Defect chemistry of p-type perovskite conductor used in solid oxide fuel cells

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Introduction

The development of solid oxide fuel cells (SOFCs) has been driven by both industry and academy for the purpose of searching for the alternative energy sources. Over last several years, operation of SOFCs in the intermediate temperature regime (500 – 700ºC) is of particular interest, which seems mandatory for SOFC commercialization. Strict materials requirements are of great importance for the electrode of SOFCs operated over the intermediate temperature region. Therefore, it is necessary to study the electrode materials by understanding the mechanisms for the conductive and catalytic behavior and developing reliable and stable experimental methods to measure defect density and catalytic ability. Perovskite type oxides are of great interest for use as the electrodes in SOFCs 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. Thus, this family of oxides was tailored to use as mixed ionic and electronic conductors, superionic conductors, and superconductors. Defect chemistry is a particularly powerful technique in understanding the mass and charge transfer properties by determining defect type, density, association and mobility. In this article, it is our intent to report the global solutions to defect chemistry models, with an emphasis on the p-type perovskite conductors which are being considered as the electrodes of SOFCs. The global defect chemistry models allow us to better understand and predict the electrochemical properties of perovskite type p-type conductors.

Defect Chemistry Modeling

The procedure is to write the defect formation reactions: 1) list the basic defect types and reactions which can occur: intrinsic, stoichiometric, oxygen excess and oxygen deficient; 2) write the overall neutrality relation and 3) combine the resulting equations to yield a relationship which can be solved for particular temperature and oxygen activity regimes. Considering a general type perovskite type oxide (ABO_3), the occupants at A site can be (Kroger-Vink notation is used) $A_A^\times$, V_A''' and Sr_A' (for simplicity, assume Sr is the low valence element substituting at the A site). The occupants at the B site are $B_B^\times$, B_B', $B_B^\bullet$ and V_B''', where $B_B^\times$ indicates a majority of B cations which are in valence of 3+, B_B' represents that some B site cations are in 2+ state and $B_B^\bullet$ shows some B site cations are in 4+ valence state. The oxygen site can have two type of occupants, $V_O^{\bullet\bullet}$ and $O_O^\times$.

Since there exist nine variables, nine equations are needed to obtain these values. Two methods can be used to solve the resulting equations: 1) divide into regions of particular neutrality conditions and solve for that particular region or 2) do not use limiting conditions, but allow a computer to make a numerical solution to the overall equation using the total neutrality condition. More detailed equations and solutions can be found elsewhere. [1] A global solution will be discussed in this article, in which the overall electron neutrality expression is used results in a term named as the ability for oxygen vacancy generation (AOG). This method is considered as a model based on delocalized electron holes.

The total electrical conductivity, σ, is given by

$$\sigma = N\mu q \tag{1}$$

where μ is the mobility, q is the carrier charge and N is the carrier concentration. Because of the mobility of either the electrons or holes is much higher than that of oxygen ions, the total conductivity in ferrites is dominated by hole conduction. The carrier concentration, N is:

$$N = [Sr_{La}'] - 2[V_O^{\bullet\bullet}] \tag{2}$$

where $[Sr_{La}']$ is the acceptor level and $[V_O^{\bullet\bullet}]$ is the oxygen vacancy concentration. For simple analysis, it is assumed that all doping centers are dissociated. Generation of oxygen vacancy, $V_O^{\bullet\bullet}$, follows:

$$O_O^\times \rightarrow V_O^{\circ\circ} + \frac{1}{2}O_2 + 2e' \cdot \tag{3}$$

The reaction constant (K_1) of reaction in Eq. (3) is:

$$K_{V_O^{\bullet\bullet}} = [V_O^{\bullet\bullet}]\, pO_2^{1/2}\, n^2 \tag{4}$$

where, pO_2 is the oxygen partial pressure and n is the electron concentration. Assuming this reaction follows the Ahrennius law:

$$K_{V_O^{\bullet\bullet}} = K_{V_O^{\bullet\bullet},0} \exp(-\frac{E_{V_O^{\bullet\bullet}}}{kT}), \tag{5}$$

where $E_{V_O^{\bullet\bullet}}$ is the activation energy for oxygen vacancy generation and k is Planck's constant. Considering np = K_i, then the expression can be rearranged to yield

$$\ln(\frac{[V_O^{\bullet\bullet}]}{([Sr_{La}'] - 2[V_O^{\bullet\bullet}])^2}) = \ln(\frac{K_{V_O^{\bullet\bullet},0}}{K_i^2}) - \frac{1}{2}\ln(pO_2) - \frac{E_{V_O^{\bullet\bullet}}}{kT} \cdot \tag{6}$$

From this expression the oxygen vacancy concentration can be derived as a function of substitution level ($[Sr_A']$), temperature, and materials properties:

$$[V_O^{**}] = \frac{(4MN+1) - \sqrt{1+8MN}}{8A} \text{ where} \tag{7}$$

$$M = \frac{K_{V_O^{\bullet\bullet},0}}{K_i^2} \cdot \exp(-\frac{E_{V_O}}{kT}) \cdot P_{O_2}^{-1/2} \text{ and } N = [Sr_{La}'] \cdot$$

The term M can be expressed as AOG*$pO_2^{-1/2}$, where AOG stands for the ability for oxygen vacancy generation, which is a function of temperature and intrinsic materials properties. Fig. 1 shows a plot of carrier concentration calculated from Eqs. (2), (6) and (7). The ability for oxygen vacancy generation as a function of temperature and oxygen activity can be determined by simulating experimental conductivity data with the current defect chemistry. Fig. 2 shows a plot of the experimental and simulated conductivity of LSM, LSF and LSCF. Table 1 lists the AOG values of these compounds. It is worthwhile to note again that the B site cation can be easily driven from 4+ to 3+ for the perovskites which possess high values of AOG, such as $(La,Sr)FeO_{3-\delta}$. For instance, δ ~ 0.2 takes place at ~1500ºC for $La_{0.60}Sr_{0.40}FeO_{3-\delta}$ in air, which indicates that all of the Fe ions are in the 3+ valence state. If the temperature is lowered to 1000ºC, the oxygen activity has to be lowered to ~ 10^{-14} atm to observe this state. Activation energy values for AOG of manganites and chromites are larger than those of ferrites, hence, it is expected that Cr and Mn cations can be reduced to 3+ in air only if the temperature is sufficiently high.

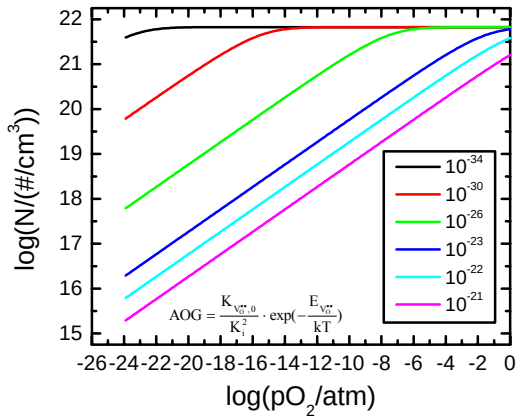

Figure 1. A plot of carrier concentration as a function of oxygen activity with various AOG values

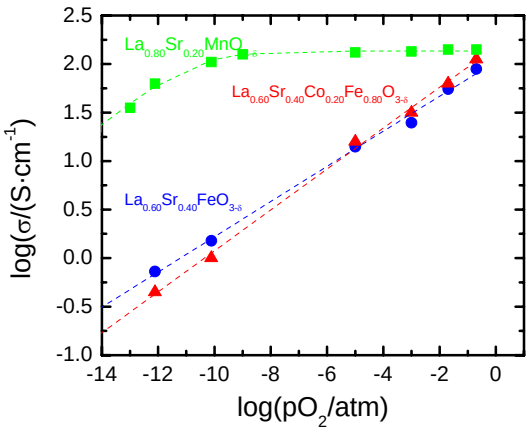

Figure 2. Plot of log(σ) vs. log(pO_2) for LSM, LSF and LSCF. The solid points are experimental data. The dash lines are fitting results from the global defect chemistry model. [2-4]

The knowledge of the values for the AOG terms can enable us to understand the maximum conductivity of many p type conductors. For example, from the previous results, we know that at temperatures < 600ºC in air LSF possesses nearly stoichiometric oxygen occupancy. Thus it can be expected that the oxygen vacancy concentration is extremely low at relatively low temperature (~ room temperature), therefore conductivity should increase with increasing temperature because of the increasing mobility. At elevated temperature, more oxygen vacancies are generated which will decrease the total carrier numbers because of the increasing oxygen vacancy concentration. The mobility, however, continuously increases with increasing temperature. Hence, a maximum conductivity at a specific temperature is expected due to an increasing mobility and decreasing carrier concentration. A shift of the temperature corresponding to the maximum conductivity is observed as shown in Table 1. As discussed previously 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.

The values of AOG and understanding of the maximum conductivity are of particular importance in the search for materials for energy conversion devices. Since oxygen vacancies are required for lower cathodic overpotentials, this temperature also represents the temperature below which a cathode can be expected to have high overpotentials. Therefore, when pure LSM is used as the cathode, it will be expect to work well when the operation temperature is ~ 1000°C because the oxygen vacancy concentrations are sufficiently high to support the required transport processes of the cathode. Below this temperature range, overpotential problems are commonly encountered. It has been found that the addition of a second ionic conducting phase to the cathode enhances the ionic transport processes, which allows lower temperature operation. Thus the use of cathodes consisting of mixtures of LSM and YSZ or LSM and CGO has become common practice in the SOFC industry, but these mixtures will not extend the temperature much below 750-800°C before cathodic overpotentials become too large because the concentration of oxygen vacancies is insufficient to support the transport processes which are required for oxygen reduction and transport of the oxygen ions to the electrolyte.

Conclusions

The understanding of the defect chemistry in the perovskite family p type conductors allows us to search for the novel materials for use in fossil energy conversion system, which requires a sufficient vacancy density, a mixed ionic and electronic conductance, high catalytic ability and stability. Examples include the electrodes used in SOFCs where the cathode component which requires high oxygen vacancy density and electronic conductance and the anode requires stability in a very reducing atmosphere, electronic conductance, and oxygen vacancy density.

Acknowledgement. This work was supported by contracts DE-FC26-02NT41563 and DE – FC36 – 01G011084.

References

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Table 1 AOG and T_{max} for four p type conductors

	LSM	LSF	LSCF	LSFCu
AOG	2.9×10^{-27}	3×10^{-21}	3×10^{-20}	
T_{max} (ºC)	900	600	550	400