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Östby, Jonas Allan; Poulsen, Finn Willy; Jacobsen, Torben

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Conductivity and defect chemistry modeling of oxygen nonstoichiometry in $Cr_{1+\varepsilon}Mn_{2-\varepsilon}O_4$ spinels

J. Östby[a], F. W. Poulsen[a] and T. Jacobsen [b]

Fuel Cells and Solid State Chemistry Division[a], Risø National Laboratory for Sustainable Energy, Technical University of Denmark, DK-4000 Roskilde, Institute of Chemistry[b], Technical University of Denmark, DK-2800 Lyngby, Denmark.

Cr- and Mn- containing oxides are present on metallic interconnects in present days SOFC's, either added deliberately as coatings – alternatively formed during high temperature oxidation of the interconnect. The electrical conductivity of such layers are of utmost importance for the performance of the SOFC. Conductivity as function of Mn-content of four $Cr_{1+\varepsilon}Mn_{2-\varepsilon}O_4$ spinels (ε = 0.25, 0.5, 0.75, 1.0) has been measured in the temperature and pO_2 ranges 523 K to 1273K and 1 atm to 10^{-4} atm, respectively.
Oxygen non-stoichiometries were measured for the Cr-Mn-O spinels using a coulometric titration technique. The compositions were both exposed to oxidation and reduction – in the latter case we entered the regime for MnO formation. The nonstoichiometry
in these spinels is very small, - i.e. the metal vacancy concentrations in air is around $3*10^{-4}$ molefraction. Cation diffusion is slow in these spinels.

The paper tries to reconcile the apparently contradicting observations summarized in the table below - especially the almost absent pO_2 dependence of the conductivity is difficult to account for.

Defect models using a disproportionation mechanism have been fitted to the data, and the resulting cation concentrations have been used to model conductance through a small polaron hopping mechanisms. Finally, the schism of treating the cation sublattice as one site, alternatively as two, a tetrahedral and octahedral one, is discussed.

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Parameter	Dependence	Explanation/comment
Mn-content	Strong influence on conductivity, increases a factor of 1000, going from Cr_2MnO_4 to $Cr_{1.25}Mn_{1.75}O_4$	Cr-site is not involved, conduction occurs via Mn-sites
Temperature	Strong influence on conductivity, 5-6 orders of magnitude; apparent activation energy in the range 0.9-1.2 eV .	The apparent activation energy is a sum of two terms
pO_2	very weak dependence of conductivity in pO_2 range 1- 10^{-4} atm.	Puzzling, since δ changes a factor 12 in the same pO_2 range