

# Highly Efficient Layer-by-Layer-Assisted Infiltration for High-Performance and Cost Effective Fabrication of Nanoelectrodes

*Yuri Choi,<sup>†,‡</sup> Sihyuk Choi,<sup>†,‡</sup> Hu Young Jeong,<sup>§</sup> Meilin Liu,<sup>‡,⊥</sup> Byeong-Su Kim,<sup>\*,‡,#</sup> and*

*Guntae Kim<sup>\*,‡</sup>*

<sup>‡</sup>Department of Energy Engineering, <sup>§</sup>UNIST Central Research Facilities (UCRF),  
Department of Mechanical and Advanced Materials Engineering, and <sup>#</sup>Department of  
Chemistry, Ulsan National Institute of Science and Technology (UNIST), Ulsan  
689-798, Korea

<sup>⊥</sup>School of Material Science and Engineering, Georgia Institute of Technology, Atlanta,  
Georgia 30332, United States

<sup>†</sup> These authors contributed equally to this work.

E-mail: gtkim@unist.ac.kr, bskim19@unist.ac.kr

## Experimental Section

*Preparation of GDC-YSZ:* The PSC-GDC-YSZ composites were prepared by conventional infiltration and LbL-assisted infiltration. This procedure requires the preparation of porous GDC-YSZ scaffolds. To prevent undesired reactions between the PSC cathode and the YSZ electrolyte, a GDC barrier layer is coated onto the YSZ scaffold. Porous YSZ scaffolds were made by mixing YSZ powder (TZ-8Y, Tosoh Corp.), a dispersant (Duramax3005, Rohm and Haas), binder (HA-12 and B1000, Rohm and Haas), and pore former (Graphite, 325 mesh, Alfa Aesar) with distilled water. This solution of YSZ slurry was dried and then sintered at 1500 °C to produce an YSZ structure with roughly 65% porosity by the Archimedes method. The GDC barrier coating is prepared by infiltrating a GDC solution into the porous YSZ scaffolds, followed by heating in air to 450 °C. Infiltration steps were repeated until the desired loading (15 wt%) was achieved. The cells were then sintered to temperature up to 1200 °C for 4 h.

*Conventional infiltration:* The procedure for conventional infiltration is similar to that reported in previous studies by our group.<sup>1-3</sup> In order to prepare a composite of PSC-GDC-YSZ, the PSC solution was prepared with stoichiometric amounts of  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (Aldrich, 99.9%),  $\text{Sr}(\text{NO}_3)_2$  (Aldrich, 99+%), and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Aldrich, 98+%) and citric acid in distilled water. After the solution was infiltrated into the GDC-YSZ scaffold, the PSC-GDC-YSZ composites were calcined in air at 450 °C to decompose nitrate ions and citric acid. Multiple infiltration steps were required to reach the final loading of 45 wt%. This composite was heated in air at 850 °C for 4 h to form the desired perovskite structure.

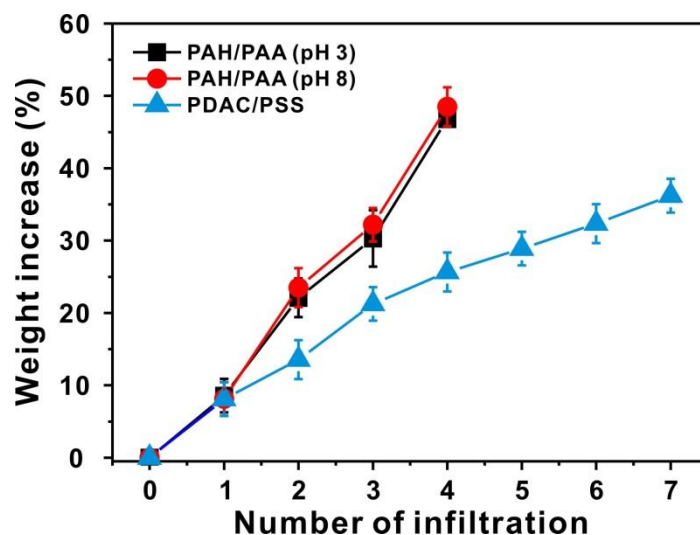
*Layer-by-Layer (LbL) assembled polyelectrolytes multilayer-assisted infiltration:* The GDC-YSZ scaffold was briefly treated with oxygen plasma to introduce a hydrophilic surface.

Poly(allylamine hydrochloride) (PAH, SigmaAldrich,  $M_w = 15,000$ ) and poly(acrylic acid) (PAA, SigmaAldrich,  $M_w = 250,000$ ) were respectively dissolved in water at a concentration of 5.0 mM and the solution was adjusted to pH 3 by 1 M HCl and NaOH. The substrate was dipped into a positively charged PAH solution for 10 min. It was then dipped into DI water for 1 min three times to remove loosely bound PAH. Subsequently, the substrate was dipped into a negatively charged PAA solution for 10 min, and washed with DI water three times for 1 min, affording a one-bilayer film of substrate/(PAH/PAA)<sub>1</sub>. The above procedure was repeated to achieve 10 bilayers. The PSC precursor solution was infiltrated into the LbL multilayer-treated YSZ scaffold, and the PSC-LbL multilayer-treated YSZ composites were calcined in air at 450 °C to decompose nitrate ions and polymer multilayers. Multiple infiltration steps were required to reach the final loading of 45 wt%. This composite was heated in air at 850 °C for 4 h to form the desired perovskite structure.

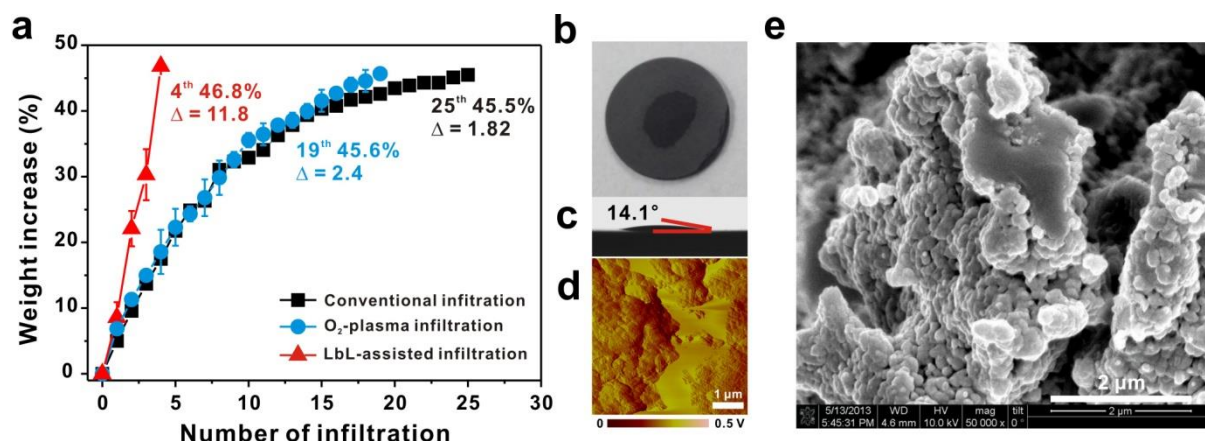
*Electrochemical characterization:* The electrochemical performance in this study was measured using symmetric cells and single cells using an electrolyte support cell. The first step in cell fabrication involved making a porous–dense–porous YSZ wafer using a tape-casting method, as described in detail elsewhere.<sup>4-5</sup> A 120 µm dense YSZ electrolyte disk was sandwiched between two 70 µm porous YSZ layers. The diameter of the active porous YSZ area was 0.36 cm<sup>2</sup>. In order to avoid solid state reaction with PSC and YSZ, a GDC barrier is coated on the porous YSZ wafer. For symmetrical cell tests, the PSC was infiltrated into both sides of porous GDC-YSZ by a multi-step process followed by heating at 450 °C. Finally, the PSC-GDC-YSZ composite was calcined in air at 850 °C for 4 h. For a single cell test, the PSC was infiltrated on the cathode side and 45 wt% CeO<sub>2</sub> and 1 wt% Pd were infiltrated into the anode side.

*Other characterizations:* X-ray powder diffraction (XRD) (Rigaku diffractometer, Cu  $K_{\alpha}$  radiation) analysis was used to confirm the crystalline structures of the samples. The microstructures and morphologies of the PSC-GDC-YSZ samples were observed using a field-emission scanning electron microscope (SEM) (Nova SEM). Transmission electron microscopy (TEM) images were acquired with a JEOL JEM 2100F with a probe forming (STEM) Cs corrector at 200 kV. The surface morphology of the samples was investigated using atomic force microscopy (AFM, Nanoscope V, Veeco) via a tapping mode. Electrical conductivity of the PSC-GDC-YSZ composite was determined in air using a four-electrode measurement. All four electrodes were made of Ag wire and Ag paste. The current and voltage were controlled and measured using a potentiostat (BioLogic) in a temperature range of 100 to 750 °C with an interval of 50 °C.

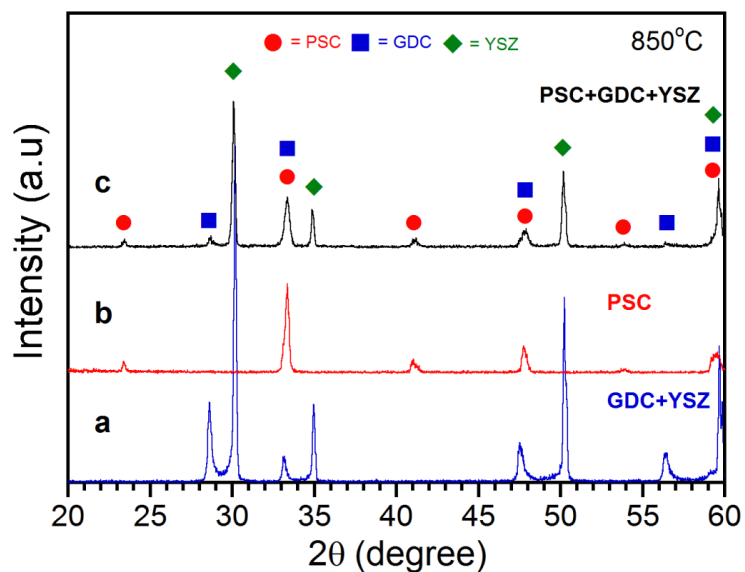
For symmetrical cells, two Ag wires were attached to each of the two electrodes using Ag paste. Each cell was mounted on an alumina tube using a ceramic adhesive (Aremco, Ceramabond 552). Impedance spectra were recorded under OCV in a frequency range of 1 mHz to 500 kHz with ac perturbation of 10 mV in a temperature range of 600 - 750 °C. For the single cell tests, each cell was mounted on an alumina tube using a ceramic adhesive. Humidified (with 3 vol%  $H_2O$ )  $H_2$  was used as the fuel at a flow rate of 100 mL min<sup>-1</sup> (passing through a water bubbler at 25 °C), whereas ambient air was used for the cathode as an oxidant. Impedance spectra and  $I$ - $V$  polarization curves were obtained with a BioLogic Potentiostat. The  $I$ - $V$  polarization curves were recorded between 600 and 750 °C.



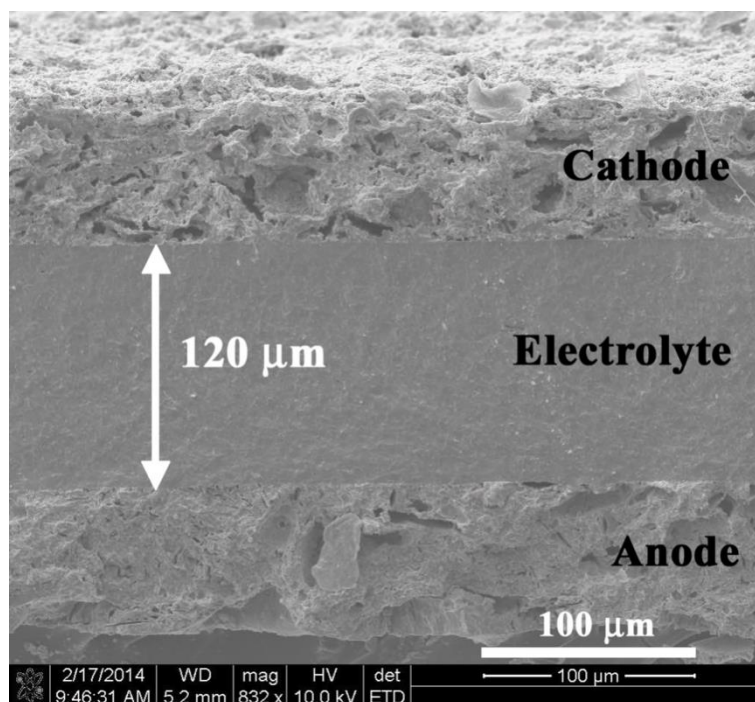
**Figure S1.** Weight changes of a single cell with the number of infiltration cycles in different polyelectrolytes. PAH/PAA (pH 3), PAH/PAA (pH 8), and poly(dimethyldiallylammonium chloride)/poly(styrene 4-sulfonate) (PDAC/PSS, 0.1 M NaCl).



**Figure S2.** Oxygen plasma treated infiltration. (a) Weight changes of a single cell with the number of infiltration cycles. (b) optical image after dropping 5  $\mu\text{L}$  of water onto a plain PSC substrate, (c) the corresponding contact angle image, (d) AFM and (e) SEM image of O<sub>2</sub>-plasma infiltration. Due to limited sites for metal ion complexations, the infiltration times of O<sub>2</sub>-plasma infiltration are not enhanced albeit the improved wettability of metal precursors. Surface root-mean-square roughness ( $R_{\text{rms}}$ ) values of O<sub>2</sub>-plasma infiltration are determined to be 60.3 nm in AFM image. Large PSC particles of roughly 150 nm diameter are coated on the surfaces of the GDC-YSZ scaffold in SEM image. The high surface roughness and large particles indicate that oxygen plasma do not act as the binder between electrode and metal precursors, resulting in aggregated and large metal particles.



**Figure S3.** X-ray diffraction profile GDC-YSZ composite, pure PSC, and PSC-GDC-YSZ composite electrode. XRD diffraction of 15 wt% GDC in the YSZ backbone is presented after sintering at 1200 °C for 4h. The pure PSC exhibits a single phase perovskite structure without any impurity phase. XRD patterns of the 45 wt% PSC-GDC-YSZ composite after sintering at 850 °C for 4h, indicating that no solid-state reactions occur for either the PSC or the GDC-YSZ composite.



**Figure S4.** The cross-sectional SEM image of a single cell with an approximately 120  $\mu\text{m}$  thick YSZ membrane.



## References

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