OPTIMAL DOPANT CONCENTRATION IN SCANDIUM DOPED CUBIC ZIRCONIUM OXIDE USED IN SOLID OXIDE FUEL CELLS

Gene Whyman, Michael Zinigrad
Ariel University, 40700, Ariel, Israel

Alexander Kalashnikov
Rock Capital Partners, Moscow, Russian Federation

ABSTRACT

Formation of complexes of oxygen vacancies and scandium ions leads to the existence of a maximum in the dependence of conductivity on dopant concentration in scandium doped cubic zirconium oxide used in solid oxide fuel cells (SOFC). A corresponding equilibrium constant in the reaction of formation of these complexes is calculated based on the comparison with the published experimental data on this dependence, as well as a diffusion coefficient of oxygen dianions in the zirconia solid electrolyte for SOFC. The change in maximal conductivity and optimal dopant concentration caused by the temperature is discussed.

1. INTRODUCTION

One of the widespread solid electrolytes used in solid oxides fuel cells (SOFC) is the fluorite-type cubic doped zirconia, ZrO$_2$ [1-2]. Addition of oxides of trivalent metals stabilizes the cubic phase of zirconia at available temperatures of the order of 600°C. The doping with these oxides also plays the other important role: substitution of tetravalent zirconium by trivalent scandium or yttrium gives rise to oxygen vacancies, which serve as guides for current carriers O$_{2-}$. In the case of scandium doping (in the Kroeger-Vink notation):

$$\text{Sc}_2\text{O}_3 \xrightarrow{\text{ZrO}_2} 2\text{Sc}^{3+}_{\text{Zr}} + V_{\text{O}}^{--} + 3\text{O}_0^x.$$

However, the increase in the dopant concentration is accompanied by formation of two types of complexes: a charged one, $[V_{\text{O}}^{--}\text{-Sc}^{3+}_{\text{Zr}}]$, and a neutral one $[V_{\text{O}}^{--}2\text{Sc}^{3+}_{\text{Zr}}]^x$ [3-7]:

$$[V_{\text{O}}^--) + [\text{Sc}^{3+}_{\text{Zr}}] \rightarrow [V_{\text{O}}^{--}\text{Sc}^{3+}_{\text{Zr}}]^,$$

$$[V_{\text{O}}^--) + 2[\text{Sc}^{3+}_{\text{Zr}}] \rightarrow [V_{\text{O}}^{--}2\text{Sc}^{3+}_{\text{Zr}}]^x.$$

These complexes prevent oxygen dianions from moving inside the crystal because of binding oxygen vacancies.

Bellow, a simple model is presented describing the movement of oxygen dianions over the free oxygen vacancies and the influence of formation of the above complexes on
this process. A more general model considering also the electronic conductivity was elaborated in [7]. However, under actual temperatures used in zirconia SOFC, the electronic conductivity is negligible.

We will focus on the ionic conductivity dependence on the concentration and will explain the existence of the optimal dopant concentration bringing the conductivity to a maximum.

2. OPTIMAL DOPANT CONCENTRATION AND EQUILIBRIUM CONSTANT OF COMPLEX FORMATION

Consider only the case of the charged complex, Eq. (1), corresponding to the real situation of low dopant concentration. Applying the mass action law to Eq. (1), one has for the equilibrium constant $K$:

$$K = \frac{[V_0^-\text{Sc}^\prime_{2Zr}]}{[V_0^-][\text{Sc}^\prime_{2Zr}]}.$$ 

Taking into account electroneutrality $2[V_0^-] = [\text{Sc}^\prime_{2Zr}]$, Eq. (3), and $[\text{Sc}^\prime_{2Zr}] = [\text{Sc}] = 2[\text{Sc}_2\text{O}_3]$, one obtains the number of oxygen vacancies which are free to move:

$$[V_0^-]_{\text{free}} = -2K\left(\frac{[\text{Sc}_2\text{O}_3]}{4K} - \frac{1}{4K}\right)^2 + \frac{1}{8K}.$$ 

Equation (4) presents a parabola, which is shifted to the right and upwards by $1/4K$ and $1/8K$, respectively. The result in Eq. (4) can be related to the experimental data of [8]. First, Eq. (4) explains the existence of a maximum in the mentioned measurements. Second, the equilibrium constant $K$ of the complex formation in Eq. (1) can be estimated from the known experimental concentration of $\text{Sc}_2\text{O}_3$ corresponding to the maximal ionic conductivity, which is equal to 0.11 mol. frac., according to [8]:

$$[\text{Sc}_2\text{O}_3]_{\text{max}} = 11\text{mol} \% = 0.11\text{mol} \cdot \text{frac.} = \frac{1}{4K},$$

$$K = 2.3(\text{mol. frac.})^{-1}.$$

The concentration of free oxygen vacancies can be connected with the electric conductivity, which is a measurable quantity. For this purpose, a current of oxygen dianions should be imagined as an equivalent current of oxygen vacancies in the opposite direction. Then, the concentration of oxygen vacancies $n$ can be used in the Nernst-Einstein equation for the conductivity $\sigma$:

$$\sigma = \frac{4e^2Dn}{kT} - \sigma_{\text{counter}},$$

where $e$ is the elementary charge, $D$ is the diffusion coefficient of oxygen vacancies, $T$ is the absolute temperature, and $k$ is the Boltzmann constant. Introducing an additive correction $\sigma_{\text{counter}}$ is dictated by the experimental fact of the vanishing of the conductivity at the nonzero dopant concentration. It may be interpreted as arising from the countercflow of other crystal defects or because of possible polarization of electrodes. Equation (6) can be cast in form
\[ \sigma = \frac{4e^2 D \cdot [V_0]_{\text{free}}}{V_{ZrO_2} kT} - \sigma_{\text{counter}}, \]  

(7)

where \( V_{ZrO_2} = 3.36 \cdot 10^{-23} \text{ cm}^3 \) is the volume of the corresponding stoichiometric unity.

Equations (7) and (4) give the calculation scheme for the conductivity of a solid electrolyte. In Fig. 1, the result (7) is plotted as a function of the scandium oxide concentration (the solid line). Numerical values of the quantities \( D \) and \( \sigma_{\text{counter}} \) are fitted to reproduce the experimental data from [8]:

\[ D = 1.1 \cdot 10^{-4} \text{ cm}^2/\text{s}, \quad \sigma_{\text{counter}} = 0.70 \text{ (} \Omega \cdot \text{ cm})^{-1}, \quad K = 2.35 \text{ (mol. frac.)}^{-1} \]

while the equilibrium constant \( K \) has been found above (see (5)).

The obtained large value of the diffusion coefficient is characteristic of the crystals with high ionic conductivity (super-ionics) at high temperatures, like doped zirconia. Comparable values in the range of \( 10^{-5} \sim 10^{-4} \text{ cm}^2/\text{s} \) were measured in [9] for oxygen vacancies at higher temperatures of order of 2000K. However, it should be taken into account that these measurements were accomplished in tetragonal pure zirconia where ionic conductivity and diffusivity should be smaller than in the cubic doped zirconia.

3. CONCLUSIONS

The increase in the concentration of the admixture of trivalent metals to tetravalent metal oxides leads to the creation of new oxygen vacancies. As a result, the oxygen ionic conductivity also increases. Unfortunately, parallel formation of complexes between oxygen vacancies and dopant atoms damps this process and eventually inverts it.
As is shown above, the use of the mass action low allows to find the optimal concentration providing a maximum to the conductivity.

In the case of the doping of zirconia with scandium, the diffusion coefficient of oxygen dianions and the equilibrium constant for formation of the mentioned complexes are obtained from the published experimental data.

From a suitable analysis of the temperature dependence of the mentioned equilibrium constant and diffusion coefficient, which is underway, it is revealed that the maximal ionic conductivity is a sharp increasing function of the temperature. The optimal dopant concentration also increases with the temperature.

REFERENCES