig. 2 shows all these structures schematically. Flow field plate channels were single serpentine with 1 mm width and 1 mm depth. Bolt torque on the cell housing varied between 5 and 10 N m. A solution of 1 M methanol was supplied to the cell with a peristaltic pump at 1 ml min⁻¹ flow rate. The fuel was not heated as it was supplied to the cell. The dry airflow rate was at 250 ml min⁻¹ with no backpressure. The cells were conditioned at open circuit voltage and also polarized to various current densities for about 5 h. Polarization data were taken at different current densities with 5–15 min open circuit rest between measurements.

Same catalyst coated membrane (CCM) was used for testing of all different cathode MTL to ensure minimal variation in CCM performance while evaluating the performance of different MTL materials. Three different temperatures (room temperature (24 °C), 40 and 80 °C) were used to observe the effect of temperature on mass transfer layer functionality.

3. Results and discussion

Permeability of various carbon graphite structures was investigated by gravitational methanol leak over time. Samples of 3 cm diameter mass transfer layers were placed on a special container and sealed at the edge with Grafoil[®] gaskets. The 5 ml methanol was placed on top of the sample and allowed to leak gravitationally to the bottom container. Total time necessary for all the methanol volume to transfer was measured and plotted in Fig. 3. This figure relatively compares different structures and shows the possible range of structural permeability with various expanded graphite based MTL technology. Even though direct comparison of MTL permeability versus fuel cell performance cannot be made due to structural (teflonization) and operational differences (flow versus diffusion), relationship exists. Plain Grafoil[®] sheet did not leak as expected due to high density (1.85 g cm⁻³) of impermeable structure. However, intrinsic mass transfer layer structure with fibers (IMTL-fiber) showed some permeability to methanol. When 80% expanded graphite, 20% carbon/PTFE mixture formed into a 150- μ m thickness (IMTL), it took 2 min to transfer 5 ml volume of methanol. This was due to additional in-plane leak paths within the structure. When IMTL, shown in Fig. 3 was perforated (PMTL), it took less than 30 s to transfer the entire methanol to the other side.

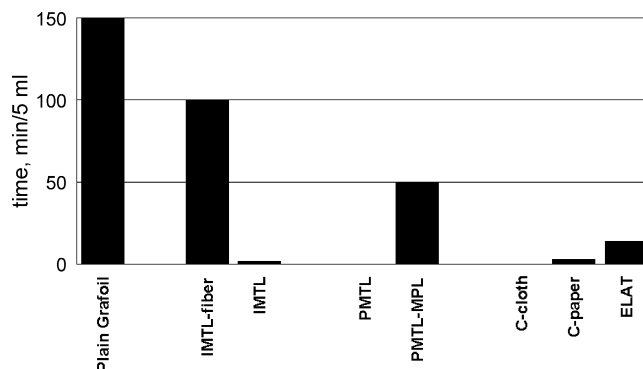


Fig. 3. Time necessary to flow 5 ml methanol through various mass transfer layer structures.

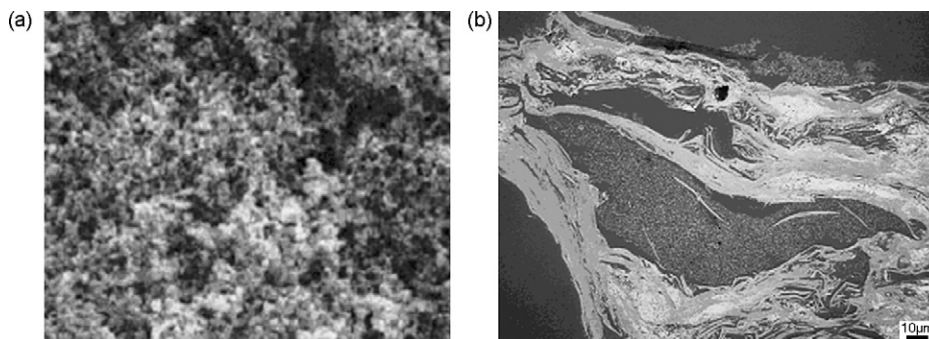


Fig. 4. Perforated mass transfer layer (PMTL) with carbon coated surface (a) and cross-section (b).

Putting a 100- μm thick MPL turned that structure (PMTL-MPL) relatively impermeable compare to IMTL due to thick nature of MPL. Similar response was measured with ELAT mass transfer layer. Absorptive nature of cloth and thinner MPL made this structure more permeable. Base material carbon cloth took less than 30 s to transfer 5 ml methanol. The ability to control the amount of leakage is an important factor for MTL functionality in DMFC operating conditions, not only for mass transfer properties but also for methanol crossover and passive operations.

Cross-section analysis confirms that the addition of carbon and PTFE increases the permeability of the graphite sheet. Fig. 4 shows the surface and cross-section of an expanded graphite mass transfer media. Carbon within the structure increases the strong attachment of the PTFE to the graphite. Macro- and micro-channels within graphite and the structure with carbon allow mass transfer in every direction for more material functionality in operating fuel cell environment.

Additional advantages of GRAFCELL[®] MTL material also come from significantly lower in-plane electrical resistivity than commercial materials. As shown in Fig. 5, an order of magnitude reduction in in-plane electrical resistivity is a significant advantage for edge current collection in planar fuel cell designs for portable electronic power source development. This, in fact, helps to get better energy and power density due to elimination of resistance losses. Thinner samples with favorable mass transport properties would be beneficial for compact packaging as well. For a highly anisotropic and conductive material such as expanded graphite, compression forces acting on GRAFCELL[®] MTL help the material take the shape of surface

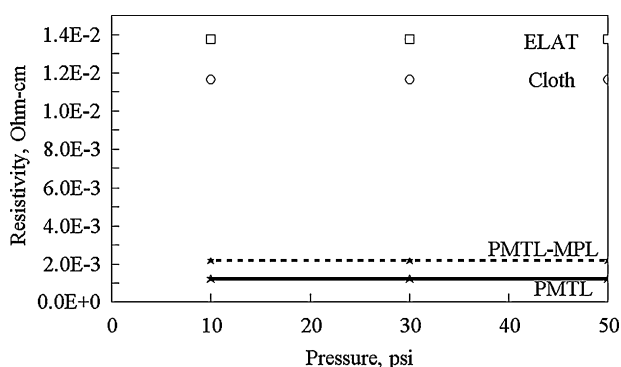


Fig. 5. Surface electrical resistivity of various carbon and graphite mass transfer layers.

it's against. Increasing density of the structure and making it thinner through higher compression reduces in-plane resistivity due to anisotropic nature of the material. Therefore, contact resistance is not a concern as the material thickness is reduced. This is a favorable property for both current collection and internal resistance reduction.

The graphite sheet with internal porosity (IMTL), as described above and in Fig. 2, were assembled into a fuel cell cathode, and cell performance was compared to a mass transfer layer that is intrinsically permeable and mechanically modified (PMTL). Responses of these mass transfer media are shown in Fig. 6 for three different temperatures. Room temperature operation gave similar responses up to 100 mA cm⁻² current density, and then sharply dropped to limiting current density for IMTL due to diffusion limitations. Differences became more obvious for 40 and 80 °C. There was not much variation with temperature for intrinsic porous material (IMTL). Simply, reactants and products could not diffuse through the media no matter what the temperature was. These samples had 3–5 times lower porosity than the best performing samples.

Similar comparison was carried out with a commercial mass transfer layer. A membrane electrode assembly (MEA) with a carbon cloth anode mass transfer layer and two different cathode mass transfer layers (commercial ELAT and GRAFCELL[®] PMTL) was operated at 1 M methanol solution at different temperatures. Performance data are presented in Fig. 7. As temperature increased, kinetics of the methanol oxidation increased, resulting in high current densities (maximum 150 mA cm⁻² at RT and 400 mA cm⁻² at 80 °C). “Solid lines” represent data for GRAFCELL[®] PMTL. This is the same PMTL as shown in Fig. 2. The performance difference was significant at room temperature operation. These results were repeatedly obtained at room temperature. It is possible that larger perforated openings and thinner expanded graphite sheet structure helped GRAFCELL[®] MTL to achieve better transport properties at room temperature operation. However, the difference disappeared with higher temperatures indicating predominance of gas phase processes.

Similar tests were carried out with larger open area GRAFCELL[®] PMTL. Fig. 8 shows polarization curves for that material with 1 M methanol at three different temperatures (room temperature, 40 and 80 °C) along with power density. These data were obtained with 1 M methanol at 1 ml min⁻¹ flow rate with 250 ml min⁻¹ dry air at atmospheric pressure with PMTL, which had 3 \times more open area

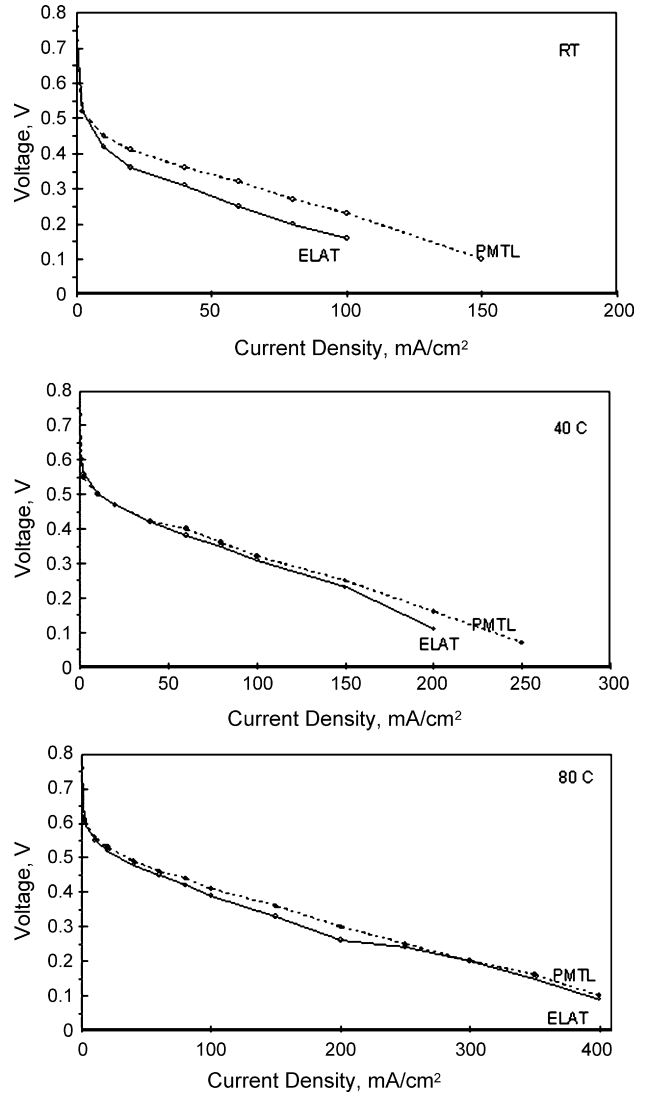
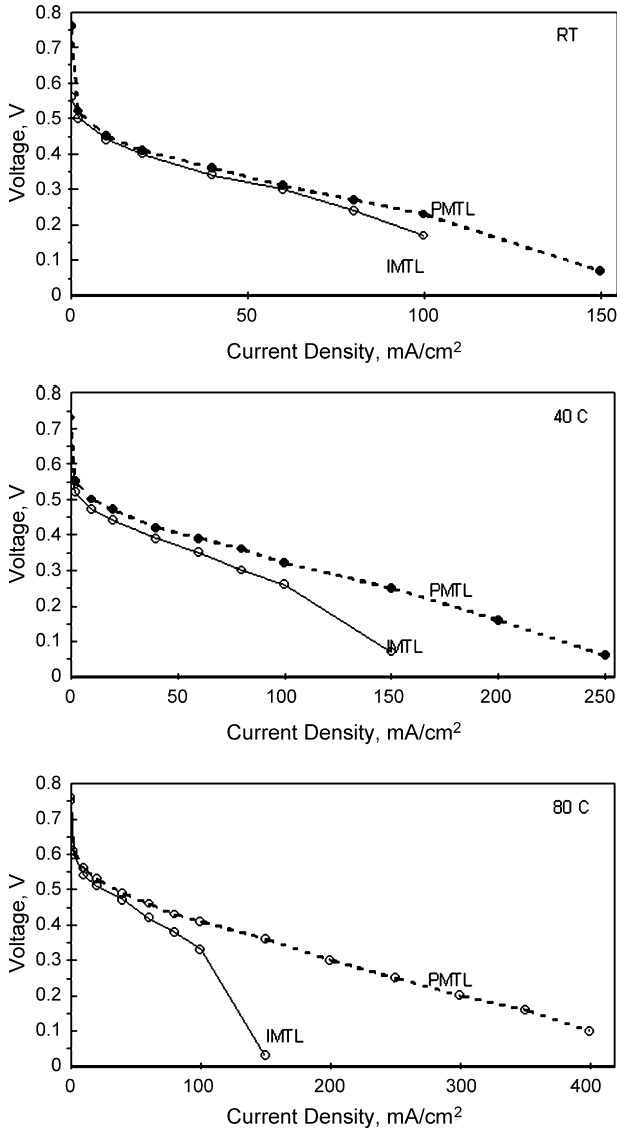


Fig. 6. Performance data for intrinsic mass transfer layer (IMTL, solid line) and perforated intrinsic mass transfer layer (PMTL, dashed line) at (a) room temperature, (b) 40 °C, and (c) 80 °C. Sample properties are same as described in Fig. 2 caption.

Fig. 7. Polarization curves for DMFC with ELAT (solid line) and PMTL (dashed line) cathode diffusion layers at RT, 40 °C, and 80 °C. Sample properties are same as described in Fig. 2 caption.

(15% open area PMTL) than data shown in Figs. 6 and 7 (5% open area PMTL). Polarization slopes got smaller with increasing temperatures (about 30 mW cm⁻² at room temperature to 85 mW cm⁻² at 80 °C). Differences between room

temperature and high temperature response were due to a combination of activation and mass transfer limitation. At room temperature operation, activation was more dominant than mass transfer. At low current densities, material variations did not impact the response unless there were significant structural differences. At high current densities,

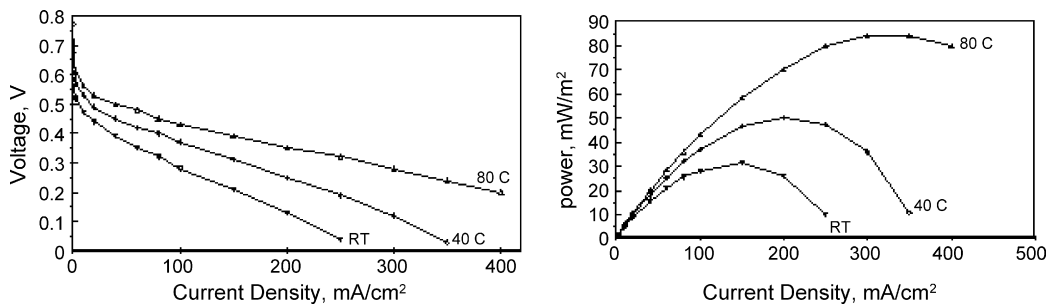


Fig. 8. Effect of temperature on single cell polarization curves and power density using GRAFCELL® cathode PMTL with 15% open area.

material-to-material variations were clearly observed at different temperatures.

4. Conclusion

The importance of cathode mass transfer media was demonstrated through extended testing with different materials. A commercial mass transfer layer as thick as 450 μm was compared to expanded graphite mass transfer layer, about 200 μm thick. Existence of large size open areas with intrinsic permeability and proper PTFE application helped effective transport of gas and liquid within the GRAFCELL[®] PMTL structure for better DMFC performance over conventional diffusion media (carbon paper or cloth) at room temperature. Proposed structure may further be optimized for porosity, permeability and open area for specific fuel and operating conditions. Similar approaches with the material can also be applied to the liquid fuel side, not only for diffusion media but also for a passive fuel supply system. Controlled hole size and pattern helps use of highly concentrated methanol solution as fuel for timely release without crossover concerns. Those results will be published separately in the future.

Acknowledgements

Help on sample preparation by Larry Jones and Rich Pachuta is greatly appreciated.

References

- [1] R. Dillon, S. Srinivasan, A.S. Aricò, V. Antonucci, J. Power Sources 127 (2004) 112–126.
- [2] B.-D. Lee, D.-H. Jung, Y.-H. Ko, J. Power Sources 131 (2004) 207–212.
- [3] D. Kim, E.A. Cho, S.-A. Hong, I.-H. Oh, H.Y. Ha, J. Power Sources 130 (2004) 172–177.
- [4] S. Litster, G. McLean, J. Power Sources 130 (2004) 61–76.
- [5] K.Z. Yao, K. Karan, K.B. McAuley, P. Oosthuizen, B. Peppley, T. Xie, Fuel Cells 4 (2004) 3–29.
- [6] A. Oedegaard, C. Hebling, A. Schmitz, S. Moller-Holst, R. Tunold, J. Power Sources 127 (2004) 187–196.
- [7] M.F. Mathias, J. Roth, J. Fleming, W. Lehnert, in: W. Vielstich, A. Lamm, H.A. Gasteiger (Eds.), Handbook of Fuel Cells—Fundamentals, Technology and Applications, vol. 3, Wiley, 2003, p. 517 (chapter 42).
- [8] P. Calarco, R.A. Mercuri, M.G. Getz, L.K. Jones, T.W. Weber, M.S. Yazici, J.H. Klug, US Patent Application UA20060091573: Gas permeable flexible graphite sheet material and process therefore.
- [9] M.S. Yazici, R.A. Mercuri, R.A. Reynolds, US Patent 6960402: Perforated cylindrical fuel cells.