Supporting Materials

Fuel Cell Tests. A PEFC single cell (Model EFC-05-02, Electrochem) was used for evaluation of replica-Pt-C as cathode catalyst at 343 K. The H_2 (> 99.99%, CO < 0.1 ppm) and dried air were flowed through anode and cathode, respectively, both with the flow rates of 100 mL min^{-1}. Water bubble via ball filter with aperture size 5 – 10 μm was inserted in the H_2 flow path at 15 cm to the inlet to anode. The temperature of water, FC, and the gas flow path between water bubble and FC was controlled at 343 K using water bath and ribbon heater.

The catalytic performance of replica-Pt-C composite was compared to that of conventional 20 wt% Pt/Vulcan XC-72 as cathode in PEFC. In the *I-V* plots per electrode area (Figure S1A), the current density using replica-Pt-C (data a and b) was by 35% greater at maximum than that using 20 wt% Pt/Vulcan XC-72 (data c). The difference between curves a and b was due to the press conditions for MEA. Nafion solution (5 – 15%) was used to disperse replica-Pt-C or 20 wt% Pt/Vulcan XC-72 on TGP-H-060H before the press to make MEA for curves b and c, whereas mechanically dispersed Pt/Vulcan XC-72 on TGP-H-060H was directly pressed as MEA for curve a. The current density for curve a extended greater in which the 50-μm Nafion film and anode 20 wt% Pt/Vulcan XC-72 constituted better interface without excess Nafion added (curve a).

The inflection point for curve b at 0.10 A cm^{-2} should be due to the lack of fuel gas because of the balance of activity and Pt amount. The Pt amount per electrode area was 0.13 mg-Pt cm^{-2} *versus* 1 mg-Pt cm^{-2} for conventional 20 wt% Pt/Vulcan XC-72. Therefore, the *I-V* plots were redrawn per Pt amount in cathode (Figure S1B). The current density using replica-Pt-C (curve a and b) was 12 times greater than that using 20 wt% Pt/Vulcan XC-72 (curve c) below the inflection point at 0.77 A $mg\text{-}Pt^{-1}$. The current density per Pt amount was 1.08 and 0.14 A $mg\text{-}Pt^{-1}$ for H_2-air PEFC with replica-Pt-C as cathode and for 20 wt% Pt/Vulcan XC-72 as cathode, respectively, at the cell voltage of 0.1 V. The current density for commercial Pt/C was relatively low (Figure S1B-c)[S1] probably because the MEA press condition was not optimized in this work. Note that the press condition of samples for curves b and c was nearly identical for comparison of PEFC tests.

The surface dispersion of Pt atoms needs to be taken into account to evaluate turnover number. The mean Pt particle sizes of 1.2 and 4.8 nm (Table 1) correspond to Pt surface dispersion of 0.8 and 0.3, respectively. Thus, the current density values corresponded to turnover numbers of 2.8 and 0.9 s^{-1}, respectively. The reason of this 3 times improvement was intimate contact of Pt with C matrix catalytically grown from C_2H_2. The quicker O_2 gas diffusion in cathode may also affect because the diameter of replica-C rod/tube should be smaller than 2.7 nm of ordered pores of Al-MCM-41 in comparison to conventional C particles of 0.1 – 1 μm.[14–17,22,23]

The possibility to reduce the Pt nanoparticle size to 1.2 nm keeping the metallic reactivity was demonstrated stabilized on/in the C matrix catalytically produced over the Pt nanoparticles, in clear contrast to structural instability of Pt[9,17] and activity decrease for oxygen reduction for Pt particles less than 3.5 nm.[22,23]

Reference of Supporting Materials

(S1) Paulus, U. A.; Schmidt, T. J.; Gasteiger, H. A.; Behm, R. J. *J. Electroanal. Chem.* **2001**, *495*, 134 – 145.

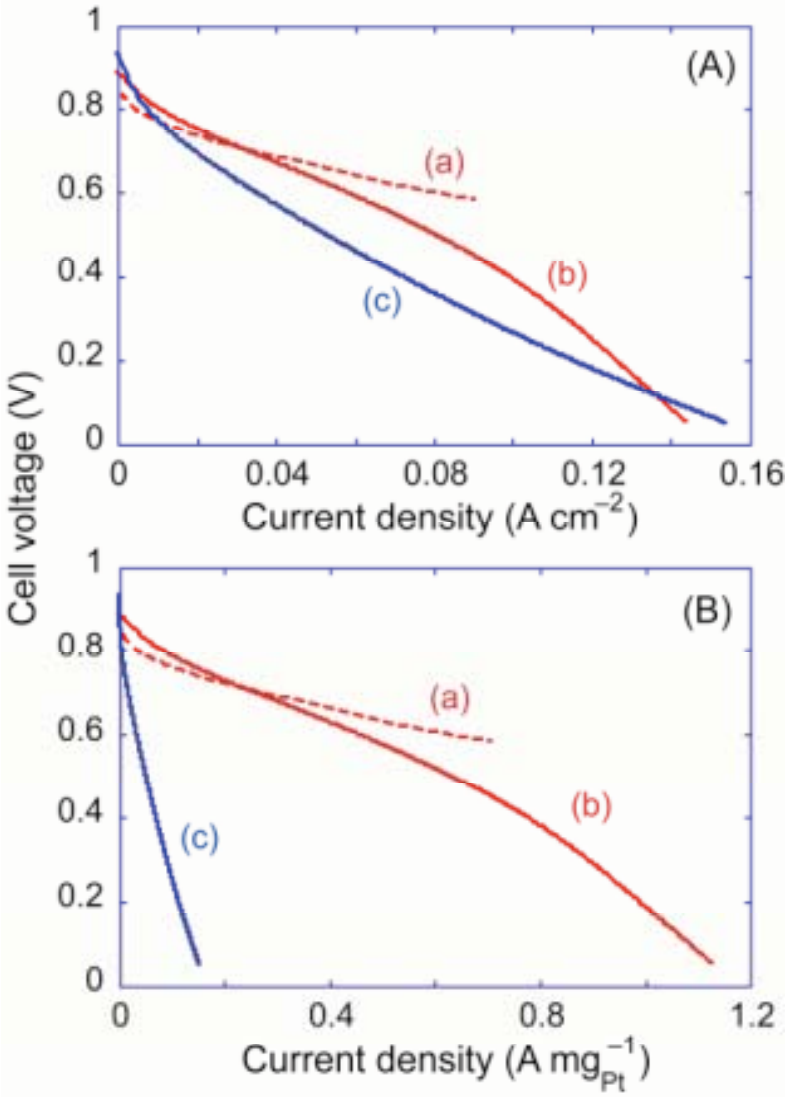

Figure S1. Dependence of cell voltage as a function of current density per electrode area (A) and per Pt weight (B) for H_2-air PEFC with replica-Pt-C (cathode) and 20 wt% Pt/Vulcan XC-72 (anode) (a, b) and with 20 wt% Pt/Vulcan XC-72 (cathode, anode) (c). The temperature of water bubble, FC, and H_2 flow path in between was controlled at 343 K.