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Supplementary Materials for

Discovery of true electrochemical reactions for ultrahigh catalyst mass activity in water splitting

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The PDF file includes:

Other Supplementary Material for this manuscript includes the following:
(available at advances.sciencemag.org/cgi/content/full/2/11/e1600690/DC1)

- movie S1 (.avi format). Phenomena of electrochemical reaction occurring at microchannel scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; channel size, 1 mm height; triangle opening size, 600 μm; duration, 0.058 s).
- movie S2 (.avi format). Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 600 μm; duration, 0.058 s).
- movie S3 (.avi format). Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 400 μm; duration, 0.069 s).

- movie S4 (.avi format). Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; circular opening size, 500 μm; duration, 0.121 s).
- movie S5 (.avi format). Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; circular opening size, 50 μm; duration, 0.112 s).
- movie S6 (.avi format). Phenomena of electrochemical reaction occurring in a triangle opening with a thin tungsten wire as conductive wire (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 600 μm).
- movie S7 (.avi format). Phenomena of electrochemical reaction occurring in a triangle opening with a plastic microfiber as nonconductive wire (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 600 μm).

Sequence of photos of electrochemical reactions in PEMEC micro-openings

A sequence of close-up images of opening-scale electrochemical reactions is shown in fig. S4. It can be observed that, with the lapse of time, oxygen bubbles are generated and grow only along the edge of the LGDL opening land. In fig. S4A, at the initial time of the video, a relatively large oxygen bubble just flows over the LGDL opening, which, along with the opening land, absorbs some small bubbles; in fig. S4B, at 0.0017s, multiple oxygen bubbles, of different sizes, can be clearly observed along the edge of the opening land; in fig. S4C, at 0.0033s, both the quantity and size of oxygen bubbles has increased; in fig. S4D, at 0.005s, the oxygen bubbles along the edge of the opening land can be seen to have gotten larger; in fig. S4E, at 0.0067s, some small oxygen bubbles have merged to form larger bubbles; in fig. S4F, at 0083s, the size of the oxygen bubbles has kept increasing, and some of them are going to detach from the surface of the catalyst layer (CL). Similar reactions are also observed in the PEMECs, with various LGDL parameters and different opening sizes (from 50 μm to 600 μm) and shapes (triangular and circular), as shown in Fig. 2. All cells were operated at a current density of 2 A/cm^2. The dynamic details can be found in the supplementary materials: movies S1 to S5.

Preliminary results for the new catalyst fabrication method

The phenomena observed in the experiments revealed the electrochemical reactions in a PEMEC and could guide future fabrication and optimization of CLs. For example, CLs might be deposited only on the edges of LGDLs as shown in Fig. 3E. To further support the findings, two groups of control experiments were conducted, as follows.

A PEMEC was designed and fabricated in the laboratory for conducting the experiments. It consists of two endplates made from commercial grade aluminum designed to provide even compressive pressure on the cell. To apply a current to the cell, a copper plate was inserted at the cathode as a current distributor. The bipolar plate was fabricated from graphite and used a parallel flow field to distribute the flow over the active area of the cell. To maintain even compression and prevent leakage, gaskets for the LGDLs were fabricated from PVC. The cell was compressed by eight evenly distributed bolts, which were tightened to 40 lbf-in. of torque during assembly. The electrolyzer had an active area of 5 cm^2 and was operated at 80°C.

The PEMEC was attached to an electrolyzer control system with a current range up to 100 A and a voltage range of up to 5 V. The hardware was connected to Bio-Logic software, EC-Lab, which was used to conduct performance testing and electrochemical impedance spectroscopy. For controlling the flow, a system of piping was connected to the PEMEC. While the cathode piping was merely intended to safely exhaust hydrogen gas that formed during electrolysis, a diaphragm liquid pump from KNF Neuberger was used to circulate water at a constant volumetric flow rate of 20 ml/min through the anode.

The only difference between the two groups of experiments was cathode catalyst fabrication. The first control group used a conventional CCM (Fuel Cells Etc, Inc.). The CCM was composed of Nafion 115, a perfluorosulfonic polymer, with a thickness of 125 μm; an anode CL with an $IrRuO_x$ catalyst loading of 3 mg/cm^2; and a cathode layer with a platinum black (Pt/B) catalyst loading of 3 mg/cm^2. The second experimental group used a single-side catalyst-coated membrane. The single-side catalyst-coated

membrane was composed of Nafion 115 with a thickness of 125 and a 15 μm thick anode CL with an $IrRuO_x$ catalyst loading of 3 mg/cm^2. The cathode catalyst platinum (approximately 15 nm thick) was sputter coated on the LGDL.

The membrane electrode assembly (MEA) was also investigated *ex-situ*. The cathode CLs were analyzed by scanning transmission electron microscopy (STEM). A Hitachi HF3300 transmission electron microscope/scanning transmission electron microscope equipped with a Bruker energy-dispersive spectrometry (EDS) detector and both high-angle annular dark field (HAADF) and secondary electron (SE) detectors was used to image the morphology and composition of different CLs. The inset HAADF-STEM images show both electrodes contain particle sizes below 10 nm (please check the pictures on the top right corner of Fig. 4C and Fig. 4D). MEA specimens were prepared by diamond-knife ultramicrotomy with a target thickness of 50–100 nm. SE/STEM images were obtained of the topside of the Pt/B electrode (Fig. 4C) and topside of the platinum thin film sputter coated directly on the titanium LGDL (Fig. 4D).

"The performance comparison is shown in Fig. 4E. Although the performance of the PEMEC with the catalyst formed by the new fabrication method is slightly worse than that of the conventional one, the difference at a current density of 2 A/cm^2 is only 0.12 V and may be the result of increased interfacial ohmic resistance and catalyst size due to the new fabrication method. The impedance testing results substantiate this assumption: the high frequency resistance (HFR) value of the control group is 0.07 Ω cm^2 and the HFR value of the experimental group is 0.1 Ω cm^2. The cathode catalyst platinum used in the experimental group is only around 1/90 of the platinum used in the control group, which significantly improves catalyst utilization. To compare the mass activity of the loading catalyst, the current was determined for each group at a fixed cell potential (1.60 V): 4.8897 A and 3.2549 A for the control group and experimental group, respectively. This translates to a 54 times higher mass activity of the loading catalyst ($A \cdot mg^{-1}_{catalyst}$) in the experimental group compared than the control group, as shown in Fig. 4F."

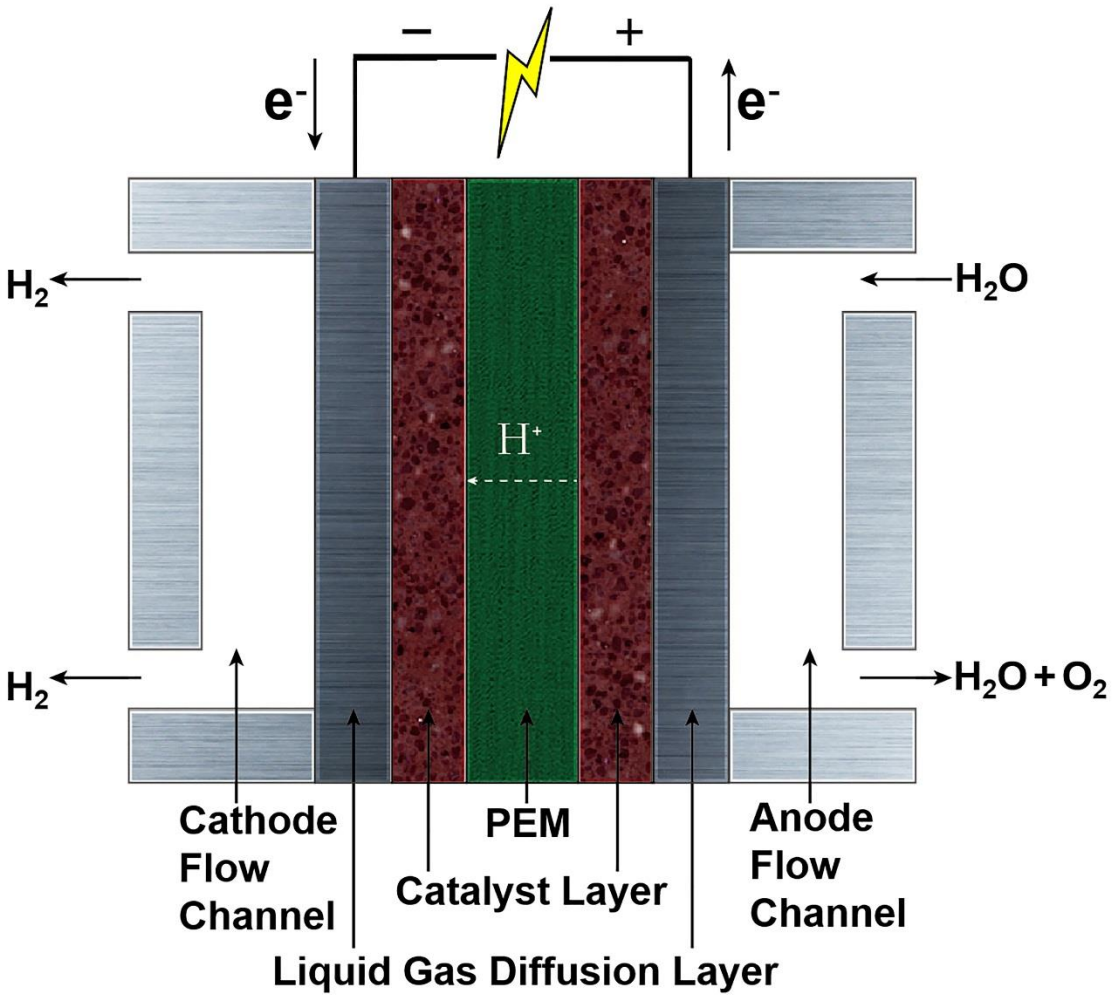

fig. S1. Schematic of a PEMEC. A sequence images of electrochemical reactions in a triangle micro-opening of the thin, highly tunable titanium LGDL.

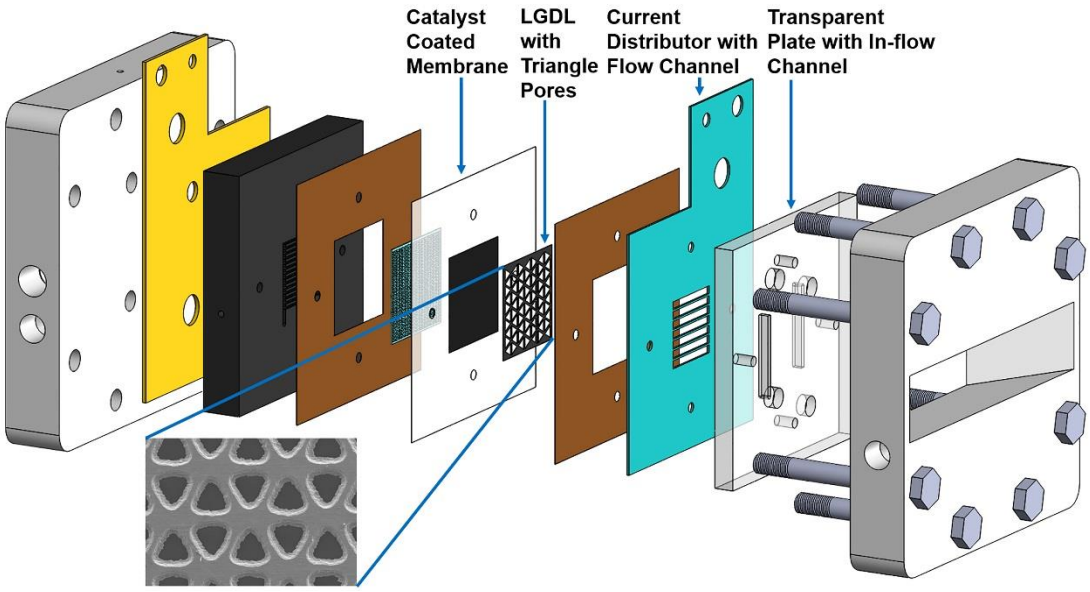

fig. S2. Schematic of the transparent, reaction-visible PEMEC and LGDLs with well-tunable and straight holes throughout.

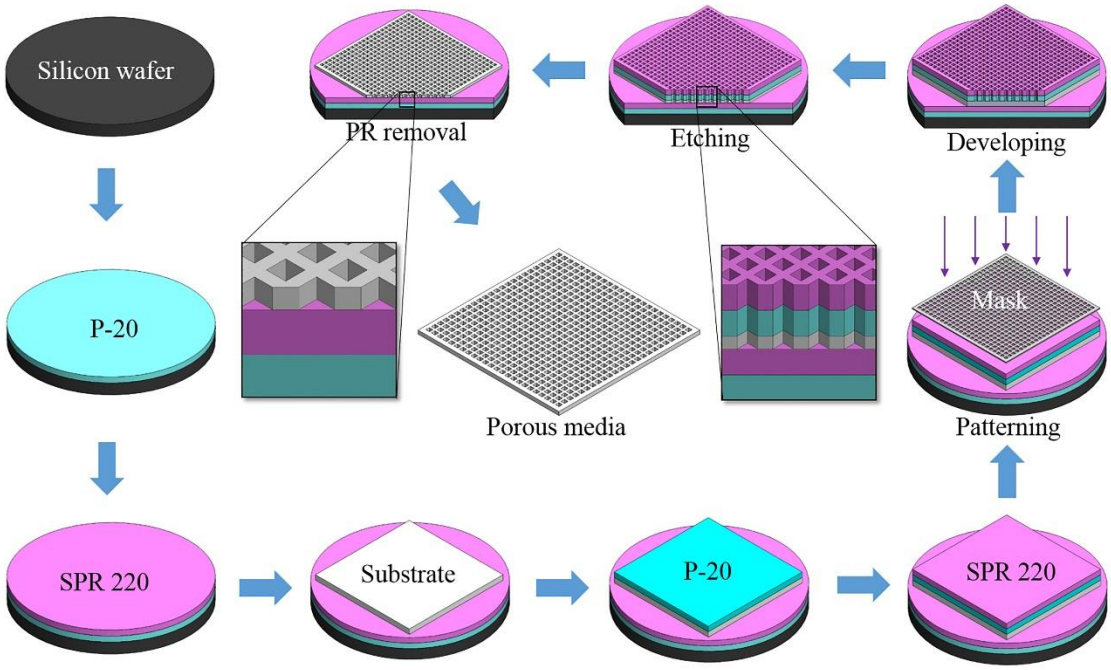

fig. S3. Schematic of a developed nanofabrication process for the titanium thin LGDL with well-tunable micro-openings.

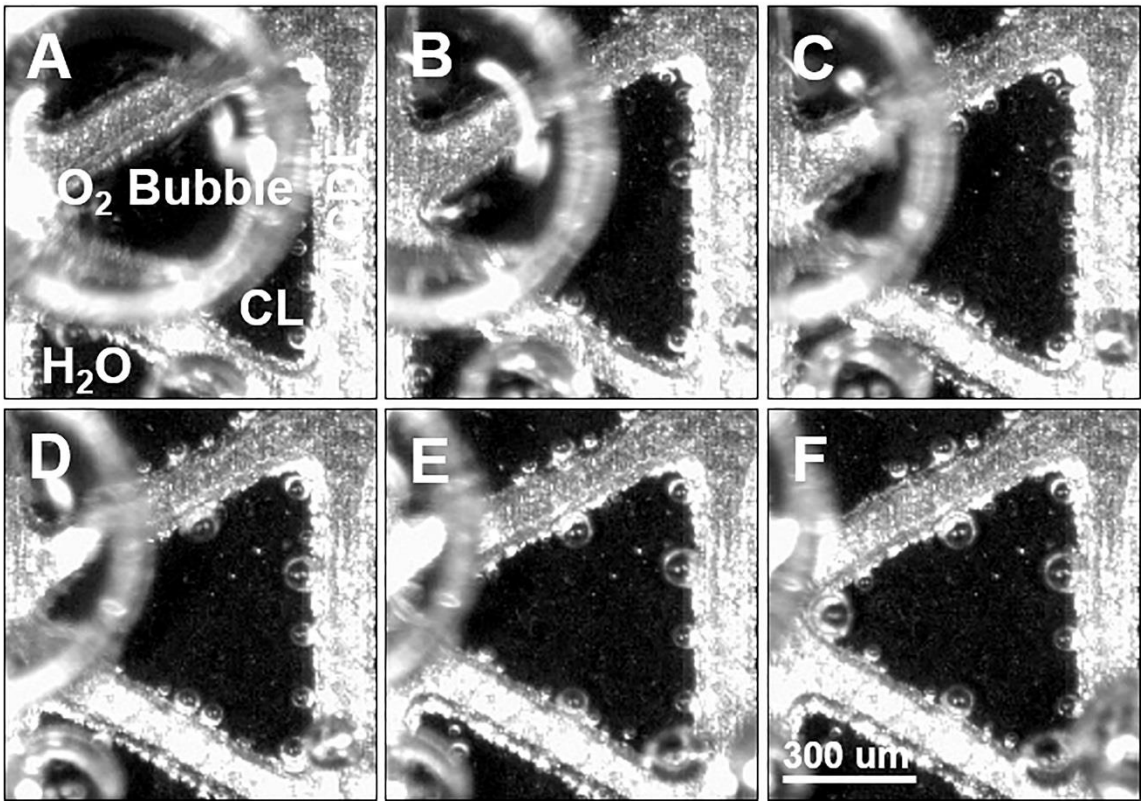

fig. S4. (triangular opening size: 600μm, water is fully filling the channel and flowing from right to left)**: (A)** initial time, t_0; **(B)** t_0 + 0.0017 s; **(C)** t_0 + 0.0033 s; **(D)** t_0 + 0.005 s; **(E)** t_0 + 0.0067 s; and **(F)** t_0 + 0.0083 s.

Descriptions of Movies

movie S1. Phenomena of electrochemical reaction occurring at microchannel scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; channel size, 1 mm height; triangle opening size, 600 μm; duration, 0.058 s).

movie S2. Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 600 μm; duration, 0.058 s).

movie S3. Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 400 μm; duration, 0.069 s).

movie S4. Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; circular opening size, 500 μm; duration, 0.121 s).

movie S5. Phenomena of electrochemical reaction occurring at micro-opening scale (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; circular opening size, 50 μm; during time, 0.112 s).

movie S6. Phenomena of electrochemical reaction occurring in a triangle opening with a thin tungsten wire as conductive wire (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 600 μm).

movie S7. Phenomena of electrochemical reaction occurring in a triangle opening with a plastic microfiber as nonconductive wire (operation current density, 2 A/cm^2; DI water flow rate, 20 ml/min; triangular opening size, 600 μm).