

Final Report

Project acronym: *GoPHy MiCO*

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Publishable project summary

GoPhy MiCO addresses one of the main challenges in the development of new efficient energy systems based on Proton Ceramic Fuel Cells and Electrolysers (PCFCs / PCEs), namely the identification of new Mixed Proton and Electron conducting Ceramics (MPECs). These are essential for the oxygen/steam electrodes, but only few are identified, and the knowledge on these materials systems is limited. By studying a large matrix of double perovskites with different transition metal B-sites, and alkali-earth and lanthanide cations on distinguishable A-sites, and by systematic substitutions of these, trends in structure, oxidation, hydration, electron structure and conductivity has been established. The structural, chemical and electrical complexity of multiple cation double perovskites necessitated a wide range of complementary characterisation techniques. Although some studies had started to investigate electronic influence on hydration prior to project start-up, the theoretical state-of-the-art of hydration of mixed conductors was mostly related to qualitative assessment of cation basicity as an indicator of hydration properties. Based on project background results from the partners, the sole focus on cation basicity was regarded as insufficient, and the main objectives therefore focused on expanding the sets of parameters to involve also electrical and structural indicators. The project has concluded that cation basicity alone is insufficient as indicator for proton stability. The local electronic structure strongly affects oxide ion basicity through the cation-anion charge transfer, and oxygen non-stoichiometry is essential for hydration. The study of the electronic structure and oxygen non-stoichiometry is strongly related to structure, and the former is also influenced by the A-site cations and their valence electrons. Powder Neutron Diffraction (PND) combined with Synchrotron Radiation Powder X-ray Diffraction (SR-PXD) was performed on a large sample matrix for a detailed structural analysis of hydrating and non-hydrating compositions, and to study hydrating compositions in dry and wet state. Conductivity measurements were performed to correlate hydrating and non-hydrating compositions to mobility and concentrations of electrons and electron holes. The effect of hydration on total conductivity was investigated by conductivity relaxation, and partial proton conductivity was directly measured by an innovative development of the Hebb-Wagner technique. Concentrations of electronic species' was obtained through iodometric titration and Thermogravimetric Analysis (TGA), and TGA was also used to investigate oxygen non-stoichiometry and hydration. Proton concentrations and diffusion was also investigated by use of Secondary Ion Mass Spectrometry (SIMS). As a support for the structural studies, Scanning Transmission Electron Microscopy (STEM) was used to investigate the cation ordering on atomistic scale, and to look for local structural domains. The combined STEM / SR-PXD / PND studies were used to establish a correlation between hydration and cation order-disorder transition, which was again related to changes in oxygen non-stoichiometry upon hydration. The electronic structure was investigated by X-ray Photon Spectroscopy (XPS) and X-ray Adsorption Spectroscopy (XAS and XANES). The spectroscopic results were used as input parameters for ab-initio atomistic modelling (DFT), where electron structure and proton stability were modelled. Electrochemical measurements – where the most promising compositions were applied as electrodes on proton conducting electrolytes – were undertaken to investigate the effect of hydration on electrode performance. Some hydrating compositions were also investigated as low temperature electrocatalysts for water oxidation. Five rounds of composition series' with increasing cation complexity has been investigated in an iterative selection process including 80 unique compositions, and the most promising compositions have been tested for stability in high steam pressures. The main conclusion of the project is that compositions of solely closed-shell A-site cations show hydration, while inclusion of non-closed shell elements suppress hydration. The project outcome brings significant contributions to the development of proton ceramic fuel cells and electrolysers and to the ongoing implementation of hydrogen-based energy systems. Partners are UiO and IFE (NO), GUT (PL) and ITQ/CSIC (ES).