

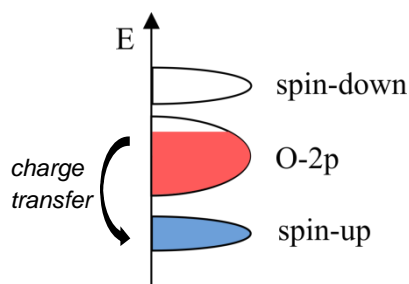
## PROTON UPTAKE IN THE MIXED IONIC AND ELECTRONIC CONDUCTORS $\text{Ba}_{1-x}\text{Sr}_x\text{FeO}_{3-dx}$

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Cathode materials for proton-conducting ceramic fuel cells (PCFC) should combine electronic conductivity with adequate proton conductivity and thereby extend the water formation process from the triple phase boundary to the entire surface of the porous cathode. A variety of such materials including perovskite-structured  $\text{Ba}_{0.95}\text{La}_{0.05}\text{FeO}_3$  has been studied experimentally with regard to proton uptake, revealing a systematically lower proton concentration than in electrolyte materials and a peculiar interaction between electronic charge carriers (i.e. holes) and ionic charge carriers (i.e. protons). [1]



In this study, the electronic structure of the model material  $\text{BaFeO}_3$  is investigated in  $2 \times 2 \times 2$  supercells by means of DFT+U (PBE functional) and hybrid DFT (HSE06 functional). Special focus is laid on the characteristics of the O2p states since they dominate the valence band in oxides, and are involved in O-H bond formation upon proton uptake (protons are incorporated in the form of hydroxide ions on oxide ion sites).

The calculations show that strong correlation effects of Fe3d electrons lead to a significant energy separation of spin-up and spin-down sub-bands. The spin-up band eventually falls below the O2p states and thus

triggers a negative charge transfer from the oxide ions to the iron ions. These results are in line with an experimental x-ray spectroscopic study on  $\text{BaFeO}_3$  thin films. [2]. The negative charge transfer reduces the absolute charge on the oxide ions and as such the oxide ion's basicity. Since the basicity of the oxide ion plays a decisive role in the hydration thermodynamics of solid oxides, the negative charge transfer could explain why the measured proton uptake [1] is lower than the threshold expected from defect chemical modelling.

The formation of oxygen vacancies is accompanied by a simultaneous annihilation of holes and thereby changes the occupancy of the O2p states. The vacancy formation energy increases with decreasing hole concentration in the system. The hydration enthalpy also depends on hole concentration (varying between zero and  $\approx -1$  eV), although the hydration reaction (dissociative water incorporation into oxygen vacancies) is a pure acid-base reaction. Both effects are discussed in the context of the electronic structure of  $\text{BaFeO}_3$ .

Finally, the implications of the electronic structure on the proton uptake are discussed for related compounds  $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{FeO}_3$  and  $\text{SrFeO}_3$ , with the latter showing the least favorable proton uptake.

[1] R. Zohourian et al., Adv. Funct. Mater. 2018, 28, 1801241

[2] T. Tsuyama et al., Phys. Rev. B., 2015, 91, 115101