

**Electronic Supplementary Information for
Intermediate-temperature alkaline fuel cells with non-platinum
electrodes**

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Ionic conduction in $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$

Acceptor-doped SnP_2O_7 compounds are unique ion conductors that exhibit high conductivity above $10^{-2} \text{ S cm}^{-1}$ in the temperature range from 50 to 300 °C. The SnP_2O_7 structure can be described as a network of MO_6 octahedra sharing corners with P_2O_7 units, characterized by the presence of intersecting zigzag tunnels delimited by pentagonal windows. This unique crystalline structure provides many ion exchange sites and transport pathways. Proton exchange capability is typically introduced into the bulk of SnP_2O_7 by charge compensation through the partial substitution of Sn^{4+} cations with low valency cations, such as In^{3+} , Al^{3+} , Mg^{2+} , Sb^{3+} , Sc^{3+} , Ga^{3+} , and Zn^{2+} . More recently, an opposite effect has been confirmed by partial substitution of Sn^{4+} cations with high valency cations, such as V^{5+} , Nb^{5+} , Ta^{5+} , and Sb^{5+} , which resulted in hydroxide ion exchange capability.

A series of $\text{Sn}_{1-x}\text{A}_x\text{P}_2\text{O}_7$ ($\text{A}^{\text{V}} = \text{V}, \text{Nb}, \text{Ta}, \text{and Sb}$) compounds were prepared and characterized. The electrical conductivity was enhanced by the partial substitution of Sn^{4+} cations with pentavalent cations, the effect of which was most significant for Sb^{5+} . The Sb^{5+} content of 8 mol% was the limit of substitution for Sb^{5+} , where the highest electrical conductivity was obtained at each temperature: 0.04 S cm^{-1} @ 50 °C, 0.08 S cm^{-1} @ 100 °C, 0.04 S cm^{-1} @ 150 °C, and 0.05 S cm^{-1} @ 200 °C.

The anion exchange capability of $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ was further evaluated using spectroscopic and electrochemical analyses. The intensities of the FT-IR absorption bands assigned to OH groups became higher with increasing Sb^{5+} content from 0 to 8 mol%. Several characteristics of $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ also were compared with those of the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ pure proton conductor. The basicity of $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ was higher than that of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$. A steam gas concentration cell with the $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$

electrolyte exhibited opposite polarity to that with the $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$ electrolyte. In contrast to the behavior of $\text{Sn}_{0.9}\text{In}_{0.1}\text{P}_2\text{O}_7$, the H/D isotope effect on the electrical conductivity was not observed for $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$, especially at 100 °C or higher. The production of H_2O vapor at the anode during the cell operation at 200 °C also was confirmed for $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$. Therefore, hydroxide ions are the predominant conduction species in $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ at intermediate temperatures.

Experimental Details

Sample preparation

A $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ membrane was synthesized as according to a procedure reported previously.² Briefly, SnO_2 and Sb_2O_5 were mixed with 85% H_3PO_4 and deionized water. The mixture was stirred at 300°C until it formed a high viscosity paste. The paste was calcined in an alumina pot at 650°C for 2.5 h and then ground into a powder with a mortar and pestle. A total of 0.04 g polytetrafluoroethylene (PTFE) powder was added to 1.00 g of $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ powder, kneaded using a mortar and pestle, and finally cold-rolled to a thickness of 110 μm using a laboratory rolling mill.

The M/C electrodes (M = Pt, Pd, Rh, Ni, Ru, Au, Cu, and Ag) were prepared using the following procedure. A commercially available carbon support (Vulcan, XC-72R) was suspended in a mixed solution of ethanol and deionized water. An aqueous solution of corresponding metal chloride or nitrate was added dropwise to the suspension using a micropipette while stirring at 90°C . After aging at this temperature overnight and then grinding using a mortar and pestle, the powder was heated under H_2/Ar (10 vol% H_2) at temperatures at 350°C for 1 h. The metal content of the catalyst powders obtained was 30 wt%. A mixture of the catalyst powder, PTFE dispersion, 2-propanol, and deionized water was dispersed using a Thinky AR-100 mixer. The slurry was deposited on the surface of a gas diffusion layer (Toray TGPH-090) using a screen printing technique and then dried at 80°C in air to remove the solvent. The loading of all metals was adjusted to *ca.* 1.5 mg cm^{-2} by controlling the time of printing.

The Pd and Ru electrodes were modified as follows. A total of 1.00 g of $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ powder was ground in 10.0 g of tetrahydrofuran (THF) using a planetary ball mill at 150 rpm for 10 h. After ultrasonic treatment for 20 min, the ink

was painted on the surface of the Pt/C electrode using a high-pressure spray coating technique, followed by heating at 50°C in air for 10 min. The loading of $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ was *ca.* 6 mg cm⁻².

Characterization

The electrode samples were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Diffraction patterns were collected using a Rigaku Miniflex II diffractometer operated at 45 kV and 20 mA with Cu K α radiation ($\lambda = 1.5432 \text{ \AA}$). Specimens for XRD measurements were electrodes synthesized without processing. TEM images were obtained using a Jeol JEM2100F microscope at an accelerating voltage of 100 kV with a beam current of 92 μA . Specimens for TEM measurements were prepared by shaving a part of the catalyst layer of the electrode, followed by dispersion of the powder in *n*-butanol in an ultrasonic bath for 10 min. A drop of the resultant suspension was evaporated on a Mo grid. SEM images were taken using a Hitachi S-4800 microscope at an accelerating voltage of 15 kV with a beam current of 0.2 nA. Specimens for SEM measurements were electrodes deposited on the surface of the gas diffusion layer.

Electrochemical measurements

The electrolyte membrane was sandwiched between the two electrodes and then pressed at room temperature at 2 MPa for 2 min. Two gas chambers were arranged by placing the membrane electrode assembly (MEA) between two alumina tubes and sealing with an inorganic adhesive. A Pt reference electrode was attached to the surface of the side of the electrolyte, which was exposed to a H₂ atmosphere. Electrochemical measurements were obtained by supplying H₂ saturated with H₂O vapor at room temperature (50 mL min⁻¹) and air saturated with H₂O vapor at 70°C (50 mL min⁻¹) to the anode and cathode,

respectively. The IR-corrected electrode potential was recorded using the current interruption method, where a sharp change in voltage corresponds to IR loss, and a slow voltage change corresponds to polarization losses. Polarization resistance was analyzed using a Solartron SI 1260 impedance analyzer and Solartron, 1287 electrochemical interface. The frequency range for the measurements was 0.1–10⁶ Hz and the AC amplitude was 10 mV. Current-voltage (*I-V*) and current-power (*I-P*) curves were measured using a Hokuto Denko HA-501 galvanostat. The cell voltage was recorded using the four-probe method and determined after a steady state was attained.

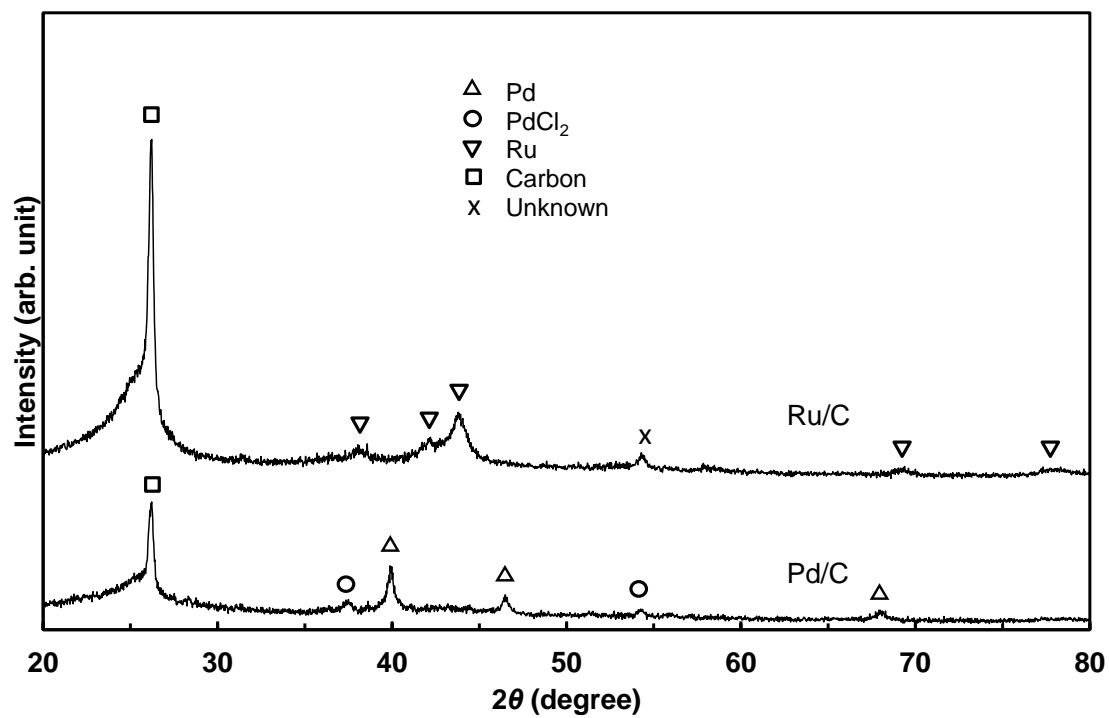


Fig. S1. XRD patterns of Pd/C and Ru/C electrodes.

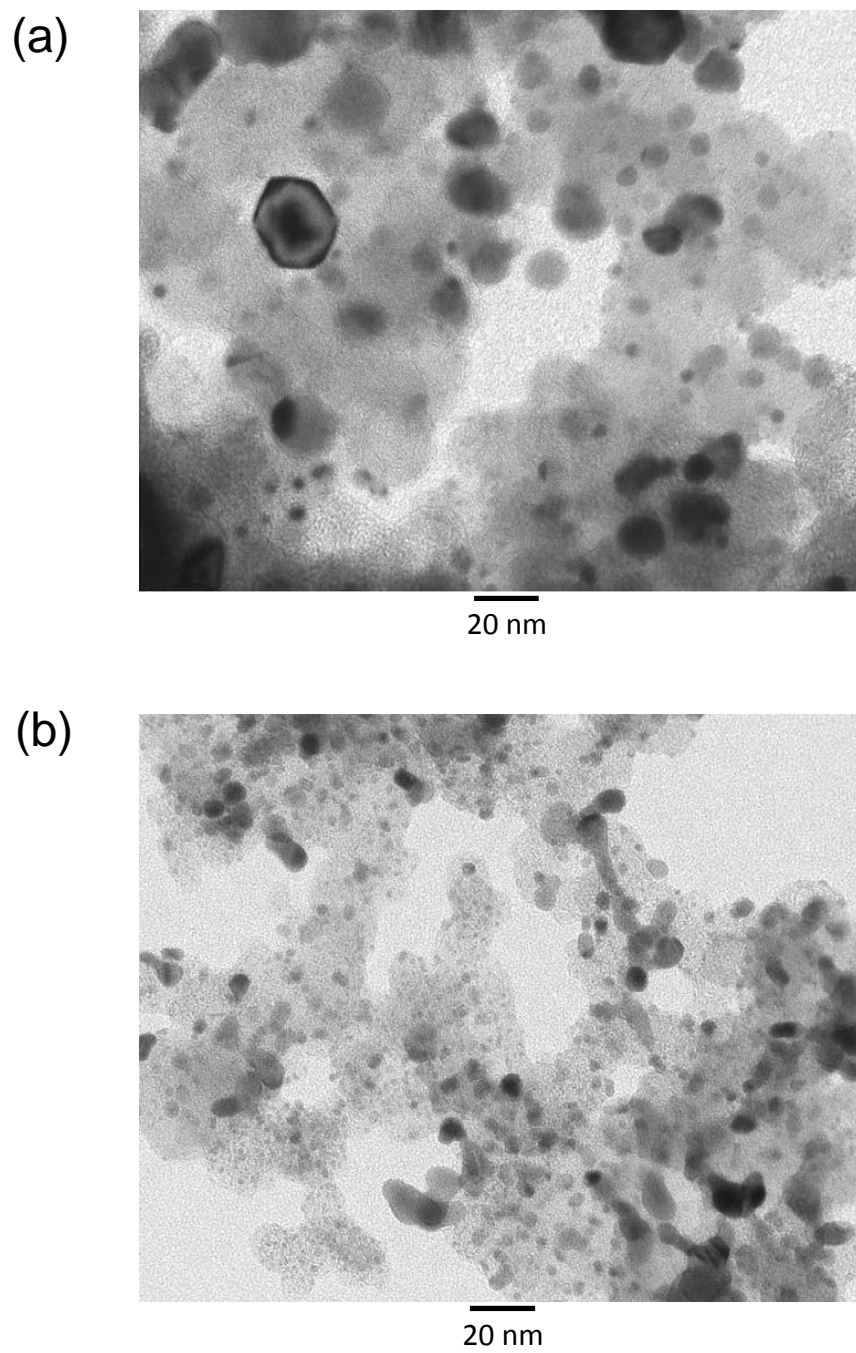


Fig. S2. TEM images of (a) Pd/C and (b) Ru/C electrodes.

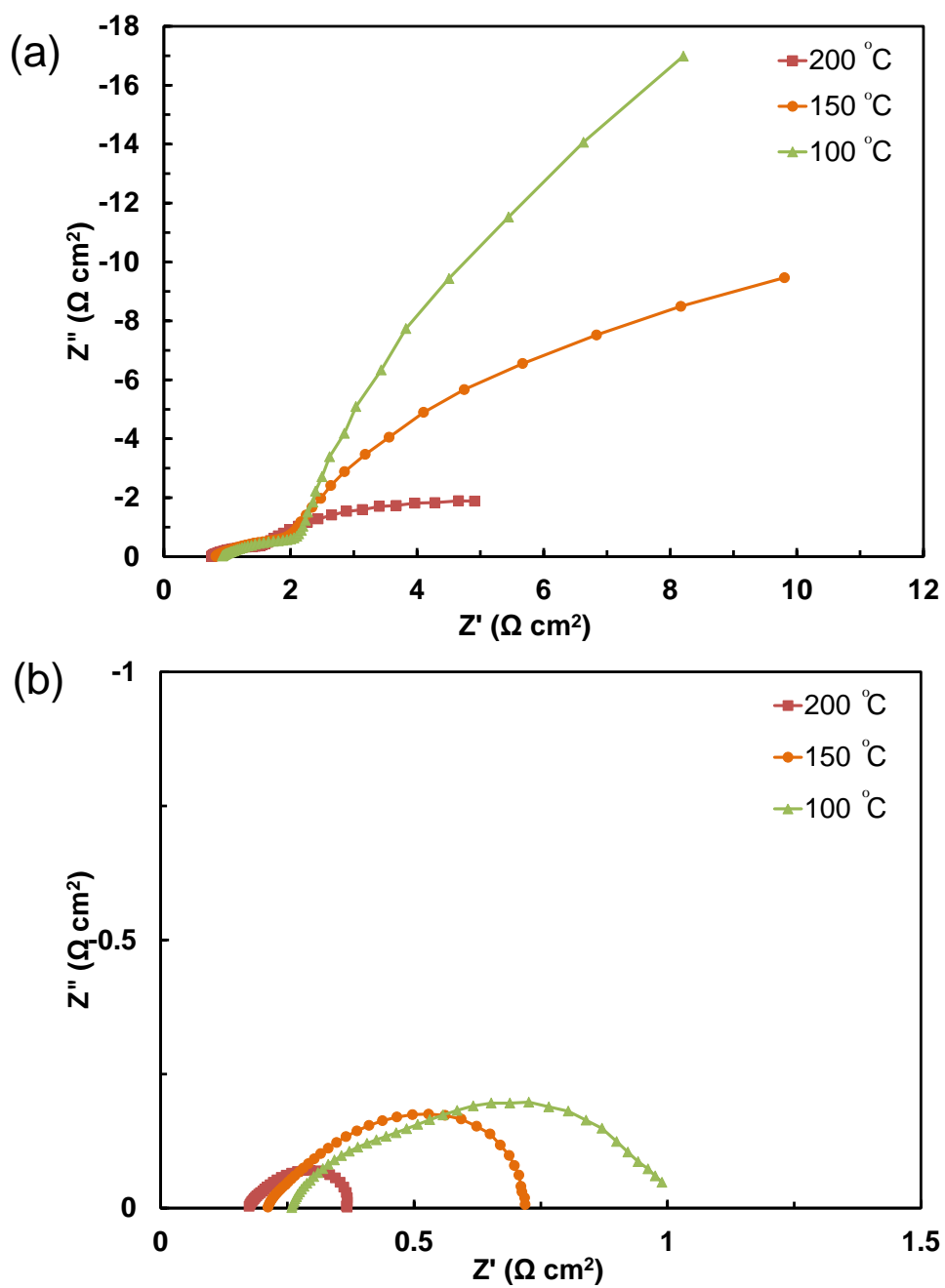


Fig. S3. Impedance spectra of half cells (a) with the Pd/C electrode under air flow and (b) with the Ru/C electrode under H_2 flow. The experiment was conducted under open-circuit voltage conditions.

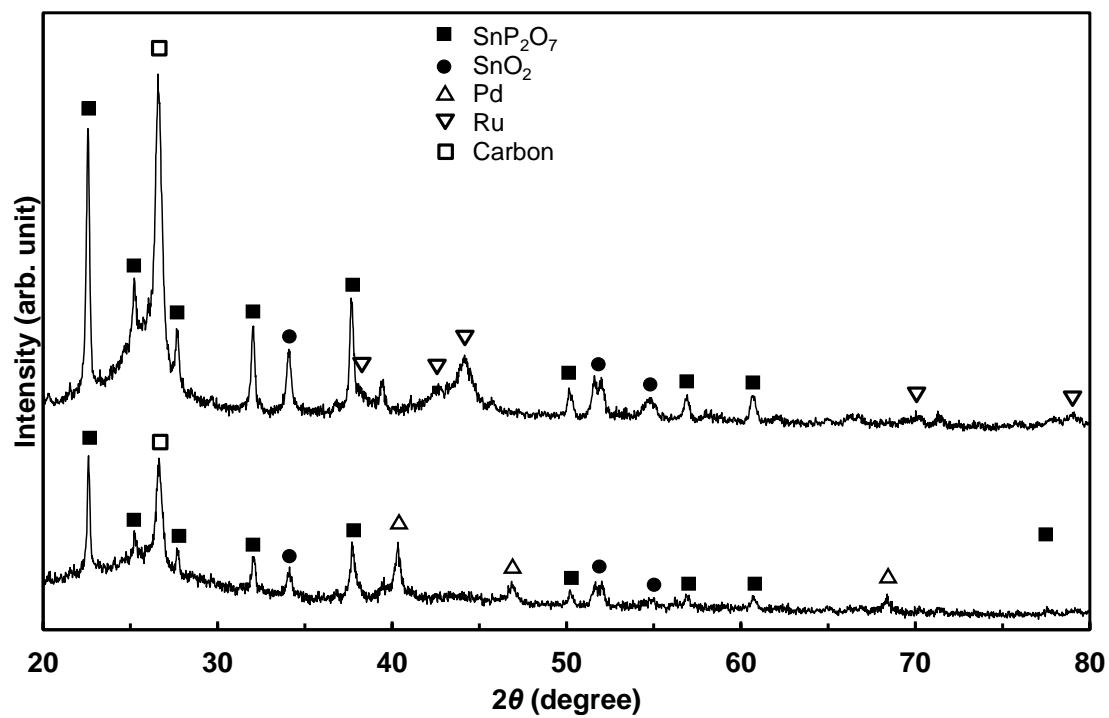


Fig. S4. XRD patterns of modified Pd/C and Ru/C electrodes.

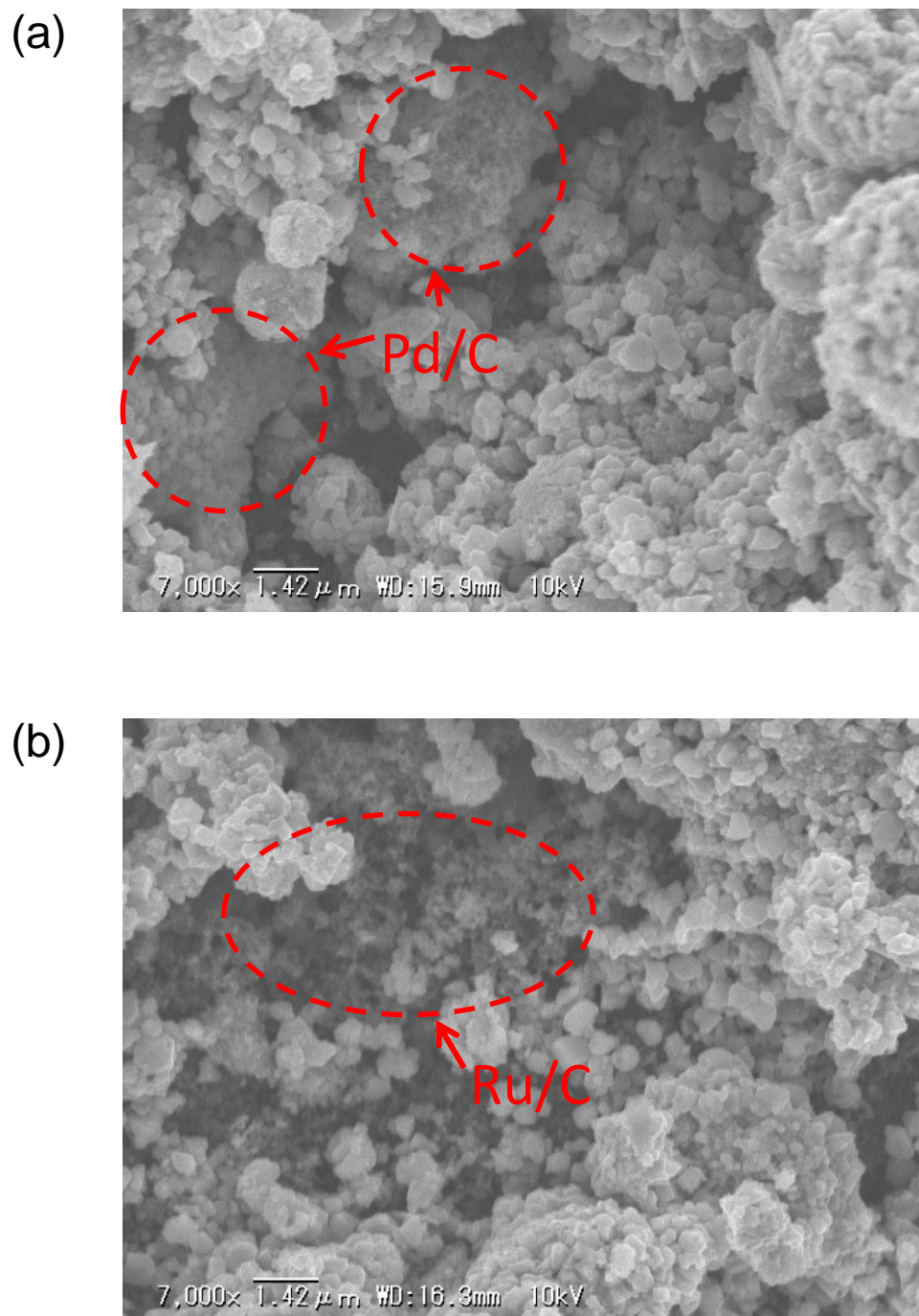


Fig. S5. SEM images of (a) modified Pd/C and (b) Ru/C electrodes.

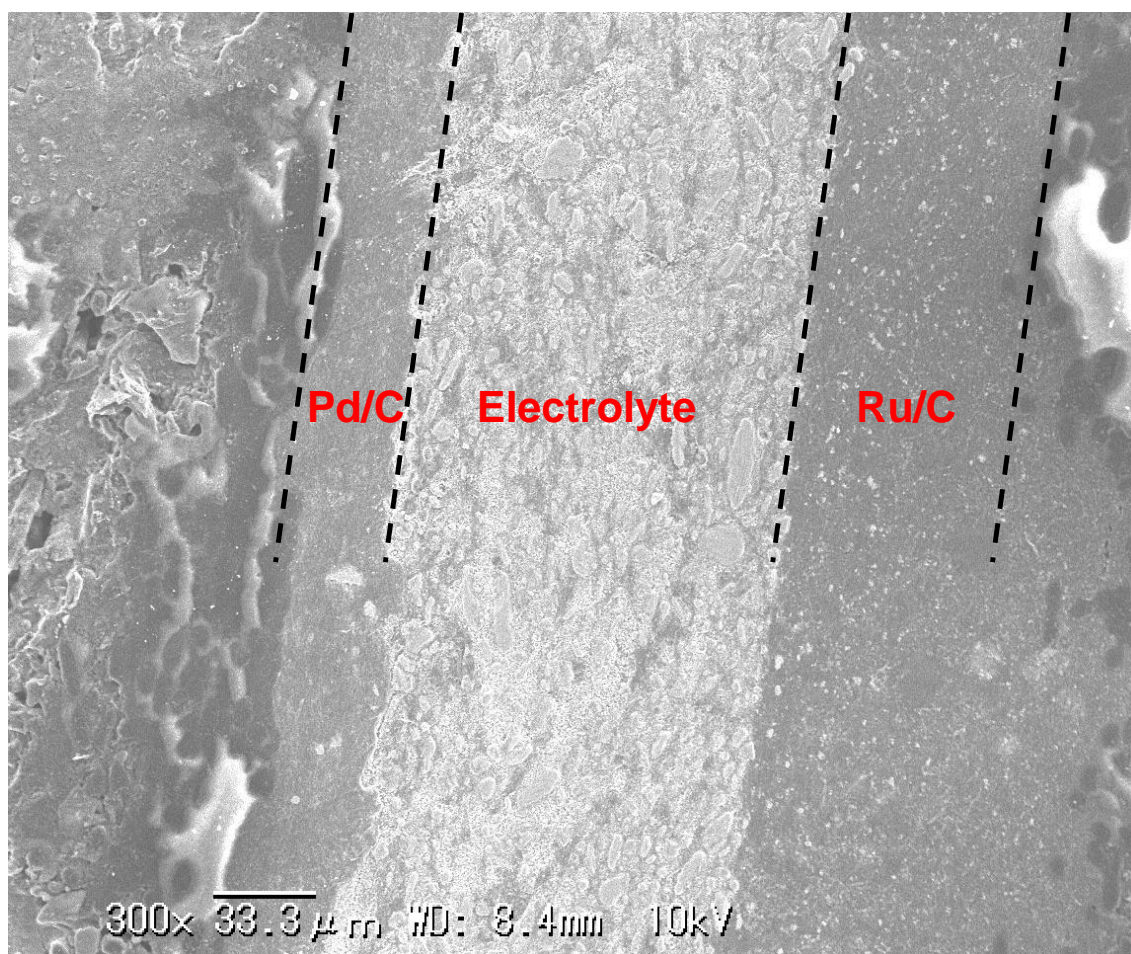


Fig. S6. Cross-sectional SEM image of a fuel cell using the $\text{Sn}_{0.92}\text{Sb}_{0.08}\text{P}_2\text{O}_7$ -PTFE composite membrane as an electrolyte with the Pd/C cathode and Ru/C anode.

References

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- 2 T. Hibino and K. Kobayashi, *J. Mater. Chem. A*, 2013, **1**, 1134.