A Sugar-Template Manufacturing Method for Microsystem Ion-Exchange Membranes

Rio V. Festarini, Minh-Hao Pham, Xinyue Liu, and Dominik P.J. Barz*

*Department of Chemical Engineering,
Queen's University, Kingston,
ON, K7L 3N6, Canada*

Abstract

In this work, we report on a novel method for producing ion-exchange membranes that can be integrated directly into polydimethylsiloxane-based micro devices. Ionomers such as NafionTM, a copolymer with high conductivity and selectivity to small cations, are generally incompatible with common micro device materials due to the chemical inertness of the tetrafluoroethylene-based skeleton and the swelling in aqueous solutions. Hence, we introduce a microfabrication concept where we use consolidated sugar granules as a template to produce a porous polydimethylsiloxane scaffold. Ionomer and scaffold are combined to a composite membrane where the cohesion of these incompatible materials is of rather mechanical nature; i.e., the ionomer is physically entrapped in the scaffold. Electrochemical Impedance Spectroscopy measurements reveal the excellent membrane conductivity for the upper electrolyte concentrations tested in this work.

Keywords: ion-exchange membrane, microfluidics, microfabrication, NafionTM, polydimethylsiloxane

* dominik.barz@queensu.ca

I. INTRODUCTION

The integration of membranes into microsystems enables various operations such as filtration, concentration gradient generation and sample pre-concentration [1]. While membranes are selective with respect to the size of a species, another important feature is selectivity with respect to the electric charge. Ion-selective membranes can be used for manifold tasks such as on-chip pumping, pH control, or electrokinetic concentration and also facilitate many electrochemical processes. Generally, a substrate is ion selective when its pores are so narrow that electric repulsion, induced by the surface charges of the pore wall, prevents the transfer of ions of the same sign. NafionTM is a nano-porous polymer and conductive to small cations while it restricts the transfer of large cations, anions and electrons. This ionomer does not directly form non-leaking bonds with other polymers or silicate materials that are traditionally used in microfluidics [2], such as polydimethylsiloxane (PDMS), due to the chemical inertness of the tetrafluoroethylene-based skeleton. The membrane volume can increase up to around 50 % in contact with aqueous solutions, resulting in swelling forces that can impact the device's proper functioning. Ion-exchange membrane integration also requires tight sealing within a microfluidic system so that no ionic current can bypass the membrane [3]. As emphasised in the review by Slouka et al., one of the main challenges of microfluidic device fabrication is the integration of ion-exchange membranes such as NafionTM [3]. Nevertheless, there are several examples where NafionTM has successfully been integrated into microsystems.

In terms of (polymeric) microfluidic systems, the common design is that NafionTM connects microfluidic channels at a junction. A typical example is the planar electrocapture device where circular punched pieces of NafionTM were mounted at the connection between channel and reservoir over the drilled holes in an adhesive tape as described in Ref. [4]. Lee et al. used a surface patterning process where a liquid layer of NafionTM precursor was printed on a glass substrate and then enclosed with a PDMS cover [5]. Kim and Han just made a cut into a PDMS chip with a blade and filled it with NafionTM precursor [6]. Another fabrication strategy mimics the concept of capillary valves and involves filling a lithographically patterned channel junction with NafionTM precursor [7, 8]. Phan et al. described a process where a solid NafionTM strip was embedded inside a PDMS mixture and then self-sealed by curing it [9]. All these methods have in common that they are based

on rather expensive microfabrication methods and/or require precision assembling while the resulting active ion-exchange area is small. In-situ NafionTM membrane fabrication also complicates quality control of the manufacturing process.

Electrochemical microsystems such as fuel cells usually utilize a sandwich design to achieve large active ion-exchange areas. There are many examples such as a polymeric Micro-Proton-Exchange-Membrane Fuel Cell (μ PEMFC) where the Poly(methyl methacrylate) substrate and the membrane (NafionTM 1135) were bonded together using an adhesive gasket [10]. Another μ PEMFC described in Refs. [11, 12] consists of a PDMS film with microchannels that is glued with epoxy to the micropatterned membrane (NafionTM 112). A clever approach for a composite membrane was proposed by Esquivel et al. [13, 14]. The membrane consists of a PDMS thin film provided with an array of through holes, fabricated by standard soft-lithography, that are filled with NafionTM precursor. Similarly, Huh et al. used a silicon wafer patterned with an array of microfabricated pillars to form uniform holes through PDMS layers [15]. Such membranes can be reversibly and irreversibly connected to glass or PDMS but these methods require expensive cleanroom tools for the microfabrication of the silicon master. A simpler yet effective strategy is the dispersion of extractable solid particles such as salt in PDMS precursor as used to produce a macro-porous biological cell scaffold [16]. Likewise, Yuen et al. filled a mixture of PDMS pre-cursor and sugar particles in a microchannel. After curing and de-molding, the sugar particles were dissolved to create a three-dimensional interconnected micro-porous PDMS microfluidic device [17].

In this work, we propose a simple and robust method using extractable dispersed solids for cleanroom-free and low-cost fabrication of a PDMS-based ion-exchange membrane. The concept comprises the combination of NafionTM and PDMS to form a composite membrane where the cohesion of these incompatible materials is not chemical but of mechanical nature. That is, NafionTM is physically encapsulated in the rubbery irregular porous structure of the PDMS scaffold. Then, the fact that NafionTM but not PDMS swells in contact with aqueous solutions, increases the mechanical joining and the sealing between the different materials. The article is structured as follows: First, we describe the methodologies and materials. Second, we describe the process which is developed to fabricate the PDMS-NafionTM composite membrane. The penetration of the ionomer precursor into the PDMS scaffold here is important. Hence, we investigate the wettability of liquid NafionTM on

PDMS; the results are compiled in the supporting information to this article. Third, we present experimental results of the characterization of the membrane and complete the article with some concluding remarks.

II. METHODS AND MATERIALS

In this section, we specify the materials and the fabrication and characterization equipment that are used for this work.

A. Materials

Composite membrane consists of a PDMS scaffold filled with NafionTM ionomer. The ionomer is purchased as NafionTM dispersion D2021 (Ion Power, DE, USA). The concentration of 1100EW NafionTM is 20 % while the continuous phase consists of 34 % water, 44 % 1-propanol and the remainder 2 % of ethanol and mixed ethers. The PDMS precursors are purchased as Sylgard 184 Silicone Encapsulant Clear from Dow Corning (Ellsworth Adhesives, ON, Canada) and mixed in the recommended weight ratio of 10 to 1. Organic solvents with a purity of $\geq 99.5\%$ are used for different purposes including: toluene, benzene, ethyl acetate (ACP Chemicals, QC, Canada), and acetone (Fisher Scientific, ON, Canada).

A mold to form the void volume in the membrane scaffold is created using white, plain granulated sugar (Lantic Sugar Limited, ON, Canada) as a template. Void volume is filled and supported during scaffold slicing with wax (FisherfinestTM Histoplast paraffin, Fisher Scientific). Paraffin wax is removed with toluene or benzene. Conductivity measurements of the membranes are performed in DI water electrolyte solutions made with sodium chloride NaCl (BioXtra $\geq 99.5\%$, Sigma Aldrich, ON, Canada) and with sulfuric acid H₂SO₄ (98 % reagent grade, Fisher Scientific).

B. Instruments

PDMS films for scaffold integration are made with a Laurell WS-650-23 spin coater (Laurell Technologies, PA, USA). Curing of PDMS is performed at higher temperature using a Corning PC-420D hot plate (Corning, NY, USA) or a Cole Parmer StableTemp

Programmable Oven (Cole Parmer, IL, USA). Cleaning and sample preparations are completed with the assistance of a Fisherbrand FB11203 ultrasonic cleaner (Fisher Scientific, PA, USA). Microtome slices of the PDMS scaffold are taken with the use of a Leica RM2255 Fully Automated Rotary Microtome (Leica Biosystems, Germany). Corona treatment is applied to PDMS (scaffold) to change its wettability in contact with NafionTM dispersion utilizing a BD-20 Corona Producer (Electro-Technic Products Inc, IL, USA). Microscopy is done with a Micromaster Premier Microscope (Fisher Scientific, PA, USA); Pixel analysis of microscopic images is performed with the open source software ImageJ (U. S. National Institutes of Health, Md, USA). The impedance of the composite membrane is measured with an Autolab potentiostat/galvanostat PGSTAT302N (Metrohm Autolab B.V., The Netherlands). All weight measurements are performed with a semi-micro balance CPA225D (Sartorius, Germany). All conductivity and pH measurements are performed by a SevenMulti Multiparameter pH and conductivity probe (Mettler Toledo, Switzerland).

FIG. 1. Fabrication process scheme of the Nafion™-PDMS composite membrane.

III. MEMBRANE FABRICATION

The composite membranes are made through an in-house fabrication process that does not require complicated microfabrication or cleanroom techniques. The fabrication of the composite membrane can be categorized in the following main steps as indicated in the process flow chart illustrated in Fig. 1.

The first fabrication step, depicted in Fig. 1a), is concerned with the preparation of the scaffold mold made from a sacrificial material. The mold's function is to create the porous structure in the PDMS that is subsequently filled with the ionomer. We use conventional sugar as a sacrificial mold template that is sized with screens of 45 to 150 μm or 150 to 250 μm sieve size. The sized sugar is spread to cover a large glass petri dish and placed to absorb moisture on a stand in a desiccator with saturated humidity. After 2 hours, the sugar is lightly packed into a 50 mL beaker which is placed in an oven at 60 $^{\circ}\text{C}$ for at least 2 hours to dry, forming a larger sugar block as sketched in Fig. 1a). The sugar block is then carved with a scalpel to a desired size. We use a cube that is approximately 1 cm $\times$ 1 cm $\times$ 1 cm in size which serves as the mold in the production step. After several attempts,

we learn that it is beneficial to use a granular size range which is close to the thickness of the final PDMS scaffold. If the size range is smaller than the scaffold size, it is difficult for the solvent to penetrate into the small pores and to dissolve the sugar granules in order to create void volume for the ionomer.

The next fabrication step fills and encompasses the sugar cube mold with PDMS. First, a container of approximately $2.5\text{ cm} \times 2.5\text{ cm} \times 3\text{ cm}$ in size is made from cardboard and coated with aluminum foil. The sugar cube is placed inside and the PDMS precursor is poured into the container. The container is placed in a desiccator which is evacuated and released to ambient pressure 2 to 3 times so that the liquid PDMS precursor penetrates uniformly into the pores of the sugar cube. After curing at room temperature for one day, a PDMS-sugar cube is created as depicted in Fig. 1b). As an alternative to this step, we also examine an approach where a PDMS thin film with a larger cavity is produced on a glass substrate. The cavity is filled with particles and liquid PDMS precursor is subsequently spread on the particles and cured. In case of very thin PDMS films, the removal from the glass substrate often ruptured the PDMS. In case of rather thick PDMS films, many template particles could not completely be dissolved as lots of particles are entirely covered by PDMS. Moreover, the control of a desired thickness is also difficult to achieve and filling with PDMS precursor can impact the particle arrangement as well. Based on the obtained results, we concluded that this thin film approach is less feasible than the cube method described above.

Next, the top and bottom PDMS layers of the PDMS-sugar cube are cut off with a scalpel to grant access to the sugar cube. The whole cube is placed in a $60\text{ }^{\circ}\text{C}$ warm ultrasonic water bath for at least 3 hours to remove the sugar, changing the water at least every hour. The result is a PDMS cube with an internal porous structure of the negative geometry of the mold as sketched in Fig. 1c). Afterwards, the cube is sliced to a 0.5 cm thick scaffold piece and dried overnight.

In the next step, the 0.5 cm thick piece is prepared for microtome slicing by filling with paraffin wax to support the scaffold structure. Scaffolds with varying thicknesses are prepared by microtome slicing. However, very thin PDMS scaffolds are too delicate since the rubbery texture is pulled by the metal blade of the microtome and ruptures. We find that a microtome slice of around $200\text{ }\mu\text{m}$ thickness maintains the structural integrity of the PDMS scaffold. Considerable downsizing of the scaffold (membrane) area is now also possible by

cutting, perforating or comparable methods. After removing the paraffin wax with toluene, the final PDMS scaffold is created as sketched in Fig. 1d) .

Next, the scaffold is embedded in a larger PDMS frame, as represented in Fig. 1e), for the sake of better handling and to facilitate the integration into the measurement cell as illustrated in Fig. 3. Here, a larger circular film of PDMS is created with an opening that matches the scaffold area. After applying corona treatment to contacting surfaces for approximately one minute, the two parts are bonded together irreversibly. In order to improve the filling of void volume with NafionTM, corona treatment is then applied for one minute on the actual scaffold area of the PDMS (cf. supporting information). The NafionTM dispersion is applied with a pipette until the scaffold void volume is filled. After 10 minutes in the fume hood, the NafionTM dispersion is dried partially and shrunk in volume. This application process is repeated 4 to 6 times until the scaffold is completely filled with NafionTM. As the NafionTM dispersion is drying, it begins to deform the PDMS scaffold which is unfavorable for the subsequent device integration. Hence, the impregnated scaffold is flattened by pressing between two teflonTM-coated metal plates in an oven heated to 100 °C. Finally, the so produced NafionTM-PDMS composite membrane can be incorporated in a micro device. Several designs are feasible, depending on the application. In Fig. 1f), we exemplarily sketch the membrane sandwiched between two microfluidic (PDMS or glass) substrates having a meandering and a straight channel. At locations, where channel, membrane and channel overlap, a transfer of small cations is enabled. This can be used for example to locally manipulate conductivity and/or pH value of the liquids or to permit local access for sensing or controlling of electrical signals. If the intention is to use the membrane in an electrochemical micro reactor, the design can be changed such that large areas of the channels are connected by the composite membrane.

FIG. 2. a) PDMS scaffold sliced to a thickness of $200\ \mu\text{m}$; b) Microscope image showing the irregular scaffold structure; c) processed image to infer scaffold porosity.

IV. MEMBRANE CHARACTERIZATION

The effectiveness of the manufactured composite PDMS-NafionTM membrane needs to be examined. Two parameters are measured: i) the porosity of the membrane scaffold and ii) the resistance (conductivity) of the ion-exchange membrane for two cation species and various concentrations.

A. Scaffold Porosity

The porosity of the membrane scaffold is an important parameter since it represents the void volume which can be filled with ionomer. Consequently, the higher the scaffold porosity, the higher the conductivity of the composite membrane. We use two different methods to estimate the scaffold porosity. One is a (microscopic) visual method and the other relies on a (macroscopic) weight difference. The measurements were conducted with three different PDMS scaffolds and also on five different regions of each scaffold in the case of the microscopic method.

Figure 2a) shows a PDMS scaffold, manufactured as described above, after microtome slicing and paraffin wax removal. A $10\times$ magnification of the scaffold is shown in part b) and gives insight into the typical irregular pore structure created by the sugar template method. This irregular geometry should be favorable for the physical entrapment of the ionomer, especially with respect to the volume change of the ionomer in contact with aqueous

solutions. We infer the scaffold porosity by identification of the void area of the membrane and subsequent integration of the corresponding pixel area using the software imageJ. In detail, Fig. 2c) shows the scaffold area depicted in part b) after image processing in order to distinguish between void and PDMS area. The integration of the void area pixels gives a porosity of around 31.7%. Since the magnified area that we evaluate is only a part of the entire scaffold, the image processing and pixel integration is repeated at five arbitrary locations. Evaluation of these data results in a scaffold porosity of $29.9\% \pm 3.6\%$. It is understood that using a two-dimensional image to infer the porosity, that is per definition a three-dimensional parameter, can have a limited accuracy. However, the thickness of the porous PDMS slices is similar to the size of the granules. Hence, we can claim that the pore structure does not considerably change over the scaffold thickness and the (planar) picture gives a good approximation of the volume. To verify the image processing approach, the porosity is additionally determined by measuring the weight of the membrane before and after the stabilizing paraffin wax is removed post microtome slicing. With a wax density of 0.9 g/cm^3 , the weight difference method gives a porosity of 25.6%. This value is only slightly outside of the statistical variation of the other imaging method and proves its suitability.

Generally, there is only a limited control of the PDMS scaffold porosity fabricated in this work. This is understood since the sugar mold (template) is made from a packed bed of a natural granular material. On the one hand, the selection of particles from the raw material is achieved by sieves. This gives hardly control over the particle shape and results in a certain size range. On the other hand, during the production of the mold, the sugar granules orient randomly in a 3D structure. The analysis of all manufactured membranes in this work gives a porosity of around $25 \pm 7\%$ while the size of the (irregular) pore openings depends only partly on the sieves used in the production process. That is, $150\mu\text{m}$ to $250\mu\text{m}$ for rather spherical particles but much larger but narrow non-spherical particles can slip through the sieves. Additionally, due to the adsorption of moisture during the consolidation process of the sugar mold, the granules partially dissolve and connect on their edges, vertices and junctions with their neighbors. All these effects limit the detailed reproducibility of the scaffold and result in a wider and irregular variation of the pore structures.

FIG. 3. a) Schematic of the composite membrane measurement cell and b) corresponding electrical equivalent circuit.

B. Membrane Conductivity

We also test the resistance (conductivity) of the final composite membrane which depends on ion species and its concentration in the surrounding aqueous electrolyte. Since NafionTM is only permeable for small cations, we choose aqueous solutions of sodium chloride and sulfuric acid to test the membrane conductivity for sodium (Na^+) and protons (H^+), respectively.

In detail, we use electrochemical impedance spectroscopy (EIS) to measure the impedance (ohmic resistance) of the composite membrane. Figure 3a) gives a sketch of the configuration of the measurement cell. The cell consists of the membrane which is sandwiched between two glass elbows filled with the test solution. A platinum (Pt) wire electrode is immersed in either glass elbow, both of which are connected to a potentiostat–frequency generator/analyzer. We choose Pt to ensure stability of the electrodes in both the acid and the saline electrolyte solution. The potentiostat induces an alternating voltage $\tilde{V}$ between the electrodes. The resulting alternating current $\tilde{I}$ is measured while the frequency of the voltage is varied

FIG. 4. Nyquist plot measured for different NaCl concentrations in the test cell with (open symbols) and without (solid symbols) composite membrane installed.

over a desired range. The ratio of the alternating voltage to the alternating current is the complex impedance $\tilde{Z} = \tilde{V}/\tilde{I}$, a measure for the resistance of an electrical setup to resist the passage of a current. Figure 3b) shows the electrical equivalent circuit (EEC), representing the elements of the measurement cell, which is required for data interpretation. The composite membrane is modelled as a linear ohmic resistor R_m . The behavior of the electrodes requires a representation with a nonlinear element, we choose a constant phase element Q_e . Since the concentrations of the tested aqueous electrolytes are rather low, the dielectric characteristics of the liquids have to be accounted for. That is, the liquid in the measurement cell is modelled as a parallel arrangement of a linear (ionic) resistance R_{el} and a nonlinear (dielectric) capacitor C_{el} . The overall measured impedance data can be plotted in the form of a Nyquist diagram. Here, the real part $Re(\tilde{Z})$ is plotted on the x-axis and the negative imaginary part $-Im(\tilde{Z})$ on the y-axis. This allows to fit the data to the EEC and to identify single or combinations of the circuit elements. The fundamental idea behind our measurements is to infer the impedance of the test cell with and without the membrane installed; differences can then be assigned to the membrane.

Figure 4 shows impedance spectra for measurements in 0.01, 0.025, 0.05 and 0.2 M NaCl in water with (open symbols) and without membrane (solid symbols) installed in the mea-

surement cell. We observe that the plots measured at different concentrations have similar shapes which can be interpreted based on the corresponding EEC. At the right hand side of a Nyquist plot, there are the impedances at lower frequencies. Here, these values form a rather straight line that is part of a very large semicircle induced by the electrical double layer of the electrodes. We find only a fraction of this semicircle because there are no electrochemical reactions at the electrodes due to the low alternating voltage. At the left hand side, the smaller, almost complete, semicircle represents the electrical phenomena of liquid and, if applicable, membrane in the measurement cell. The radius of this semicircle is small compared to the other semicircle since the liquid (bulk) capacitance C_{el} is much smaller than the electrode double layer capacitance. If there were no bulk capacitance, the large semicircle would intersect the x-axis. Then, the corresponding sole real value would correspond to the sum of all ohmic resistances in the test cell; that is, $2R_{el} + R_m$ and $2R_{el}$ for the test cell with and without membrane, respectively.

If we compare the Nyquist plots measured at the concentration of 0.01 M NaCl with and without membrane installed, we observe that the semicircle joint location is shifted on the real axis. The difference is assigned to the ohmic resistance of the membrane. When we increase the electrolyte concentration, two characteristics are observed: i) The circles are shifted towards lower real values due to the higher conductivities of the liquids. ii) The radius of the smaller semicircles decreases since the dielectric nature of the liquid diminishes.

All Nyquist plots are fitted to the EEC, using the NOVA software from Autolab, in order to extract the resistance of the membrane. Figure 5a) gives the relation between membrane resistance and concentration of aqueous NaCl electrolyte. The membrane immersed in the lowest NaCl concentration of 0.01 M has a resistance of around $200\ \Omega$. We see that the resistance decreases if the electrolyte concentration increases. At the highest concentration of 0.2 M, the resistance is around $2.8\ \Omega$. Figure 5b) shows the membrane resistance vs. the H_2SO_4 concentration in the aqueous solution. We find the same qualitative behavior as for the NaCl solutions. That is, the membrane resistance decreases when the electrolyte concentration increases. However, we observe that the membrane resistance immersed in a H_2SO_4 solution is significantly lower than in an equivalent NaCl solution. We can compute the specific conductivity of the electrolyte in our composite membrane based on the correlation $\sigma \approx t\tau^2/(AR_m\phi)$. Here, t is the thickness of the membrane, τ is the tortuosity, A

FIG. 5. Membrane resistance in contact with aqueous a) NaCl and b) H_2SO_4 electrolyte of various concentrations. Connection between data point is just for a better visualization.

is the base area of the membrane (scaffold), and ϕ is the porosity. Assuming a reasonable tortuosity of $\tau = 1.5$, the specific membrane conductivity for the lowest and highest concentration of NaCl corresponds to around 0.002 S/cm and 0.1 S/cm, respectively. In case of the membrane being immersed in sulfuric acid, we estimate the lowest conductivity to be around 0.01 S/cm and the highest conductivity to be around 0.09 S/cm. The conductivities of a commercial NafionTM 117 foil in pure water, 0.1 M H_2SO_4 and 0.1 M NaCl are reported to be 0.08 S/cm, 0.0875 S/cm and 0.011 S/cm, respectively [18, 19]. We realize that the conductivities of the composite membrane in very low electrolyte concentrations are lower than that of a commercial membrane in water. However, a similar performance is achieved when

the membrane is immersed in electrolytes having higher concentrations. Possible reasons for the deviations at very low concentrations could be the fundamental differences in the materials. That is, we compare values of a plain industrially-casted NafionTM foil to an entity with complex 3D structure which has been made layer by layer. Further differences are the different pretreatments of the NafionTM film and the composite membrane. Industrial NafionTM membranes are usually cleaned and activated before utilization with H₂O₂ and concentrated H₂SO₄ solutions at elevated temperatures. We abstain from this harsh treatment due to the delicate character of our composite membranes. Nevertheless, the fact that the composite membrane at higher electrolyte concentrations achieves the performance of a commercial NafionTM membrane is a sign for self-activation.

V. CONCLUDING REMARKS

In this work, we develop a fabrication method for an ion-exchange composite membrane, consisting of PDMS and the ionomer NafionTM. The membrane fabrication strategy is to consolidate sugar granules to create a mold in a cube shape. Liquid PDMS precursor is then poured into the mold void volume. After curing of the PDMS precursor, the sugar granules are dissolved, resulting in a void volume with an irregular pore structure. To obtain the membrane scaffold, the PDMS is sliced with a microtome. The PDMS scaffold is repeatedly filled and cured with NafionTM dispersion. Finally, to maintain the shape of the composite membrane, it is pressed at elevated temperatures. The irregular void structure of the PDMS scaffold physically entraps the ionomer. In contact with aqueous solutions (microfluidics) or humid gases (fuel cells), the combination of ionomer swelling and rubbery PDMS scaffold secures the physical entrapment.

Through electrochemical impedance spectroscopy, the conductivity of the composite membrane is tested in multiple concentrations of aqueous H₂SO₄ and NaCl solutions. We measure specific conductivities similar to those of a commercial NafionTM membrane for the upper electrolyte concentrations tested in this work, which proves the concept of the novel fabrication approach.

The present strategy is cleanroom-free, cost-effective and the fabricated composite membrane allows for simple reversible or irreversible bonding via corona treatment to a larger PDMS or glass/silicon-based microsystem for ion-exchange capability. The membrane re-

quires a sandwich-like design of the microsystem, where it is stacked between adjacent layers containing the structures to be ionically connected. Hence, the application of our composite membranes can rather be found in a micro electrochemical system, such as a miniaturized fuel cell, battery or an electrolyzer, than in an analytical micro device where only localized ion transfer capacity is required. Here, the good ion conductivity contributes to an efficient performance while the film structure (thickness of 200 μm) constructed from the porous PDMS scaffold allows its secure integration onto silicon-based substrates. In contrast, a commercial NafionTM film can only be glued, with the risk of severe impact of the membrane functionality, or mechanically integrated by using additional external casings which makes a bulky rather than a micro device.

The fabrication of membranes with an area below a few mm^2 is rather difficult with the present approach. However, the membrane can be used to achieve both large and localized ion-exchange if the design of the adjacent structures is adapted accordingly. It is necessary to note that this membrane cannot transport the same quantity of small cations at the same rate as a similar-in-area film of NafionTM because of the PDMS scaffold's limited porosity. Also, a precise control of the scaffold porosity is difficult due to the nature of the packed bed approach used to manufacture the sugar template from a raw natural material.

It should be possible to improve the present production process for the composite membrane by varying certain key points in the fabrication. For example, different sacrificial materials can create PDMS scaffolds with different structures. Or contrary to the current fabrication method, it may be possible to create solid NafionTM plugs that are embedded inside of liquid PDMS which is then cured. Opening the surface with slicing might provide a porous network of NafionTM consistently through the PDMS film. Another alternative is to design PDMS pores for enhanced NafionTM entrapment using microfabrication methods similar to those in Ref. [13]. Here, layering of thin PDMS layers with regular holes of different diameter, created by multiple lithography processes, has the potential to create 3D pore designs that can effectively hold NafionTM. Finally, this method of physical entrapment in a PDMS scaffold can be considered as a general fabrication strategy and could be expanded to other functional polymers.

Supplemental Material

Supplemental material on the wettability of NafionTM dispersion, DI water and 1-propanol

on PDMS surfaces is available online from the publisher.

Acknowledgments

The authors gratefully acknowledge the financial support from DuPont Canada, the Natural Sciences and Engineering Research Council of Canada (NSERC). We thank Oliver Jones of the Queen's Laboratory for Molecular Pathology for the microtome slicing.

-
- [1] Xueye Chen, Jienan Shen, Zengliang Hu, and Xuyao Huo. Manufacturing methods and applications of membranes in microfluidics. *Biomed. Microdevices*, 18(6):104, December 2016.
- [2] Kenneth A. Mauritz and Robert B. Moore. State of understanding of nafion. *Chem. Soc. Rev.*, 104(10):4535–4586, oct 2004.
- [3] Zdenek Slouka, Satyajyoti Senapati, and Hsueh-Chia Chang. Microfluidic Systems with Ion-Selective Membranes. *Annu. Rev. Anal. Chem.*, 7(1):317–335, 2014.
- [4] Mats Jönsson and Ulf Lindberg. A planar polymer microfluidic electrocapture device for bead immobilization. *J. Micromech. Microeng.*, 16(10):2116, aug 2006.
- [5] Jeong Hoon Lee, Yong-Ak Song, and Jongyoon Han. Multiplexed proteomic sample preconcentration device using surface-patterned ion-selective membrane. *Lab. Chip*, 8(4):596–601, 2008.
- [6] Sung Jae Kim and Jongyoon Han. Self-sealed vertical polymeric nanoporous-junctions for high-throughput nanofluidic applications. *Anal. Chem.*, 80(9):3507–3511, 2008.
- [7] Vincent Liu, Yong-Ak Song, and Jongyoon Han. Capillary-valve-based fabrication of ion-selective membrane junction for electrokinetic sample preconcentration in PDMS chip. *Lab. Chip*, 10(11):1485–1490, 2010.
- [8] Chun-Hao Chang and Ruey-Jen Yang. Enhanced sample preconcentration in microfluidic chip using graphene oxideNafion membrane. *Microfluid. Nanofluid.*, 20(12):168, dec 2016.
- [9] Dinh-Tuan Phan, Chun Yang, and Nam-Trung Nguyen. Fabrication of nanoporous junctions using off-the-shelf Nafion membrane. *J. Micromech. Microeng.*, 25(11):115019, 2015.
- [10] Siew Hwa Chan, Nam-Trung Nguyen, Zetao Xia, and Zhigang Wu. Development of a polymeric micro fuel cell containing laser-micromachined flow channels. *J. Micromech. Microeng.*, 15(1): 231, 2004.
- [11] Keyur Shah, W. C. Shin, and R. S. Besser. Novel microfabrication approaches for directly patterning PEM fuel cell membranes. *J. Power Sources*, 123(2):172–181, 2003.
- [12] Keyur Shah, W. C. Shin, and R. S. Besser. A PDMS micro proton exchange membrane fuel cell by conventional and non-conventional microfabrication techniques. *Sens. Actuators, B*, 97(2):157–167, 2004.
- [13] J. P. Esquivel, N. Sabaté, A. Tarancón, N. Torres-Herrero, D. Dávila, J. Santander, I. Gràcia,

- and C. Cané. Hybrid polymer electrolyte membrane for silicon-based micro fuel cells integration. *J. Micromech. Microeng.*, 19(6):065006, may 2009.
- [14] N. Sabaté, J. P. Esquivel, J. Santander, J. G. Hauer, R. W. Verjullo, I. Gràcia, M. Salleras, C. Calaza, E. Figueras, C. Cané, and L. Fonseca. New approach for batch microfabrication of silicon-based micro fuel cells. *Microsyst. Technol.*, 20(2):341–348, mar 2014.
- [15] Dongeun Huh, Hyun Jung Kim, Jacob P Fraser, Daniel E Shea, Mohammed Khan, Anthony Bahinski, Geraldine A Hamilton, and Donald E Ingber. Microfabrication of human organs-on-chips. *Nat. Protoc.*, 8(11):2135–2157, 2013.
- [16] Eileen Pedraza, Ann-Christina Brady, Christopher A Fraker, R Damaris Molano, Steven Sukert, Dora M Berman, Norma S Kenyon, Antonello Pileggi, Camillo Ricordi, and Cherie L Stabler. Macroporous three-dimensional pdms scaffolds for extrahepatic islet transplantation. *Cell Transplant.*, 22(7):1123–1135, 2013.
- [17] Po Ki Yuen, Hui Su, Vasiliy N Goral, and Katherine A Fink. Three-dimensional interconnected microporous poly (dimethylsiloxane) microfluidic devices. *Lab Chip*, 11(8):1541–1544, 2011.
- [18] Bryan S. Pivovar, William H. Smyrl, and Edward L. Cussler. Electro-osmosis in Nafion 117, polystyrene sulfonic acid, and polybenzimidazole. *J. Electrochem. Soc.*, 152(1):A53–A60, 2005.
- [19] Albert Lehmani, Pierre Turq, Michelle Périé, Jacques Périé, and Jean-Pierre Simonin. Ion transport in Nafion 117 membrane. *J. Electroanal. Chem.*, 428(1-2):81–89, may 1997.