REDOX-ACTIVE IMPURITY IONS IN SOLID ELECTROLYTES AND THEIR INFLUENCE ON TRANSPORT PROPERTIES

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ABSTRACT

The importance of redox-active impurities in solid electrolytes is discussed. As long as the content of these impurities is negligible with respect to the aliovalent oxide content (e.g., the yttria concentration in stabilized-ZrO$_2$), the equilibrium concentrations of electrons and holes are not affected by the impurities. However, they may have a considerable influence on the chemical diffusion of oxygen by the internal source/sink effects as well as on the electronic conductivity directly under conditions where the interaction with the gas phase is frozen in. Defect chemistry and transport equations for solid electrolytes are given including the ionization equilibrium reactions of ions of variable charges. The valence state and its change of doped transition metal ions (Ti, V, Cr, Mn, Fe, Co, Ni, Cu) and selected rare earth ions (Ce, Pr, Gd) in 9.5 mol%Y$_2$O$_3$-stabilized ZrO$_2$ single crystals as a model solid electrolyte are identified by electron paramagnetic resonance (EPR/ESR) and optical absorption spectroscopy (NIR, VIS, UV). The single crystals, annealed at 800°C in a p$_{O_2}$ range from 1.0 down to 10$^{-20}$ bar, are used in this study. The redox-active impurity ions in the solid electrolyte are specified by both methods.

INTRODUCTION

The influence of charge-variable impurity ions on the transport and electrochemical properties of ionic solids is of significant scientific and technological interest. The introduction of electronic conductivity in solid electrolytes by heavily doping with transition metal or rare earth ions has been discussed (e.g., 1-6). The mixed ionic and electronic conduction has been considered to enlarge the three phase boundaries at the electrolyte/electrode interface (1). Electrocatalytic effect and an enhancement of the oxygen exchange by transition metal oxides at the electrolyte surface have been reported (1,4-6). A mixed conduction should be avoided especially in case of very thin electrolytes. They may be used in order to reduce the operation temperature of fuel cells from 1000°C down to about 800°C or even lower (5,7,8).

The influence of dopant ions with variable charges is a general issue in solid state ionics affecting transport properties. Therefore, transport equations should be modified with respect to internal source and sink terms (9). If the redox-active impurity ions are present, the transport equations should include the following internal source/sink terms:

$$
\frac{\partial n_i}{\partial t} = \nabla \cdot \left( D_i \nabla n_i \right) + \sum_{j} n_j \lambda_{ij} \left( \frac{A_{ij}}{A} - 1 \right)
$$

where $n_i$ is the concentration of ion $i$, $D_i$ is the diffusion coefficient of ion $i$, $\lambda_{ij}$ is the ionization equilibrium constant of the reaction $i \rightarrow j$, $A_{ij}$ is the activity coefficient of ion $j$, and $A$ is the activity of the electrolyte.
content is very large, typical doping effects occur: If they are important in the
electroneutrality equation, they modify electronic and ionic concentrations directly; also
they may even change activity coefficients and equilibrium constants. In those cases,
conductivities and chemical diffusion coefficients are affected. If the interaction of the
gas phase with redox-active impurities at the surface itself is important, the surface rate
constants are modified, too. Owing to segregation effect, this may even be relevant at
lower overall concentrations.

In this paper, we mainly consider the more sophisticated effects which are also
of relevance if the redox-active impurity concentrations are small. Their influence is not
state-of-the-art. One effect is the significant influence on chemical diffusion
quantitatively predicted by theoretical work in our group (8), which has been confirmed
for YSZ and Fe-doped SrTiO₃ (9-11). The deeper reason for this lies in the fact that the concentration changes with oxygen stoichiometry are decisive through which the influence of the redox-active impurities is magnified. The second effect refers to the
impact of redox-active impurities under conditions where the oxygen stoichiometry is
frozen-in. Note here that the oxygen ions can still be quickly transported through the
electrolytes under these conditions. This is highly significant especially at lower
temperatures. There the oxygen incorporation reaction (and thus stoichiometry) is
frozen-in and the redox-active impurities are the only sources and sinks for the
electronic carriers. First, as a model case, the defect chemistry of doped solid
electrolytes including ions of variable charges is considered, both in equilibrium and
frozen-in cases. The various transport properties are briefly described including partial
conductivities, defect diffusion coefficients, and the chemical diffusion coefficient of
oxygen including the internal source/sink effect, as well as the surface exchange
coefficient. Emphasis is then given on the identification of valence state changes of
transition metal and rare earth ions in yttria-stabilized zirconia. Valence changes of
dopants are studied after annealing under typical (reduced temperature) fuel cell
operational conditions. The use of single crystals enables one to compare EPR spectra
with optical absorption after the defined heat-treatments, and to avoid a possible effect
of inhomogeneities between grains and grain boundaries.

DEFECT CHEMISTRY AND TRANSPORT PROPERTIES
INCLUDING IONS OF VARIABLE CHARGES

We consider equilibrium and partially frozen-in situations. Since the solid
electrolyte is usually used within the temperature and pO₂ ranges in which the ionic
cconductivity is predominant in general, the defect chemistry is considered only for the
situations where \([V^{n-}]\gg[\delta^+]\), \([\delta^-]\) and \([V^{n+}]\gg[\text{impurity (M)}\text{of variable charges}]\approx c_M\).

Defect Chemistry in Equilibrium

Defect chemical relations are given for YSZ as a model. The equilibrium defect
chemistry at a temperature, T, is described by the oxygen incorporation equilibrium:
Since $[V_o^{**}] > [h^+]$, $[e']$, $[M_{Zr}]$, $[M_{Zr'}]$ ($\approx 10^{-20} \leq p_{O_2} \leq 1$ bar for YSZ), the overall electroneutrality condition,

$$2[V_o^{**}] + [h^+] - [M_{Zr}] - [e'] - [M_{Zr'}] - 2[M_{Zr'}] = 0$$

is then reduced to:

$$[V_o^{**}] = \frac{[Y_{Zr}]}{2}.$$  

Therefore, the electron and hole concentrations are fixed by $K_1$, $p_{O_2}$, and $[Y_{Zr}]$, as

$$[h^+] = K_1(T)^{\frac{1}{2}} \cdot [V_o^{**}]^{\frac{1}{2}} \cdot p_{O_2}^{-\frac{1}{4}} \equiv K_1(T)^{\frac{1}{2}} \cdot \left(\frac{[Y_{Zr}]}{2}\right)^{\frac{1}{2}} \cdot p_{O_2}^{-\frac{1}{4}}$$

$$[e'] = \frac{K_1(T)}{[h^+]} \equiv K_1(T)^{-\frac{1}{2}} \cdot K_1(T) \cdot \left(\frac{[Y_{Zr}]}{2}\right)^{-\frac{1}{2}} \cdot p_{O_2}^{\frac{1}{4}}$$

where $K_1(T) = [h^+] \cdot [e']$ refers to the band-band equilibrium. Impurity equilibria such as

$$K^{(n+1)+} \leftrightarrow M^{(n+1)+} + h^+; \quad K_1(T) = \left[\frac{[M^{(n+1)+}][h^+]}{[M^{(n)+}]}ight]$$

are not of influence on $[h^+]$, rather the ratio $[M^{(n)}]/[M^{(n+1)+}]$ is fixed through Eq. 4. Therefore the electron and hole concentrations and their conductivities are not affected by the redox-active impurities, as long as the simplification of the overall electroneutrality condition (Eq. 2 to 3) is valid. Using the mass conservation condition,

$$c_M = \left[\frac{[M^{(n+1)+}][h^+]}{[M^{(n)+}]}ight]$$

the concentrations $[M^{(n+1)+}]$ and $[M^{(n)+}]$ can be easily calculated. It follows:

for low $p_{O_2}$: $[M^{(n)+}] \equiv c_M$ and $[M^{(n+1)+}] \equiv c_M \cdot K_1^{\frac{1}{2}} K_2^{-1} \cdot \left(\frac{[Y_{Zr}]}{2}\right)^{\frac{1}{2}} \cdot p_{O_2}^{\frac{1}{4}}$  

for high $p_{O_2}$: $[M^{(n+1)+}] \equiv c_M$ and $[M^{(n)+}] \equiv c_M \cdot K_1^{-\frac{1}{2}} K_2^{-1} \cdot \left(\frac{[Y_{Zr}]}{2}\right)^{-\frac{1}{2}} \cdot p_{O_2}^{\frac{1}{4}}$.

The relations for the strongly reducing condition are analogous and not considered separately here. These defect chemical relations are, of course, different if the total $M$-concentration, $c_M$, becomes comparable with $[Y_{Zr}]$ (Eq. 3 invalid). Moreover, at much higher $M$-concentrations, the hopping conduction between $[M^{(n+1)+}]$ and $[M^{(n)+}]$ may not be negligible (13). However, contrary to the conductivities, there is a serious effect on $D$ as shown in detail in ref. (9).
**Transport Properties**

The partial conductivities of charged particle species, \( i \), are correlated with the particle diffusion coefficients via the Nernst-Einstein relation (e.g., 14),

\[
\sigma_i = |z|e \cdot [i] \cdot \mu_i = \frac{(|z|e)^2}{kT} \cdot [i] \cdot D_i
\]

where \( \sigma_i \) is the partial conductivity, \( D_i \) the particle diffusion coefficient, \( \mu_i \) the mobility, \( |z|e \), charge, \( k \) and \( T \) have the usual meanings, and \( i \) may be \( V_a^* \), \( h^* \), or \( e^- \) in ionic and mixed-conducting oxides. Charge carrier concentrations may be determined by equilibrium defect chemical relations or be frozen-in. The chemical diffusion coefficient, determined as the ambipolar diffusion of oxygen ions and electrons, is described as (9,14),

\[
\overline{D} = t_{v^*} \cdot D_{eon} + t_{eon} \cdot D_{v^*}
\]

where the subscript \( eon \) denotes \( h^* \) (or \( e^- \)), and the transference numbers are defined as \( t_{v^*} = \sigma_{v^*}/\sigma_{total} \) and \( t_{eon} = \sigma_{eon}/\sigma_{total} \). If ions of variable charges are involved, acting as sink or source of electrons or electron holes, the chemical diffusion coefficient must be modified and generalized as (9),

\[
\overline{D} = \chi \cdot t_{v^*} \cdot D_{eon} + t_{eon} \cdot D_{v^*}
\]

where \( \chi \) denotes the trapping factor (or more precisely the differential fraction of free holes (or electrons)) involving the constants of the ionization equilibrium reactions of the impurity ions. For solid electrolytes where \( t_{v^*} \approx 1 \gg t_{eon} \), the equation 12 can, if \( \chi \cdot D_{eon} \) is not very much lower than \( D_{v^*} \), be reduced to (9-12):

\[
\overline{D} \approx \chi \cdot D_{eon}
\]

The trapping factors, \( \chi_{h^*} \) (and \( \chi_{e^-} \)), \( 0 < \chi \leq 1 \) are given, using the ionization equilibrium constant (in Eq. 6), as (9),

\[
\chi_{h^*}^{-1} = 1 + \frac{c_M \cdot K_2}{(K_3 + [h^*])^2}
\]

in oxidizing \([h^*] > [e^-]\), the ionization with holes involved) conditions, and analogous for reducing \([h^*] < [e^-]\), the ionization with electrons involved) conditions. The presence of the trapping factors indicates the importance of redox-active ions for the chemical diffusion.

The chemical diffusion coefficients are typically measured by detecting the rate of reequilibration, as the partial pressure of the oxygen over an oxide is suddenly changed. Since the amount of oxygen exchanged is appropriately correlated with the change in the defect concentration, \( c \), via the above given defect chemical relations, the time(t)-dependent relaxation of the concentration yields the chemical diffusion coefficient \( \overline{D} \) using the relation (10,15).
\[
\frac{c_{\text{int}} - c_{\text{int}0}}{c_{\text{int}} - c_{\text{int}0}} = 1 - \frac{4}{\pi} \sum_{j=0}^{\infty} \frac{(-1)^j}{2j+1} \exp\left(-D(2j+1)^2 \pi^2 t / 4l^2\right) \cos\left(\frac{(2j+1)\pi x}{2l}\right)
\]  \[15\]

for a thin slab sample, that is, a parallelepiped with two sides much larger than the third with a thickness 2l. The equation is valid under the conditions that the surface exchange kinetics are fast enough and not rate-limiting.

If the surface exchange is rate-limiting instead of the chemical diffusion, the relaxation of concentrations is governed by the surface exchange coefficient \( \tilde{k} \) as (10,15):

\[
\frac{c_{\text{int}} - c_{\text{int}0}}{c_{\text{int}} - c_{\text{int}0}} \cong 1 - \exp\left(-\frac{\tilde{k} t}{l}\right) \approx \frac{\tilde{k} t}{l} .
\]  \[16\]

\( \tilde{k} \) may be influenced even at low \( c_M \) if there are segregation effects to the surface. The same is valid with respect to the diffusion through space charge regions (16). \( \tilde{D} \) and/or \( \tilde{k} \) describe the kinetics of the reequilibration. Slow kinetics at lower temperatures, therefore, may cause time-dependent (Eq. 15 and/or 16) or frozen-in (Eq. 18 mentioned later instead of Eqs. 4 and 5) electronic defect concentrations and conductivities. Electronic conductivities in quenched situations have been observed in SrZrO3 (17). Using the relaxation of optical absorption, the chemical diffusion and surface exchange coefficients of Fe-doped SrTiO3 and the chemical diffusion coefficients of Ni- Ti-, and Ce-doped YSZ could be determined (10-12).

Defect Chemistry in Partially Frozen-in State

Nearly exclusively neglected has been the effect of the redox-active impurities on \( \sigma_{\text{ev}} \) (and thus also on \( \tilde{D} \)) at a temperature, T, at which the oxygen incorporation is no longer in equilibrium, but the trapping reaction is still reversible. Let us assume that the incorporation equilibrium is maintained at a (higher) temperature, \( T_E \), but frozen in at lower T, we have to give up Eqs. 1, 4, and 5 for \( T < T_E \). Instead, the conservation of the hole ensemble has to be considered,

\[
[h^+] + [M^{(n+1)+}] = [h^+]_E + [M^{(n+1)+}]_E = S_E
\]  \[17\]

where \( S \) is the concentration of the total ensemble and the index E denotes the values at \( T_E \). Owing to the gain of Coulomb energy by trapping, the concentration of free holes will decrease at the expense of an increased concentration of trapped holes. This leads to a dependence of \( \sigma_h \), not only on \( c_M \) but also on T (through \( K_2 \)). It is well possible that high apparent migration energies of electronic carriers are often simply caused by this effect, (see ref. 17) and misinterpreted in polaron-pictures. It is straightforward to show that for \( T < T_E \), it holds that (since \([h^+], [M^{(n+1)+}], [M^n] \geq 0\))

\[
[h^+] = \left( \frac{c_M + K_2 - S_E}{2} \right) + \sqrt{\left( \frac{c_M + K_2 - S_E}{2} \right)^2 + K_2 \cdot S_E}
\]  \[18\]
where

\[ S_E = \left[ M^{(n+1)*}_E \right] + \left[ h^* \right]_E = \frac{c_M \cdot \left[ h^* \right]_E}{K_{2E}} + \left[ h^* \right]_E \]  

\[ \left[ h^* \right]_E = K_1(T_E)^{1/2} \cdot \left( \frac{Y_{Zr}}{2} \right)^{1/2} \cdot \rho_0 \cdot \frac{1}{\nu} \]  

The relations for the strongly reducing condition are analogous. If the internal ionization equilibrium (Eq. 17) also freezes below a temperature \( T_F \) \((\leq T_P)\), the conductivities for \( T<T_F \) are only activated by true migration barriers. Owing to the importance of redox-active impurity ions mentioned above, we identify and specify such ions in YSZ as a model (and an important) electrolyte material.

**EXPERIMENTAL**

The yttria (9.5 mol%) stabilized zirconia single crystals used had a dopant content of \(<0.1\) wt\% transition metal (Ti, V, Cr, Mn, Fe, Co, Ni, Cu) or rare earth (Ce, Pr, Gd) oxides. These crystals were cut into a dimension of \(3.8\times10\times0.5\) mm\(^3\), with (100) orientations of all surfaces, followed by mechanical polishing using 1 \(\mu\)m diamond paste and then chemically polished to ensure optically transparent surfaces. The crystals were annealed at 800°C for 16 h under a corresponding atmosphere using O\(_2\)-Ar or H\(_2\)-H\(_2\)O-Ar mixtures and then quenched at a cooling rate of \(\approx100^\circ\)C/min. X-band EPR experiments were made above 100 K (model EMX, Bruker Analytische Messtechnik GmbH). Selected single crystals were used to quantify the EPR absorption intensity change as a function of oxygen partial pressure. Single crystal EPR measurements were performed with the (100) largest surfaces perpendicular to the applied static magnetic field. For the quantitative EPR, care was taken to place the samples in the same position in the microwave cavity of the EPR spectrometer, and to maintain the experimental conditions identical. For powder EPR, the quenched samples were then crashed and milled to ensure a statistical distribution of all crystal orientations. Optical absorption spectroscopy was carried out on these specimens in a wave length range from 1100 nm to 190 nm (near-infrared, visible, and ultra-violet range) at room temperature (model Lambda 2, Perkin-Elmer Corp.).

**RESULTS AND DISCUSSION**

**Electron Paramagnetic Resonance**

Figure 1(a) shows EPR spectra obtained at 125K from the powdered crystals with specific dopants. The results are summarized in Table 1. EPR signals from 6
The effective g-factor is correlated with the applied static magnetic field \( B \) by the relation \( h\nu = g \cdot \mu_B \cdot B \), where \( \nu \) is the microwave frequency, \( \mu_B \) Bohr magneton, and \( h \) Planck constant. Three absorption peaks, corresponding to Cr\(^{3+} \) (19), were found in Cr-doped YSZ; one main signal at \( g=3.814 \) and other two absorption-like peaks at \( g=5.878 \) and \( g=1.966 \). EPR of Mn-doped YSZ revealed 3 sets of hyperfine split sextet signals. Since the 100\% of Mn exist as \(^{55}\)Mn with a nuclear spin of \( I=5/2 \) (18), the presence of the hyperfine interaction between electron spin and nuclear spin, leading to \( 2I+1=6 \) peaks, has been observed. The EPR of Fe was observed at \( g=4.279 \) in addition to a small absorption-like peak at \( g=2.006 \). The \( g=4.3 \) peak has been attributed to Fe\(^{3+} \) (18,20,21). This signal was found in almost all crystals confirming that Fe is a major impurity in YSZ.

EPR spectra at 125 K of powdered crystals after reduction in (5%H\(_2\)-Ar)+3%H\(_2\)O at 800°C are shown in Fig. 1(b). Upon reduction, EPR signals from Ti and Ce appeared. The Ti\(^{3+}(3d^1) \) signal was found in almost all crystals after reduction, confirming that Ti is a common impurity in YSZ (e.g., 16,20,21). Within the po\(_2 \) range studied, the g-factors of Cr\(^{3+} \), Mn\(^{2+} \), and Fe\(^{3+} \) did not show appreciable change. With decreasing po\(_2 \) (pure O\(_2\)->(5%H\(_2\)-Ar)+3%H\(_2\)O), the peak due to Ti\(^{3+} \) appeared, the intensity from Cr\(^{3+} \) remained the same, that from Mn\(^{2+} \) slightly increased, and the Fe\(^{3+} \) signal almost vanished. Figure 2 shows the EPR absorption intensities of Ti-, Cr-, Mn-, Fe-doped YSZ single crystals as a function of oxygen partial pressure for annealing, measured at room temperature for Cr-, Mn-, and Fe-doped YSZ, and at 125K for Ti-doped YSZ. Within the po\(_2 \) range studied, Cr\(^{3+} \) is stable, while the valence change Mn\(^{3+} \leftrightarrow \)Mn\(^{2+} \) occurs under weakly reducing conditions (O\(_2\)-Ar), and that of Fe\(^{3+} \leftrightarrow Fe^{2+} \) and Ti\(^{4+} \leftrightarrow Ti^{3+} \) under strongly reducing conditions (H\(_2\)-H\(_2\)O-Ar). The EPR signals of Pr and Gd were identical in line shape and intensity upon oxidation and reduction. A very broad EPR signal from Ce-doped YSZ was observed after reduction in (5%H\(_2\)-Ar)+3%H\(_2\)O, but not after oxidation in pure O\(_2\).

Optical Absorption Spectroscopy

The optical absorption of the following elements was observed after annealing at 800°C: Ti, V, Cr, Mn, Fe, Co, Ni, Ce, and Pr. The results are summarized in Table 1. Figure 3 shows the optical absorption coefficients of YSZ doped with (a) transition metal ions and (b) selected rare earth ions after oxidation, and (c) transition metal ions and (d) selected rare earth ions after reduction. The optical absorption coefficient, \( \alpha \), is derived using the relation, \( \alpha = A \cdot \ln 10/l \), where \( A \) is the optical density or absorbance, and \( l \) the sample thickness. The qualitative results of the optical absorption investigations within 10\(^{-20} \) \( \leq \) po\(_2 \) \( \leq 1 \) bar can be summarized as follows:

(i) absorption changed under weakly reducing conditions (O\(_2\)-Ar): Mn, V
(ii) absorption changed under strongly reducing conditions (H\(_2\)-H\(_2\)O-Ar): Ti, Fe, Ce
(iii) absorption unchanged: Cr, Co, Pr
(iv) no absorption observed: Cu, Gd

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With decreasing \( p_{O_2} \) of annealing atmosphere (pure \( O_2 \rightarrow (5%H_2-Ar)+3%H_2O \)), changes in optical absorption occurred. The optical absorption coefficient of Cr remained the same, that of Mn and Fe decreased, and that of Ti and Ce increased. The \( p_{O_2} \) dependence of EPR and optical absorption was correlated for Ti, Cr, Fe, and Ce, while anti-correlated for Mn, indicating that \( Ti^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, \) and \( Ce^{3+} \) were observed in optical absorption. The decrease in absorption due to V in YSZ with decreasing \( p_{O_2} \) was attributed to \( V^{4+} \leftrightarrow V^{3+} \) (22). The positions of absorption peaks in Co-, Ni-, and Pr-doped YSZ were consistent with literature (23), and can be attributed to \( Co^{2+}, Ni^{2+}, \) and \( Pr^{3+} \).

**Defect Chemistry**

EPR of YSZ doped with different concentrations of Mn revealed that the EPR absorption intensity was proportional to the \( Mn^{2+} \) concentration, and the quantification by EPR was possible in a dilute dopant concentration range (24). As shown in Figure 2, the EPR absorption intensity of \( Cr^{3+} \) within the \( p_{O_2} \) range studied, of \( Mn^{2+} \) below \( 10^{-5} \) bar, and of \( Fe^{3+} \) above \( 10^{-10} \) bar remained constant. In strongly reducing atmosphere, the \( p_{O_2} \) dependence of the EPR absorption of \( Fe^{3+} \) and \( Ti^{3+} \) revealed a +1/4 and -1/4 dependence, respectively. These \( p_{O_2} \) dependencies are analogous to those expected from the defect chemical relations in equilibrium as Eqs. 8 and 9, even though the EPR experiments were carried out at much lower temperatures where the oxygen exchange equilibrium reaction is frozen-in.

It is very unlikely that the electronic equilibrium also freezes at \( T_E \). Evaluating Eq. 18 furtheron, it turns trivially out that the equilibrium behavior is obtained for a negligible \( c_M \)-value (simply because few trapping sites exist). This is immediately verified by setting \( K_2 \cdot \Delta E = K_2 \cdot [h^+]_E \). The other case of interest is the case of a high \( c_M \)-value, such high that also at high \( T, S_E \approx [M^{(n+1)+}]_E \gg [h^+]_E \) (e.g., in YSZ at \( 800^\circ C \) (25)). Then,

\[
[h^+] = \frac{-c_M + K_2 - [M^{(n+1)+}]_E}{2} + \sqrt{\left(\frac{c_M + K_2 - [M^{(n+1)+}]_E}{2}\right)^2 + K_2 \cdot [M^{(n+1)+}]_E} \quad [23]
\]

follows. If at high \( T \), all \( M \) are in the high valence state (\( c_M \approx [M^{(n+1)+}]_E \gg [M^{(n+1)+}]_E \)), a \( p_{O_2} \) independent \( [h^+] \)-value is obtained.

We are more interested in the other extreme that all \( M \) are in the reduced state. Then \( c_M \approx [M^{(n+1)+}]_E \gg [M^{(n+1)+}]_E \):

\[
[h^+] = \frac{-c_M + K_2}{2} + \sqrt{\left(\frac{c_M + K_2}{2}\right)^2 + K_2 \cdot [M^{(n+1)+}]_E} \quad [24]
\]

In the first approximation, \( K_2 \cdot [M^{(n+1)+}]_E \) is neglected against the mixed factors of the first term under the square-root, leading to \( [h^+] \approx 0 \). In the second approximation...
(\sqrt{1+x} = 1 + x/2 \text{ for } x \ll 1), \text{ we obtain (since } (K_2/c_M) \ll 1 \text{ following from } [M^{m*}] \approx c_M \text{ and } [h^+] \ll [M^{(m+1)*}] \text{ in particular at low temperatures):}

\[
[h^+] \approx c_M \cdot \frac{K_2}{K_{2E}} \cdot \frac{[h^+]_E}{c_M + K_2} = \frac{c_M}{c_M + K_2} \cdot \frac{K_2}{K_{2E}} \cdot K_1E^{1/2} \cdot \left(\frac{[Z]}{2}\right)^{1/2} \cdot pO_2^{1/4} \tag{25}
\]

\[
[M^{(m+1)*}]_E \equiv \frac{c_M}{c_M + K_2} \cdot [M^{(m+1)*}]_E = \frac{c_M}{c_M + K_2} \cdot \frac{1}{K_{2E}} \cdot [h^+]_E
\]

\[
= \frac{c_M}{c_M + K_2} \cdot \frac{1}{K_{2E}} \cdot K_1E^{1/2} \cdot \left(\frac{[Z]}{2}\right)^{1/2} \cdot pO_2^{1/4} \tag{26}
\]

where \( K_{1E} \equiv K_1(T_E) \) and \( K_{2E} \equiv K_2(T_E) \). Since the hole concentration is already small at \( T_E \), it will not be able to change the redox ratio significantly when \( T \) is increased. Thus, \( K_2 \ll c_M \) and \([h^+]\) is independent of \( c_M \) and \([M^{(m+1)*}]\) and \([M^{m*}]\) independent of \( T \). More importantly here, the \( pO_2 \)-dependencies are indeed analogous to the ones under equilibrium conditions, \((\partial \ln [M^{m*}] / \partial \ln pO_2) = \pm 1/4 \) or 0.

**SUMMARY**

(1) The influence of redox-active impurities on transport properties is explained in the light of defect chemistry. It is shown in particular that comparably low concentrations of redox-active impurities, which are of no influence on the electronic conductivities via equilibrium conditions, can modify \([h^+]\) and \([e^+]\) significantly when the stoichiometry is frozen in, as well as the chemical diffusion of oxygen.

(2) Various ions in their specific valence states have been identified by EPR and optical absorption:

(i) Valence states observed by EPR at \( T > 105K \)

YSZ annealed in pure \( O_2 \):

\( Cr^{3+}, Mn^{2+}, Fe^{3+} \) (V, Pr, Gd)

YSZ annealed in \((5\% H_2 - Ar) + 3\% H_2O\):

\( Ti^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+} \) (Ce, Pr, Gd)

(ii) Valence states observed by optical absorption at \( T = R.T. \)

YSZ annealed in pure \( O_2 \):

\( Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pr^{3+} \) (V)

YSZ annealed in \((5\% H_2 - Ar) + 3\% H_2O\):

\( Ti^{3+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Ce^{3+}, Pr^{3+} \)

(3) Redox-active ions in YSZ have been specified:

(i) changes under weakly reducing conditions: \( Mn^{3+} \leftrightarrow Mn^{2+}, V^{4+} \leftrightarrow V^{3+} \)

(ii) changes under strongly reducing conditions: \( Ti^{4+} \leftrightarrow Ti^{3+}, Fe^{3+} \leftrightarrow Fe^{2+}, Ce^{4+} \leftrightarrow Ce^{3+} \)

(iii) no change found within the experimental condition: \( Cr^{3+}, Co^{2+}, Pr^{3+}, Gd^{3+} \)

(4) The \( pO_2 \) dependencies, as observed from the EPR experiments, can be explained by the fact that the oxygen incorporation reaction in contrast to the ionization equilibrium freezes and that \([M^{m*}] \gg [M^{(m+1)*}] \gg [h^+].

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Table 1: Electron paramagnetic resonance and optical absorption of transition metal and rare earth ions in yttria-stabilized zirconia single crystals*1

|       | EPR absorption*2 (powdered crystals) (po2=1.0) | EPR absorption*2 (powdered crystals) (po2=1.4x10^-19) | Valence state observed by EPR | Optical absorption peak*3 (10^-6<po2<1) | Valence state observed by optical absorption | Valence state/change (annealed T=800°C, 10^-6<po2<1) |
|-------|-----------------------------------------------|------------------------------------------------------|-------------------------------|-----------------------------------------|---------------------------------------------|--------------------------------------------------|
| Ti    | not observed (T>105K)                          | g//c=1.947±0.001                                      | Ti³⁺ (in reducing atm.)         | 397±5nm (3.12eV)                        | Ti³⁺ (in reducing atm.)                      | Ti³⁺<->Ti³⁺ (po2<10^-20)                         |
| V     | g^eff=1.987±0.002                               | not observed (T>105K)                                | (V²⁺(VO²⁻)[22])                | 322±5nm (3.86eV)                        | V⁴⁺ [22] (in oxidizing atm.)                  | V⁴⁺<->V⁴⁺ (po2<10^-5)                           |
| Cr    | g^eff=3.81±0.003                                | g^eff=5.87±0.006                                      | Cr³⁺ (both in oxidizing and reducing atm.) | 699.7±0.7nm (1.77eV) | 518.5±0.5nm (2.43eV) | Cr³⁺ (both in oxidizing and reducing atm.) | no change Cr³⁺                                      |
| Mn    | g^eff=2.019±0.001                               | g^eff=2.02±0.001                                     | Mn²⁺ (Mn³⁺:V⁶⁻[24]) (both in oxidizing and reducing atm.) | 670±5nm (1.85eV) | 514.9±1.0nm (1.91eV) | Mn²⁺ (in oxidizing atm.)                         | Mn²⁺<->Mn²⁺ (po2=10^-10)                         |
| Fe    | g^eff=4.279±0.003                               | g^eff=4.28±0.003                                     | Fe³⁺ (in oxidizing atm.)         | 298±5nm (3.06eV)                        | Fe³⁺ (in oxidizing atm.)                      | Fe³⁺<->Fe³⁺ (po2=10^-15)                         |
| Co    | not observed (T>105K)                           | not observed (T>105K)                                |                               |                                         | Co⁷⁺ [23]                                   | no change Co⁷⁺                                      |
| Ni    | not observed (T>105K)                           | not observed (T>105K)                                |                               |                                         | Ni⁷⁺ [23]                                   | (Ni⁷⁺+Ni⁷⁺ [11])                                  |
| Cu    | not observed (T>105K)                           | not observed (T>105K)                                |                               |                                         |                                            |                                                 |
| Ce    | not observed (T>105K)                           | (observed but very broad)                            | Ce³⁺                         | 463.6±1.7nm (2.68eV) | Ce³⁺ (in reducing atm.)                      | Ce³⁺<->Ce³⁺ (po2<10^-15)                         |
| Pr    | (observed but very broad)                      | (observed but very broad)                            |                               | 606mm2.05eV) | 589mm2.10eV | Pr⁷⁺ [23]                                   | no change Pr⁷⁺                                      |
| Gd    | (very broad, no po2 dependence)                | not observed                                         |                               |                                         |                                            |                                                 |

*1 YSZ: 9.5mol% Y₂O₃-90.5mol%ZrO₂. Specimens annealed at 800°C within 10^-10<po2<1 for 16 hours followed by quenching.

*2 V exists 99.75% as V²⁺(I=7/2), and Mn 100% as Mn⁴⁺(I=5/2). Fe³⁺ impurity peak (g=4.28) observed in almost all crystals, after oxidation. Ti³⁺ impurity peak (g//c=1.947, g^eff=1.869) found in some crystals (V, Cr, Co, Ni-doped), after reduction.

*3 E(eV)=1239.842/X(nm) where E is energy and X is wave length.

*4 The oxygen partial pressure where the concentrations of both valence states are the same, at the temperature measured.

See text for references denoted as [ ].
Figure 1: EPR spectra of YSZ powdered crystals, annealed at 800°C in (a) pure O₂ and (b) (5%H₂-Ar)+3%H₂O. EPR experiments were carried out at 125K.

Figure 2: EPR absorption intensity of YSZ single crystals, annealed at 800°C at various oxygen partial pressure (10⁻²⁰≤pO₂≤1 bar).
Figure 3: Optical absorption coefficients of YSZ doped with (a) (c) transition metal and (b) (d) rare earth oxides, annealed at 800°C in (a) (b) pure O₂ and (c) (d) (5%H₂-Ar) +3%H₂O.