



Forum Inżynierii Materiałowej

Materials Engineering Forum

- **The Materials Engineering and Metallurgy Committee of the Polish Academy of Sciences**
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Hydration, stability and electrochemistry of electrode materials for proton ceramic electrochemical cells

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Mixed Proton and Electron conducting Ceramics (MPEC's) are central in the development of efficient electrodes for Proton Ceramic Electrochemical Cells. Mass transfer overpotential is limiting the electrode performance, and the interplay between catalytic activity and the inherent partial proton conductivity determines the electroactive surface. The electronic conductivity is important for low ohmic overpotential, but mobile electronic defects also affects proton stability. The stability of protons correlates with anion basicity, and electron structure and mobility is therefore essential with respect to both red-ox activity and partial proton conductivity. A wide range of double perovskites with A- and B-site substitutions has been investigated for proton concentration, stability in high steam pressures and electrochemical performance. Thermogravimetric Analysis (TGA) has been used to investigate proton concentrations and Electrochemical Impedance Spectroscopy (EIS) under positive, zero and negative DC bias was used to investigate polarization resistance for model electrodes and porous electrodes in both anodic and cathodic operation. The results reveal that while acceptor doping on the B-site promotes hydration and oxygen reduction, donor doping promotes hydrogenation and anodic water oxidation. Stability in high steam pressures is closely related to the A-site ionic radii ratio (IRR), where increased IRR gives increased oxygen non-stoichiometry, increased hydration and lowered stability in steam. Some of the reported MPEC materials[1] are therefore not stable at 600°C and 10 bar H₂O. They may, however, be stabilised for high steam pressures, and we present several ways to do so while maintaining MPEC functionality.

Acknowledgements: The Research Council of Norway (Grant n 272797 "GoPHyMiCO" and n 299736 "FunKey Cat")

[1] R. Strandbakke, V.A. Cherepanov, A.Y. Zuev, D.S. Tsvetkov, C. Argirusis, G. Sourkouni, S. Prünke, T. Norby, *Solid State Ionics* 278 (2015) 120.