Defect Chemistry and Conduction Mechanism of p Type Mixed Ionic and Electronic Conductors

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Understanding the defect formation and conduction mechanisms of the mixed ionic and electronic conductors (MIECs) allows us to improve technologically important systems such as solid oxide fuel cells, sensors and catalytic reactors. The p type perovskite family oxides are of great interest for use as the MIECs because (1) site occupancy is determined mainly by ionic radius so lattice site location of a particular cation is fairly certain; (2) electronic conductivity (σ) is determined by B site ion; and (3) ionic conductivity results from the presence of oxygen vacancies. Defect chemistry is a particularly powerful technique in understanding the mass and charge transfer properties by determining defect type, density, association and mobility. Questions on the defect chemistry in p type MIECs remain such as the origin of the ionic compensation and/or electronic composition in acceptor doped ferrites, manganites and cobaltites, and the degree of non-stoichiometry of these compounds. In this presentation, it is our intent to report our latest results of defect density and to present the global solutions to defect chemistry models of a variety of p type MIECs, including chromites, manganites, ferrites, and other B site substituted ferrites. The global defect chemistry models allow us to better understand and predict the electrochemical properties of perovskite type p-type conductors. Experiments were conducted to further understand this model, which include the electrical conductivity measurements, thermogravimetric analysis, neutron diffraction, and Mössbauer spectroscopy.

The term AOG is defined as the ability for oxygen vacancy generation, which possesses a similar electrochemical implication as that of reaction constant for oxygen vacancy generation, $K_{V_O^{\bullet\bullet}}$. Both of these terms have been simulated through two global defect chemistry models as a function of temperature and oxygen activity. Fig. 1 shows a plot of simulated conductivity as a function of oxygen activity for three types of perovskites, from which $K_{V_O^{\bullet\bullet}}$ can be obtained.

The B site cation can be easily driven from 4+ to 3+ for the perovskites which possess high values of AOG or $K_{V_O^{\bullet\bullet}}$, such as LSF, either by increasing the temperature or by decreasing oxygen activity. For instance, $\delta \sim 0.2$ for $La_{0.60}Sr_{0.40}FeO_{3-\delta}$ when heated to ~1500°C in air, which indicates that all of the Fe ions are in the 3+ valence state. If the temperature is lowered to 1000°C, the oxygen activity has to be lowered to $\sim 10^{-14}$ atm to observe this state. The activation energy values for AOG or $K_{V_O^{\bullet\bullet}}$ of manganites and chromites are larger than those of ferrites, hence, it is expected that Cr (4+) and Mn (4+) cations can be reduced to 3+ in air only if the temperature is sufficiently high. In these systems, oxygen vacancies are generated by a thermally activated process, which in turn results in a maximum conductivity for many p type conductors measured at elevated temperature. This maximum in conductivity represents the temperature at which the oxygen vacancy concentration starts to influence the carrier concentration. It does not mean that the oxygen vacancy concentration is negligible at this temperature, but on the other hand, the influence of oxygen vacancy concentration on total carrier concentration is negligible below this temperature and the concentration of oxygen vacancies is so small that their contribution to transport processes becomes minimal.
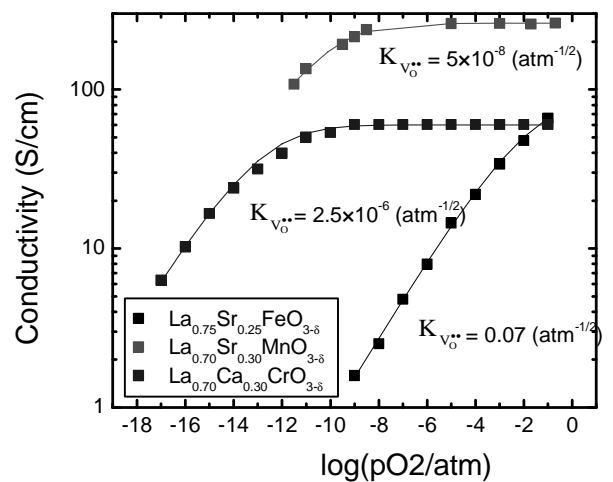

Fig. 1 A plot of simulated conductivity as a function of oxygen activity for three types of perovskites, from which $K_{V_O^{\bullet\bullet}}$ can be achieved.

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