Proceedings of the ASME 2010 3rd Joint US-European Fluids Engineering Summer Meeting and 8th International Conference on Nanochannels, Microchannels, and Minichannels
FEDSM-ICNMM2010
August 1-5, 2010, Montreal, Canada

FEDSM-ICNMM2010-30305

DESIGN OF AN EXPERIMENTAL SETUP TO STUDY MASS TRANSPORT IN MICRO-NANO CAPILLARIES AND POROUS MEDIA

Lalit M. Pant
Energy Systems Design Laboratory
Department of Mechanical Engineering
University of Alberta
Edmonton, Alberta, T6G 2G8
CANADA
Email: lalit@ualberta.ca

Marc Secanell
Energy Systems Design Laboratory
Department of Mechanical Engineering
University of Alberta
Edmonton, Alberta, T6G 2G8
CANADA
secanell@ualberta.ca

Sushanta K. Mitra*
Micro and Nano Scale Transport Lab.
Department of Mechanical Engineering
University of Alberta
Edmonton, Alberta, T6G 2G8
CANADA
sushanta.mitra@ualberta.ca

ABSTRACT

Study of gas diffusion is critical in understanding the process of mass transfer in porous media, which is an integral part of polymer electrolyte membrane fuel cells (PEMFCs). An experimental method is presented to study the mass transfer processes in micro-nano capillaries, which is further extended to study the transport in the porous media of fuel cells. A diffusion bridge setup, similar to the one presented by Remick and Geankoplis [1] has been used. The experimental setup facilitates the study of binary and multicomponent mixture transport through micro-nano capillaries and porous media. The setup can perform studies for two cases viz., pure diffusion and convection-diffusion. Using pressure controls in both channels, the pressure gradient across the capillaries is varied to study the convection diffusion process in detail. The results obtained from the study will be used to review various models of mass transport available in literature.

INTRODUCTION

The polymer electrolyte fuel cell (PEMFC) technology has emerged as a promising future alternative for energy, due to zero-emission, silent operation and higher efficiency compared to internal combustion engines. These advantages make fuel cells an excellent power source for remote and backup power generators, forklifts and automobiles [2]. However, in order to make fuel cells a viable choice for consumers, further cost, durability and reliability improvements are necessary. The catalytic efficiency of the catalyst layer has to be increased, as the platinum (Pt) catalyst used in fuel cells is very costly and constitutes a major part of overall cost of the system. The catalyst layers (CL) are composite porous media made of Pt supported on carbon, a polymer electrolyte and a pore network, with pore sizes ranging from 2nm to 100nm. In order to improve fuel cell performance and reduce cost, it is imperative to understand and enhance mass transport in the CL. To proceed for optimization of catalyst layers, a reliable set of theoretical models is necessary. Several recent studies [3, 4] have examined the effective diffusivities in fuel cells, and it has been found that most of the available models highly overpredict the effective diffusivities in the CL.

A catalyst layer (CL) can be simplified by a network of interconnected micro- nano capillaries in which fuel and reactant gases are transported by diffusion. Thus the problem reduces to understanding the mass transport process in micro-nano capillaries. The conventional Fickian approach towards mass transfer is known to be inaccurate, when dealing with multicomponent mixtures [5]. The Maxwell-Stefan approach discussed by Krishna and Wesselingh [5] takes into account all the driving

*Address all correspondence to this author.

and frictional forces. The Maxwell-Stefan equations account for multicomponent mixtures, but this approach performs momentum balance with an average mixture velocity. The assumption of an average mixture velocity is applicable only when the diffusion velocities are negligible compared to mixture velocities. However this approach gives inaccurate results when dealing with very low mixture velocities. For mass transfer, major forces on the species are the chemical potential gradient, drag forces from other species (interspecies friction) and the friction from walls (accounted by Knudsen diffusion). At very small dimensions the collisions between molecules and wall becomes more prevalent than between molecule and molecule, thus the Knudsen diffusion becomes significant. The binary friction model (BFM) presented by Kerkhof [6] takes into account both interspecies friction and Knudsen diffusion, and can be used for modeling the diffusion process. Kerkhof and Geboers [7] presented a new solution of the Boltzmann equation, where the three constitutive equation i.e., conservation of mass, momentum and energy are combined with the Boltzmann equation. The solution of multicomponent mass transfer has been decomposed into, simultaneous equations of motion for each species, with a different velocity for all species, instead of a diffusion equation for each species and a momentum equation for the mixture. Thus the average mixture velocity has been eliminated from the solution, providing a way to understand individual species behavior. However, apart from a few limiting cases, Kerkhofs theory has not been experimentally validated. A numerical model based on Kerkhofs approach is being developed by MalekpourKoupaei et al. [8]. The results from this study will be used, to validate the novel mathematical model developed by Kerkhof and Geboers [7].

Diffusion at micro-nano scales has been studied by several researchers. Most of the experimental work has been done in studying diffusion coefficients in porous media [3, 4] and zeolites [9, 10]. Zamel et al. [4] recently presented an experimental study of diffusion coefficients in carbon paper. A Loschmidt cell apparatus was used to find effective diffusivities and tortuosity of the porous media, and it was found that conventionally used correlations overpredict diffusivity. Similar results were also presented by Yu and Carter [3] for a CL. Theoretical modeling of porous media becomes very challenging due to its complex structure. Using zeolites like graphite, in the diffusion measurement gives some advantage in terms of structured pores, compared to the very complex pore network in a porous media. An extensive study on diffusivity of graphite have been done by Evans III et al. [9, 10]. The studies have been done with and without pressure gradients across the permeable graphite, to study both pure diffusion and convection diffusion. The porous media can also be simplified as a network of capillaries, for the ease of study and theoretical modeling. The models and theories for micro-nano capillaries can then be extended to study the more complex problem of porous media. Only a few experimental results are available for micro-nano capillaries, and thus most of the recent theories for mass transfer in capillaries have not been thoroughly validated. Remick and Geankoplis [1, 11] have conducted binary and ternary diffusion experiments in capillaries in the transition region between Knudsen and molecular diffusion. In their experiment, pure Knudsen diffusion and momentum balance in transition region was validated, by using a diffusion bridge setup with a bundle of 644 capillaries, each with diameter of 39.1μm.

Several techniques are available in literature for measurement of diffusion coefficients. A detailed discussion on numerous techniques have been presented by Marrero and Mason [12]. In literature, mostly unsteady diffusion measurement techniques such as; Loschmidt cell, two bulb apparatus have been used as they provide high accuracy and control. However in the present study a steady diffusion measurement technique: a diffusion bridge has been used, because this method provides the ability to study convection dominated diffusion which is not possible with unsteady techniques. A similar technique has been used to study convection diffusion in zeolites by Evans III et al. [10], and to study pure diffusion in micro capillaries by Remick and Geankoplis [1]. The current study facilitates the study of pure diffusion as well as convection dominated diffusion in micro-nano capillaries and porous media. The reported experiments in literature [1, 10] date back nearly 40 years. Using state of the art micro-fabrication techniques, only now we can fabricate micro-nano capillaries with desired design accuracies. Also the instruments used in current experiment provide much higher degree of control and accuracy.

In this paper, a detailed description and schematics of the experimental setup is presented in experimental method section. The experimental method used is the diffusion bridge technique [1]. The central part of the system holds the chip which contains either the capillaries or the porous media, depending on the study. The fabrication process for the capillaries and the chip are discussed in the same section under capillary chip fabrication and porous media chip fabrication subsections.

EXPERIMENTAL METHOD

Experimental Apparatus

The experimental setup used is based on the diffusion bridge setup used by Remick and Geankoplis [1]. The schematic diagram of the experimental setup is shown in fig. 1. Also the photograph of the assembled setup is shown in fig. 2. The central part of the setup consists of the chip, where two parallel flow channels carrying two different gases are connected by capillaries or porous media. The flow rates of gases in the

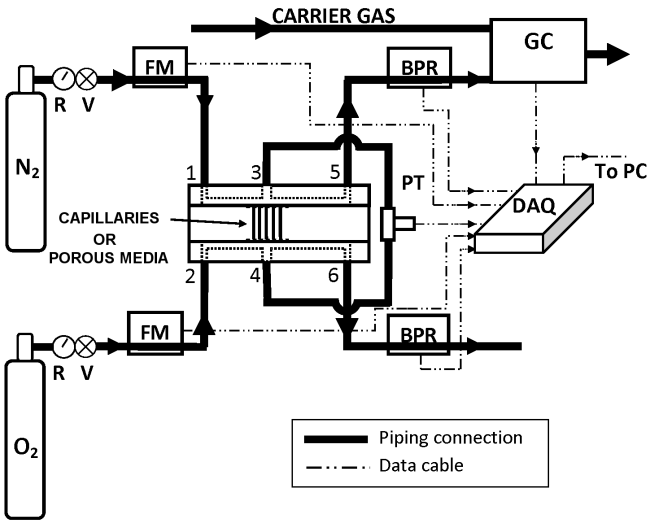

FIGURE 1. SCHEMATICS OF THE EXPERIMENTAL SETUP, BPR-BACK PRESSURE REGULATOR; DAQ-DATA ACQUISITION; FM-MASS FLOW CONTROLLER; GC-GAS CHROMATOGRAPH; PT-DIFFERENTIAL PRESSURE TRANSDUCER; R-REGULATOR VALVE; V-STOPCOCK.

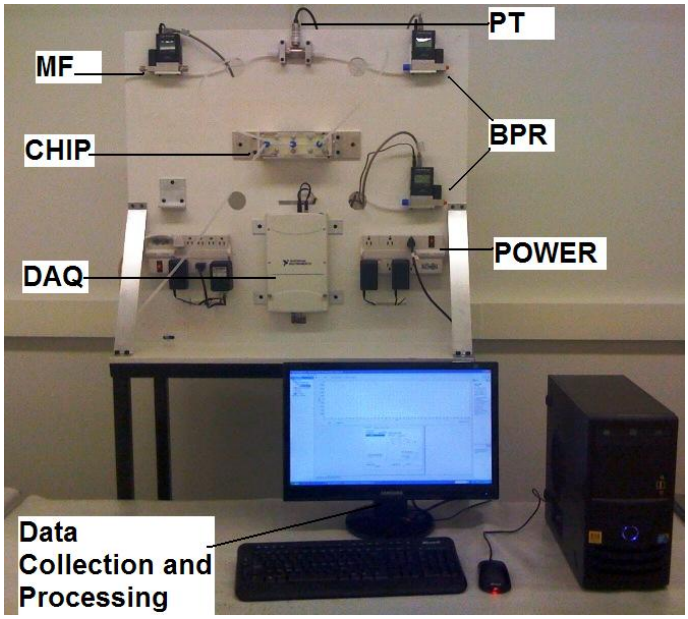

FIGURE 2. PHOTOGRAPH OF THE ASSEMBLED SETUP, ACRONYM MEANINGS ARE SAME AS IN FIG. 1

channels are controlled by mass flow controllers (Cole-Parmer, Model RK-32907-57) with a capacity of 0.5–50 mL/min. The mass flow controllers have an accuracy and repeatability of $\pm 0.2\%$, thus the maximum uncertainty will be ± 0.1 mL/min. Points 1 and 2 in the figure are the inlets of the flow channels for nitrogen and oxygen respectively. A pressure transducer (Omega, Customized Model MMDDB10WBIV10H2A0T1A2) of range 0–25 mBar, is connected to points 3 and 4 across the capillaries, to measure the pressure gradient across the capillaries. For pure diffusion case the pressure gradient should ideally be zero. With an accuracy of $\pm 0.05\%$, the pressure transducer can record very small pressure gradients. The outlets (points 5 and 6) of the flow channels are connected to back pressure regulators (Cole-Parmer, Model NCI-00240MM) of range 0-5 psig, to control the gas pressure in the flow channels. The accuracy of the pressure controllers is $\pm 0.25\%$, thus the uncertainty is only ± 0.0125 psi. After the pressure regulator, the nitrogen stream is sent to a micro gas chromatograph (Varian, Model CP-2003P) for analysis, and the oxygen stream in vented to the atmosphere. A carrier gas is used to run the nitrogen sample in the GC loop. The carrier gas is optimized to give best response and fast elution times. The gas chromatograph uses a thermal conductivity detector (TCD) to analyze the composition of the stream. The resolution of the micro-GC is 1ppm. A data acquisition card (NI, model USB-6221) is used to collect data from all the equipments.

Capillary Chip Fabrication

The capillary chip used in this experiment was fabricated at Nanofabrication Laboratory (NanoFab), University of Alberta, using microfabrication techniques described in literature. Kumar et al. [13] have presented a detailed review of microfabrication and bonding techniques for making microfluidic devices. The chip was made in two steps of macromachining and micromachining. The schematics of the final chip is shown in fig. 3. In first step, two pieces of borofloat glass were taken and the main flow channels were cut on it by water jet machining. The channels are parallel in the center and curve outwards near edges to give more strength to glass between channels.

In second step, micro channels were etched on one piece of glass. The process flow diagram for etching and bonding is shown in figure 4. The glass was first sputtered with chrome and gold. The gold layer is used to protect the non exposed glass during etching, and the chrome layer provides stability to the gold layer. The channel pattern was printed on the substrate by photo lithography, then the gold layer and glass were etched. A microscopic image of the channels is shown in fig. 5. The photolithography technique can make capillaries of size as small as 5μm. To make smaller sizes, electron beam lithography can be used. Electron beam lithography can make features of size as small as 100 nm. Once the capillaries are etched, the

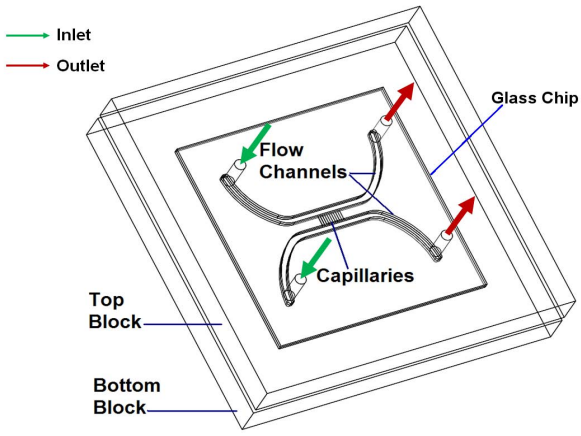

FIGURE 3. FINAL VIEW OF ASSEMBLED CAPILLARY CHIP

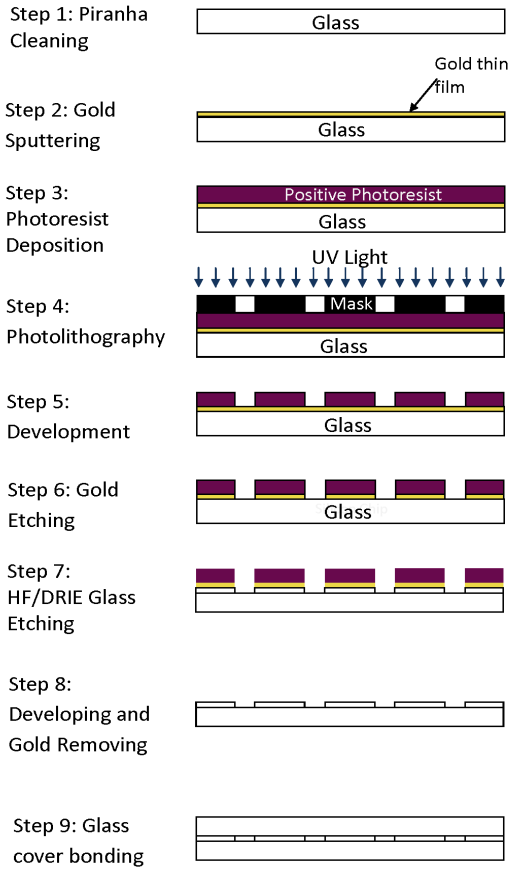

FIGURE 4. PROCESS FLOW CHART FOR CAPILLARY CHIP FABRICATION.

second piece of glass was thermally bonded on top of it to seal the microchannels and make capillaries. The bonded glass chip is placed between two acrylic blocks and sealed with silicon gaskets. The acrylic chip contains fittings which can connect pipings with the glass chip.

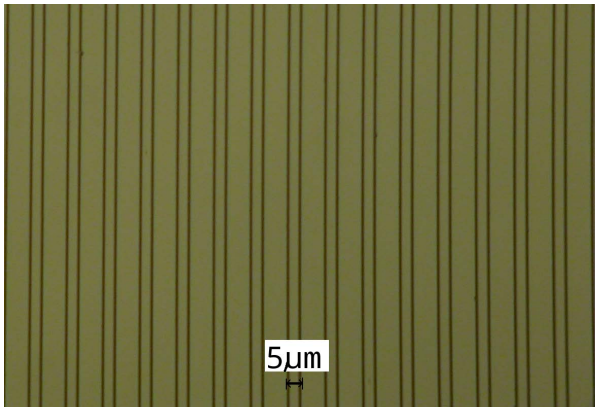

FIGURE 5. THE MICROSCOPIC IMAGE OF CHANNELS ON GLASS

Porous Media Chip Fabrication

To study mass transport in porous media a different kind of chip was designed. The overall setup of experiment remains the same as in fig. 1, but the central chip changes. The schematics of the chip is shown in fig. 6.

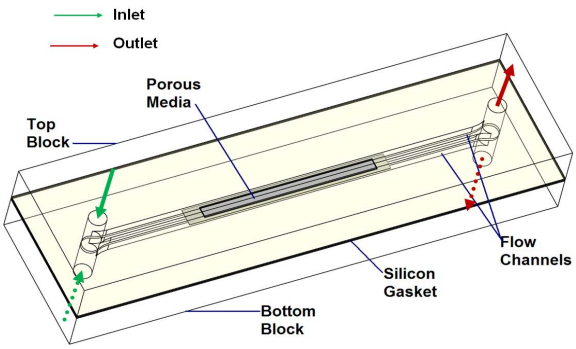

FIGURE 6. SCHEMATICS OF POROUS MEDIA CHIP

In first step two acrylic blocks were machined to make channels and connection fittings. The blocks are then assembled in such a way that the channels on both blocks face each other. To

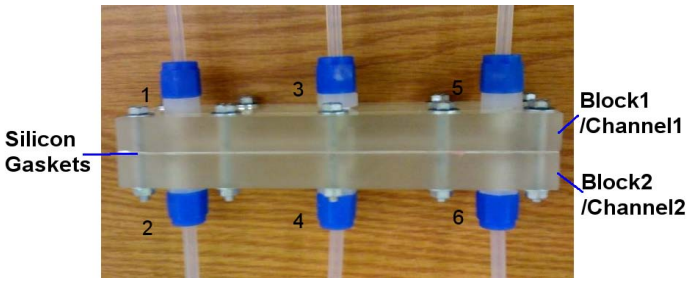

FIGURE 7. THE CHIP TO STUDY MASS TRANSPORT IN POROUS MEDIA

make the block seal proof and also to separate these two channels, two silicon gaskets are placed in between. The silicon gaskets have a slot at the location of the channel. A carbon paper is placed between the two gaskets in this slot and the hole assembly is tightened. The carbon paper connects the flow channels and provides pathway for convection and diffusion. A photograph of the chip is shown in figure 7. The carbon paper can be changed by disassembling the chip, and parametric studies can be performed.

CONCLUSIONS AND FUTURE WORK

A brief overview of the theoretical models available for study of mass transport was given. A steady-state measurement technique was chosen for the experiment to study both convection and diffusion. The description of the experimental setup to measure mass transport in micro-nano capillaries and porous media was presented. The fabrication process of micro-nano capillaries was also discussed. The chip design for study on capillaries and porous media was discussed in detail.

The experimental setup is mostly complete, and the experiments are yet to be carried out. The experiments will be carried out using this setup, and various theories available in literature will be validated by comparing the experimental results to the numerical model developed by MalekpourKoupaei et al. [8]. Also the mass transport in porous media will be studied in detail to find effective transport properties. The theory for capillaries will be extended to explain the process in porous media. The proposed setup provides an ideal platform to study pure diffusion and convection-diffusion problems in multicomponent systems. The results from the experiment will aim at increasing our understanding of mass transport.

REFERENCES

[1] Remick, R., and Geankoplis, C., 1973. "Binary diffusion of gases in capillaries in the transition region between knudsen and molecular diffusion". *Industrial and Engineering Chemistry,* ***12***(2), pp. 214–220.

[2] Wishart, J., Dong, Z., and Secanell, M., 2006. "Optimization of a PEM fuel cell system for low-speed hybrid electric vehicles". In ASME Design Engineering Technical Conference,. Philadelphia, Pennsylvania, USA, no. DETC2006–99606.

[3] Yu, Z., and Carter, R., 2010. "Measurement of effective oxygen diffusivity in electrodes for proton exchange membrane fuel cells". *Journal of Power Sources,* ***195***(4), pp. 1079–1084.

[4] Zamel, N., Astrath, N., Li, X., Shen, J., Zhou, J., Astrath, F., Wang, H., and Liu, Z.-S., 2010. "Experimental measurements of effective diffusion coefficient of oxygen-nitrogen mixture in pem fuel cell diffusion media". *Chemical Engineering Science,* ***65***(2), pp. 931–937.

[5] Krishna, R., and Wesselingh, J. A., 1997. "The maxwell-stefan approach to mass transfer". *Chemical Engineering Science,* ***52***(6), pp. 861 – 911.

[6] Kerkhof, P., 1996. "A modified maxwell-stefan model for transport through inert membranes: The binary friction model". *Chemical Engineering Journal and the Biochemical Engineering Journal,* ***64***(3), pp. 319–343.

[7] Kerkhof, P., and Geboers, M., 2005. "Toward a unified theory of isotropic molecular transport phenomena". *AIChE Journal,* ***51***(1), pp. 79–121.

[8] MalekpourKoupaei, A., Mitra, S., and Secanell, M., 2010. "Numerical modelling of mass transfer through micro and nano capillaries". *Submitted* in International Conference on Nanochannels, Microchannels, and Minichannels,. Montreal, Canada, no. FEDSM-ICNMM2010–30910, ASME.

[9] Evans III, R., Watson, G., and Truitt, J., 1962. "Interdiffusion of gases in a low permeability graphite at uniform pressure". *Journal of Applied Physics,* ***33***(9), pp. 2682–2688.

[10] Evans III, R., Watson, G., and Truitt, J., 1963. "Interdiffusion of gases in a low-permeability graphite. ii. influence of pressure gradients". *Journal of Applied Physics,* ***34***(7), pp. 2020–2026.

[11] Remick, R., and Geankoplis, C., 1974. "Ternary diffusion of gases in capillaries in the transition region between knudsen and molecular diffusion". *Chemical Engineering Science,* ***29***(6), pp. 1447–1455.

[12] Marrero, T., and Mason, E., 1972. "Gaseous diffusion coefficients". *Journal of Physical and Chemical Reference Data,* ***1***(1), pp. 3–118.

[13] Kumar, G. N. S., Mitra, S. K., and Rao, V. R., 2009. "Fabrication of dielectrophoretic microuidic device". In International Conference on Nanochannels, Microchannels and Minichannels,. Pohang, South Korea, no. ICNMM2009–82170, ASME.