Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Proton-conducting phosphate glass and its melt exhibiting high electrical conductivity at intermediate temperatures

Takuya Yamaguchi,[†a] Satoshi Tsukuda,[a] Tomohiro Ishiyama,[b]
Junji Nishii,[c] Toshiharu Yamashita,[d] Hiroshi Kawazoe[d] and Takahisa Omata[*a]

[a] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan*
[b] *Fuel Cell Materials Group, Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan*
[c] *Research Institute for Electronic Science, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, Japan*
[d] *Kawazoe Frontier Technologies Corporation, Kuden-cho 931-113, Sakae-ku, Yokohama 247-0014, Japan*

* Corresponding author. Tel.: +81-22-217-5832, fax: +81-22-217-5832
e-mail: takahisa.omata.c2@tohoku.ac.jp

† Present address: Fuel Cell Materials Group, Research Institute for Energy Conservation, National Institute of Advanced Industrial Science and Technology (AIST), AIST Central 5, Higashi 1-1-1, Tsukuba, Ibaraki 305-8565, Japan

Table S1 Glass transition temperature (T_g) of $35NaO_{1/2}$-$1WO_3$-$8NbO_{5/2}$-$5LaO_{3/2}$-xMO_y-$(51-x)PO_{5/2}$ ($MO_y = GeO_2$ and $BO_{3/2}$, and $x = 0$, 1 and 3) glasses. T_g was determined by differential thermal analysis (DTA).

Compositions	T_g / °C
$35NaO_{1/2}$-$1WO_3$-$8NbO_{5/2}$-$5LaO_{3/2}$-$51PO_{5/2}$ ($x = 0$)	420
$35NaO_{1/2}$-$1WO_3$-$8NbO_{5/2}$-$5LaO_{3/2}$-$1GeO_2$-$50PO_{5/2}$ ($MO_y = GeO_2$, $x = 1$)	437
$35NaO_{1/2}$-$1WO_3$-$8NbO_{5/2}$-$5LaO_{3/2}$-$1BO_{3/2}$-$50PO_{5/2}$ ($MO_y = BO_{3/2}$, $x = 1$)	427
$35NaO_{1/2}$-$1WO_3$-$8NbO_{5/2}$-$5LaO_{3/2}$-$3GeO_2$-$48PO_{5/2}$ ($MO_y = GeO_2$, $x = 3$)	469
$35NaO_{1/2}$-$1WO_3$-$8NbO_{5/2}$-$5LaO_{3/2}$-$3BO_{3/2}$-$48PO_{5/2}$ ($MO_y = BO_{3/2}$, $x = 3$)	441

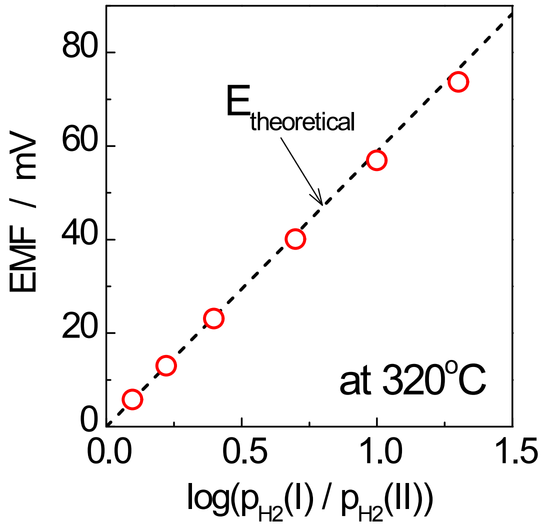

Fig. S1 Electromotive force (emf) as a function of logarithmic p_{H2} ratio of Gas (I) to Gas (II) of the hydrogen concentration cell using 36H-glass as the electrolyte measured at 320 °C. Gas (I) was constant at 100% H_2 gas. The dashed black line indicates the theoretical emf determined using the following Nernst equation: $E = \frac{RT}{2F} \ln\left(\frac{p_{H2}(I)}{p_{H2}(II)}\right)$.

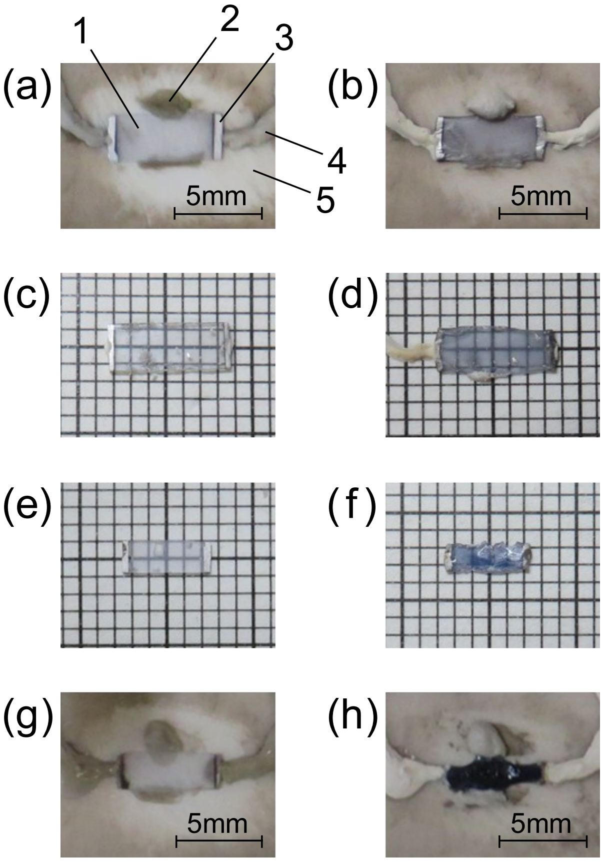

Fig. S2 Optical images of 36H-glass (a, c, e, g) before and (b, d, f, h) after the conductivity measurements at 280, 320, 360 and 400 °C, respectively. The numbers in the image indicate, respectively, 1: 36H-glass, 2: ceramic paste used to hold the glass on ceramic support, 3: Pd electrode, 4: Ag conductive paste, and 5: ceramic support.

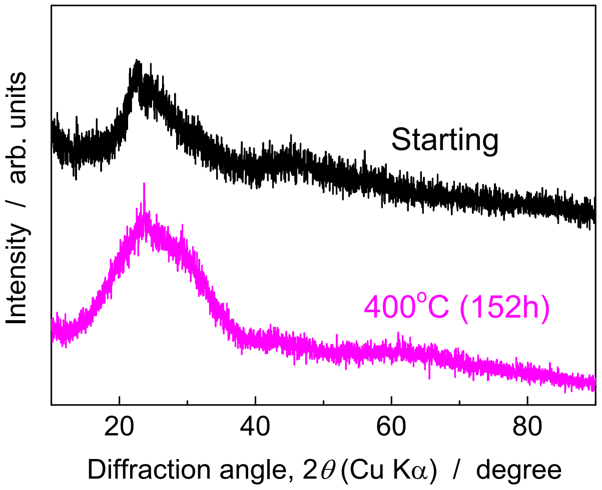

Fig. S3 XRD pattern of 36H-glass before (black line) and after the conductivity measurement at 400 °C for 152 h (pink line). The XRD pattern of the sample after the conductivity measurement (pink line) may contain some backgrounds from the glass sample holder because the amount of the sample was small.

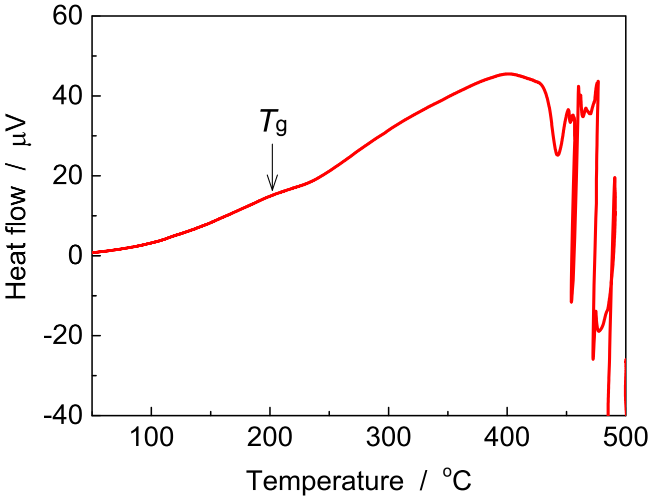

Fig. S4 DTA curve of 36H-glass obtained in dry 3% H_2/97% Ar at a heating rate of 10 °C min^{-1}.

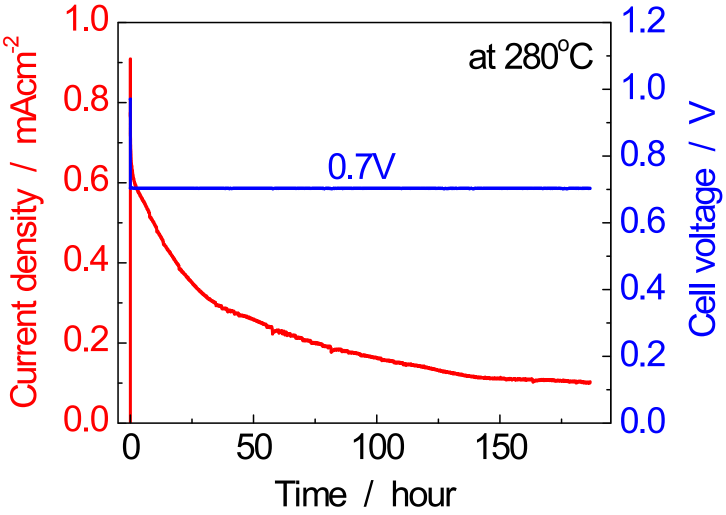

Fig. S5 Time evolution of the output current of the ITFC with the structure dry 100% H_2, Pd | 36H-glass | Pd, dry air at a fixed voltage of 0.7 V.

Viscosity of 36H-glass at 280 °C

The viscosity of typical glasses at glass transition temperature (T_g) is known to be ~10^{12} Pa s, and the viscosity at dilatometric softening temperature (T_d) can be calculated from the thermal expansion curve using following equation [K. Asaoka et al., *Dent. Mater. J.*, 1990, **9**, 193.]:

$$\eta = 1/\sigma \times \alpha(T_d) \times q. \qquad \text{(S1)}$$

where η is viscosity at T_d in Pa s, σ is applied load in N m^{-2}, $\alpha(T_d)$ is thermal expansion coefficient at T_d in °C^{-1} and q is heating rate in °C s^{-1}. In this study, σ was 3.5×10^4 N m^{-2}, $\alpha(T_d)$ was determined to be 6.1×10^{-5} °C^{-1} from the thermal expansion curve (Fig. 2 in the main text), and q was 0.167 °C s^{-1}. Assigning these values to the equation S1, η at T_d was calculated to be $10^{9.5}$ Pa s. The viscosity at T_g and T_d were plotted as a function of T_g/T, as shown in Fig. S5. Of course, it is well known that the viscosity of glass forming liquid generally deviated from Arrhenius behavior [C. A. Angell, *J. Non-Cryst. Solids.*, 1991, **131–133**, 13.]; however, the deviation is not significant in the temperature range between $0.8<T_g/T<1$, especially in oxide glasses that are categorized as "strong" glass. Therefore, the viscosity at 280 °C corresponding to $T_g/T = 0.817$ was extrapolated to be $10^{7.5}$ Pa s based on the plot shown in Fig. S5.

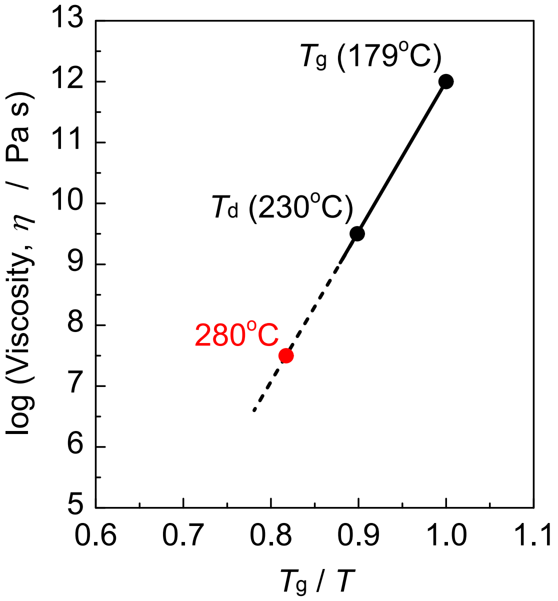

Fig. S6 Viscosity of 36H-glass as a function of T_g / T.

Reactivity of 36H-glass with Pd electrode

We checked the reactivity of 36H-glass with Pd electrode by cross-sectional Pd element mapping image (STEM-EDX image) of the Pd/36H-glass interface after the fuel cell test at 300 °C, and we confirmed that Pd did not dissolve into the glass-melt (Fig. S7). This indicates that the acidity of the present glass-melt is sufficiently low to suppress the reaction with Pd, so that various materials can be applicable in the fuel cell using glass-melt electrolytes.

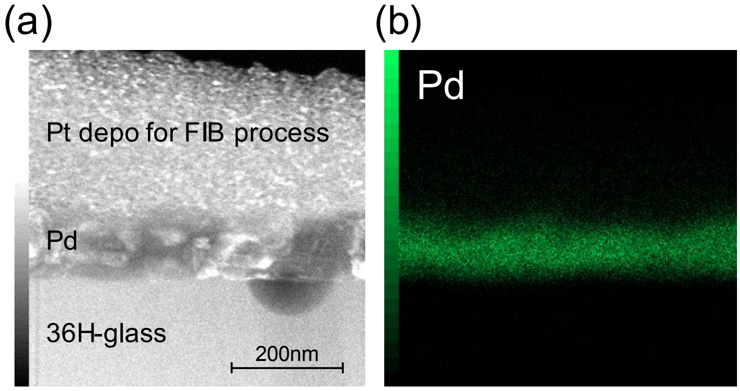

Fig. S7 (a) Cross-sectional STEM image and (b) STEM-EDX Pd element mapping image of the Pd/36H-glass interface after the fuel cell test at 300 °C.