

ABSTRACT

Mobile Protons in Triple-Conducting Perovskites - Similarities and Differences to Electrolyte Materials

R. Merkle¹, C. Berger,¹ A. Chesnokov,² D. Gryaznov,², E. Kotomin,^{1,2} J. Maier¹

¹Max Planck Institute for Solid State Research, Stuttgart, Germany.

²Institute of Solid State Physics, University of Latvia, Riga.

Triple-conducting oxides with mobile oxygen vacancies, protons and electronic defects are of fundamental interest, and find application as electrodes of protonic ceramic electrochemical cells (PCFC, PCEC). In electrolysis mode, PCECs enable the direct generation of dry, compressed H₂ with high efficiency. Compared to Ba(Zr,Ce,Acc)O_{3-z} electrolytes, the degree of hydration in triple-conducting Ba(Fe,Co,Zn,Y)O_{3-δ} perovskites is significantly lower. This is attributed to the high covalency of (Fe,Co)-O bonds, which decreases the basicity of the oxide ions.[1]

The experimental determination of proton mobility in triple-conducting perovskites is challenging. Proton diffusivities from SIMS measurements will be presented.[2] They are complemented by extended DFT calculations for BaFeO_{3-δ}, which indicate the presence trapping effects, and the appearance of a repulsive zone for strongly oversized acceptors.[3] Based on the obtained proton and oxygen vacancy conductivities of Ba(Fe,Acc)O_{3-d} perovskites the extension of the zone(s) active for oxygen reduction/oxidation in a porous PCFC/PCEC air electrode is discussed.

A.C. and D.G. thank the Latvian Council of Science (project no. lzp-2021/1-0203) for financial support, E.A.K. acknowledges the M-Era.Net HetCat project for funding.

[1] R. Zohourian, R. Merkle, G. Raimondi, J. Maier, *Adv. Funct. Mater.* 28 (2018) 1801241; R. Merkle, M. F. Hoedl, G. Raimondi, R. Zohourian, J. Maier, *Ann. Rev. Mater. Res.* 51 (2021) 461-493

[2] C. Berger et al., to be submitted (2024)

[3] M. F. Hoedl, A. Chesnokov, D. Gryaznov, R. Merkle, E. A. Kotomin, J. Maier, *J. Mater. Chem. A* 11 (2023) 6336-6348; A. Chesnokov et al. (2024) submitted