DEFECT CHEMISTRY OF MIXED CONDUCTING DOUBLE PEROVSKITES

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Barium Gadolinium Lanthanum Cobaltites with the general formula $Ba_{1-x}Gd_{0.8-y}La_{0.2+x+y}Co_2O_{6-\delta}$ (BGLC) are reported as Mixed Proton and Electron Conducting materials (MPECs), and have been utilized as positrode (positive electrode) materials for Proton Ceramic Electrochemical Cells (PCECs) [1]. A defect chemical model, treating various charge carrying defects in BGLC was published in 2017 [2] and in this work we expand the model to also comprise formation of protons in BGLC. Protons can be incorporated by two different reactions, in a ratio depending on measurement conditions and the oxidation state of the material. Low temperatures and high pO_2 leaves BGLC oxidized, and with increasing electron hole concentration, the hydrogenation reaction is promoted with respect to hydration. Hydrogenation is confirmed by use of isothermal Dry-H_2O-D_2O switches in thermogravimetric measurements, revealing a larger concentration of protons than expected from hydration only (Figure 1, left). The reduction of BGLC by hydrogenation is slowly counteracted by oxygen uptake combined with an expected cation reordering, bringing the material back to its initial oxidation state after equilibration in wet conditions. By combining oxidation and hydration thermodynamics, hydrogenation entropy and enthalpy can be obtained, making it possible to model proton concentrations from hydration and hydrogenation separately by use of advanced defect chemistry (Figure 1, right). Hydration is proposed to be facilitated by a minor concentration of oxygen vacancies in the O-Co-O layers, where acidic vacancies may accommodate basic hydroxyl groups. These vacancies are neighboured by more basic oxide ions in the O-Ba-O and O-Ln-O layers which in turn may accommodate protons.

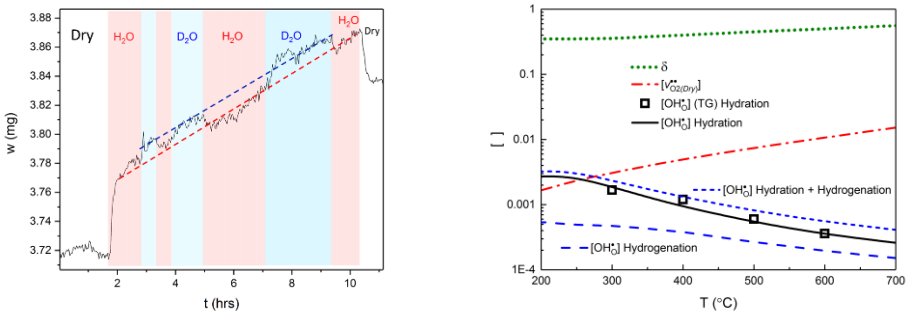

Figure 1 Left: Weight gain in BGLC (x = 0, y = 0.5) in dry air, 2 % H_2O and 2% D_2O at 300°C. Right: Total oxygen non-stoichiometry (δ), oxygen vacancies available for hydration, protons from hydrogenation, protons from hydration, total, modelled proton concentration, and measured hydration by TG in air versus temperature.

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