Conductivity and Defect Chemistry Modeling of Oxygen Nonstoichiometry in Cr1+B;Mn2-#B;O4 Spinels

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Conductivity and defect chemistry modeling of oxygen nonstoichiometry in Cr\textsubscript{1+}\,ε\,Mn\textsubscript{2-}\,ε\,O\textsubscript{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\textsubscript{1+}\,ε\,Mn\textsubscript{2-}\,ε\,O\textsubscript{4} spinels (ε = 0.25, 0.5, 0.75, 1.0 ) has been measured in the temperature and pO\textsubscript{2} ranges 523 K to 1273K and 1 atm to 10\textsuperscript{-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\times10\textsuperscript{-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\textsubscript{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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<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dependence</th>
<th>Explanation/comment</th>
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</thead>
<tbody>
<tr>
<td>Mn-content</td>
<td>Strong influence on conductivity, increases a factor of 1000, going from Cr\textsubscript{2}MnO\textsubscript{4} to Cr\textsubscript{1.25} Mn\textsubscript{1.75}O\textsubscript{4}</td>
<td>Cr-site is not involved, conduction occurs via Mn-sites</td>
</tr>
<tr>
<td>Temperature</td>
<td>Strong influence on conductivity, 5-6 orders of magnitude; apparent activation energy in the range 0.9-1.2 eV</td>
<td>The apparent activation energy is a sum of two terms</td>
</tr>
<tr>
<td>pO\textsubscript{2}</td>
<td>very weak dependence of conductivity in pO\textsubscript{2} range 1- 10\textsuperscript{-4} atm.</td>
<td>Puzzling, since δ changes a factor 12 in the same pO\textsubscript{2} range</td>
</tr>
</tbody>
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