

Supporting Information

Connected nanoparticle catalysts possessing a porous, hollow capsule structure as carbon-free electrocatalysts for oxygen reduction in polymer electrolyte fuel cells

*Takanori Tamaki, Hidenori Kuroki, Shun Ogura, Teruaki Fuchigami, Yoshitaka Kitamoto,
Takeo Yamaguchi**

Experimental Section

Catalyst Synthesis: The connected Pt–Fe catalysts were synthesised as follows.^{1,2} Briefly, amorphous silica particles with an average diameter of 320 nm (Nippon Shokubai, KE-P30) were first modified with poly(diallyldimethylammonium chloride) (PDDA) and then Pt–Fe nanoparticles were synthesised on the PDDA-modified silica particles via the polyol method using tetraethylene glycol as a reducing agent and Fe(III) acetylacetonate and Pt(II) acetylacetonate as the metallic precursors. The connected Pt–Fe catalysts were then fabricated via supercritical treatment of the Pt–Fe nanoparticle/PDDA/silica composite particles. The particles were dispersed in ethanol (5 mL) and then placed in a sealed supercritical reaction cell with a volume of 11 mL. The sealed cell was heated to 290 °C, which corresponds to 25 MPa and maintained at that temperature for 3.5 h. The silica particles were then dissolved by heating the samples in an aqueous 3 M NaOH solution at 80 °C for 1 h. A commercial catalyst supplied by Tanaka Kikinzoku Kogyo, TEC10E50E with 45.8 wt% Pt supported on carbon black (TKK Pt/C) and laboratory-made Pt–Fe/C was used for comparison. The Pt–Fe/C was fabricated using our previously reported procedure.³ Briefly, the metallic precursors, i.e. hexachloroplatinic acid and vinyl ferrocene were mixed with carbon black (Ketjen black) and ground well. An appropriate volume of isopropyl alcohol was then added and the paste-like mixture ground well. The mixture was then reduced in a tube furnace for 2 h at 800 °C using 20% H₂ in N₂ as the carrier gas. The weight ratio of the metallic precursors was adjusted to an atomic ratio of Pt/Fe = 1, and the total quantity of metallic precursors was set such that the metal content of the catalysts was 40 wt%.

Catalyst Characterization: The catalyst compositions were determined using inductively coupled plasma-atomic emission spectroscopy (ICP–AES) on an ICPS-8100 (Shimadzu) after dissolving the catalysts in aqua regia. The Pt/Fe molar ratio of

the connected Pt–Fe catalysts was 0.94 ± 0.04 , which is close to the feed ratio. XRD data obtained using a Ultima IV (Rigaku) with a Cu K α ($\lambda = 1.5406 \text{ \AA}$) X-ray source operating at 40 kV and 40 mA and a scanning rate of 1 or 2° min⁻¹. TEM was performed using an H8100 electron microscope (Hitachi) with an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM)-EDX line-scan measurements were performed using an HD-2700 Cs-corrected STEM (Hitachi High Technologies Corporation). Cross-sectional SEM observation was performed according to our previous report using a specially designed focused ion beam stage for FB-2000A and an MEA sample holder for the S-4800 (Hitachi High Technologies Corporation).⁴

Electrochemical characterization of the catalysts in acid solution (0.1 M HClO₄) was performed on a rotating disk electrode (RDE) at room temperature. The electrodes for the RDE were prepared as follows. The working electrode was prepared by coating a mirror-polished glassy carbon electrode with a geometric area of 0.196 cm² with 10 μ L of a catalyst dispersion composed of the connected Pt–Fe catalysts (2.5 mg), a 5 wt% Nafion solution (12.5 μ L) and a 25% aqueous isopropyl alcohol solution (6.3 mL), or the TKK Pt/C or Pt–Fe/C (18.5 mg), a 5 wt% Nafion solution (100 μ L) and a 24% aqueous isopropyl alcohol solution (25 mL) and then drying it overnight at room temperature. A Pt wire and a reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. Prior to electrochemical characterization, electrochemical pre-treatment was performed in nitrogen saturated 0.1 M HClO₄ solution by cycling the potential between 0.05 to 1.2 V at a sweep rate of 50 mV s⁻¹ until the voltammograms were stabilized. CVs were obtained under nitrogen over the potential range 0.05–1.2 V with a sweep rate of 20 mV s⁻¹. Polarization curves were obtained via linear sweep voltammetry (LSV) under nitrogen and oxygen from 0.05 V to 1.2 V at a sweep rate of 20 mV s⁻¹ and at an electrode

rotational speed of 1600 rpm. The CVs and LSVs were obtained using an HZ-3000 (Hokuto Denko) or a Solartron 1287 (Toyo Corporation).

MEA Fabrication and Characterization: The MEA was fabricated using the connected Pt–Fe catalysts as the cathode catalyst, TKK Pt/C as the anode catalyst, and Nafion NR-211 (DuPont) as the electrolyte membrane. The catalyst ink for the cathode was prepared by mixing the connected Pt–Fe catalysts (20 mg), a 20 wt% Nafion solution (13 mg), and a 56 wt% aqueous isopropyl alcohol solution (10 mL). After ultrasonication for 2–3 h and bubbling of nitrogen through the mixture for 10 min, the ink was treated in an autoclave (TVS-N2, Taiatsu Techno Corporation) at 200 °C for 24 h. The ink was then ultrasonicated again and then coated onto a Nafion NR-211 membrane via pulsed spray (Nordson K.K., Japan). The anode of the MEA was fabricated using the decal method; the catalyst ink for the anode, which was composed of TKK Pt/C and Nafion ionomer at an ionomer to carbon weight ratio = 1, was applied on a poly(tetrafluoroethylene) sheet using a bar-coating machine, and then this film was hot-pressed with the Nafion-cathode assembly at 135 °C and 5.11 kN for 5 min. The Pt loading for the cathode and the anode were 0.32 and 0.22 mg cm⁻², respectively. The fabricated MEA was placed in a 5 cm² single-cell test holder (ElectroChem, Inc.) containing gas diffusion media (SIGRACET GDL 24 BC, a carbon paper with a microporous layer) for each electrode. The performance of the MEA was determined at 80 °C, with gas flow rates of 100 and 500 mL min⁻¹ for H₂ and O₂, respectively, using an HJ1010SM8A charge-discharge unit (Hokuto Denko). Relative humidities of the anode and cathode were 90% and 70%, respectively. The procedures for the start-stop durability test and CV analysis followed the revised FCCJ protocols.^{5,6} The durability test was outperformed by applying a triangular wave between 1.0 and 1.5 V vs. a RHE at a scan rate of 0.5 V s⁻¹. The CV measurements were performed at 80 °C and 100% relative humidity using a potential sweep from

0.05 to 0.9 V vs. RHE, a sweep rate of 50 mV s⁻¹ and with flow rates of 100 mL min⁻¹ of H₂ for the anode and 500 mL min⁻¹ of N₂ for the cathode. The flow of N₂ gas was halted just prior to the CV measurements. In addition, prior to the recording of data, several CVs were obtained until the voltammograms were stabilized. Because the CVs were affected by hydrogen evolution reaction (HER), two methods were employed to calculate the ECSA according to the previous reports.⁶⁻⁸ The first method was based on extraction of the HER current from the total reduction current⁸ as shown in Figure S4(a). The Tafel curve for HER was calculated using a Tafel slope and an intercept approximated at low potential region where the voltammogram is logarithmically linear.⁸ The second method assumed that a shaded part in Figure S4(b) corresponded to the adsorption of hydrogen, from which ECSA was calculated.^{6,7} Both the methods gave similar values, 13.9 and 14.2 m² g⁻¹, and the first method was used for the calculation in Figure 3d. After performing the durability test, the cathode catalysts were evaluated using TEM. The samples for TEM analysis were obtained by scratching the catalyst off the cathode layer.

Figure S1

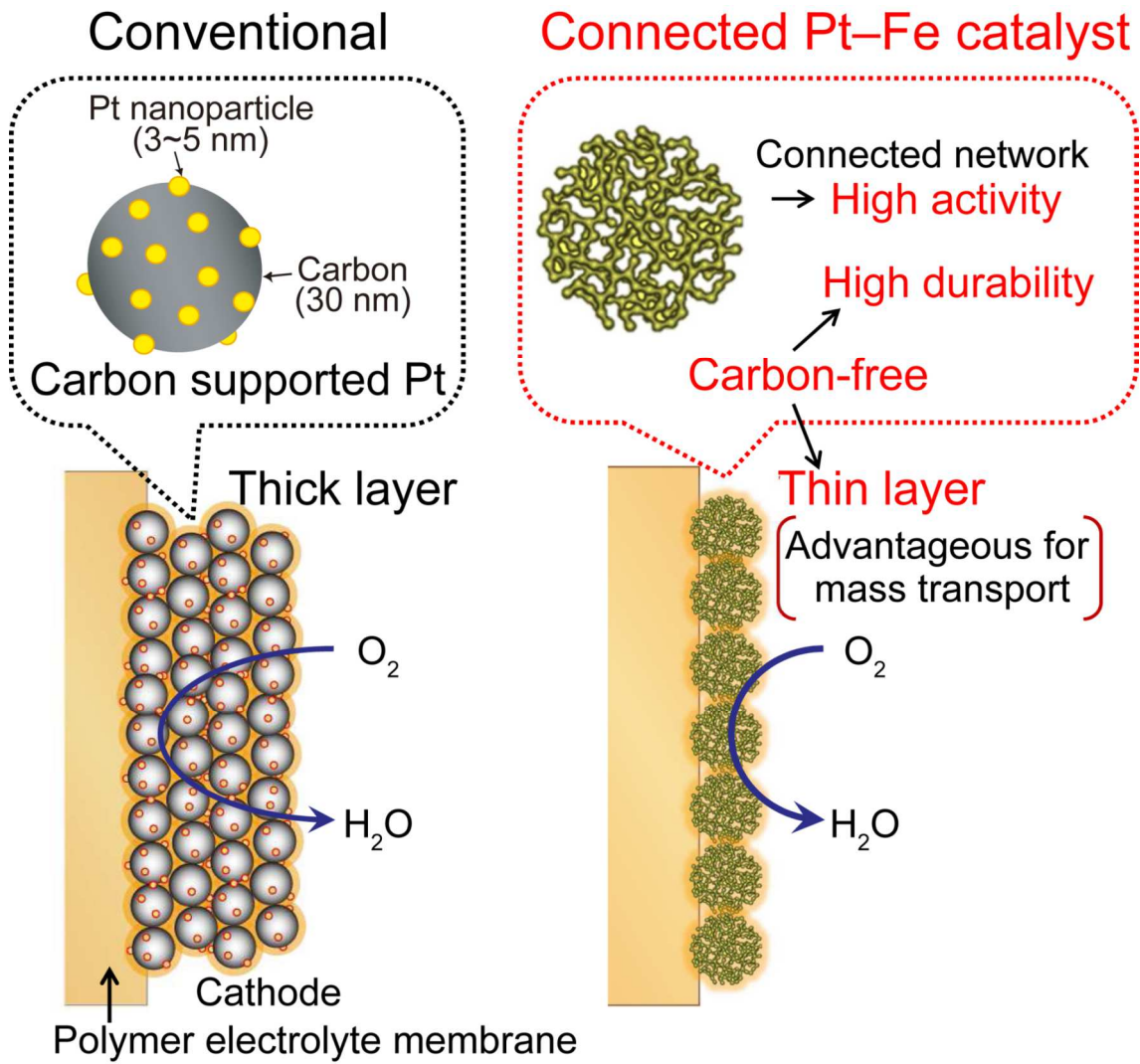


Figure S1. Schematic illustration of the present study. Connected Pt-Fe nanoparticle catalysts can solve all of the problems of PEFC cathode catalysts.

Figure S2

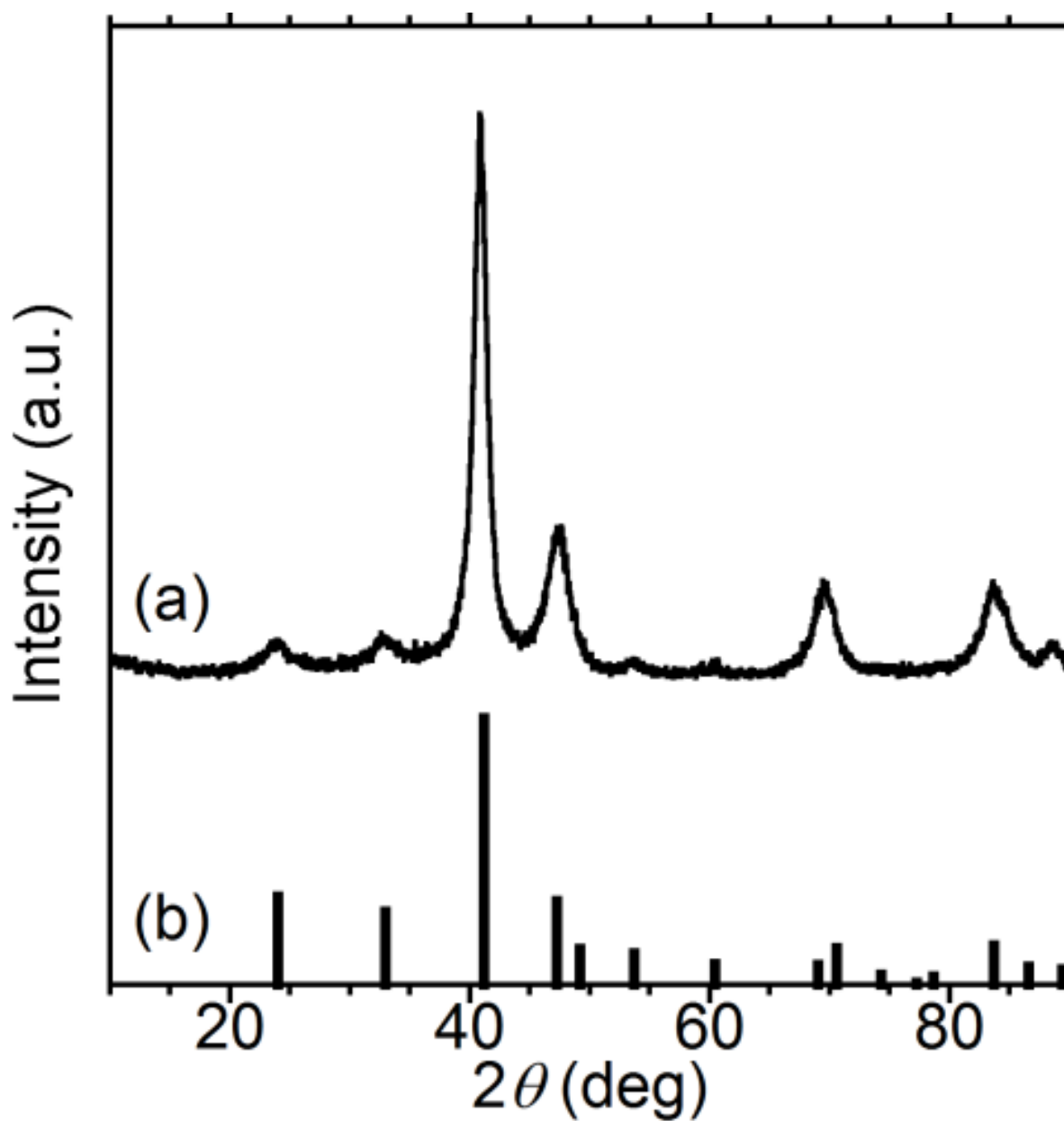


Figure S2. (a) XRD pattern of the connected Pt–Fe catalysts. (b) Powder Diffraction File #03-065-9121 (L1₀ ordered iron platinum) of the International Centre for Diffraction Data.

Figure S3

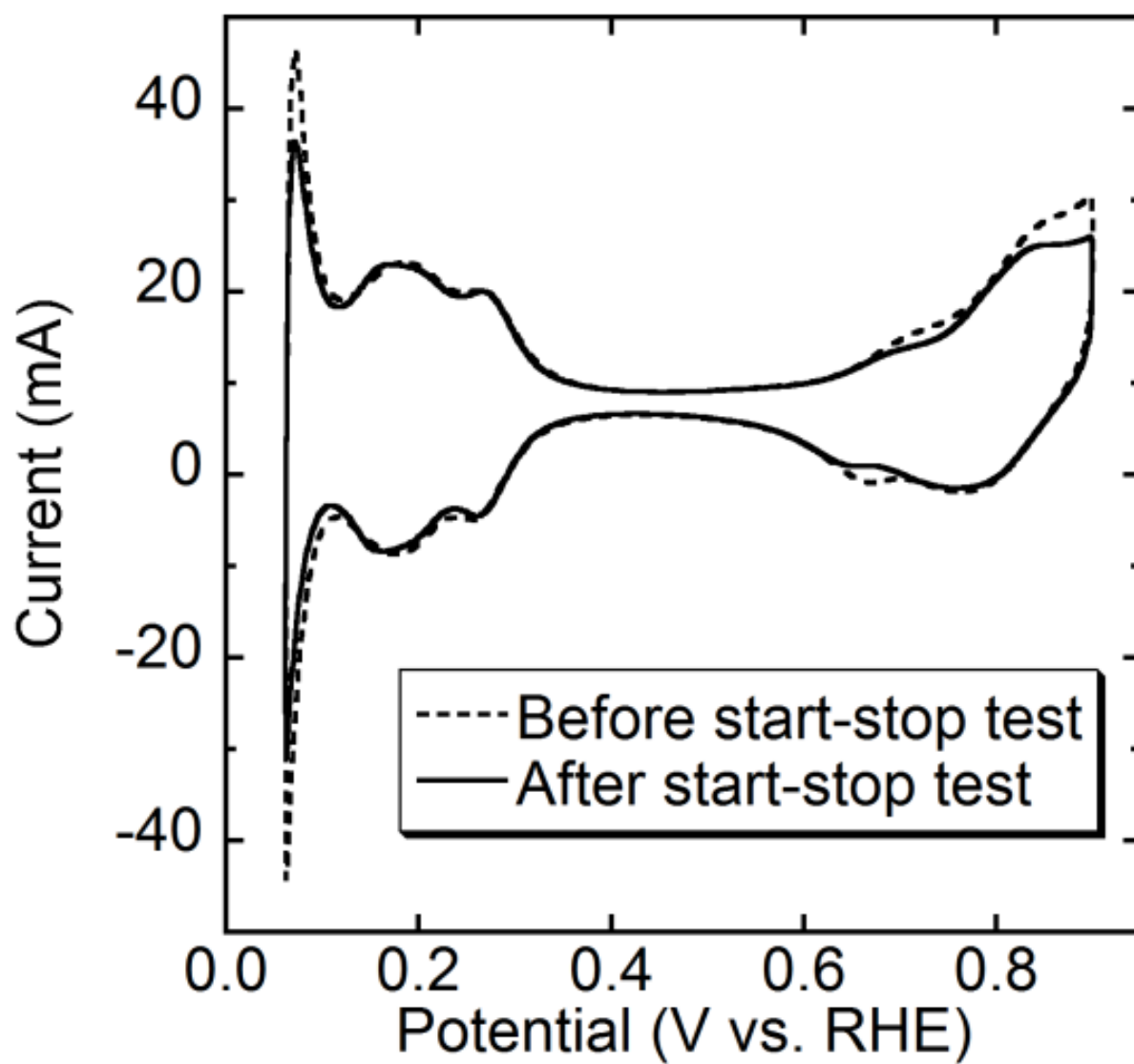


Figure S3. CVs of the connected Pt-Fe catalysts in the cathode of the MEA before and after 10,000 cycles of the start-stop durability test at 80 °C.

Figure S4

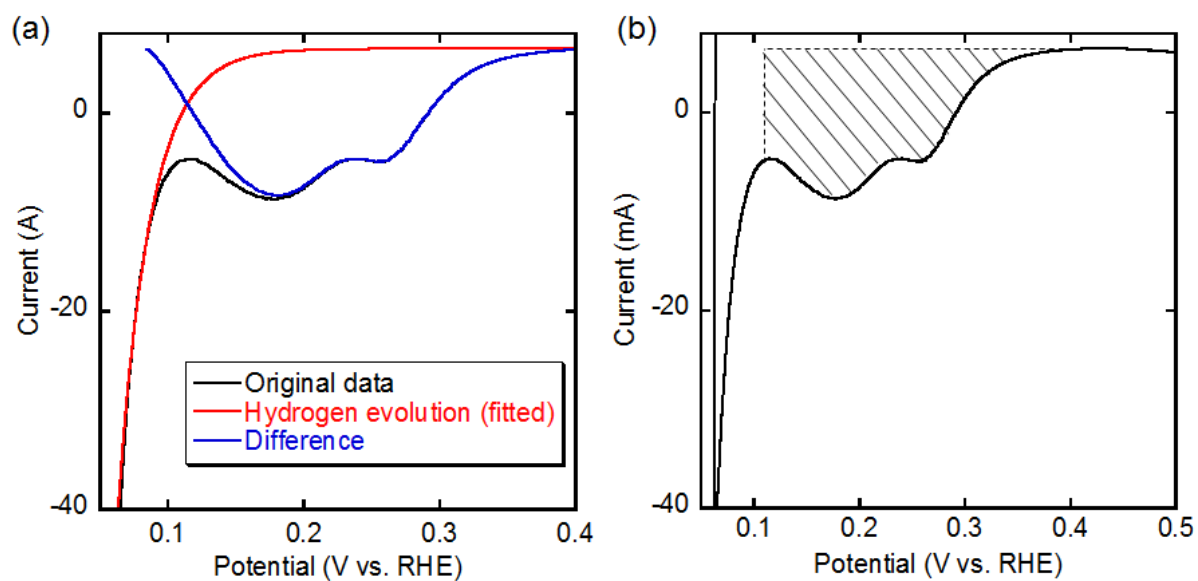


Figure S4. Two methods employed in the calculation of the ECSA in the MEA from the CV data. (a) ECSA was calculated by extracting hydrogen evolution reaction current (red line) from total reduction current (black line).⁸ (b) ECSA was calculated from the shaded part.⁶

Figure S5

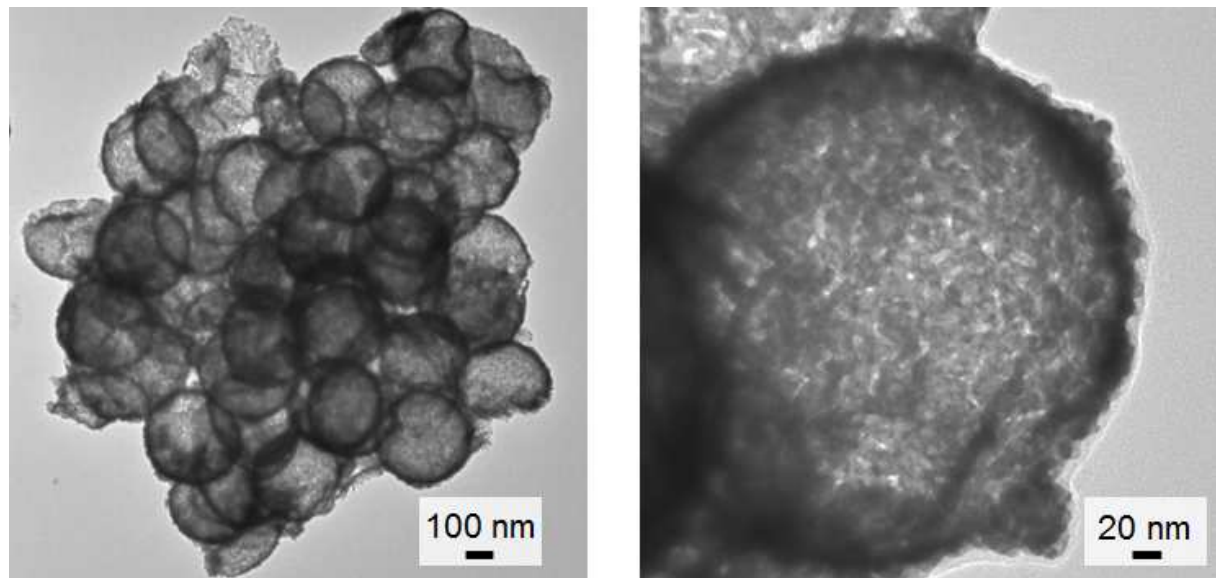


Figure S5. TEM images of the connected Pt–Fe catalysts in the cathode of the MEA after 10,000 cycles of the start-stop durability test at 80 °C.

Figure S6

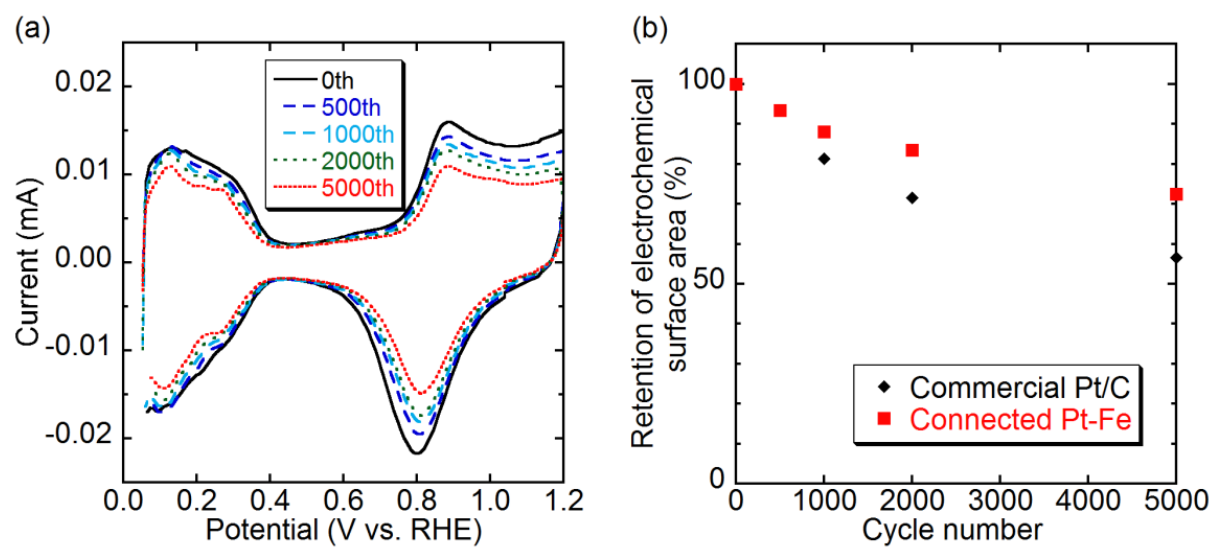


Figure S6. (a) CVs of the connected Pt–Fe catalysts in N_2 -saturated 0.1 M $HClO_4$ during the load-cycle durability test at 60 °C. (b) Change in the ECSA of the connected Pt–Fe catalysts and commercial Pt/C during the load-cycle durability test as a function of the number of cycles in N_2 -saturated 0.1 M $HClO_4$ at 60 °C.

Supporting Information References

- 1 T. Fuchigami, R. Kawamura, Y. Kitamoto, M. Nakagawa and Y. Namiki, *Langmuir*, 2011, **27**, 2923-2928.
- 2 T. Fuchigami, R. Kawamura, Y. Kitamoto, M. Nakagawa and Y. Namiki, *Biomaterials*, 2012, **33**, 1682-1687.
- 3 B. Arumugam, B. A. Kakade, T. Tamaki, M. Arao, H. Imai and T. Yamaguchi, *RSC Adv.*, 2014, **4**, 27510-27517.
- 4 Y. Katayanagi, T. Shimizu, Y. Hashimasa, N. Matsushita, Y. Yamazaki and T. Yamaguchi, *J. Power Sources*, 2015, **280**, 210-216.
- 5 A. Ohma, K. Shinohara, A. Iiyama, T. Yoshida and A. Daimaru, *ECS Transactions*, 2011, **41**, 775-784.
- 6 Proposals of the development targets, research and development challenges and evaluation methods concerning PEFCs (Japanese), Fuel Cell Commercialization Conference of Japan (FCCJ), 2011, http://fccj.jp/pdf/23_01_kt.pdf, (accessed September 2015).
- 7 T. Biegler, D. A. J. Rand and R. Woods, *J. Electroanal. Chem.*, 1971, **29**, 269-277.
- 8 H. Iden and A. Ohma, *J. Electroanal. Chem.*, 2013, **693**, 34-41.