Proton uptake in mixed conducting perovskites

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A cathode material in a protonic-conducting ceramic fuel cell (PCFC) requires a high catalytic activity, electronic conductivity, sufficient proton conductivity, phase stability, to achieve good performance. The proton conductivity allows to extend the oxygen reduction reaction from the triple phase boundary to the whole surface of the cathode (so-called "bulk path"). For (Ba,Sr,La)(Fe,Co,Zn,Y)O_{3-d} mixed-conducting perovskites the hydration thermodynamics was studied by thermogravimetry.[1-3]
While these cathode materials have a high concentration of oxygen vacancies, the degree of the hydration is significantly smaller compared to typical electrolytes (acceptor doped $BaZrO_3$). Interestingly, partial substitution of iron by redox-inactive and oversized Zn^{2+} and Y^{3+} drastically increases the proton uptake, while partial substitutuion by cobalt decreases it.
Measurements of oxygen nonstoichiometry and proton uptake exhibit pronounced deviations from ideally dilute defect chemistry. They can be assigned to hole-hole and hole-proton defect interactions, and phenomenologically quantified using a first-order correction.[1,4] Physically, these interactions can be related to the partial delocalization of holes from iron to the adjacent oxygen ions, which in turn makes their protonation less favorable. This interpretation is supported by DFT calculations as well as EXAFS and XRS measurements of (Ba,La)(Fe,Zn,Y)O_{3-d}. This defect chemical understanding may serve as the basis for further PCFC cathode development, in particular since the desired properties (proton uptake, catalytic activity, electronic conductivity, etc.) have conflicting trends.

References
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