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## Supporting Information

# Investigating the role of GeO<sub>2</sub> in enhancing the thermal stability and proton mobility of proton-conducting phosphate glasses

Takahisa Omata<sup>a\*</sup>, Aman Sharma<sup>a</sup>, Takuya Kinoshita<sup>b</sup>, Issei Suzuki<sup>a</sup>, Tomohiro Ishiyama<sup>c</sup>, Shinji Kohara<sup>d, e, f, g</sup>, Koji Ohara<sup>g</sup>, Madoka Ono<sup>b</sup>, Tong Fang<sup>h</sup>, Yang Ren<sup>h</sup>, Masaya Fujioka<sup>b</sup>, Gaoyang Zhao<sup>h</sup>, and Junji Nishii<sup>b,\*</sup>

<sup>a</sup> Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan <sup>b</sup> Research Institute for Electronic Science, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo 001-0021, Japan <sup>c</sup> 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 <sup>d</sup>Center for Materials Research by Information Integration (CMI2), Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science (NIMS), Ibaraki 305-0047, Japan <sup>e</sup>Research Center for Advanced Measurement and Characterization, NIMS, Sayo-gun, Hyogo 679-5148, Japan. <sup>f</sup>PRESTO, Japan Science and Technology Agency, Chivoda-ku, Tokvo 102-0076, Japan. <sup>g</sup>Diffraction and Scattering Division, Japan Synchrotron Radiation Research Institute (JASRI), Sayo-gun, Hyogo 679-5198, Japan <sup>h</sup> School of Materials Sciences and Technology, Xi'an University of Technology, Xi'an 710048, China

\* Corresponding author.

takahisa.omata.c2@tohoku.ac.jp (T. Omata) and nishii@es.hokudai.ac.jp (J. Nishii).



**Figure S1**. EDX spectra of the glasses before and after APS. (a) 4Ge, (b) 6Ge, (c) 8Ge and (d) 10Ge glasses. The right, middle and left panels show the glass before APS, the anode side and the cathode side for the glass after APS, respectively.

#### **S2.** Proton conductivity



**Figure S2**. emfs for the hydrogen concentration cell as a function of logarithmic hydrogen partial pressure,  $p(H_2)$ , ratio. (a) 4Ge, (b) 6Ge, (c) 8Ge and (d) 10Ge glasses after APS. The  $p(H_2)_{high}$  was fixed at  $4.9 \times 10^3$  Pa. The theoretical emfs calculated using the Nernst equation,  $E = (RT/2F)\ln(p(H_2)_{high}/p(H_2)_{low})$  are shown as black lines.



Figure S3. DC polarization characteristics at 250 °C under 5% $H_2/95$ % N<sub>2</sub> atmosphere of the glasses after APS. (a) 4Ge, (b) 6Ge, (c) 8Ge and (d) 10 Ge glasses.

#### S3. Glass structure



**Figure S4**. Summary of the previously reported mean coordination number of Ge as a function of the mean Ge-O distance. ● ref. S1, ● ref. S2, ● refS.3, ● ref. S4, ● ref.S5 and ● ref. S6.



**Figure S5**. Raman spectra of the glasses before and after APS. (a) 4Ge, (b) 6Ge, (d) 8Ge and (d) 10Ge glasses.

### S4. XPS spectra of Ge 2p core level



Figure S6. XPS spectra of Ge 2p core level of the glasses (a) before and (b) after APS.

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