

On the metafunction of protons in ceramic electrolytes

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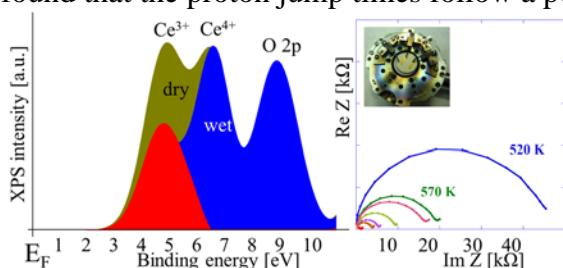
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Abstract

Protons in solids are not always welcome. They can cause brittleness in pressure vessels. They can make electric shorts in semiconductors. They can promote dielectric breakdown in insulators. Because of the abundance of humidity (H_2O) in ambient environment and the crystalline imperfections (defects) in materials, water molecules like to enter some materials and settle as hydrates or hydrides structures. Oxygen and protons become part of the structure. Upon thermal excitation, the hydroxyl bonds may become hydrogen bonds which eventually “melt”. The protons may then liberate and become electric charge carriers, which lend them a particular new function in solid electrolytes as proton conductors.

We have in the last couple of years observed and investigated the biography and lifestyle of such protons from localization to de-localization. The proton is an elusive player and not always easy to make out. With a combination of neutron and synchrotron based scattering and spectroscopy methods, along with electroanalytical techniques, we have increased our understanding of the proton dynamics and its structural origin, which is important for super-protonic conductivity.

We have investigated the oxygen vacancy filling of engineered oxygen deficient BCY by water molecules with impedance spectroscopy and ambient pressure XPS [1], which enabled us to sketch a detailed picture of the correlation of molecular and electronic structure changes, with concomitant onset of proton conductivity at higher temperatures. We thus could design experiments, where the proton-phonon coupling was quantitatively investigated with high p-T impedance spectroscopy combined with quasi-elastic neutron scattering [2,3]. Supported by pressure dependent XRD and Raman scattering data [4,5] we correlated the proton jumping parameters with the temperature and found that the proton jump times follow a polaron relation [6,7].



VB XPS spectra spectral signature of oxygen defects in BaCeY-oxide, recorded in resonant condition for Y/Ce. Maxima are shifted by about 0.5 eV, revealing that gap state of oxygen vacancies near Y is 0.5 eV closer to Fermi level than gap state from vacancy next to Ce.

- [1] Q. Chen et al., Chem. Mater. 25 (23), 4690 (2013).
- [2] Q. Chen et al., Solid State Ionics 252, 2 (2013).
- [3] Q. Chen et al., High Pressure Research 32(4), 471 (2012).
- [4] Q. Chen et al., J. Phys. Chem. C 115 (48), 24021 (2011).
- [5] Q. Chen et al., J. Eur. Ceram. Soc. 31 (14), 2657 (2011).
- [6] Q. Chen et al., Appl. Phys. Lett. 97, 041902 (2010)
- [7] A. Braun et al., Appl. Phys. Lett., 95, 224103 (2009).