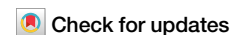


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Synergistic proton conduction via Ca-vacancy coupled with Li⁺-bridge in Ca₅(PO₄)₃OH



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Proton conductivity plays a crucial role in the advancement of materials for proton ceramic fuel cells (PCFCs) and a variety of electrochemical devices. Traditional approaches to enhancing proton conductivity in perovskites have largely relied on doping strategies to induce structural oxygen vacancies. However, these methods have yet to overcome the challenges associated with achieving desired proton conductivity. Here, we introduce an approach wherein intermediate Li⁺ ions act as a bridge linked to Ca vacancies, fostering a mechanism for accelerated proton transport. Utilizing protonated Ca₅(PO₄)₃OH-H(Li) as an electrolyte, we achieve a proton conductivity of 0.1 S cm⁻¹ and a fuel cell performance of 661 mW cm⁻² at an operational temperature of 550 °C for realizing low temperature PCFCs. This proton transport synergy overcomes traditional doping limitations, enabling the advancement of proton-conducting electrolytes and enhancing the efficiency of proton conducting electrolyte fuel cells, with implications in energy conversion and storage technologies.

PCEFCs emerge as trailblazers in the dynamic landscape of electrochemical energy conversion, navigating the complexities of both high and low-temperature domains (HT and LT)^{1–7}. Discerning the nuances between HT and LT proton fuel cells proves pivotal in comprehending the tailored characteristics of these fuel cells designed for diverse operational ranges^{8–11}. The proton ceramic fuel cells (PCFCs) are robust challenger because of their operational temperature is typically above 300 °C^{12–16}.

PCFCs do not utilize noble catalyst metals in electrodes and electrochemical reactions; instead, they heavily rely on proton conductivity in ceramic electrolyte materials. Notably, commonly employed PCFC electrolytes, grounded in yttrium-doped BaZrO₃ and BaCeO₃ perovskite oxides, exhibit a constrained proton conductivity ranging from 10⁻² to 10⁻³ S cm⁻¹ at approximately 600 °C^{17–19}. Therefore, there is a growing demand for developing materials with high proton conductivity, around 0.1 S cm⁻¹ at temperatures between 300 and 500 °C^{20,21}. This temperature range is ideal for combining the advantages of high-temperature and low-temperature fuel cells while minimizing their drawbacks, thus facilitating in the commercialization of fuel cells²². Conversely, LT-PCEFCs, such as PEMFCs that operate at lower temperatures, require noble catalyst electrodes like Pt and

depend on specific high humidity levels to maintain sufficient proton conductivity for optimal power output^{23,24}.

Both HT and LT fuel cells present distinctive advantages and disadvantages but LT PCFCs hold even more attractive potential in certain aspects especially in low cost for future commercialization. The global landscape of research and development evinces heightened interest in both types of fuel cells. Notably, PEMFCs have already achieved notable commercialization milestones, finding application especially in the automotive and some interest in power generation sectors^{24,25}.

Notably, Qian et al. recently spotlighted the potential of proton conducting materials, demonstrating exceptional proton conductivity through Cd vacancies in a CdPS₃-based membrane²⁶. However, their achievement primarily resides in the LT domain, evident in the material's dependence on high relative humidity levels and operational temperatures not surpassing 100 °C.

In clarifying this distinction, this work propels the mechanism of metal vacancy-induced proton transport into PCFCs, elucidating the synergistic interplay between Ca vacancies and Li⁺ bridging ions, exemplified in Ca₅(PO₄)₃OH. This breakthrough not only bridges the gap between LT and

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HT PCEFCs but also underscores the pivotal role of PCFCs in the broader context of energy conversion technologies.

$\text{Ca}_5(\text{PO}_4)_3\text{OH}$, characterized by the hydroxyapatite structure, emerges as a focal point of our investigation^{27–29}. While extensively studied for its crystal structure and properties, our research unveils an intriguing phenomenon of significant enhancement in proton conductivity facilitated by calcium vacancies within $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.

In addition, Furuseki, Horiuchi, and Bystrov's previous study provides vital insights into the proton-conducting properties of hydroxyapatite (HAp) composites, displaying the variety and possible applications of this material^{30–32}. Our study uniquely focuses on characterizing calcium vacancies and protonation within $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$, incorporating insights derived from nuclear magnetic resonance (NMR) spectroscopy.

The apex of our investigation reveals an exceptional proton conductivity approaching 0.1 S cm^{-1} at 500°C for $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$, presenting a compelling avenue for augmenting fuel cell performance. In the subsequent sections, we delve into experimental details, results, and the far-reaching implications of our findings, offering a comprehensive exploration of the remarkable properties of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and its potential transformative impact on future energy technologies. This discovery represents advancement towards developing efficient and cost-effective proton-conductive materials. It also introduces new possibilities in energy conversion and storage applications, highlighting the importance of high-temperature PCFCs in sustainable energy solutions.

Results and discussions

Structure and morphology

Figure 1A presents the XRD patterns of the four samples which well match with the XRD diffraction pattern of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (JCPDS No.73-0293) with a space group structure of P63/m. The diffraction angle of about 29° in K- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and Li- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ belongs to CaCO_3 (JCPDS No. 86-0147), and this diffraction peak disappeared in acetic acid treated H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, which further indicates that the peak belongs to CaCO_3 ³³. Since Ca^{2+} is partially replaced by other ions K^+ , Li^+ and H^+ which have different ion radii, the unit cell dimensions of the material will be affected, resulting in different degrees of deviation of the diffraction peak in the XRD patterns³⁴.

In order to further analyze changes in crystal structure the XRD patterns were refined using GSAS II software. The refinement results are presented in Fig. 1B. As shown in Supplementary Fig. S1, due to H^+ ($8 \times$ The ionic radius of $10^{-6} \text{ \AA}$) and Li^+ ($0.69 \text{ \AA}$) is smaller than that of Ca^{2+} ($1 \text{ \AA}$), and

the lattice parameters of Li- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ are smaller compared to $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, indicating that Li^+ and H^+ enter the interior of the lattice. Although the ionic radius of K^+ ($1.38 \text{ \AA}$) is larger than that of Ca^{2+} , the decrease in crystal cell parameters has also been mentioned in other literature. This abnormal phenomenon is mainly due to the charge imbalance caused by the substitution of K^+ for Ca^{2+} , which creates vacancies and leads to abnormal changes in crystal cell parameters³⁵.

Supplementary Fig. S2 presents Scanning Electron Microscopy (SEM) measurements which show that both $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ are plate structure, and the morphology remains consistent before and after ions substitution. However, due to the acid treatment the particle size has reduced from 120 nm ($\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$) to 70 nm ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) as acid treatment can introduce functional groups or alter the surface roughness of a material, which may result in a decrease in apparent size.

Supplementary Fig. S3 shows the high-resolution transmission electron microscopy (HR-TEM) image of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$. The particle displays well-defined crystalline fringes with a lattice spacing of 0.27 nm correspond to the (112) plane of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, indicating that the crystal structure was not affected by the protonation. Through EDS observation of element distribution, it can be seen that Ca, P and O are uniformly distributed in H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, and the content of K is lower compared to other elements. This is mainly ascribed to multiple washing and ion exchange processes during the preparation of H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Due to the limitations of quantitative EDS analysis, the distribution of H and Li light elements cannot be observed.

Characterization of calcium vacancies and protonation in $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-Li}$ samples

As above mentioned, because of the EDS quantitative testing limitation, the light elements cannot be routinely analyzed. Hence, ICP-AES was performed to determine the concentration of various elements in the $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-Li}$ samples, and the results are listed in Supplementary Table S1. According to the relative atomic mass of each element, the corresponding molar concentration of each element can be calculated. The chemical formula of calcium hydroxy phosphate is $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, and the P content is constant during protonation. Therefore, we assume that the molar ratio of P in $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ is 3.1159312842. Based on the calculated molar concentration, it can be determined that the molar ratio between the various elements is approximately K: Li: Ca: P = 0.0075:0.1225:19:3.11. It can be seen that there is an order of magnitude difference between the content of K and other elements, which can be

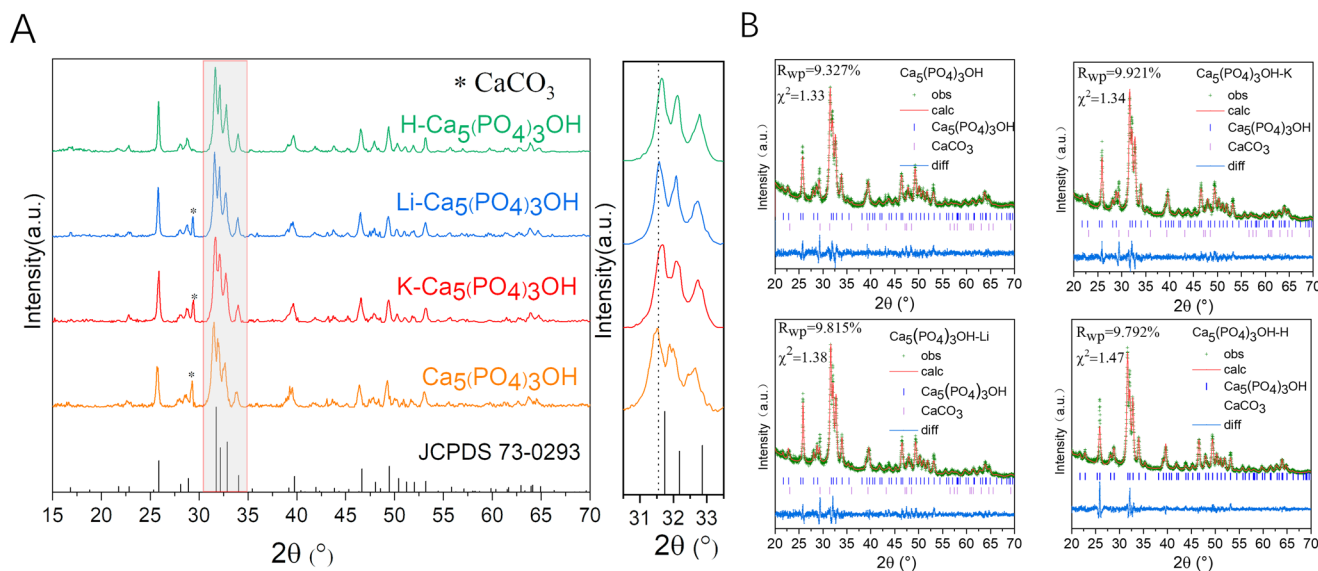


Fig. 1 | X-ray Diffraction analysis. (A) XRD patterns of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, $\text{Ca}_5(\text{PO}_4)_3\text{OH-K}$, $\text{Ca}_5(\text{PO}_4)_3\text{OH-Li}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$. (B) Refined XRD patterns of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, $\text{Ca}_5(\text{PO}_4)_3\text{OH-K}$, $\text{Ca}_5(\text{PO}_4)_3\text{OH-Li}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$.

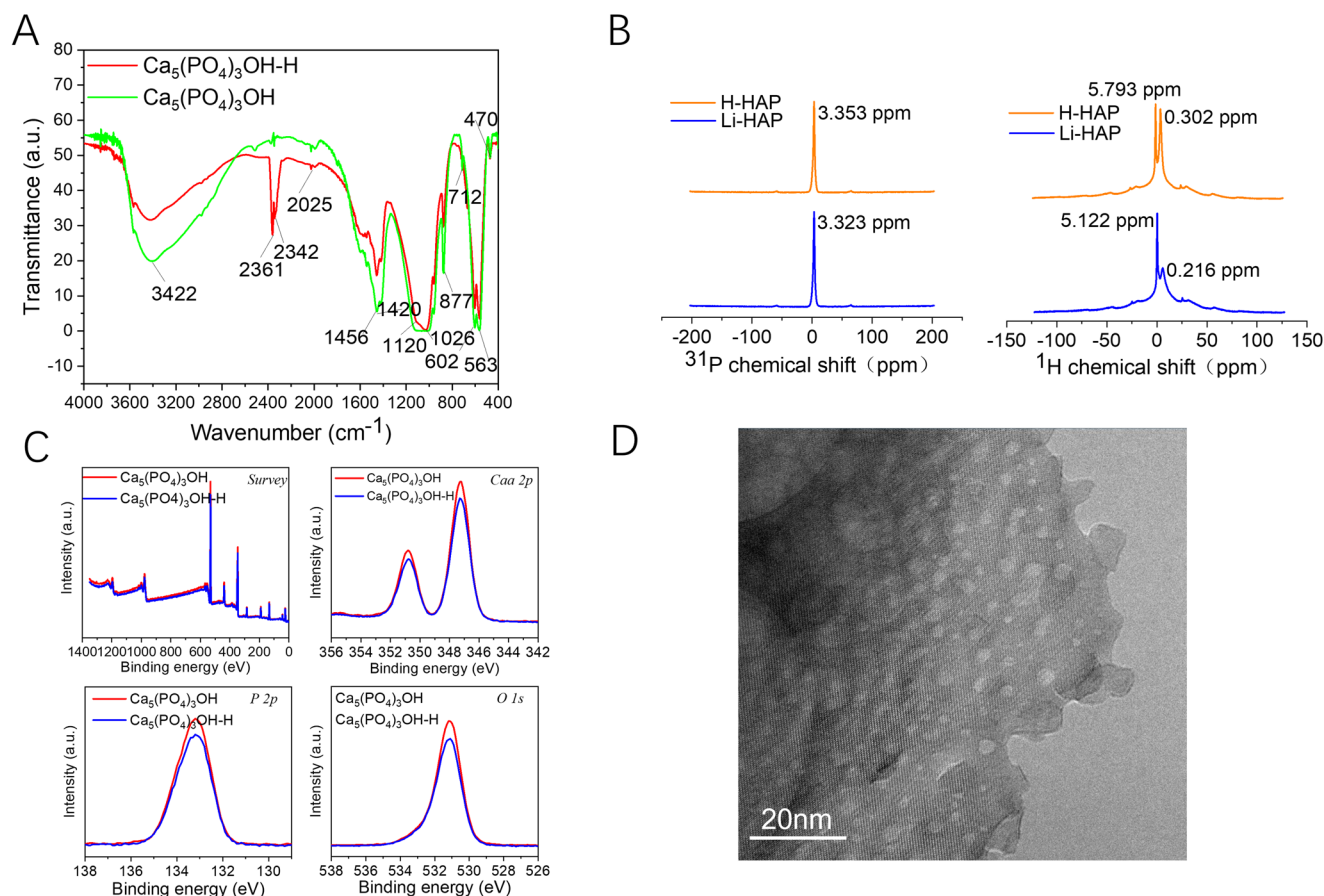


Fig. 2 | Structural characterizations. A FTIR spectra of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (B) (a) ^{31}P NMR spectra of H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (C) XPS Spectra of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ (D) HR-TEM image of H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ powder.

ignored, and this is also consistent with EDS results. Based on the charge balance and valence states of other elements, the molar ratio of H in $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ can be calculated, thereby determined the chemical formula of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ as $\text{Ca}_{4.89}\text{Li}_{0.03}\text{H}_{0.19}(\text{PO}_4)_3\text{OH}$. Ca-vacancy promotes proton transport as it creates a defect site with a low activation energy for proton hopping. In oxide materials the Ca-vacancy can act as a proton acceptor, which can facilitate the dissociation of protonic species like H_2O into H^+ and OH^- ions. The generated H^+ ions then migrate through the Ca-vacancy site via proton hopping, which has a lower activation energy compared to other pathways. Therefore, the presence of Ca-vacancy defects can significantly enhance the proton conductivity of the materials³⁶. In addition, the presence of Ca vacancies influences the hydration dynamics within the material, creating favorable hydration shells around the protonic species. These hydration effects promote the mobility of protons and contribute to their facilitated transport through the lattice, ultimately enhancing the overall proton conductivity of the material. The Ca vacancies are not merely empty spaces but act as active sites that significantly influence proton dynamics within the material.

Figure 2A shows the FTIR results of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$. The functional groups contained in $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ can be clearly identified by infrared spectroscopy. The absorption peak at about 3408 cm^{-1} is attributed to the stretching vibration of O-H, and 1026 cm^{-1} belongs to the antisymmetric stretching vibration of PO_4^{3-} . The absorption peaks of 602 cm^{-1} and 563 cm^{-1} are due to the asymmetric angular vibration of PO_4^{3-} . The absorption peak located around 877 cm^{-1} belongs to the bending vibration of CO_3^{2-} ^{36,37}. The content of CaCO_3 in $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is higher than that in $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$, which is consistent with the change in peak intensity in FTIR. The absorption peak located at 1456 cm^{-1} belongs to a variable angle vibration of H_2O . As the preparation process does not undergo high-

temperature sintering, this may be due to residual H_2O in the material during the preparation process. More interestingly, the absorption peak at 2361 cm^{-1} could be attributed to the tensile vibration of P-H, while the absorption peak of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ is much stronger than that of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, which is the result of the presence of Ca vacancies and proton insertion.

The ^{31}P and ^1H NMR spectra of Li- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ are shown in Fig. 2B. When a calcium vacancy is occupied by protons, the extranuclear environment around the atom changes, which can be detected by nuclear magnetic resonance spectroscopy (NMR). When the chemical environment of the atomic nucleus changes, the conditions that can trigger resonance also change³⁸. The same functional group has the same ppm value, but different chemical environments can produce different chemical shifts³⁹. The phosphate group has a tetrahedral structure. According to the number of oxygen atoms bridged by each tetrahedron, the phosphate bond is divided into four categories, represented by Q_n ($n=0,1,2,3$). In the NMR spectra of ^{31}P of H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and Li- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, there is only one single chemical shift peak, 3.353 ppm and 3.323 ppm , respectively. This indicates that P exists in the form of Q_0 , i.e., free PO_4^{3-} , in H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and Li- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. The difference in chemical shifts between the two may be due to changes in the chemical environment around P caused by protons entering the $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ lattice, and due to the relatively low content of embedded H, the difference is relatively small, which is also consistent with the ICP-AES results. There are significant differences in the ^1H spectra of H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and Li- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. The chemical shifts at 5.793 ppm and 5.122 ppm , respectively, belong to the adsorbed water on the material surface, while the chemical shifts at 0.302 ppm and 0.216 ppm reflect the O-H within the crystal structure. It can be seen that the O-H intensity in H- $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ is

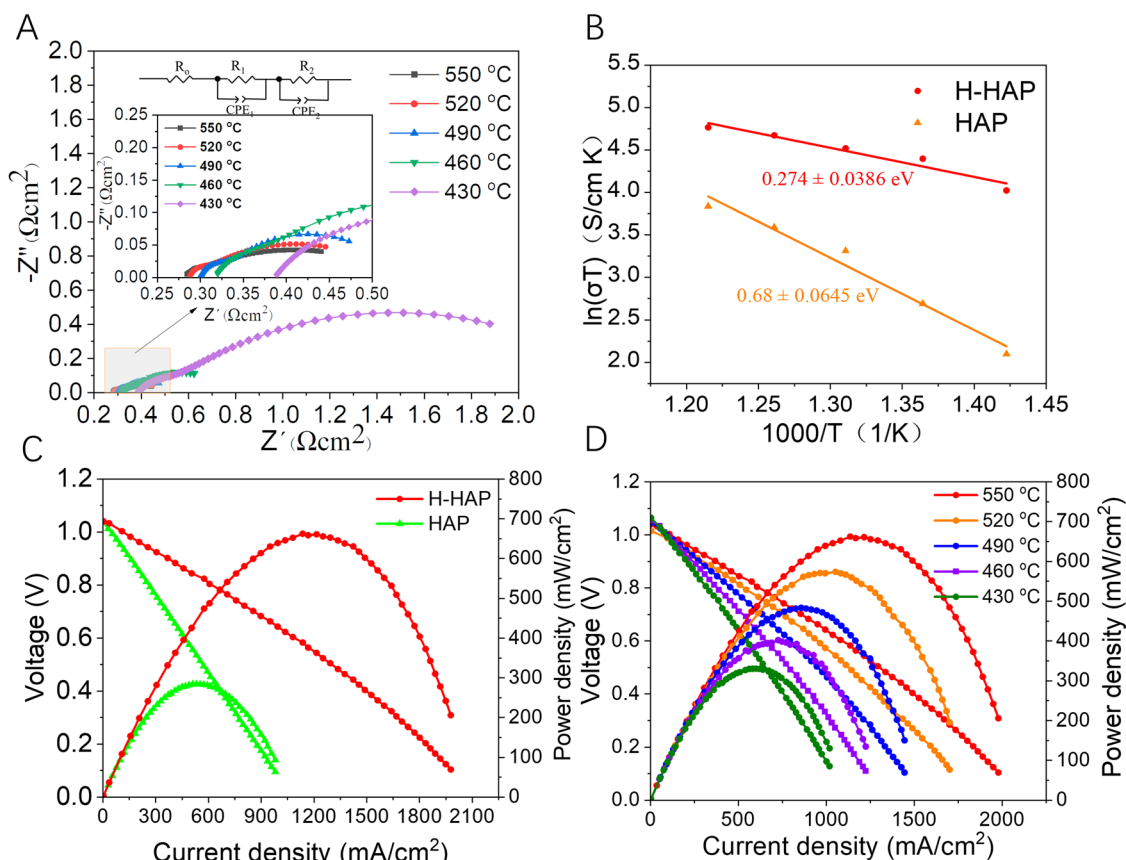


Fig. 3 | Electrical and electrochemical performances. (A) EIS spectra obtained for $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ (Li) at various temperatures and (B) Arrhenius curves and calculated activation energies for $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ (C) Fuel cell

performance comparison of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ at 550 °C, and (D) I - V and I - P curves of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ at different temperatures.

much higher than that in $\text{Li-Ca}_5(\text{PO}_4)_3\text{OH}$, which indicates that after protonation treatment, more H^+ enters the $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ crystal, which is also consistent with the FTIR results.

According to the X-ray photoelectron spectroscopy (XPS) spectra shown in Fig. 2C, the valence states of Ca, P, and O (+2, +5, and -2, respectively) remain same in both samples $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$, suggesting that all the samples keep charge balance though protons are incorporated into the structure, the charge is balanced by forming calcium vacancies. However, the intensity of the peaks of Ca 2p, P 2p and O 1s have been changed after protonation. Which can be attributed to the alteration in the chemical environment of the atoms after protonation, leading to shifts in the binding energies and changes in the relative intensities of the spectral peaks. These changes provide valuable insights into the chemical bonding and electronic structure variations induced by protonation. The presence of calcium vacancies (Ca-vacancies) induces alterations in the local environment and the surrounding crystal structure, resulting in the creation of distinctive proton-conductive pathways. These modified pathways play a crucial role in facilitating the movement of protons through the material. By reducing energy barriers, these pathways contribute to an enhanced efficiency of proton transport within the material^{40,41}. Further analysis through HRTEM as shown in Fig. 2D we directly find that $\text{H-Ca}_5(\text{PO}_4)_3\text{OH}$ contains a large number of tiny pores with diameters ranging from 3 to 5 nm, which may be caused by the partial dissolution of Ca^{2+} during the preparation process, that directly proves the existence of Ca vacancies in $\text{H-Ca}_5(\text{PO}_4)_3\text{OH}$.

EIS measurements were conducted on $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ under open circuit conditions in a fuel cell, and the impedance spectra obtained are shown in Fig. 3A. The EIS data was fitted based on the fitting circuit $R_0(R_1\text{CPE}_1)(R_2\text{CPE}_2)$ for $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. In the equivalent circuit, R_0 represents the ohmic resistance which can be obtained by

calculating the intercept on the real axis at high frequencies, R_1 and R_2 represent the grain-boundary resistances of the electrolyte and the polarization resistance of the electrode, respectively, whereas CPE is the constant phase element. The fitting data are listed in Supplementary Tables S2 and S3. As the temperature decreases for $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the bulk resistance of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ increases from $0.606 \Omega \text{ cm}^2$ to $2.134 \Omega \text{ cm}^2$, and at different temperatures, the bulk resistance is higher than the grain boundary resistance, indicating that ions in $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ tend to transport through the grain boundary. The conductivity of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ at 550 °C is calculated from the EIS to be 0.056 S cm^{-1} using formula $\sigma = \frac{L}{RA}$, and continues to decrease as the temperature decreases, reaching 0.012 S cm^{-1} at 430 °C. The EIS pattern of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ with temperature is consistent with that of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$.

Compared to $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the bulk resistance of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ at 550 °C decreased from $0.606 \Omega \text{ cm}^2$ to $0.277 \Omega \text{ cm}^2$, the grain boundary impedance decreased from $0.104 \Omega \text{ cm}^2$ to $0.003 \Omega \text{ cm}^2$, and the conductivity increased from 0.056 S cm^{-1} to 0.143 S cm^{-1} , an increase of nearly 2.5 times. As the temperature decreases, the impedance of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ gradually increases, with R_0 and R_1 increasing to 0.386 and $0.116 \Omega \text{ cm}^2$ at 430 °C, respectively. The corresponding conductivity is 0.080 S cm^{-1} , which is lower than 0.1 S cm^{-1} , but still higher than that of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ at 550 °C. This indicates that the conductivity of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ can be effectively improved by constructing a Ca vacancy. According to the above formula, the activation energy corresponding to $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ can be obtained from the slope of the Arrhenius curve⁴². The activation energies of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ are $0.68 \pm 0.064 \text{ eV}$ and $0.274 \pm 0.038 \text{ eV}$, respectively as shown in Fig. 3B.

Figure 3C shows the I - V (current voltage) and I - P (current power) curves of a fuel cell with $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ as electrolytes at 550 °C. It can be seen that at 550 °C, the OCV of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ is

Table 1 | Comparing our work with other fuel cell performances at 550 °C

Composition	OCV(V)	Power density(mW cm ⁻²)	Ref.
Ni-NCAL/3C-SiC/ZnO/NCAL-Ni	1.1	270	45
Ni-NCAL/BCFZY-ZnO/NCAL-Ni	1.01	643	1
Ni/LCN-NSDC/Ag	0.8	500	46
Ni-NCAL/SrTiO ₃ (STO)/NCAL-Ni	0.99	620	47
Ni-NCAL/ZnO/NCAL-Ni	1.06	482	48
Ni-NCAL/Film TiO ₂ /NCAL	1.1	364	49
NCAL/BCZY/ Ca ₅ (PO ₄) ₃ OH-H(Li) /BZCY/NCAL	1.04	661	Our work

1.04 V, and the maximum power density (MPD) is 661 mW cm⁻². This power output is about 2.3 times the power density of Ca₅(PO₄)₃OH at 550 °C, similar to the change in conductivity. The *I*-*V* and *I*-*P* characteristic curves of a Ca₅(PO₄)₃OH-H electrolyte fuel cell at lower temperatures are shown in Fig. 3D. Ca₅(PO₄)₃OH-H electrolyte fuel cell performance comparison with other fuel cell performances at 550 °C is presented in Table 1. The OCV and MPD are 1.015 V, and 573.6 mW cm⁻², 1.046 V and 483.4 mW cm⁻², 1.053 V and 402.2 mW cm⁻², 1.064 V and 330.5 mW cm⁻² at 520, 490, 460 and 430 °C, respectively. The power outputs of the fuel cell using Ca₅(PO₄)₃OH-H as the electrolyte is much higher than that of using the Ca₅(PO₄)₃OH electrolyte, further demonstrating that constructing metal cation vacancies can effectively improve the conductivity of the material. The electrostatic interactions between the Ca vacancies and protonic species exert a significant influence on the transport behavior of protons within the lattice. The vacancies induce changes in the local electric field, thereby facilitating the directional movement of protons⁴¹. This alteration in the electric field, coupled with the pathways created by the vacancies, promotes the efficient transport of protons through the material. Consequently, this phenomenon leads to an enhanced power output in applications such as fuel cells, underscoring the pivotal role of Ca vacancies in optimizing the electrochemical performance of the material. NCAL was utilized as an electrode material due to its excellent conductivity and catalytic properties. Oxides with a similar structure, like LiAl_{0.5}Co_{0.5}O₂, have demonstrated a conductivity of 0.1 S cm⁻¹ at 500 °C and strong catalytic activity for the oxygen reduction reaction (ORR). At specific temperatures, an amorphous layer may develop on the surface of NCAL, which enhances the formation of multiple oxygen vacancies, thereby facilitating improved oxygen ion conduction. Moreover, the introduction of Li⁺ ions into the material can positively influence its catalytic characteristics and the performance of fuel cells. Liu et al. have highlighted the significant potential of NCAL as an electrode material⁴³. Additionally, Chen et al. have reported promising results for NCAL electrodes in both the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR)¹.

To further investigate proton conducting feature, the following experiments were carried out: i) Conductivity vs hydrogen concentration; ii) Hydrogen concentration cell (HCC); iii) Conductivity isotopic effect; iv) Conductivity measured using the proton conducting filter cell.

First, we determined the conductivity of Ca₅(PO₄)₃OH-H in hydrogen at a different partial pressures or concentrations. According to relevant literature, protons dissolved in oxides are considered to be interstitial protons H_i⁴⁴. The diffusion of protons in oxides is positively proportional to the partial pressure of hydrogen, as indicated by

Equation (1).

$$\frac{1}{2} \text{H}_2(\text{g}) = \text{H}_i + e^- K_1 = [\text{H}_i] n \text{P}_{\text{H}_2}^{-1/2} \quad (1)$$

The proton conductivity should be proportional to the concentration of hydrogen. As shown in Fig. 4A as the concentration of hydrogen peroxide increases, the arc of the impedance spectrum gradually decreases. The specific impedance data are summarized in Supplementary Table S4. It can be seen that with the increase in hydrogen concentration, R₀ decreases from 0.287 Ω cm² to 0.194 Ω cm², and R₁ also decreases from 0.101 Ω cm² to 0.051 Ω cm². As shown in Fig. 4B, the conductivity of Ca₅(PO₄)₃OH-H(Li) increases with increasing hydrogen concentration, and at 20% and above hydrogen concentration, it exhibits a conductivity of more than 0.1 S cm⁻¹.

To determine the proton transfer number (t_{H+}) for Ca₅(PO₄)₃OH-H(Li), hydrogen concentration cells (pure and 5% H₂) were applied using silver as electrode and results are shown in Fig. 4C. The theoretical electromotive force is calculated according to the Nernst equation. The t_{H+} is the ratio of the measured electromotive force to the theoretical electromotive force. The measured proton transference number is in the range of 0.7 to 0.87 between 430 and 550 °C. Silver is not ideal electrode for hydrogen, the measured proton transfer number may be lower than the real value.

Furthermore, we fabricated a cell with a configuration of NCAL/BCZY/ Ca₅(PO₄)₃OH-H(Li) /BZCY/NCAL, where BaZr_{0.3}Ce_{0.6}Y_{0.1}O_{3-δ} (BCZY) serves as a filter to block other ions and BCZY is a proton conductor at low-temperature. The *I*-*V* and *I*-*P* curves are shown in Fig. 4D where the cell exhibits a maximum power output of 485 mW cm⁻², which is 73.3 % of the cell without BCZY. Possible causes of performance degradation include i) the increased impedance of the BZCY layer itself, ii) two additional interfaces between Ca₅(PO₄)₃OH-H(Li) and BZCY layers, leading to more polarization resistance⁴⁴. The EIS in Fig. 4E could further prove the above conclusion with the fitting data listed in Supplementary Table S6. The ohmic resistances increased from 0.43 to 0.60 Ω and the grain boundary resistances increased from 0.0045 to 0.0106 Ω, for the cells with and without BZCY layers. The results show that proton conduction is the dominant contribution to the conductivity. Finally, the isotopic effect measurements further provide evidences for proton transport property as shown in Fig. 4F where EIS measurements were obtained from H₂ and D₂ atmospheres, respectively, a significant difference between them and larger resistance displays that D⁺ diffusion is slower than that of H⁺ as a clear indication of proton diffusion isotopic effect.

We further studied the proton transport isotope effect (KIE) of Ca₅(PO₄)₃OH-H(Li) and the results are presented in Fig. 4F and the EIS fitting data is listed in Supplementary Table S5. For the Grotthuss mechanism, the KIE is usually bigger than (mD/mH)^{1/2} ~ 1.4 because the mass of D (mD) is twice that of H atom (mH). By contrast, the KIE for vehicle mechanism is equal to the viscosity ratio of D₂O to H₂O, ~1.2. At 550 °C, the conductivity of Ca₅(PO₄)₃OH-H(Li) in H₂/air atmosphere is 2.04 times higher than that of Ca₅(PO₄)₃OH-H(Li) in D₂/air atmosphere, confirming that the proton transport is governed by the Grotthuss mechanism. The difference in isotopic mobility between H⁺ and D⁺ ions can be attributed to the influence of Ca vacancies. The presence of Ca vacancies alters the local environment and energetics of proton transport within the material. Consequently, any observed variations in the mobility of H⁺ and D⁺ ions can be indirectly linked to the impact of these vacancies on the mechanisms of proton transport. This disparity in isotopic mobility serves as a valuable indicator, providing insights into how Ca vacancies affect and modulate proton transport processes within the material.

The Ca vacancy plays a key role in improving proton ion conductivity. Calcium vacancy generation is further induced by doping trivalent La ions to form Ca₅(PO₄)₃OH-La, by high-temperature solid-phase reaction. The fuel cell performances of Ca₅(PO₄)₃OH-La were tested which displayed a maximum power density of 600 mW cm⁻² at 550 °C, approximately 2 times that of the original Ca₅(PO₄)₃OH as shown in Supplementary Fig. S4 (A)), and the electrochemical performance was measured, see Supplementary Fig. S4(B). The power output of 392 mW cm⁻² is obtained at 460 °C, which is higher than the power density of original Ca₅(PO₄)₃OH at 550 °C. According to the EIS in Supplementary Fig. S4(C) the ionic conductivity of Ca₅(PO₄)₃OH-La reaches 0.118 S cm⁻¹ at 550 °C (Supplementary Fig. S4 (D)) which is approximately 2 times higher than that of original

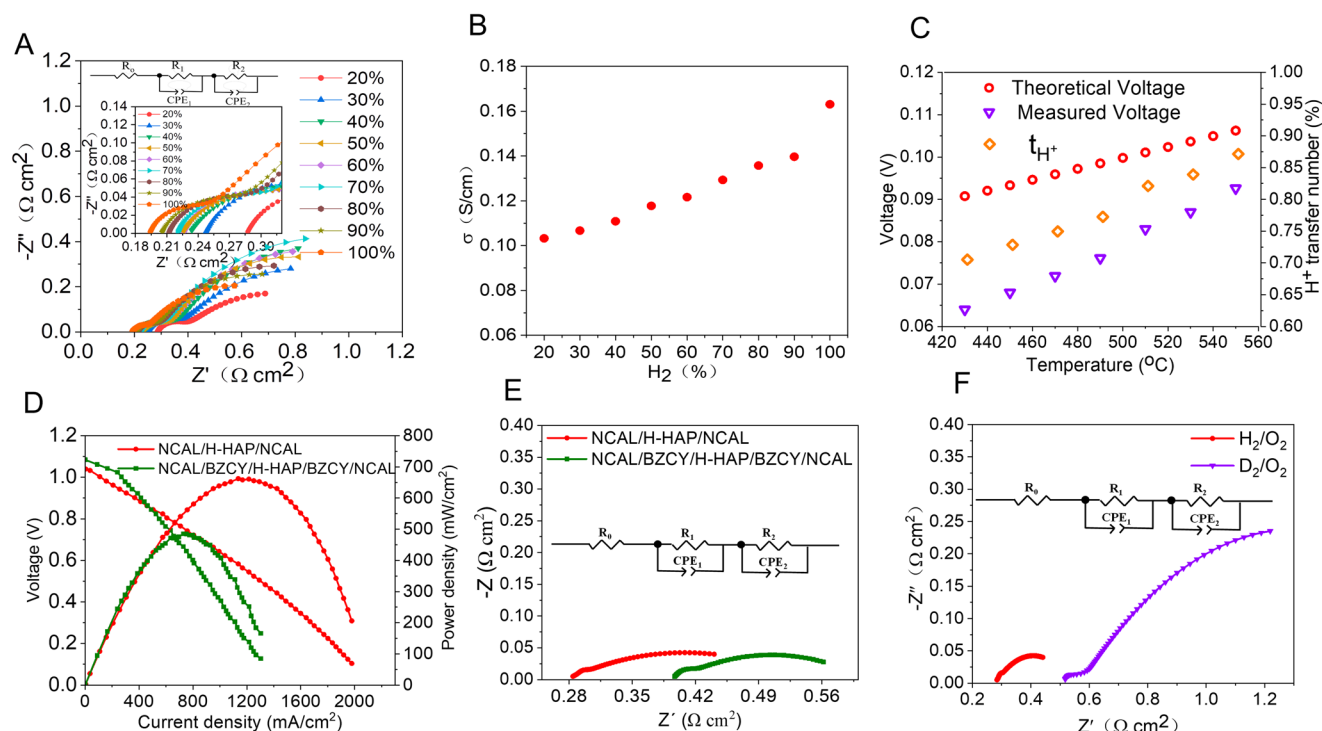


Fig. 4 | Conductivity analysis. (A) EIS spectra and (B) conductivity of $\text{Ca}_5(\text{PO}_4)_3\text{OH-H}$ varying with hydrogen concentration. (C) The measured electromotive force, theoretical electromotive force, and H^+ transfer number from a hydrogen concentration cell based on $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ electrolyte. (D) I - V and I - P characteristics of the $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ electrolyte fuel cell with and without BZCY layer

under H_2/air atmosphere at 550°C . (E) Corresponding electrochemical impedance spectroscopy of the cells with and without BZCY layer and EIS fitting results are listed in Supplementary Tables 3, 6. (F) Typical Nyquist plots for the $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ in the presence of H_2 (red) and D_2 (blue) at 550°C and fitting results are listed in Supplementary Tables 3, 5.

$\text{Ca}_5(\text{PO}_4)_3\text{OH}$. It can be seen that the cation vacancy produced by different ways can effectively improve the conductivity of the materials.

We have further carried out theoretical modeling and calculations to study proton transport mechanism. The schematic diffuse paths and calculated energy barriers for Li^+-H^+ pair or H^+ are shown in Fig. 5A. The corresponding relaxed structures of initial state and final state used for energy barriers calculation are also shown in Fig. S5. We calculated and compared various proton transport mechanisms and paths, e.g. i) The calculated Li^+-H^+ pair diffusion barrier along adjacent Ca vacancies is 2.73 eV, which is very high. The Li-H bonds in the Ca vacancies are relatively weak (~ 2.45 Å) and should not be able to move simultaneously, see Supplementary Fig. S6(a). This result is not quite as expected; ii) The diffusion barrier of Ca vacancies filled with adjacent Li^+ associated bare H^+ diffusion is approximately 0.35 eV; iii) while undoped by Li^+ , the initial result of H along adjacent Ca vacancies is approximately 1.89 eV, which is also very high being not a favorable path/mechanism. After the formation of the Ca^{2+} vacancy in $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, single H^+ is prone to enter into the vacancy region, bond with the surrounding O atom to form a stable structure Supplementary Fig. S6(b). However, the imbalance of valence state still exists, just like the presence of a negative charge in the vacancy region. Therefore, when H^+ migrates between Ca^{2+} vacancies, it will subject to additional electrostatic attraction from the vacancy region, which leads to a high ion diffusion barrier of 1.89 eV. Based on these theoretical calculations, Fig. 5A illustrates the most favorable theoretical calculations for proton transport paths/mechanism, while is the most feasible in agreement with experimental results presented in Fig. 2B, where 0.274 eV is obtained for the proton transport activation energy. Based on both theoretical and experimental results, we proposed the proton transport mechanism via a H^+ coupled Li^+ transport mechanism as presented by Fig. 5A.

When the Ca^{2+} vacancy is filled by H^+ and Li^+ simultaneously as shown in Supplementary Fig. S6(c), the valence state of the vacancy region is balanced, and the electrostatic attraction on H^+ from vacancy region is

eliminated. In addition, the interaction between H^+ and Li^+ somewhat weakens that between H^+ and O atom (The DFT results show that the H-O bond length increases from 0.98 Å without Li to 1.01 Å with Li doped). The above two factors lead to a large reduction of ion diffusion barrier of H^+ when migrating between Ca^{2+} vacancies. Therefore, in H^+ and Li^+ filled $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, the diffusion barrier of H^+ along Ca^{2+} vacancies is only ~ 0.35 eV (Fig. 5A).

Overall, Li^+ filling can effectively reduce the diffusion barrier of the H^+ atom along the Ca vacancies, which may result in an enhanced proton conduction. Figure 5B presents a detailed proton transport in $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. The existence of Ca vacancies introduces additional hopping sites for protons within the lattice, facilitating easier and faster proton migration through the material. These hopping sites create pathways that enable protons to move more freely, ultimately enhancing proton conductivity overall. The study aims to elucidate the facilitated hopping mechanism, considering factors such as electrostatic interactions, hydration and protonation dynamics, and defect-mediated diffusion pathways. Through this comprehensive analysis, the research contributes to a deeper understanding of the proton transport mechanism facilitated by Ca vacancies in $\text{Ca}_5(\text{PO}_4)_3\text{OH}$. Introducing a H^+ -coupled Li^+ mechanism to occupy the Ca vacancies could indeed facilitate proton transport. Li^+ ions associated with the Ca vacancies, acting as intermediaries or bridges for proton transport. They create sites or pathways for proton transfer. Protons (H^+) could then hop from one Li^+ site to another, utilizing these occupied vacancies as stepping stones for their movement. On the other hand, the presence of Li^+ ions within the vacancies facilitates a more controlled and guided path for protons. This coupling mechanism allows for leveraging Li^+ ions within the Ca vacancies introducing a potential strategy to enable proton transport, addressing the size disparity between Ca vacancies and protons. It creates a favorable scenario where the Li^+ ions act as intermediaries, aiding in the movement of protons through the crystal lattice. Further exploration and experimental validation of this proposed

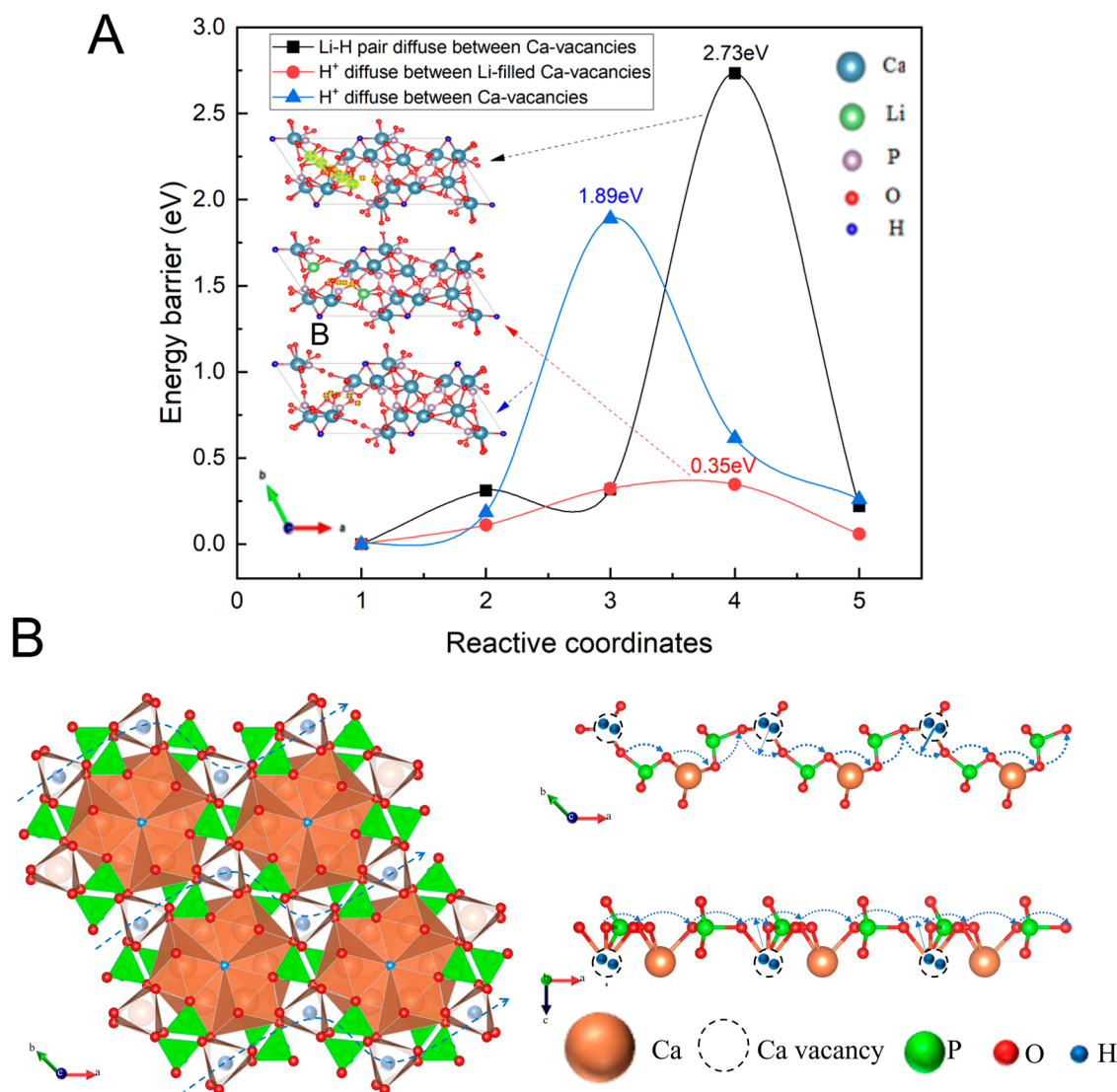


Fig. 5 | DFT Calculations. (A) The energy barrier of Li-H pair or H⁺ diffuses between adjacent Ca vacancies of CaPOH, and H⁺ diffuses between Li⁺ filled Ca vacancies of CaPOH. The schematic diffuse pathways for Li-H pair and H⁺ are also shown in the insets. **B** Proton conduction mechanism in Ca₅(PO₄)₃OH.

mechanism could significantly contribute to understanding and enhancing proton conductivity in Ca₅(PO₄)₃OH-based materials. To enhance the accuracy of the computational model, the formation energies of Ca vacancies in Ca₅(PO₄)₃OH were calculated using spin-polarized calculations. There exist two kinds of Ca vacancies in Ca₅(PO₄)₃OH, see clearly their structures in Fig. S7(b, c). The spin-polarized calculations reveal that a 7-coordinated Ca vacancy configuration (Ca-v2) exhibits a slightly lower formation energy (Supplementary Table S7), indicating that it may be easier to form. This finding supports the presence of both 9- and 7-coordinated Ca vacancies in the structure, offering additional diffusion pathways. The path 2 (Ca-v1 → Ca-v2 → Ca-v1) is also included [Fig. S7(d)], which takes advantage of these energetically favorable vacancies.

Regarding defined direction of bulk diffusion, there is a possibility of proton diffusion along the c-axis, thereby introducing an additional pathway [(Path 3: Ca-v1 → Ca-v1 along the c-axis, see in Fig. S7(e)]. This approach aligns with our experimental observations, suggesting that the diffusion mechanism is not confined to a single direction. These modifications provide a more comprehensive understanding of the diffusion behavior in different directions, ensuring alignment with experimental diffusion characteristics. The insights gained from this detailed examination will significantly advance the knowledge of proton-conductive materials, potentially impacting their applications in various energy-related technologies.

Conclusions

This study represents a significant leap in materials science by unveiling a pioneering method to boost proton conductivity via calcium vacancy and lithium-ion bridging. The development of protonated Ca₅(PO₄)₃OH-H(Li) introduces a groundbreaking proton conduction mechanism, achieving unprecedented material performance with exceptional proton conductivity of 0.1 S cm⁻¹ at 300–550 °C and superior PCFC performance, peaking at 661 mW cm⁻² at 550 °C. This achievement not only advances the field of ceramic proton conductors but also demonstrates the potential of Ca₅(PO₄)₃OH-H(Li) as a leading electrolyte for future PCFCs. The integration of calcium vacancies with lithium-ion bridging, fostering proton transport pathways, enhances our understanding of proton conduction and signifies the material's broader impact on energy conversion and storage technologies, marking a stride towards sustainable energy solutions.

Methods

Materials synthesis and fuel cell fabrication

The Ca₅(PO₄)₃OH power was bought from Jiuding Chemical Co., Ltd., China. For the synthesis of Ca₅(PO₄)₃OH containing Calcium (Ca) vacancies, 10 g of Ca₅(PO₄)₃OH power was firstly soaked in 400 mL of 0.25 M KCl solution and stirred for 2 h at room temperature. The resulting suspensions were washed by deionized water to remove excess K⁺ ions.

During the above treatments, the hydrated K ions inserted into $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ powder, and caused an equivalent loss of divalent Ca ions, consequently leaving Ca vacancies. 400 mL of 0.25 M LiCl solution was then added into the washed $\text{Ca}_5(\text{PO}_4)_3\text{OH-K}$ and stirred for 2 h at room temperature, in which K ions were replaced by Li ions. The resulting suspensions were washed by deionized water to remove excess Li^+ ions. To synthesize $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ power, the resulting $\text{Ca}_5(\text{PO}_4)_3\text{OH-Li}$ power was redispersed in 0.5% Acetic acid solution for 3 h to exchange partial Li ions with protons.

To verify further Ca-vacancy effect, we employed lanthanum-doped $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ ($\text{La}_{0.25}\text{Ca}_{4.75}(\text{PO}_4)_3\text{OH}$), which was prepared by high-temperature solid-phase reaction. Firstly, $\text{La}(\text{NO}_3)_3$ and $\text{Ca}_5(\text{PO}_4)_3\text{OH}$ were fully ground according to stoichiometric ratios. The above powder was then calcined at 1000 °C with a heating rate of 5°/min in air for 4 h, followed by adequately grounding of the powders to get the final sample. In this way, two higher valency La^{3+} replaced Ca^{2+} , to maintain neutrality, one extra Ca-vacancy must be created thus to enhance the Ca-vacancy concentration in the sample.

To prepare $\text{BaZr}_{0.3}\text{Ce}_{0.6}\text{Y}_{0.1}\text{O}_{3-\delta}$ (BZCY), Ba, Zr, Ce, and Y metal nitrates were dissolved in distilled water and citric acid was added as a reacting agent. The solution was stirred and heated at 70 °C for 2 hours. The composition was supposed to be $\text{BaZr}_{0.3}\text{Ce}_{0.6}\text{Y}_{0.1}\text{O}_{3-\delta}$. The attained solution was heated at 250 °C for 4 h, and a dark grey-black colored ash was found. Finally, the resulting ash was successively calcined at 1000 °C for 3 hours to yield BZCY powder. To authenticate the H^+ ion conduction of the fuel cell, a distinct fuel cell device was fabricated using the similar assembly but adding two O^{2-} ion blocking very thin layers of $\text{BaZr}_{0.3}\text{Ce}_{0.6}\text{Y}_{0.1}\text{O}_{3-\delta}$ on both sides of electrolyte. The fuel cell device was assembled in a design of NCAL/BCZY/ $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ /BZCY/NCAL having same parameters regarding active area and thickness, as used for the cell mentioned before i.e. NCAL-Ni/ $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ /NCAL-Ni.

Structural characterizations

The phase structure was measured by X-ray diffraction (XRD; Bruker D8 ADVANCE) with Cu K α radiation source over the 2θ range of 10–80°, operating at 45 kV and 40 mA. Morphological properties were characterized by scanning electron microscopy (SU8010, Hitachi Japan). The elemental composition was characterized by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Agilent 5110). Transmission electron microscopy (TEM, Talos F200S G2) was used to characterize the materials. The functional groups were analyzed by Fourier Transform Infrared Spectrometer (FTIR) conducted with PerkinElmer Frontier. X-ray photoelectron spectra (XPS) was performed through Thermo Fisher, ESCALAB 250Xi+ with the source of Al-K α ($h\nu=1486.6$ eV).

To determine the chemical composition of each material, the sample was measured by ICP-AES. We set the mole concentration of P as 1, and the mole concentration of other elements, including Ca, O and Li, and the corresponding chemical formula were determined relative to that of P. The mole concentration of H was determined based on the principle of charge balance and the valence states of other elements. Measurements of ion conductivity 0.1 g powders were pressed under a hydraulic press pressure of 200–220 MPa to get electrolyte pellet with active area of 0.64 cm². As prepared pellet was sandwiched between two NCAL ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) symmetric electrodes pasted on Ni foam. The electrochemical impedance spectra (EIS) were measured with a potentiostat (CHI) with the temperature from 550 °C to 400 °C. The applied frequency range was 1 MHz to 0.1 Hz with 10 mV bias voltage. The digital instrument (ITECH8511) was used for measuring $I-V$ (current-voltage) and $I-P$ (current-power) characteristics. The conductivity was calculated according to the simulated resistance in the EIS results.

Measurements of electronic conduction contribution

Response current testing under direct-current (DC) voltage was carried out to identify the possible electronic conduction contribution to the conductivity of the $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$. Ag blocking electrodes were used to

measure the electronic conduction in the configuration of Ag/ $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ /Ag under N_2 atmosphere.

The electronic conduction for fuel cell condition is measured by quasi in-situ measurement. After the end of the fuel cell test, N_2 is introduced into the anode and cathode immediately. Then the response current testing under direct-current (DC) voltage was measured in the configuration of NCAL/ $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ /NCAL under N_2 atmosphere.

Proton transference number measurements

The proton transfer number was test through the hydrogen concentration cell in the configuration of Ag/ $\text{Ca}_5(\text{PO}_4)_3\text{OH-H(Li)}$ /Ag. 5% H_2 and pure H_2 were passed into the cathode and anode of the cell respectively with the same flow rate. The electromotive force (EMF) of the cell was recorded on a computerized instrument (IT8511A+, ITECH Electrical Co., Ltd., China). The theoretical electromotive force was test according to the Nernst equation Eq. 2,

$$E = \frac{RT}{2F} \ln \frac{P_1}{P_2} \quad (2)$$

R is the gas constant; T is the absolute temperature; F is Faraday's constant, P_1 is the hydrogen partial pressure on the anode side and P_2 is the hydrogen partial pressure on the cathode side. The proton transfer number (t_{H^+}) is the ratio of the actual electromotive force to the theoretical electromotive force.

KIE measurements and analyses

The impedance spectra of the two fuel cells were tested in H_2/O_2 and D_2/O_2 atmospheres, respectively. If protons are the dominant charge carriers in the material, there will be a significant difference for the H^+/D^+ conductivity due to the isotopic effect. The KIE is the ratio of ion conductivity of membrane in H_2/O_2 atmosphere to the value in D_2/O_2 atmosphere. For the Grotthuss mechanism, protons are transported by hydrogen bond breaking and recombination. In comparison with the case of H_2/O_2 , the proton conductivity is decreased in D_2/O_2 , whose mass (mD) is twice that of H atom (mH). Theoretically, the KIE for Grotthuss mechanism is (mD/mH)^{1/2} ~ 1.4. The experimentally obtained KIE is usually in the range of 1.4 to 3.3 due to the influence of material's structure and chemical condition. In contrast, the KIE for vehicle mechanism is ~1.2 due to the different transport groups.

Computational details and modeling

The density functional theory (DFT) calculations were implemented in the Vienna ab initio simulation package (VASP) based on projector-augmented wave (PAW) pseudopotentials. The generalized gradient approximation with the exchange-correction function of Perdew-Burke-Ernzerhof form (GGA-PBE) was employed and the kinetic energy cutoff was set to be 400 eV for plane wave basis expansion. During structure optimization, the convergence criteria of electronic self-consistent energy and atomic force were respectively set to 10⁻⁵ eV and 0.01 eV. To investigate the migration property of H^+ along Ca vacancies in CaPOH material, a (2×1×1) supercell was adopted with Brillouin zone (BZ) sampled by a Γ -centered (2×4×5) Monkhorst-Pack grid, and the energy barrier was calculated by using the climbing image nudged elastic band (CI-NEB) method.

Data availability

The data that support the findings of this study are available from the authors on reasonable request, see author contributions for specific data sets.

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Author contributions

Z.B. conceptualize the study and wrote the initial draft of the manuscript. Y.L. fabricated the fuel cells and conducted the electrochemical measurements. N.A. further worked on the manuscript to its final version. F.W. took charge of designing and supervising the electrochemical experiments. Q.P. carried out DFT calculation under the supervision and instructions from S.Y., and Y.J. evaluated and analyzed the data. M.S. and J.W. provided valuable assistance in interpreting and analyzing the results. All authors engaged in collaborative discussions to refine the findings and enhance the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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