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Proton conductivity of multifunctional metal phosphonate frameworks

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Metal phosphonates exhibit attractive characteristics for proton conductivity, such as tunable functionality, chemical and thermal stability and the existence of H-bond networks with acidic protons within their structure.¹

In the present work, we examine the relationship between crystal structure and proton conductivity for several metal (mono-, di- and tri-valent) phosphonates containing rigid: (5-(dihydroxyphosphoryl)isophthalic acid, PiPhtA and 2-hydroxyphosphonoacetic acid, HPAA) or flexible: (hexa- or octamethylenediamine-N,N,N',N'-*tetrakis*(methylenephosphonic acid, H₈HDTMP or H₈ODTMP) multifunctional ligands. The crystalline hybrid derivatives prepared show a great structural diversity, from 1D to 3D open-frameworks possessing hydrogen-bonded water molecules and phosphonic and carboxylic acid groups. The rigid 3D framework of Ca-PiPhtA, that exhibits a proton conductivity of $5.7 \cdot 10^{-4}$ S/cm as synthesized, transforms into a layered compound upon exposure to ammonia vapors² with increased proton conductivity ($6.6 \cdot 10^{-3}$ S/cm). The flexible frameworks of magnesium or lanthanide phosphonates, with 1D channels, present conductivities higher than 10^{-3} S/cm. Their activation energies fall in the range corresponding to a Grotthuss mechanism.^{3,4} For M(I)-HPAA solids conductivities up to $5.6 \cdot 10^{-3}$ S/cm were measured.

References

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