THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Proton conductivity in acceptor-doped lanthanide based pyrochlore oxides

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Abstract:

A high interest in developing new materials for SOFC applications in the temperature range of approximately 200–500 °C has been growing lately. The lower activation energies for proton (H^+) mobility can give higher conductivity in this temperature range. A demand on finding new H^+ conducting materials as electrolytes in fuel cells is thereby the result. The materials should preferably have high H^+ concentration and mobility, be chemically stable at the required operating temperatures and be electronically insulating. Although structure-types other than the well known perovskites, such as pyrochlores, have been of interest as novel materials for protonic devices, significantly less research has been carried out on these systems. This makes further detailed investigation of proton conduction in pyrochlores an important step on the way to finding the next family of materials for proton conducting applications.

This thesis presents the synthesis and characterization of the structure and conductivity of several pyrochlore oxide compounds. The synthesis for all the studies was concentrated on traditional solid state sintering, while characterization have been conducted with X-ray diffraction (XRD), thermogravimetric analysis (TGA), infrared spectroscopy (IR), scanning electron microscopy (SEM) and electrochemical impedance spectroscopy (EIS). Determination of particle size distribution (PSD), calculations of transport numbers via the electromotive force method (EMF) and EIS in a controllable gas cell for the $Sm_{2-x}Ca_xTi_2O_{7-x/2}$ material were carried out (Paper IV).

The proton conductivity in pyrochlore materials has been examined for several acceptor doped compounds, such as $A_{2-x}Ca_xB_2O_{7-x/2}$ (A = La, Sm, Yb; B = Ti, Sn, Zr, Ce) and $A_2B_{2-x}Y_xO_{7-x/2}$ (A = Sm; B = Ti, Sn). The materials exhibit high purity and chemical stability. The effects of A- and B-site doping, the significance of the B-site ion, and the importance of the lanthanide size at the A-site were all studied in relation to their impact on proton conductivity.

Expansions or reductions of the cell depending on doping site or choice of A- and B-site ions were confirmed by 2θ-shifts in the XRD patterns. TGA gave affirmative results regarding the loss of protons from the hydrated samples at expected temperatures. The results were linked with IR spectra confirming peaks at characteristic positions for O-H stretch vibrations as well as a isotopic shifts for samples treated under heavy water.

The EIS measurements showed overall elevated conductivities under wet gas conditions and isotope effects with deuterated water. The A-site doped samples showed close to one order of magnitude higher conductivities compared to the B-site doped samples. Varying the B-site ion with increasing ionic radius (Ti, Sn, Zr, Ce) showed higher proton conductivity levels for the B-site ions with smaller ionic radii and higher electronegativity. Further, the effect of the lanthanide contraction on proton conduction could be seen through varying the A-site constituent along the lanthanide group. The EMF and the EIS measurements carried out under controlled gas atmospheres gave transport numbers supporting dominant proton conductivity in $Sm_{1.92}Ca_{0.08}Ti_2O_{7-\delta}$. Large electrode polarization resistances were noted for all temperatures and gas concentrations. The Gorelov method was used for correction.

This work provides a wider understanding of the influence of the doping site, choice of A and B-site ions and microstructure on proton conduction in pyrochlore systems.

Key words: Pyrochlore, Rietveld refinement, Proton conductivity, Electrical impedance spectroscopy, Concentration Cell Electromotive Force Method.

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