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Conductivity and defect chemistry modeling
of oxygen nonstoichiometry in
Cr_{1+ε} Mn_{2-ε}O₄ spinels

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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+ε} Mn_{2-ε}O₄ spinels (ε = 0.25, 0.5, 0.75, 1.0) has been measured in the temperature and pO₂ 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 pO₂ 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 ₂ MnO 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