

## Anhydrous superprotonic conductivity in a new zirconium acid phosphate: application of the BVSE method to proton conducting materials

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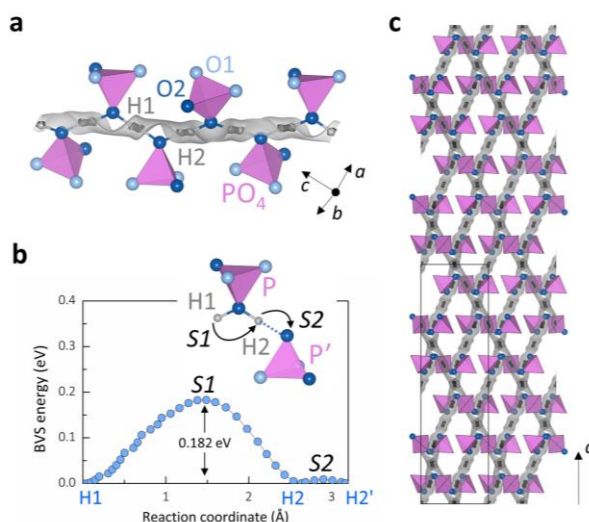
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Solid-state proton conductors (SSPCs) are ionic conductors in which the diffusion of  $\text{H}^+$  ions is responsible for charge transfer. SSPCs with target proton conductivity of  $10^{-2} \text{ S cm}^{-1}$  at low temperatures ( $\leq 150^\circ\text{C}$ ) are in demand for the development of fuel cells and other hydrogen-related technologies for portable and automotive applications [1]. However, at such low temperature, high relative humidity ( $\text{RH} > 90\%$ ) is required to attain sufficiently high proton conductivity. The requirement for active humidification forces the implementation of complex water management systems, thus imposing considerable limitations on the deployment of these technologies [2].

We have recently discovered a new zirconium solid acid triphosphate,  $\text{ZrH}_5(\text{PO}_4)_3$  (ZP3), with record-high superprotonic conductivity of  $0.5 - 3.1 \times 10^{-2} \text{ S cm}^{-1}$  in anhydrous conditions ( $\text{RH} \ll 1\%$ ). This value of anhydrous proton conductivity is unprecedented and comparable with benchmark polymer electrolytes and other proton conductors operating under high relative humidity [3]. Here, we report on the use of the bond-valence sum energy (BVSE) method for the characterization of the proton transport in this novel SSPC. We have successfully employed the BVSE method for the characterization of the proton and oxide ion diffusion in complex solid oxide ionic conductors [4], and we will first discuss these reports to show that this method can indeed be extended to systems other than Li-ion and alkali-metal conductors [5].

Our BVSE analysis on ZP3 revealed that equilibrium proton positions can be located around non-bridging oxygen atoms within disordered phosphate  $\text{PO}_4$  units. Protons are bistable on two off-centre sites between two non-bridging oxygen atoms which compete as hydrogen bond donor and acceptor due to short  $-\text{O}2\cdots\text{O}2-$  distance. Protons can diffuse on a 1-dimensional conduction pathway along the hydrogen bond network (Fig. 1a), following a Grotthius like mechanism composed by the rotation of a proton from position H1 to H2 (or vice versa) and hopping onto an adjacent oxygen atom (Fig. 1b). These hydrogen bond chains form an extended network running through the entire crystal structure and enabling long-range correlated proton motion (Fig. 1c).

These findings are of strong fundamental relevance as they evidence a conduction mechanism never seen before in a solid acid. In addition, the example of ZP3, suggests that the BVSE method could be successfully used to screen candidate materials containing native protonic defects, in search for innovative low temperature SSPCs.



**Figure 1.** a) BVSE map for a test  $\text{H}^+$  (isosurface levels are drawn at  $< 0.19 \text{ eV}$ ). b) BVSE barrier and schematic of the proton diffusion mechanism. c) Proton migration network within the ZP3 structure.

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