Supplementary Information

First-principles calculations of proton defect properties in Ca-doped YPO₄

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Table S1. Optimized lattice constants for YPO4, as calculated using various exchange-correlation interactions; experimental values are shown for comparison.

Method	<i>a</i> (Å)	<i>c</i> (Å)	V (Å ³ /formula unit)	Ref.
PBE	6.962	6.059	73.43	-
PBEsol	6.881	6.005	71.08	-
r ² SCAN	6.895	6.034	71.70	-
HSE06	6.894	6.015	71.47	-
Experimental	6.895	6.028	71.64	[S1]
Experimental	6.907	6.035	71.65	[S2]

Table S2. Optimized binding energies for O_2 molecules are calculated using various exchange-correlation interactions; experimental values are shown for comparison.

Method	Binding Energy (eV)	Bond length (Å)	Ref.
PBE	-6.08	1.233	-
PBEsol	-6.59	1.227	-
r ² SCAN	-5.43	1.222	-
HSE06	-5.19	1.209	-
Experimental	-5.23	-	[S3, S4]
Experimental	-5.12	1.21	[S5]



Fig. S1. Electronic band structure and density of states (DOS) of the YPO₄ unit cell. The calculated bandgap of 6.705 eV in YPO₄ is characterized by oxygen (O) having a higher density of states just below the valence-band maximum (VBM), whereas yttrium (Y) exhibits a larger DOS just above the conduction-band minimum (CBM).

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Fig. S2. Results of the search for stable positions of OH_0^{\bullet} in YPO₄. The relative energies are 0.11 eV for pink, 0.53 eV for cyan, and 1.38 eV for blue, with the purple sphere at 0 eV as the reference state. The views are from the (a) [001], (b) [010], and (c) [100] directions.



Fig. S3. An illustration of how the proton at the stable site in YPO₄ bonds to the neighboring oxygen. Stable positions of OH_0^{\bullet} in YPO₄ were sought. The relative energies are (b) 0.11 eV for pink, (c) 0.53 eV for cyan, and (d) 1.38 eV for blue in comparison with the purple sphere (a) as the reference state.



Fig. S4. Comparison of the concentrations of Ca substituted for Y in YPO₄, as calculated under various conditions. The Ca concentration was calculated to be lower when $Ca_2P_2O_7$ was used as the coexisting phase for determination of the chemical potential of Ca. In the case of CaHPO₄, which was used as a raw material in the previous experimental study by Amezawa *et al.* [S6], a sufficient amount of Ca was found to be soluble. Notably, the doped amounts evaluated by the conventional constant- μ method vary with temperature.



Fig. S5. Defect concentration in undoped YPO_4 (a) at 700 K and an oxygen partial pressure of 0.1 atm, (b) at 700 K and a water-vapor partial pressure of 0.01 atm, and (c) at an oxygen partial pressure of 0.1 atm and a water-vapor partial pressure of 0.01 atm.



Fig. S6. Defect concentration in Ca-doped YPO₄ as a function of the Ca doping amount at an oxygen partial pressure of 0.1 atm and a water-vapor partial pressure of 0.01 atm. Panels (a)–(f) illustrate the variation in defect concentration with changing Ca doping levels ranging from 1 to 10^{-5} mol%.



Fig. S7. The long-range a-axis proton diffusion pathway in Ca-doped YPO₄, as determined from NEB calculations. The black spheres represent stable initial sites, whereas white spheres depict intermediate images for long-range a-axis diffusion. Proton diffusion paths in a-axis viewed (a) from [001] and (b) from [010] are shown. (c) Plot showing that the migration barrier for long-range diffusion in a-axis is 1.33 eV.



Fig. S8. Activation energies derived from graphs in previous studies in which the conductivity for YPO_4 doped with 3 mol% Ca [S6]. The association energies of the *c*-channel migration barrier and proton complex in undoped YPO_4 were compared based on the value when $P(H_2O)$ is 1.4 kPa.

References

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