Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary information

Enhancing proton mobility and thermal stability in phosphate glasses with WO_3: The mixed glass former effect in proton conducting glasses

Aman Sharma,[a] Issei Suzuki,[a] Tomohiro Ishiyama,[b] and Takahisa Omata*[a]

[a] *Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.*

[b] *Research Institute for Energy Conservation, Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

S1. Proton injection by APS

Figure S1 depicts the depth profiles of C_{Na} and C_{OH} for all glasses after alkali-proton substitution (APS). The profiles indicate that over 90% of Na ions were discharged from the glasses, and a large amount of OH was introduced into the glasses through APS. The electrochemical substitution of Na^+ ions with protons was successfully conducted, as evidenced by the comparable absolute values of the changes in C_{Na} and C_{OH}, ΔC_{Na}, and ΔC_{OH}, before and after APS.

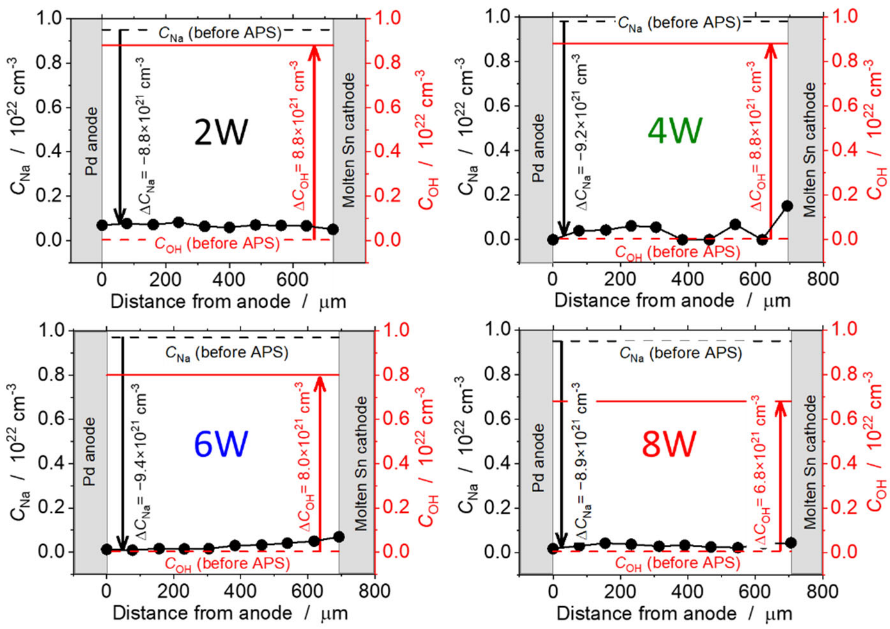

Fig S1 Depth profiles of C_{Na} (black dots) and C_{OH} (red solid line) for *x*W-glass after alkali-proton substitution (APS). The black and red dashed lines indicate C_{Na} and C_{OH}, respectively, for the *x*W-glass before APS.

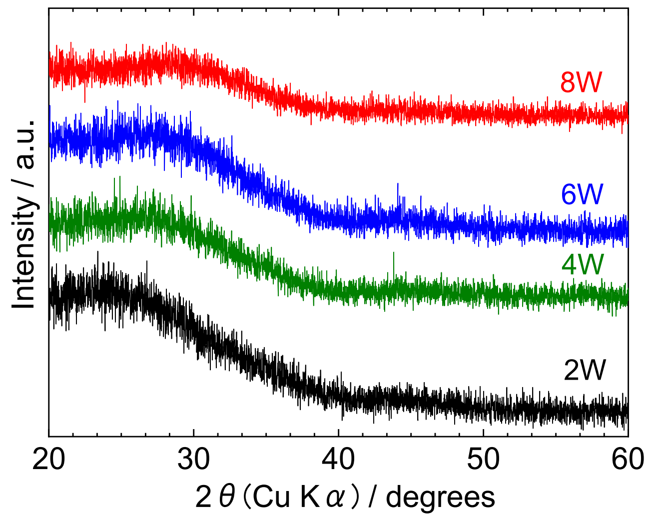

Figure S2. XRD patterns of the *x*W glasses after APS.

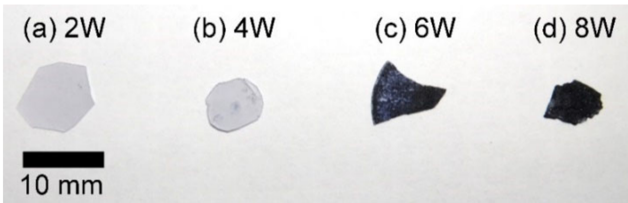

Fig S3 Photographic images of the glasses after alkali-proton substitution (APS) for the (a) 2W-, (b) 4W-, (c) 6W-, and (d) 8W-glasses.

S2. Proton conductivity

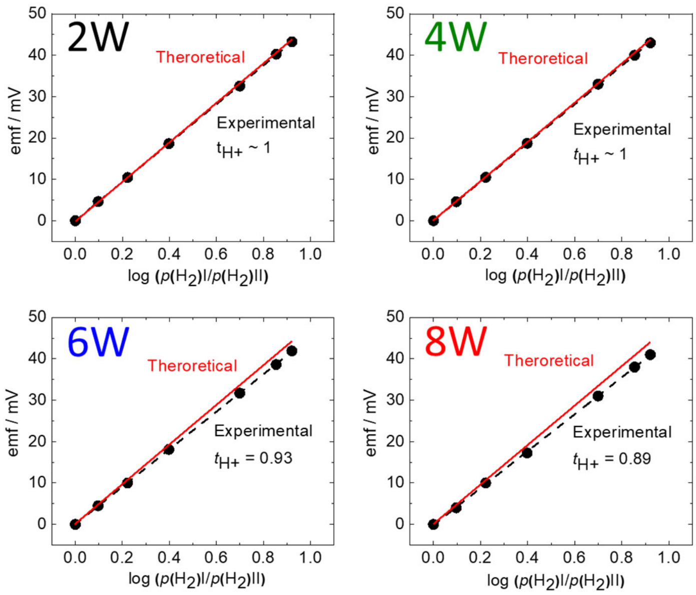

Fig S4 Electromotive forces (EMFs) for the hydrogen concentration cell as a function of logarithmic hydrogen partial pressure, $p(H_2)$, ratio at 207 °C for *x*W glass after alkali-proton substitution (APS). The theoretical emfs calculated using the Nernst equation, $E = (RT/2F)\ \ln(p(H_2)_{high}/p(H_2)_{low})$ are shown as red lines.

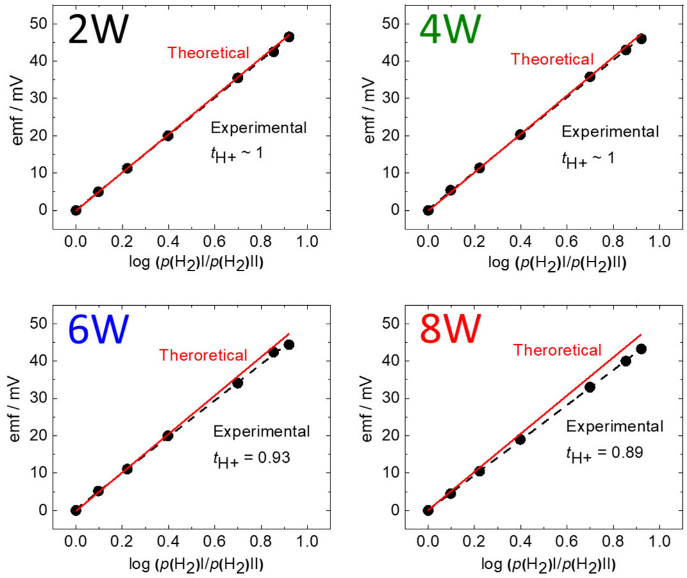

Fig S5 Electromotive forces (EMFs) for the hydrogen concentration cell as a function of logarithmic hydrogen partial pressure, $p(H_2)$, ratio at 243 °C for *x*W glass after alkali-proton substitution (APS). The theoretical emfs calculated using the Nernst equation, $E= (RT/2F)\ \ln(p(H_2)_{high}/p(H_2)_{low})$ are shown as red lines.

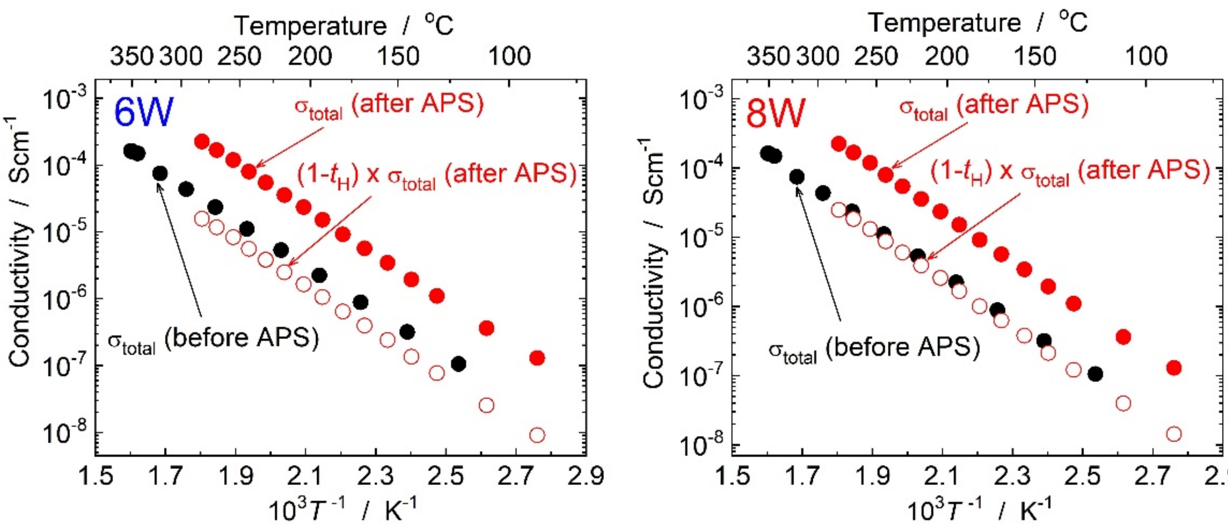

Fig S6 Arrhenius plot of the total conductivity (σ_{total}) and partial conductivity due to non-proton contributions ($(1-t_H)\times\sigma_{total}$) of the 6W- and 8W- glasses after APS comparing with the total conductivity, i.e., approximately Na^+ ion conductivity, of the corresponding glasses before APS.

S3. Raman spectra

Table S1 Assignment of the Raman bands observed for *x*W-glass after alkali-proton substitution (APS).

Assignment[a]	Position / cm^{-1}					Ref.
	2W	4W	6W	8W		
$\delta_{O\text{–}M\text{–}O}$	265	265	265	265	Bending mode of O–*M*–O of MO_6 octahedra	S1-S4
$\delta_{O\text{–}M\text{–}O^-}$	380	380	380	380	Bending mode of O–*M*–O^- of MO_6 octahedra	S1-S4
$\delta_{O\text{–}M\text{–}O} + \delta_{O\text{–}P\text{–}O}$	508	509	512	514	Combination mode of the O–*M*–O bending mode with the O–P–O bending mode	S1-S4
$\nu_{M\text{–}O}$	598	596	595	594	Stretching mode of the *M*–O bond of MO_6 octahedra	S1-S4
$\nu_{P\text{–}O\text{–}P,\ sym}\,(Q^2)$	714	724	738	746	Symmetric stretching mode of the P–O–P bond for the Q^2 unit	S5-S6
$\nu_{M\text{–}O^-}$	917, 950	912, 954	907, 956	902, 956	Stretching mode of the *M*–O^- bond of MO_6 octahedra	S1-S4
$\nu_{O\text{–}P\text{–}O,\ sym}\,(Q^2)$	1163	1159	1157	1153	Symmetric stretching mode of NBOs for the Q^2 unit	S5-S6
$\nu_{O\text{–}P\text{–}O,\ assym},\ (Q^2)$	1246	1244	1242	1240	Asymmetric stretching mode of NBOs for the Q^2 unit	S5-S6

[a] *M* denotes Nb or W

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