

**Electronic Supplementary Information for
Compact bipolar plate-free direct methanol fuel cell stacks**

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Experimental Details

PtAu/C and Pr-doped Mn₂O₃/C were synthesized in the same manner as reported previously [1]. Briefly, the PtAu/C anode with an Au content of 0.45 mol% was prepared by the chemical reduction of an Au precursor (HAuCl₄·4H₂O) on the surface of a commercially-available Pt/C powder (30 wt% Pt, Tanaka Kikinzoku Kogyo) using NaBH₄ as a reducing agent. The Pr-doped Mn₂O₃/C cathode (60 wt% Mn₂O₃) with a Pr content of 7 mol% was prepared by impregnation of the surface of carbon powder by an Mn precursor (Mn(NO₃)₂·6H₂O) and a Pr precursor (Pr(NO₃)₃·nH₂O). The catalyst/support powder was mixed with a polytetrafluoroethylene (PTFE) binder in a glycerin solvent using a mortar and pestle. The mixture was coated on the surface of a carbon-coated gas diffusion layer (Toray, TGPH-090), followed by heating in an Ar flow at 350°C for 1 h. The characteristics of these electrode materials, including the microstructure and crystalline structure, are described in the next section. The electrode area of both the anode and cathode was 1.0 cm². A composite membrane comprised of Sn_{0.9}In_{0.1}P₂O₇ and PTFE was used as an electrolyte. The Sn_{0.9}In_{0.1}P₂O₇ powder (0.92 g) was mixed with the PTFE powder (0.08 g) in a mortar and then cold-rolled to a thickness of 600 μm using a laboratory rolling mill.

The catalytic and electrocatalytic properties of the PtAu/C anode and the Pr-doped Mn₂O₃/C cathode were studied in a dual-chamber mode, as shown in Fig. S1. The PtAu/C or Pr-doped Mn₂O₃/C working electrode was attached to the bottom side of the electrolyte membrane. A commercially-available Pt/C electrode (10 wt% Pt/C, 0.6 mg Pt cm⁻²) was used as a counter electrode and attached to the top side of the electrolyte membrane. The working chamber was supplied with a gas mixture of 8% methanol, 8%

H₂O, 4% oxygen and argon, at a flow rate of 60 mL min⁻¹ in the temperature range from room temperature to 75°C. The counter chamber was supplied with air at a flow rate of 60 mL min⁻¹. The catalytic activity of the working electrode was measured by analyzing the composition of the outlet gas from the chamber using Shimadzu GC-2014 flame-ionization and Varian CP-4900 thermal-conductivity detectors. The potential and resistance of the working electrode were evaluated using a Solartron SI 1260 impedance analyzer with an SI 1287 electrochemical interface. The electrode potential was measured against the counter electrode. The electrode impedance was separated using an Au reference electrode, which was exposed to ambient air.

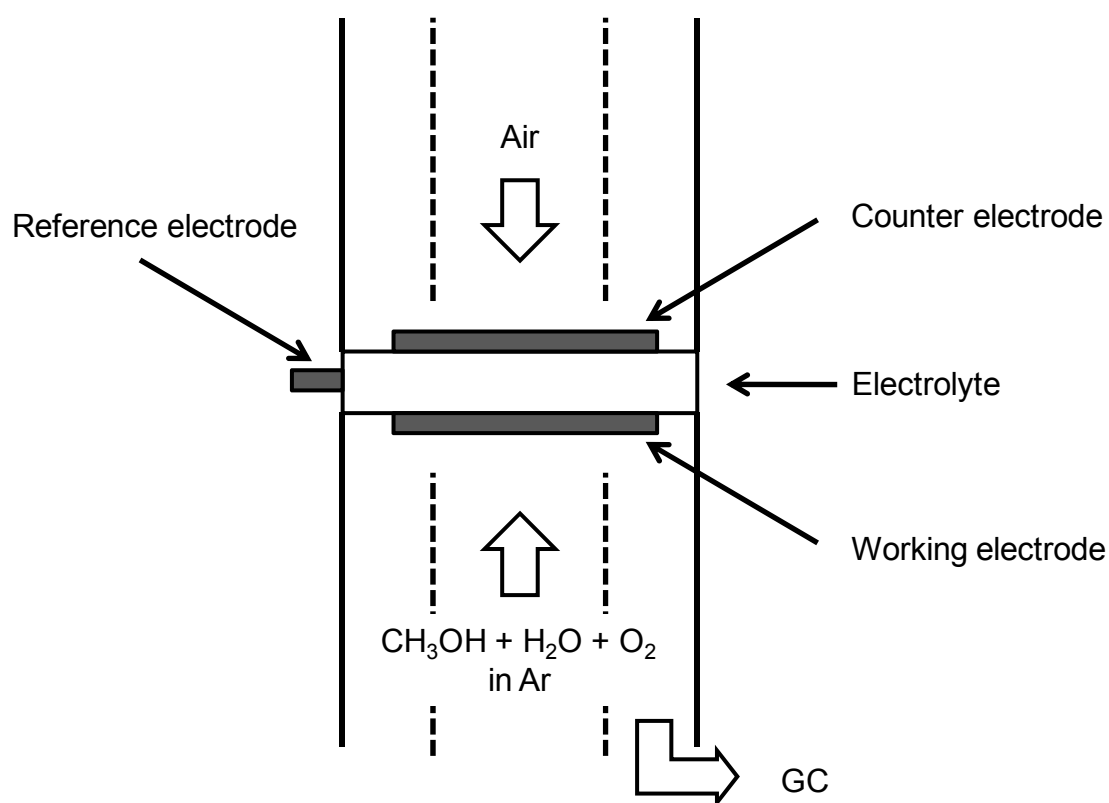


Figure S1. Schematic diagram of the cell configuration for measurements of catalytic and electrocatalytic activities of the working electrode.

Performance tests of single and stacked cells were carried out in a single-chamber mode. The PtAu/C anode and the Pr-doped Mn₂O₃/C cathode were attached on opposite sides of the electrolyte membrane. For stacked cell tests, several cells were tightly connected without a bipolar plate. Single or stacked cells were set up in a stationary methanol aqueous solution bubbled with air. Unless otherwise stated, the methanol concentration was 1 M, the flow rate of air was 60 mL min⁻¹, and the operating temperature was room temperature. Current–voltage curves were measured using a Hokuto Denko HA-501 galvanostat.

Characteristics of Sn_{0.9}In_{0.1}P₂O₇ [2]

We previously reported that 10 mol% In-doped SnP₂O₇ (Sn_{0.9}In_{0.1}P₂O₇) has a cubic structure with SnO₆ octahedra and P₂O₇ units at the corners and edges, respectively. Such closely packed P₂O₇ units could provide many proton bonding sites and associated transport pathways in the bulk, resulting in high proton conductivities above 0.1 S cm⁻¹ between 150 and 350°C under unhumidified conditions. The electromotive force values of a hydrogen concentration cell with this material were very close to the theoretical values calculated from Nernst's equation, indicating that the ionic transport number was 0.97. Thus, Sn_{0.9}In_{0.1}P₂O₇ was found to be an almost purely ionic conductor in a hydrogen atmosphere.

Correction of the potential of the working electrode

In our previous studies, the Pt/C counter electrode usually showed a potential of +920 mV against a hydrogen electrode under the present conditions (for example, P. Heo et al., J. Electrochem. Soc., 153, A897 2006). Therefore, in the present work, we estimated

the potential of the working electrode vs. the hydrogen electrode using the above potential value as a correction value.

Characterizations of PtAu/C and Pr-doped Mn₂O₃/C by transmission electron microscopy (TEM), energy dispersive X-ray (EDX), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) measurements [1]

Specimens for TEM and EDX measurements were prepared by ultrasonic dispersion in *n*-butanol, placing a drop of this suspension onto a Mo grid, and then evaporating the solvent. Bright-field transmission images and EDX spectra were obtained using a JEOL JEM2100F and JED-2300T instrument, respectively, at an accelerating voltage of 200 kV with a beam current of 92 μ A. The XRD patterns were recorded using a Rigaku Miniflex II diffractometer with Cu K α radiation ($\lambda = 1.5432 \text{ \AA}$). The diffractometer was operated at 45 kV and 20 mA. Powder diffraction patterns were recorded in the 2θ range from 20 to 80°. XPS analyses of Mn and Pr were conducted using a VG Escalab220i-XL with Al K α radiation (1486.6 eV). The photoemission angle was set at 45° to the sample surface, allowing for a reduction in the escape depth to a few nm.

TEM observations of PtAu revealed spherical-shaped crystals with diameters from a few to 10 nm grown on the carbon surface. EDX analysis of various locations in the TEM image confirmed that the composition of the crystals was almost pure Pt, independent of the particle size. The Au content of 0.45 mol% is below the detection limit of the EDX measurement. These results correspond to the XRD profile, where the Pt peaks were not shifted by the addition of Au.

The microstructure of Pr-doped Mn_2O_3 was somewhat complex, with particle sizes of 50–200 nm. In all crystals, the EDX intensity was in the order of $\text{Mn} > \text{Pr}$, where the Pr content was in the range from 3 to 8 mol%. The XRD profile revealed only diffraction peaks attributable to Mn_2O_3 , which suggests that most of the doped Pr atoms substitute for Mn atoms. Moreover, the Mn $2p_{3/2}$ and Pr $3d_{5/2}$ XPS spectra had large peaks at 642 and 934 eV, respectively, which provides evidence for the presence of Mn^{2+} (640–642 eV) or Mn^{3+} (641–643 eV) ions and Pr^{3+} (933–934 eV) or Pr^{4+} (935 eV) ions in the sample.

References

- [1] M. Nagao, M. Takahashi, T. Hibino, *Energy Environ. Sci.*, 2010, **3**, 1934.
- [2] M. Nagao, A. Takeuchi, P. Heo, T. Hibino, M. Sano, A. Tomita, *Electrochem. Solid-State Lett.*, 2006, **9**, A105.