

Supporting Information

Patterning Catalyst Layers with Microscale Features by Soft Lithography Techniques for Proton Exchange Membrane Fuel Cells

Michael T. Y. Paul¹, Dongho Kim¹, Madhu S. Saha²,
Juergen Stumper², and Byron D. Gates^{1,*}

1) Department of Chemistry and 4D LABS, Simon Fraser University, 8888 University Drive, Burnaby, BC V5A 1S6, Canada

2) Automotive Fuel Cell Cooperation, 9000 Glenlyon Pkwy, Burnaby, BC V5J 5J8, Canada

*Corresponding Author

e-mail: bgates@sfu.ca

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Methods and Materials

In this study, templates prepared from an elastomer were used to create patterned catalyst layers with arrays of hexagonally arranged microscale features for use in proton exchange membrane fuel cells (PEMFCs). These features consist of either arrays of cylindrical discs, or perforations (holes) in an otherwise continuous film containing a mixture of Pt and C nanoparticles that make up the cathode catalyst layers (CCLs) coated onto Nafion[®] 211 membranes. The patterned CCLs were characterized to verify their physical dimensions and the densities of their Pt loadings. These samples were further incorporated into membrane electrode assemblies (MEAs) with a 5 cm² active area for determining their performance in a proton exchange membrane fuel cell (PEMFC).

Preparation of Elastomeric Templates

In this study, elastomeric templates were used for the microcontact printing (μ CP) and microtransfer molding (μ TM) of catalyst materials onto Nafion[®] membranes. These elastomeric templates were prepared by curing the elastomeric pre-polymer materials over a series of masters. These masters consisted of photolithographically patterned SU-8 (SU-8 2025, MicroChem, Germany) supported on the polished surfaces of silicon (100) wafers (International Wafer Service, Inc., USA). Photomasks of chromium patterned on borosilicate glass, which were used in the photolithographic processes, were purchased from 4D LABS at Simon Fraser University (www.4dlabs.ca). Photolithographic patterning of the SU-8 was performed according to the manufacturer's protocols (<http://www.microchem.com/Prod-SU82000.htm>; as of July, 2019). The photolithographically defined features consisted of 50- μ m diameter cylindrical pillars or recesses arranged in a hexagonal pattern with a minimum edge-to-edge feature spacing of 25 μ m. The SU-8 pillars and recesses were controlled to a thickness of 15, 20, or 25 μ m. The general photolithographic process to prepare the masters is shown in **Figure S1**.

To create the elastomeric templates used for both patterning and transferring the CCLs, poly(dimethylsiloxane) (PDMS; Dow Corning Sylgard[®] 160) were cast and cured against the patterned SU-8 masters. These hard templates were first treated with a release layer (Alfa Aesar, 1H, 1H, 2H, 2H-perfluorooctyldimethylchlorosilane, 95%; referred to as perfluoro-silane) to minimize adhesion of the PDMS to the SU-8 masters. The procedure for preparing the release layer coating included the following steps: (i) treatment of the masters with an air-based plasma at

~30 W for 5 min; (ii) immersion of plasma treated masters in a 0.1% (v/v) solution of the perfluoro-silane prepared in toluene for 5 min; and (iii) rinsing of the silane coated masters with isopropanol and drying under a flow of filtered nitrogen gas (99.998 % N₂, Praxair, Canada). After coating the SU-8 masters with the release layer, the uncured elastomer and the curing agent were mixed according to the manufacturer's protocol and cast to a thickness of ~5 mm upon these release layer treated hard templates. These relatively thick layers of uncured elastomer were degassed in a vacuum chamber for at least 15 min. After the removal of gas bubbles from the uncured elastomer by degassing, the elastomer was cured at 70 °C for 2 h. Once cured, the elastomer was peeled from the master for use as an ink patterning template. The elastomeric template was also treated with a release layer [Sigma Aldrich; octadecyltrichlorosilane (OTS); >90%] before use in printing or molding of the PEMFC catalyst ink. The release layer assisted with the transfer of ink from the templates onto the Nafion[®] membranes. Coating of the release layer onto the elastomeric templates was performed in the same manner to the aforementioned procedures that were used for coating release layers onto the masters. Quality of the release layers on the masters and elastomeric templates were evaluated using a VCA Optima water contact angle (WCA) measurement system (AST Products, MA, United States). These measurements were performed with 1 µL droplets of deionized (DI) water (Barnstead DIAMOND[™] with an output of 18 MΩ·cm), and the average WCA values were obtained using measurements from at least 5 different regions of each substrate. An example of the WCA measurements performed on the elastomeric stamps is presented in **Figure S2**.

Catalyst Ink Preparation

To prepare the microscale patterned CCLs, catalyst ink was coated onto the PDMS templates with microscale patterned features, and the ink subsequently transferred onto Nafion[®] 211 membranes. The catalyst ink consisted of a mixture of Pt and C nanoparticles (50 wt % Pt content, TEC10E50E, Tanaka Kikinzoku Kogyo, Japan) that was blended with a 30 wt % loading of ionomer (Nafion[®] DE2020, Dupont, USA). This catalyst formulation was dispersed in a 3:1 (v/v) solution of 2-propanol (Anachemia, Canada, ACS grade) and DI water prepared in different overall volumes to achieve different solid contents of the ink solution as needed for the various coating applications. The ink suspensions were mixed using ultra-sonication applied for intervals of 1 s "on" and 3 s "off" for a total duration of 1 h (and a total of 15 min of sonication during the

collective "on" time) using a probe sonicator (Fisher Scientific, USA, Sonic Dismembrator 500) with a 12-mm diameter probe, operating at 40% of its maximum power.

Ink Coating Procedures

For preparing the catalyst coated membranes (CCMs), the CCLs were transferred onto the Nafion[®] membranes by microtransfer molding or microcontact printing techniques through the use of the elastomeric templates. The elastomeric templates were coated with catalyst materials using techniques that are described in the following sections. After transfer of the CCLs onto the Nafion[®] 211 membranes, the Pt loadings for each of the samples were verified by X-ray fluorescence (XRF) techniques using a Niton XL3t system (Thermo Scientific, United States) operating at 40 kV. The XRF system was calibrated with a series of standard Pt samples with loadings in the range of 0.01 to 0.40 mg_{Pt}/cm² as prepared by MICROMATTER (Surrey, BC, Canada) for the quantification of the Pt loadings.

For microtransfer molding of the CCLs, multiple coatings of catalyst ink with 10 % (wt/wt) solids content were deposited onto the elastomeric templates using a Mayer-bar coater. The elastomeric templates were first coated with the ink using a Mayer-bar process and the ink was dried at 50 °C on a heated stage for 10 min. Once dried, a piece of 3M[™] Magic tape[™], which was prepared to cover the entire area of the elastomeric template, was placed on top of the template. The tape was smoothed over the surfaces of the elastomeric template with a very light pressure, and immediately peeled away from the template with a gentle, steady force. This process removed the "skin" layer of catalyst ink covering the template. Catalyst ink was left within the recessed regions of the templates. These operations were all performed by hand, but could be automated in the future. The CCLs created by this molding process were determined by XRF techniques to have a Pt loading of 0.15 ± 0.01 mg_{Pt}/cm².

For microcontact printing of the CCLs, multiple coatings of a catalyst ink solution with a 2 % (wt/wt) solids content (described in the previous section) were deposited onto the elastomeric templates using an ultrasonic spray coater (ExactaCoat, Sono-Tek, USA). The elastomeric templates were placed on a heated vacuum stage (held at 80 °C) in the spray coating chamber for fast drying between each coat of the catalyst ink onto the elastomeric templates. An air shaping parameter of 0.6 (arbitrary unit), and a spray flow rate of 0.2 mL/min were used for coating the elastomeric templates. The spray coater was programmed with four repeating serpentine patterns

that were each perpendicular to the pattern of ink deposited in the previous layer. A dwell time of 30 s was used between the deposition of each layer of the catalyst ink to ensure an even drying of the ink and to assist in the formation of a uniform coating on top of the elastomeric templates. The CCLs prepared by μ CP with arrays of hexagonally arranged cylindrical discs and holes were determined by XRF to have Pt loadings $\sim 0.08 \pm 0.005 \text{ mg}_{\text{Pt}}/\text{cm}^2$ and $\sim 0.13 \pm 0.005 \text{ mg}_{\text{Pt}}/\text{cm}^2$, respectively.

For the comparative study of the CCLs, control CCLs were prepared with a continuous film was coated onto sheets of poly(ethylene-co-tetrafluoroethylene) (ETFE) using a Mayer-bar coater. A 20 % (wt/wt) solids content of catalyst ink was used with the Mayer-bar coater to achieve a continuous catalyst film with a Pt loading of $0.15 \pm 0.01 \text{ mg}_{\text{Pt}}/\text{cm}^2$ with a single pass of the Mayer-bar. The coated ETFE sheets were placed on a heated stage (held at 50°C) for 10 min for drying of the ink films. Continuous films with a Pt loading of $0.05 \pm 0.01 \text{ mg}_{\text{Pt}}/\text{cm}^2$ were also coated onto ETFE sheets using the same technique, but for use as the anode catalyst layers (ACLs). These ACLs were used in all of the samples for the preparation of the MEAs.

Physical Characterization of Templates and MEAs

The morphologies of the elastomeric templates and the transferred CCLs were characterized by a series of techniques that included laser profilometry, optical microscopy, and scanning electron microscopy (SEM). To verify the morphologies of the elastomeric templates, scanning laser profilometry was performed using a Keyence VK series 3D laser scanning confocal microscope. The laser based profilometry was used to determine the aspect ratios of the hexagonally arranged cylindrical pillars or recesses on the elastomeric templates. The morphologies of the transferred CCLs were verified by SEM and optical microscopy. The optical images were obtained using a Zeiss Axio M1m optical microscope operating under a bright field mode. The SEM analyses were performed using an FEI Helios SEM/ focused ion beam (FIB) dual beam system operating at 10 kV. Furthermore, SEM images of sample cross-sections were also obtained by epoxy impregnation of the MEAs, and polishing the embedded samples to reveal materials in a cross-sectional manner. The MEAs were impregnated with an EpoxyCure™ 2 (Buehler, Illinois Tool Works Inc., United States) epoxy according to the manufacturer's specifications (<https://www.buehler.ca/epoxy-mounting-systems.php>, accessed July, 2019), degassed in a vacuum chamber for 30 min, and cured overnight at room temperature. The epoxy

embedded samples were polished using an EcoMet™ 300 polisher (Buehler, Illinois Tool Works Inc., United States) with a series of Buehler brand silicon carbide sand papers (i.e., P280, P400, P800, P1200) to reveal the cross-sections of the epoxy embedded samples. The exposed surfaces were finely polished by a series of MetaDi Supreme™ and MasterPrep™ (Buehler, Illinois Tool Works Inc., United States) polishing suspensions (i.e., diameters of 9 μm, 3 μm, 1 μm, and 0.05 μm). The finely polished epoxy embedded samples were coated with a 1-nm thick layer of carbon using a Leica EM ACE600 high vacuum deposition system (Leica Microsystems, Germany) prior to imaging with the SEM system to reduce sample charging. Examples of the MEA cross-sections are presented in **Figure S3**.

Preparation of MEAs

The CCLs with either patterned or continuous (i.e., control sample) films of catalyst ink were used to prepare a series of catalyst coated membranes (CCMs). These CCMs were incorporated into MEAs and analyzed for their performance within PEMFCs. The catalyst ink coated materials (including ETFE and the elastomeric templates with microscale patterned features) were hot-bonded with a proton exchange membrane (PEM) to form the CCMs. All CCM anodes were prepared by hot-bonding a piece of catalyst ink coated ETFE (Pt loading of 0.05 mg_{Pt}/cm²) to Nafion® 211 membranes (NRE 211, DuPont, United States). To form the CCLs, either an elastomeric template coated with catalyst ink (for either the microtransfer molding or microcontact printing processes), or a continuous catalyst ink coated ETFE film (Pt loading of 0.15 mg_{Pt}/cm²) were used during the hot-bonding procedure. For microtransfer molding of the cathodes, the cathode and anodes catalyst layers were bonded to the Nafion® membrane at 20 bar of pressure and 150 °C for 5 min using a Carver® 25 ton hydraulic unit (Carver Inc., United States). For microcontact printing of the CCLs, the bonding pressure was reduced to 5 bar, while all of the other parameters were unchanged as previously described. The control samples for each of the different CCLs were prepared with identical hot-bonding conditions for an equivalent comparison between the patterned and control samples. During the hot-bonding process, a sheet of 0.05-mm thick polytetrafluoroethylene (PTFE; Teflon®) was placed on top of the layered CCM materials, followed by a sheet of 2-mm thick polyurethane rubber. This layered set of materials was used to ensure an even distribution of the bonding pressure across the CCMs. After 2 min of bonding, the layered CCM materials were immediately removed from the Teflon® sheet and cooled to room

temperature for at least 10 min. The ETFE films and elastomeric templates were gently removed by hand when the assembly was cooled sufficiently. A schematic of the CCM hot-bonding procedure is outlined in **Figure S4**. The MEAs were prepared by hot-bonding the CCM with a 5 cm² square section of a macroporous layer (MPL) coated gas diffusion layer (GDL) (Freudenberg Fuel Cell Components, Germany), and a piece of G10 gasket (Saint-Gobain Performance Plastics Corporation, NH, USA) with a square opening in the center (5 cm²). The same MPL/GDL and G10 gaskets materials were used for both the anode and cathode of the CCMs. The hot-bonding was performed with the same procedure as the one outlined for the preparation of the CCMs, with 20 bar of pressure at 150 °C for 2 min. Additional Mylar[®] gaskets (DuPont Teijin Films, UK) were used to adjust the thickness of the gaskets to induce a 25 % compression of the MPL/GDL materials when assembled into the PEMFCs. The fuel cell assembly pressure was adjusted by a manual process during a pre-assembly procedure with the use of a piece of Fuji prescale[®] pressure sensitive film (Super Low 0.5-2.5 MPa, LLW, Fujifilm, Japan).

Fuel Cell Testing of MEAs

The MEAs were analyzed within PEMFCs for comparing the performance of the patterned CCLs in contrast to the continuous CCLs. Fuel cell testing was performed using equipment provided by the Centre for Soft Materials in 4D LABS at SFU. These analyses were performed with a 50 W, Teledyne Medusa/Scribner systems (United States). Graphite plates with parallel gas flow-fields and landings were used in the assembly of the single stack fuel cells. The active cell size was 5 cm² and a maximum backpressure of 5 psi applied to both the anode and cathode. The gas flow rates for the cathodes and anodes were set to 1 L/min (maximum set point of the system). Electrochemical analyses, such as cyclic voltammetry (CV) conditioning, an assessment of the electrochemically active surface area (A_{ecsa}), and hydrogen cross-over analyses, were performed using a VersaSTAT 4 potentiostat (Princeton Applied Research, USA) operating in a two electrode configuration. The CV conditioning and A_{ecsa} determination were performed at a scan rate of 100 mV/s with a sweep range from 0 to 1.2 V. The hydrogen cross-over was analysed by linear scan voltammetry (LSV) performed over the range of 0.05 to 0.6 V at a scan rate of 5 mV/s (e.g., **Figure S5**). These electrochemical experiments were performed while the fuel cell was held at 80 °C with 100 % relative humidity (RH), and with H₂ (g) (99.95 %, Praxair Canada) and N₂ (g) (99.999 %, Praxair Canada) supplied to the anode and cathode, respectively. The microtransfer molded CCLs

were analyzed under conditions that included conditions similar to the United States Department of Energy (US DOE) standard fuel cell test conditions (e.g., a cell temperature of 80 °C, at 100 % RH, 5 psi of backpressure, and with H₂ (g) and compressed air supplied to the anode and cathode, respectively), "start-up" conditions (e.g., a cell temperature of 65 °C, at 70 % RH, 5 psi of backpressure, and with H₂ (g) and compressed air supplied to the anode and cathode, respectively), and "hot" conditions (e.g., a cell temperature of 95 °C, at 100 % RH, 5 psi of backpressure, and with H₂ (g) and compressed air supplied to the anode and cathode, respectively).¹ The microtransfer molded CCLs were polarized under potentiostatic conditions at a series of potentials that included an open circuit voltage (OCV), 0.8, 0.6, 0.4, 0.2, and 0.1 V with a 10 min dwell time at each set-point voltage.

The microcontact printed CCLs were also analyzed at a cell temperature of 80 °C, 100 % RH, without backpressure, and with H₂ (g) and O₂ (g) supplied to the anode and cathode, respectively. The microcontact printed CCLs were conditioned by LSV from 0.95 to 0.1 V, with the voltage stepped in 50 mV increments, and a 60 s dwell time per voltage step. A total of 12 LSV experiments were performed to condition the MEAs while aiming to achieve a deviation in fuel cell current densities of less than 0.5 mA/cm² for 3 consecutive LSV scans. A gradual increase and stabilization of the peak currents produced by the fuel cell can be observed in **Figure S6**. After the LSV plots reached stabilization, 3 additional scans were performed, averaged, and analyzed to assess the fuel cell performance for each of the MEAs (e.g., **Figure S6**). The microcontact printed samples and the microtransfer molded CCLs were each analyzed through the preparation of triplicate samples.

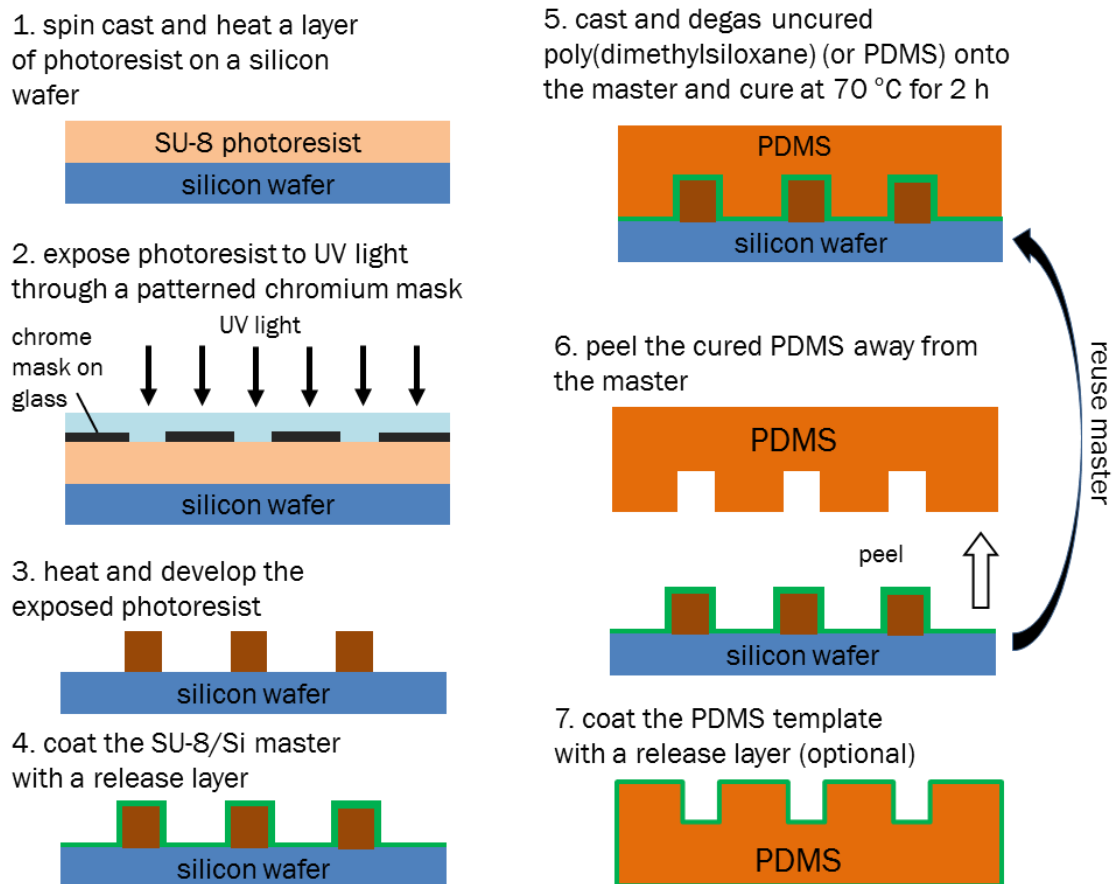


Figure S1. Schematic illustration of the preparation of the hard masters, and their use as templates to prepare the elastomeric stamps or molds.

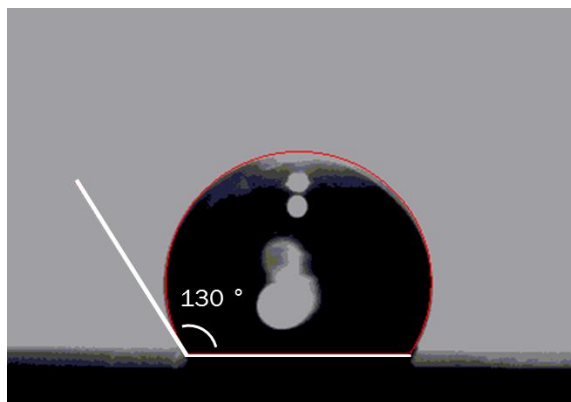


Figure S2. Optical image of a 1 μL droplet of deionized (DI) water on an octadecyltrichlorosilane (OTS) coated elastomeric template with a hexagonally arranged array of cylindrical recesses used for the microtransfer molding (μTM) of cathode catalyst layers (CCLs).

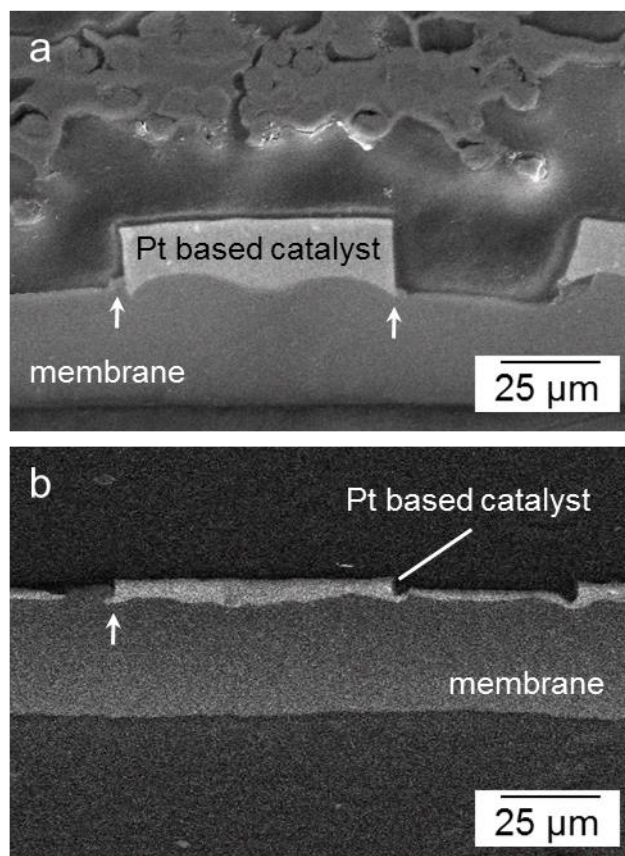


Figure S3. Cross-sections of membrane electrodes assemblies (MEAs) with patterned CCLs (i.e., containing the ink patterned with an array of cylindrical holes) after PEMFC testing were imaged by scanning electron microscopy (SEM). These cross-sections were prepared after embedding the sample in epoxy. Imaging was performed by SEM techniques with the system operated at 15 kV using a backscattered electron detector. (a) An example of a catalyst ink transferred by μ TM to a Nafion[®] membrane after removal of the catalyst skin layer. Note that the edges of the patterned ink exhibited relatively sharp features (see regions indicated by the white arrows), which was indicative of deformation to the Nafion[®] membrane. This deformation resulted from the molding process. (b) An example of a catalyst ink transferred by μ TM onto a Nafion[®] membrane without the removal of a 3- μ m thick catalyst skin layer that was present on the elastomeric template.

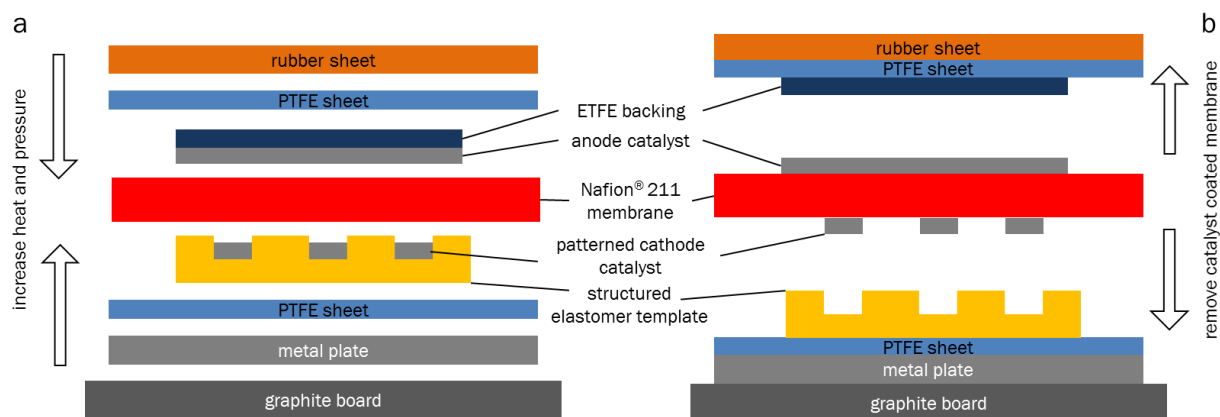


Figure S4. Schematic illustration of the hot-bonding process for preparing the catalyst coated membranes (CCMs): (a) the assembly and hot-bonding of various components of the CCMs; and (b) the bonded CCMs after removal of the backing materials and other components of the support. PDMS: poly(dimethylsiloxane); ETFE: poly(ethylene-co-tetrafluoroethylene); and PTFE: polytetrafluoroethylene.

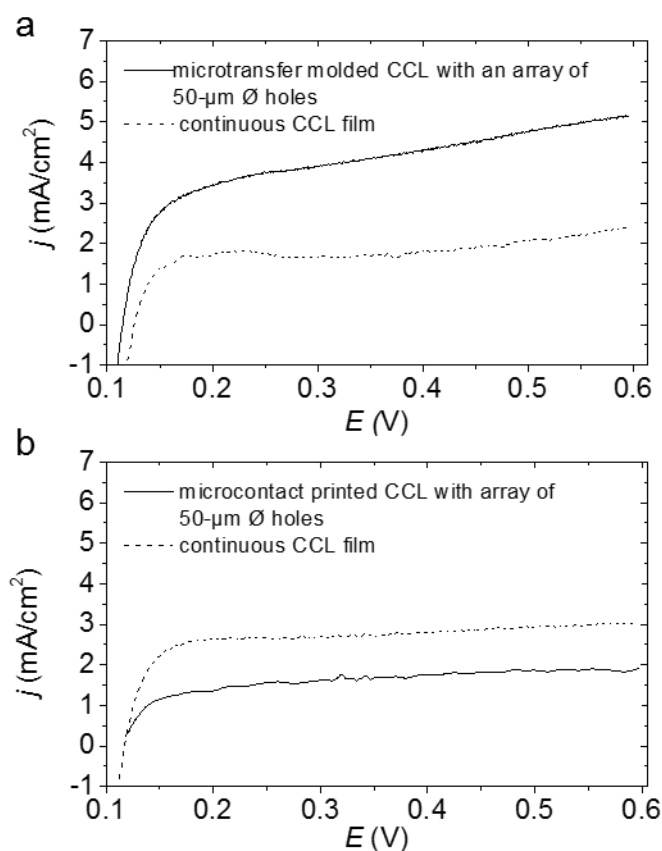


Figure S5. Hydrogen cross-over currents for MEAs prepared from (a) microtransfer molded CCLs and (b) microcontact printed CCLs in comparison to control samples with continuous, unpatterned CCLs. These hydrogen cross-over currents were obtained at a cell temperature of 80 °C, 100 % RH, and with H₂ (g) and N₂ (g) supplied to the anode and cathode, respectively. The MEAs in (a) were tested under 5 psi of gas pressure to the anode and the cathode. The MEAs in (b) were unpressurized during this test.

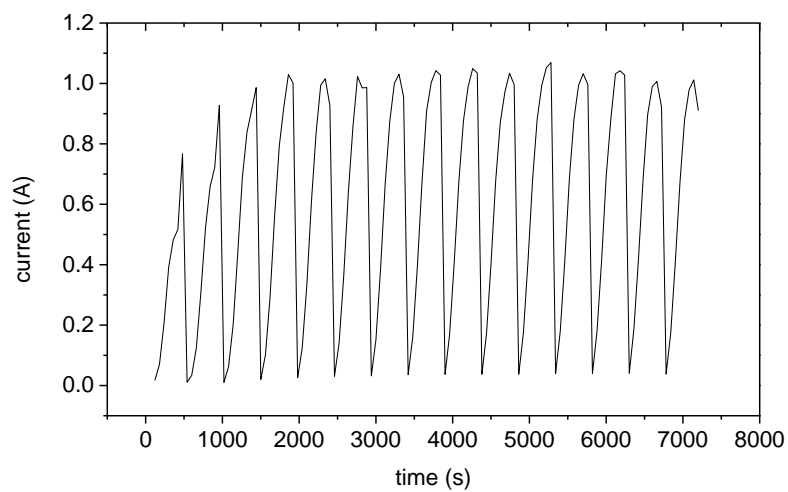


Figure S6. A series of fuel cell polarization profiles, from 0.95 V to 0.1 V, which were used to condition the MEAs. The profiles demonstrated here were from a reference sample ($0.20 \text{ mg}_{\text{Pt}}/\text{cm}^2$), which was conditioned at 80°C , 100 % RH, and with H_2 (g) and O_2 (g) supplied at 1 L/min to the anode and cathode, respectively.

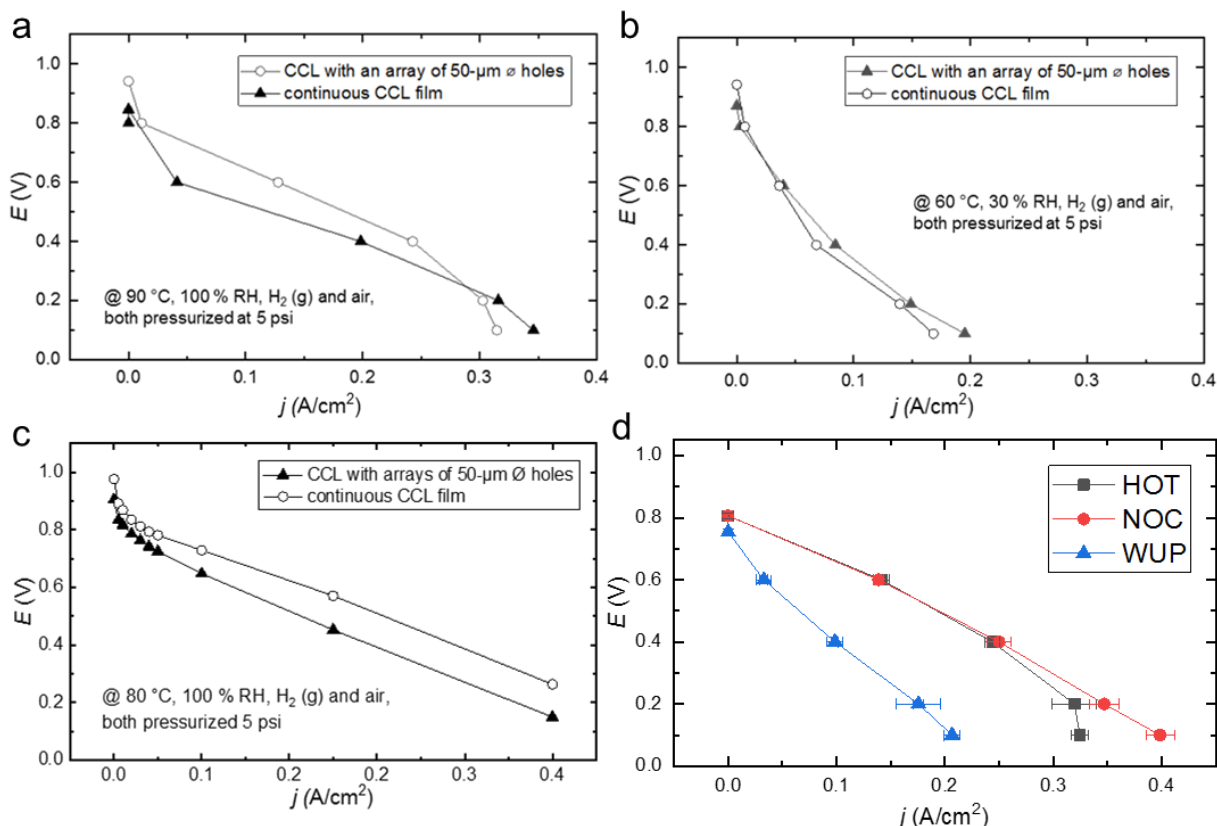


Figure S7. Fuel cell polarization profiles of microtransfer molded CCLs prepared with the catalyst ink patterned in arrays 50 μm -diameter holes (a-c). Polarization profiles were also obtained from reference samples containing CCLs prepared with thin, continuous films of catalyst ink. These profiles were normalized against the geometric surface areas, in contrast the normalization against Pt loadings used for the data plotted in the main article for the hot and start-up conditions. These plots were prepared from the average profiles of triplicate samples. (d) A summary is provided for the average values and their calculated standard deviations for these replicate measurements obtained from the patterned samples under various testing conditions including hot operating conditions (HOT), normal operating conditions (NOC), and warm-up conditions (WUP).

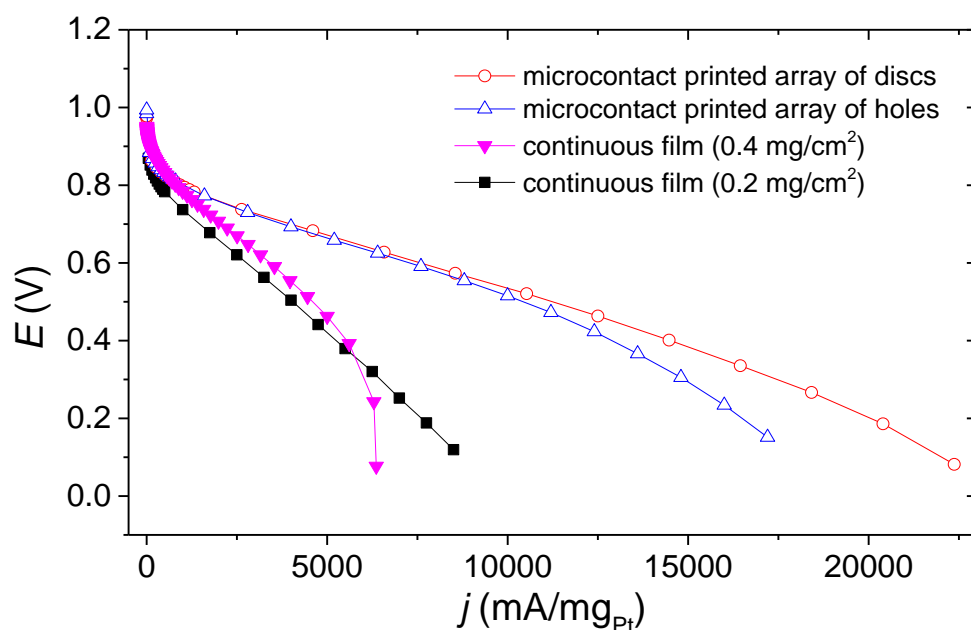


Figure S8. Fuel cell polarization profiles for microcontact printed CCLs prepared with the catalyst ink patterned in arrays of either hexagonally arranged discs or holes. Polarization profiles were also obtained from reference samples containing CCLs prepared with thin, continuous films of catalyst ink. The profiles were each normalized against their Pt loadings as determined by XRF spectroscopy techniques. These polarization curves were collected at fuel cell operating conditions of 80 °C and 100 % RH with H₂ (g) and O₂ (g) supplied at 1 L/min to the anode and cathode, respectively.

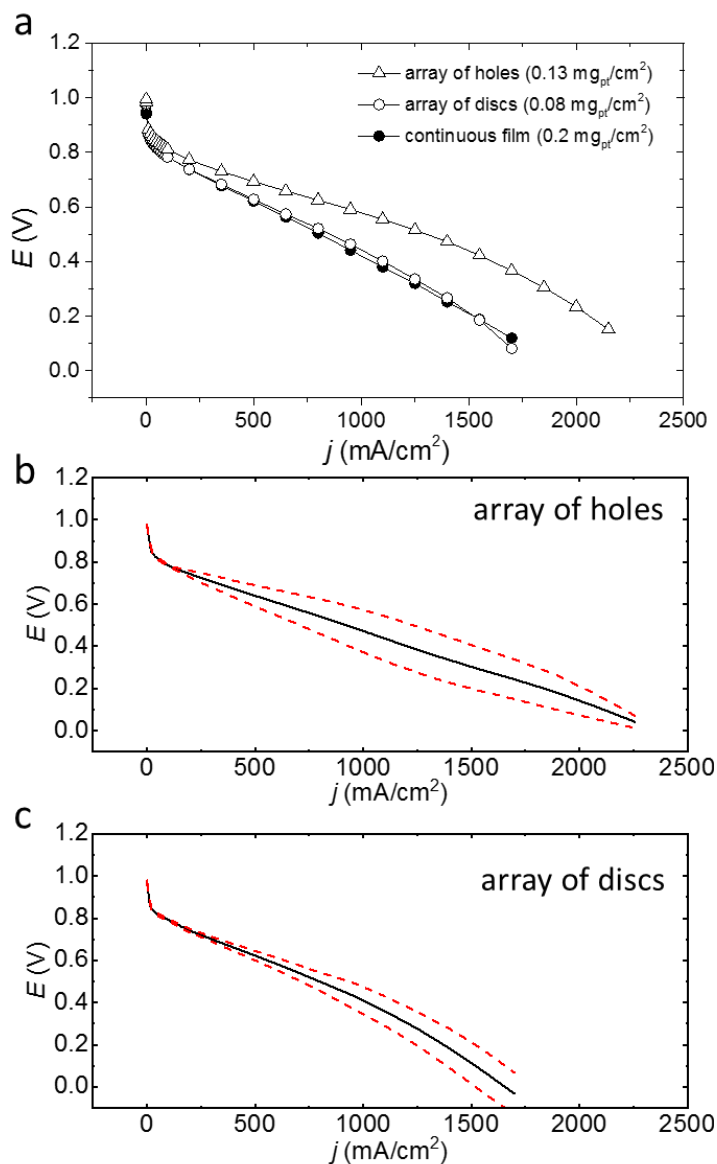


Figure S9. Fuel cell polarization profiles of microcontact printed CCLs prepared with the catalyst ink patterned in arrays of either hexagonally arranged discs or holes. (a) Polarization profiles of patterned and continuous CCL samples collected with operating conditions of 80 °C and 100 % RH with H₂ (g) and O₂ (g) supplied at 1 L/min to the anode and cathode, respectively. (b-c) The polarization profiles depicting the average values and their calculated standard deviation obtained from the analysis of the patterned samples (i.e., arrays of holes or discs, respectively), each prepared in triplicate.

Reference

- (1) Garland, N.; Benjamin, T.; Kopasz, J. DOE Fuel Cell Program: Durability Technical Targets and Testing Protocols. *ECS Transactions*, **2007**, 11, 923–931.