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Published in:
Meeting Abstracts - Electrochemical Society

Publication date:
2010

Document Version
Publisher's PDF, also known as Version of record

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

Acknowledgements
PhD- grant (JÖ) from Danish Programme Committee for Energy and Environment is acknowledged. Erik Johnson, Niels Bohr Institute, University of Copenhagen, and Peter Vang Hendriksen, Risø DTU are thanked for stimulating discussions.

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