

MIXED-CONDUCTING CATHODE MATERIALS FOR PROTONIC CERAMIC FUEL CELLS: PROTON UPTAKE AND DEFECT INTERACTIONS

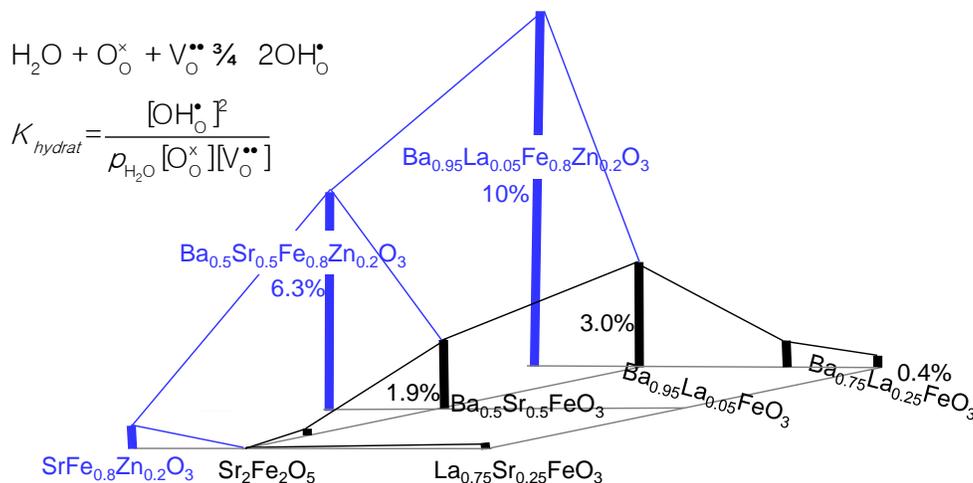
Rotraut Merkle, Max Planck Institute for Solid State Research, Stuttgart, Germany
r.merkle@fkf.mpg.de

Reihaneh Zohourian, Max Planck Institute for Solid State Research
Giulia Raimondi, Max Planck Institute for Solid State Research
Joachim Maier, Max Planck Institute for Solid State Research

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A cathode in a proton-conducting ceramic fuel cell (PCFC) should meet several criteria including high catalytic activity, electronic conductivity, sufficient proton conductivity, phase stability, etc. to achieve good performance. The proton conductivity allows the oxygen reduction reaction to extend from the triple phase boundary to the whole surface of the cathode (so-called "bulk path").

The present work studies the hydration thermodynamics of $(\text{Ba,Sr,La})(\text{Fe,Co,Zn,Y})\text{O}_{3-\delta}$ mixed-conducting perovskites using thermogravimetry.[1] The degree of the hydration is significantly smaller for cathode perovskites compared to typical electrolytes (acceptor doped $\text{Ba}(\text{Zr,Ce})\text{O}_{3-\delta}$) which are fully hydrated below ≈ 400 °C).[1-3] The cathode materials typically have a less negative hydration enthalpy and more positive hydration entropy. The highest proton uptake in this family was found for $(\text{Ba}_{0.95}\text{La}_{0.05})(\text{Fe}_{0.8}\text{Zn}_{0.2})\text{O}_{3-\delta}$ with 10% of protons per formula unit at 250 °C in 17 mbar water partial pressure. The proton mobility of $(\text{Ba,Sr})(\text{Fe,Zn})\text{O}_{3-\delta}$ was found to be comparable to that $\text{Ba}(\text{Zr,Y})\text{O}_{3-\delta}$ in electrolytes.[2] Based on these results, the bulk path is expected to be active for Ba-rich cathode materials.



The figure shows the proton uptake at 250 °C for various cation compositions. The increase with Ba content indicates that the proton uptake is closely related to the oxide ion basicity. A partial substitution of Zn on the B-site increases the proton uptake, while Co has the opposite effect due to increased covalency of the Co-O bond that decreases the oxide ion basicity. These experimental results will be compared to DFT calculations. The defect concentrations measured as a function of temperature and partial pressures indicate the presence of detrimental hole-hole and hole-proton interactions.[4] Qualitatively, they can be explained by partial delocalization of holes from the transition metal to the adjacent oxide ions, which increases the effective volume influenced by one hole and in parallel decreases the oxide ion basicity. Quantitatively, one can describe this effect by a first order correction (linear decrease of oxidation and hydration enthalpies with the hole concentration).

This detailed defect chemical insight may serve as the basis for further PCFC cathode development, in particular since a number of desired properties (proton uptake, catalytic activity, electronic conductivity, etc.) have conflicting tendencies and an insightful optimization strategy is required.

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[2] D. Poetzsch, R. Merkle, J. Maier, *Phys. Chem. Chem. Phys.* 2014, 16, 16446.

[3] R. Zohourian, R. Merkle, J. Maier, *Solid State Ionics* 2017, 299, 64.

[4] R. Zohourian, R. Merkle, J. Maier, *ECS Transact.* 2017, 77(10), 133.