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Supplementary Information

Low humidity dependence of proton conductivity in modified zirconium (IV)-hydroxy ethylidene diphosphonates

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I. Several synthesis conditions and the ICP-AES results

Other synthesis conditions were tested to synthesize ZrHEDP with various P/Zr. The nitric acid concentration and the weight ratio of HEDP/Zr-precursor were changed, and the obtained ZrHEDP was characterized by ICP-AES measurement. Table S1 presents their conditions and P/Zr, where the same heating and washing processes in the main text were employed. A high concentration of nitric acid and a large weight ratio of HEDP/Zr-precursor lead to a high P/Zr. However, even if we use their high values, ZrHEDP with P/Zr > 3 was not obtained. ZrHEDP with P/Zr > 3 should have fewer "bridging HEDPs," resulting in more open space for water adsorption and free -PO_3H_2s, and overly hydrophilic properties. It might be the reason that ZrHEDP with P/Zr > 3 dissolved in water in washing processes, and then we could not obtain it.

Table S1 P/Zr values of ZrHEDP samples synthesized under several conditions

HEDP/Zr-precursor	P/Zr (ICP-AES results)		
(Weight ratio)	0.08 M HNO_3	1.00 M HNO_3	5.00 M HNO_3
2.00			2.9
1.70	2.5	3.0	
1.50	2.6	2.9	
1.30		3.0	3.0
1.10	2.5	2.8	
0.90	2.1	2.5	
0.65		1.8	

II. Experimental results

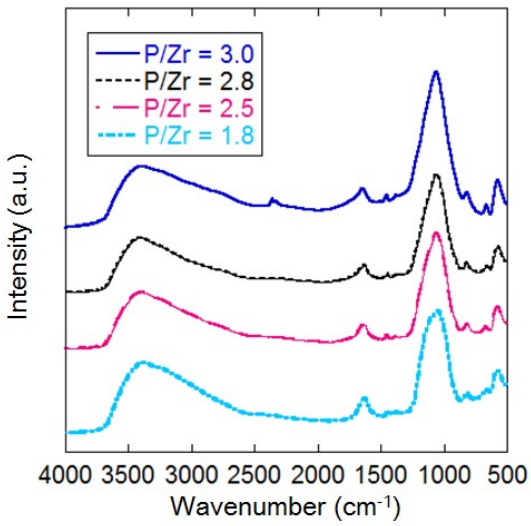

Figure S1 FTIR spectra of ZrHEDPs.

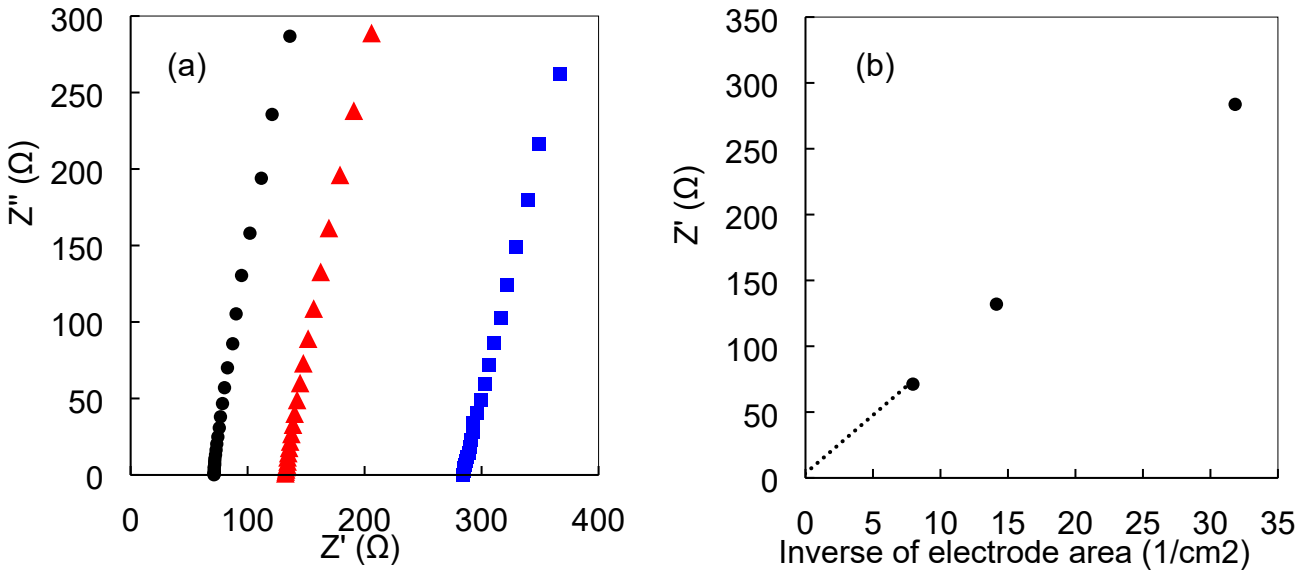

Figure S2 (a) Cole–Cole plots of the ZrHEDP with P/Zr = 2.8 at 95% RH and 90°C using different areas of electrodes. Black, red, and blue plots show the results employing the electrodes with the diameter values of 4 mm, 3 mm, and 2 mm, respectively. (b) The plots of resistivities against the inverse of the electrode areas. We observed the linear relation between them. According to Equation (S1), resistivity is linearly related to the inverse of an electrode area if the sample is in the same conditions and shows the same proton conductivity.

$$\sigma = \frac{d}{RA} \#(S1)$$

where σ is the proton conductivity, d is the distance between electrodes, A is the electrode area, and R is the resistivity. This means that these Cole–Cole plots are derived from the resistivities of the ZrHEDP sample.

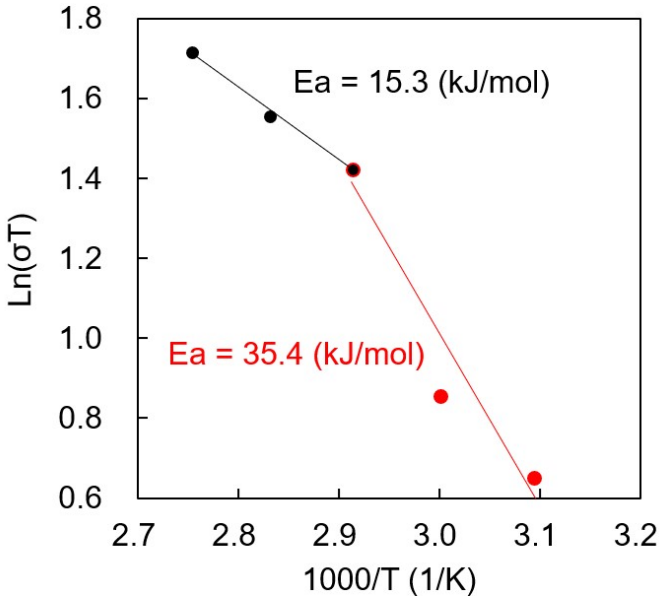

Figure S3. Arrhenius plots vs. T^{-1} from 50°C to 90°C at 95% RH. The slope seems to change at 70°C, which might be derived from the change in framework flexibility. The E_as (kJ/mol) are shown for the two slopes, calculated through Equations (S2)–(S3). Both are below 0.4 eV, which is typically considered to be the E_a of the Grotthuss mechanism.[S1]

$$\sigma = \frac{D_T c e^2}{k_B T} = \frac{C}{T} exp\left(-\frac{E_a}{k_B T}\right) \#(S2)$$

$$D_T = D_0 exp\left(-\frac{E_a}{k_B T}\right) \#(S3)$$

where T, c, e, k_B, D_T, D_0, and C are the absolute temperature, proton concentration, elementary charge, Boltzmann constant, temperature-dependent diffusivity coefficient, reference diffusivity coefficient, and pre-exponential factor, respectively.[S2]

III. The estimation method of the average distance between -PO_3H_2 moieties in ZrHEDP samples

The average distance between -PO_3H_2 moieties in ZrHEDP samples is estimated based on the phosphorous (-PO_3H_2) concentrations per the volume of pellets for proton conductivity measurements, explained as follows. Table S2 presents all the data for the calculation.

The weight density per volume (ρ) of the ZrHEDP pellets is simply calculated from the weight and volume of the pellets for proton conductivity measurements. ICP-AES results indicate the phosphorous molar concentration per weight of ZrHEDP samples (C_P). We can then estimate a

phosphorous molar concentration per volume of the pellets (ρC_P).

Two phosphorous per zirconium, at least, have to be included in the ZrP frame [see Fig. 1(c)]. Therefore, the value of {(P/Zr)–2)/(P/Zr)} represents the "minimum" ratio of -PO_3H_2 per whole phosphorus in a ZrHEDP. The ratio is the "minimum" because there is a possibility that ZrHEDP samples have remained ZrO_2, which misleadingly decreases P/Zr, and then the samples actually include more dense -PO_3H_2 in the structures of ZrHEDP with P/Zr = 4. In addition, the remaining HEDP in ZrHEDP samples is denied by NMR results.

Multiplying the phosphorous concentration per volume (ρC_P) by the values of {(P/Zr)–2)/(P/Zr)}, we obtain -PO_3H_2 molar concentration per volume of the pellets. Assuming a cubic around -PO_3H_2 with r as one side, r is the average distance between -PO_3H_2s. One -PO_3H_2 in the single cubic is equal to the number of -PO_3H_2s per volume, [$\rho C_P N_A \times$ {(P/Zr)–2)/(P/Zr)}], described as follows:

$$\left(\frac{1}{r}\right)^3 = \left\{\rho C_P N_A \times \left[\frac{(P/Zr)-2}{(P/Zr)}\right]\right\} \#(S4)$$

where N_A is the Avogadro constant (mol^{-1}). The average distances are then calculated through Eq. (S4) (7.4, 9.0, and 10.7 Å for P/Zr = 3.0, 2.8, and 2.5, respectively). As for the ZrHEDP P/Zr = 1.8, the above method cannot be applied because {(P/Zr)–2)/(P/Zr)} is a negative value.

The phosphorous density per volume of ZrHEDP pellets (distance between phosphorous) can be obtained objectively at least using the ICP-AES results and the volume and weight of pellets. As presented in Table S2, the distance between phosphorus is around 5 Å, approximately the same as the P-P distance in the ZrP framework (see Fig. 1). It verifies that the above method is sufficient to estimate the distance roughly.

The average distance of ZrHEDP with P/Zr = 3.0 was 7.4 Å, which is shorter than the expected average distance [9–11 Å, Fig. 1 (d)] along with the zirconium phosphonate plane. It should be because the pellets were formed by pressing and the acid distance between the 2D planes of the ZrHEDPs became close. In addition, as the value of P/Zr increases among P/Zr = 2.5, 2.8, and 3.0, the distance between phosphorus seems short. This might be because less "bridging HEDPs" make the 2D planes close.

Table S2 Data for the average distance between -PO_3H_2 moieties in ZrHEDP samples

P/Zr	3.0	2.8	2.5	1.8
Area of pellet (cm^2)	1.327	1.327	1.327	1.327
Thickness of pellet (cm)	0.085	0.075	0.039	0.078
Weight of pellet (g)	0.210	0.201	0.100	0.204
Weight density of pellet (ρ, g cm^{-3})	1.855	2.008	1.950	1.974
Phosphorous amount per weight by ICP-AES results, (C_P, mol g^{-1})	0.00668	0.00573	0.00547	0.00554
Density of phosphorus ($\rho C_P N_A$, nm^{-3})	7.46	6.94	6.43	6.59
{(P/Zr)–2/(P/Zr)}	0.325	0.195	0.126	−0.055
Density of -PO_3H_2 ($\rho C_P N_A \times$ {(P/Zr)–2)/(P/Zr)}, nm^{-3})	2.425	1.354	0.810	N/A
Distance between phosphorus (Å)	5.1	5.2	5.4	5.3
Distance between -PO_3H_2 (Å)	7.4	9.0	10.7	N/A

References

1. S.-S. Bao, G. K. H. Shimizu and L.-M. Zheng, Proton conductive metal phosphonate frameworks, *Coord. Chem. Rev.*, 2019, **378**, 577-594.
2. P. W. Atkins, J. De Paula and J. Keeler, *Atkins' Physical Chemistry*, Oxford University Press, 2018.