Polarization Studies of the Electronic Minority Charge Carriers in Ag⁺⁻β⁺⁻-Alumina

Werner Wepner and Jun Liu
Max-Planck-Institut für Festkörperforschung, Stuttgart, Germany

The partial electronic conductivity of Ag⁺⁻β⁺⁻-alumina was determined in the temperature range 180–200 °C, using Wagner’s asymmetric galvanic polarization cell Ag|Ag⁺⁻-alumina|Pt. The electron conductivity is $4.5 \times 10^{-8} \text{cm}^{-1}$, while the hole conductivity is about seven orders of magnitude lower at the silver activity $a_{\text{Ag}}$ at 200 °C. These results are compared with earlier data on β⁺⁻-alumina. The polarization mechanism and the effect of the electronic conductivity on the application of Ag⁺⁻-β⁺⁻-alumina are discussed.

Key words: Electronic conductivity, Ag⁺⁻-β⁺⁻-alumina, Solid electrolyte, Hebb-Wagner technique.

Introduction

β⁻ and β⁺⁻-alumina solid electrolytes are widely used in solid state batteries and chemical sensors. Only little attention has been paid so far to the conductivity, mobility and concentration of the electronic minority charge carriers as a function of the activities of the mobile and immobile species, in spite of their importance with respect to partial short-circuits and the redox processes occurring at the electrodes. In addition, the electronic conductivity and concentration are important fundamental parameters which provide insight into the defect properties, conduction mechanism and stability of the solid electrolyte.

In the early work by Whittingham and Huggins [1] the electronic conductivity of Ag⁺⁻-β⁺⁻-alumina single crystals was studied at high temperature (550–790 °C) and at low polarization potentials (below about 0.7 V), while in practical cases the operating temperature is lower than about 350 °C (and for some chemical sensors even lower than 200 °C) and the applied voltage is generally much higher.

A large influence of the surrounding oxygen partial pressure on the open circuit voltage and the electrical current has been observed [1] which shows that the material acts as an oxygen sensor. An increase of the oxygen activity results in a decrease of the sodium activity according to Duhem-Margules’ equation, and accordingly in an increase of the o.c. cell voltage with reference to elemental sodium. In this way, the electronic concentration is changed locally by the equilibrium with the oxygen. The applied voltage generates an additional variation of the chemical potential of the electrons and that of sodium and oxygen.

In this paper, polarization and relaxation measurements were carried out on polycrystalline ceramic samples at 180–200 °C. The polarization potential was up to about 1.6 V (which is lower than the decomposition voltage of about 3.2 V). The Hebb-Wagner technique [2, 3] was employed to block the ionic current, and the exchange of oxygen at the electrodes was prevented by employing dense electrodes and Ar gas environment. Relaxation processes are related to the mobility of the electronic species in the predominantly ionically conducting Ag⁺⁻-β⁺⁻-alumina.

Theoretical Considerations

The total conductivity $\sigma$ of solid electrolytes is

$$\sigma = \sigma_{\text{ion}} + \sigma_{e} + \sigma_{h},$$

where $\sigma_{\text{ion}}$, $\sigma_{e}$, $\sigma_{h}$ are the partial conductivities of ions, electrons and holes, respectively. Their contributions are commonly also expressed by their transference numbers:

$$t_{\text{ion}} + t_{e} + t_{h} = 1. \tag{2}$$

For measuring $\sigma_{e} + \sigma_{h}$ of Ag⁺⁻-β⁺⁻-alumina by Wagner’s polarization method, the following cell was employed:

$$(-)\text{Ag}|\text{Ag}^{+}=\beta^{-}\text{-alumina}|\text{Pt}(+) \ (\text{Ar atmosphere}).$$

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A d.c. potential lower than the decomposition voltage of Ag$^+$/Ag$^0$-alumina is applied with the Ag electrode as cathode and the Pt electrode as anode. Initially all the charge carriers migrate, but since there is no silver ion source provided by the Pt blocking electrode, in the final state only the electrons and holes will be kept moving.

The steady state electron (e) and hole (h) current is, in general, caused by both the electrical field and the concentration gradients. As the conduction electrons and holes are at low concentrations and more independently, the Nernst-Einstein relation

$$D_i = (kT/q) u_i, \quad i = e, h$$

with $D_i$ the diffusion coefficient, $q$ the elementary charge and $u_i$ the mobility will hold, and expressing the concentrations $c_i$ by the chemical potentials (per particle) $\mu_i$,

$$dc_i = (c_i/kT) d\mu_i; \quad u = e, h,$$

one has [4]

$$i = -\sigma_e \frac{d\varphi}{dx} - \sigma_h \frac{d\varphi}{dx} + \sigma_e \frac{d\mu_e}{dx} + \sigma_h \frac{d\mu_h}{dx}, \quad (3)$$

where $i$, $\varphi$, and $x$ are the current density, electrostatic potential, and coordinate in the direction of the current, respectively. It is common to consider the electrical and chemical driving forces also combined as the gradient of the electrochemical potential $\eta_i = \mu_i + z_i q \varphi$, where $z_i$ is the charge number of the species. Under the assumption of local equilibrium for the reaction

$$e + h \rightleftharpoons 0 \quad (4)$$

one has

$$\mu_e + \mu_h = 0. \quad (5)$$

Equation (3) may then also be written as

$$i = (\sigma_e + \sigma_h) \frac{d\mu_e}{q dx} - (\sigma_e + \sigma_h) \frac{d\varphi}{q dx} = (\sigma_e + \sigma_h) \frac{d\eta_e}{q dx}. \quad (6)$$

The applied voltage $U$ establishes a difference in the electrochemical potential (or Fermi level) of the electrons between the two electronic leads Ag and Pt,

$$U = \frac{1}{q} (\eta_e^{\text{Ag}} - \eta_e^{\text{Pt}}). \quad (7)$$

This equation is a balance of the electrical energy $qU$ and the chemical energy $(\eta_e^{\text{Ag}} - \eta_e^{\text{Pt}})$ related to the transport of one electron through the arrangement.

The current-voltage characteristics are obtained by integration of (6) between the two electrodes and then application of (7) for the electrochemical potential gradient. If $\sigma_e$ and $\sigma_h$ are independent of $\eta_e$ or the location $x$ within the electrolyte, the result is Ohm’s law for the electronic minority charge carriers current:

$$i \sim (\sigma_e + \sigma_h) U. \quad (8)$$

This equation holds if no chemical potential (or concentration) gradient is present. In more general and in all practical cases of solid electrolytes, the current-voltage relationship is more complicated than the linear relationship (8).

Since the ionic current is zero under steady state conditions, the electrostatic potential gradient has to balance in any case the diffusion of the ions $i$ in their chemical potential gradient:

$$\frac{d\varphi}{dx} = \frac{1}{z_i q} \frac{d\mu_{ion}}{dx}. \quad (9)$$

Insertion of this expression for the electrostatic gradient into (6) yields

$$i = (\sigma_e + \sigma_h) \left( \frac{d\mu_e}{q dx} + \frac{1}{z_i q} \frac{d\mu_{ion}}{dx} \right) = (\sigma_e + \sigma_h) \frac{d\mu_i}{z_i q dx}, \quad (10)$$

where $i^*$ stands for the neutral species $i$. In case of a low concentration of ionic defects (low disorder, poor ionic conductor) compared to the concentration of electrons (good electronic conductor), the chemical potential gradient of the electrons may be neglected compared to that of the ions. The electrons and holes are in this case transported by the electrical field, and the electronic conductivities are locally independent. Ohm’s law holds. If, however, the concentration of ionic defects is high (good ionic conductor) and the concentration of the electrons is small (poor electronic conductor), the chemical potential gradient of the ions is negligible and the electrons and holes are transported by their chemical potential gradient. The high concentration of ionic majority charge carriers does not allow to build up an internal electrical field. Fick’s law of diffusion holds:

$$i = \frac{\sigma_e + \sigma_h}{q} \frac{d\mu_e}{dx}. \quad (11)$$

The conductivity $\sigma_i$ may be expressed by the product of the concentration $c_i$ and electrical mobility $\mu_i$ of the charge carriers [4],

$$\sigma = |z_i| q u_i c_i \quad (12)$$
where \( z_f \) is the charge number (−1 for electrons, +1 for holes). For sufficiently small concentrations, the chemical potentials of the electrons and holes may be expressed as \( \mu = \mu^0 + kT \ln(c/c^0) \), where \( \mu^0 \) is the chemical potential in the standard state \( (c = c^0) \). Then, integration of (11) over the entire length \( L \) of the electrolyte and considering (5) yields

\[
 i_L = u_e kT (c_e^l - c_e^r) - u_h kT (c_h^l - c_h^r) \\
= \frac{\sigma_e}{q} \left( \frac{c_e^l}{c_e} - 1 \right) - \frac{\sigma_h}{q} \left( \frac{c_h^l}{c_h} - 1 \right),
\]

(13)

which is the integral form of Fick’s law of the proportionality between the current and the concentration gradient of electrons and holes over the entire electrolyte. The upper indices \( l \) and \( r \) indicate the left and right hand sides of the solid electrolyte, respectively.

In terms of the chemical potential (13) may be rewritten as

\[
i = \frac{kT}{qL} \left[ \sigma_e \left( \exp\left( \frac{\mu_e - \mu^0}{kT} \right) - 1 \right) \\
+ \sigma_h \left( 1 - \exp\left( \frac{\mu_h - \mu^0}{kT} \right) \right) \right].
\]

(14)

The differences of the chemical potentials of the electrons and holes at both sides of the electrolyte correspond to the applied voltage according to (7) since the electrochemical potentials of the electrons in the Pt and Ag leads correspond to those within the electrolyte (across the interface) and the electrolyte is free of electrical fields, i.e., \( d\eta_e, h = d\mu_e, h \). The result is

\[
i = \frac{kT}{qL} \left[ \sigma_e \left( \exp\left( \frac{-U q}{kT} \right) - 1 \right) + \sigma_h \left( 1 - \exp\left( \frac{U q}{kT} \right) \right) \right].
\]

(15)

For cationic conductors such as the \( \beta^+ \)-aluminas, the current approaches a plateau caused by the electron conductance and an exponential increase caused by the hole conductance. The conductivities of the electrons and holes at the composition of the reversible reference electrode (left hand side) are determined from the height of the plateau and the intersection of the exponential increase with the \( i \)-axis, respectively.

The conditions for the validity of (15) are:

1. The electronic charge carriers obey Boltzmann’s statistics (ideal behavior),
2. The mobilities of the electrons and holes are independent of the concentration,
3. The contact resistances at the electrode-electrolyte interfaces are negligible,
4. The conductivity and concentration of the ionic defects are large compared to those of the electrons and holes in order to avoid the build-up of an electrical field.

Under ideal blocking conditions, there is no steady-state ionic current. Each time the applied potential is changed, a redistribution of the ions in the \( \beta^+ \)-alumina according to the new potential is observed and the ionic current falls to zero more or less rapidly. The current becomes an electron and hole current, where the Ag-electrode fixes the electron or hole concentration at the left hand side and the applied potential determines the silver activity at the right hand side.

The defect chemical equilibrium for the exchange of silver with another phase in contact with the \( Ag^+ - \beta^+ \)-alumina may be written in terms of structure elements

\[
Ag(a_{Ag}) + V_i = Ag_i + e',
\]

(16)

where \( V_i \), \( Ag_i \), and \( e' \) represent vacancies at interstitial positions, silver ions at interstitial positions and excess electrons, respectively. The mass action law for this reaction reads

\[
\frac{a_{Ag}}{a_{Ag}} = \text{const},
\]

(17)

where \( a \) represents the activity of the indicated building unit [4]. Assuming ideal behavior (or concentration independent activity coefficients) for the interstitial silver ions and the electrons and considering the electroneutrality condition

\[
c_{Ag_i} = c_{e'},
\]

(18)

the following relation between the silver activity and the concentration of electrons is obtained:

\[
\frac{d \log c_e}{d \log a_{Ag}} = \frac{1}{2},
\]

(19)

Taking into account that the partial conductivity is proportional to the concentration of the corresponding species, it will be expected that

\[
d \log \sigma_e = \frac{1}{2} d \log a_{Ag}.
\]

(20)

Because of the equilibrium between electrons and holes,

\[
d \log c_e = -d \log c_h,
\]

(21)

an inverse slope holds for the silver activity dependence of the hole conduction:

\[
d \log \sigma_h = -\frac{1}{2} d \log a_{Ag}.
\]

(22)
Experimental Aspects

Na\textsuperscript{+}-β\textsuperscript{″}-alumina solid state electrolytes were cut from a bar (Ceramatec, Salt Lake City) into cylindrical pellets of 9 mm in diameter and 0.53 mm in thickness and then ion exchanged in an AgNO\textsubscript{3} melt to form Ag\textsuperscript{+}-β\textsuperscript{″}-alumina.

A Pt film of 500 Å thickness was evaporated as blocking electrode onto Ag\textsuperscript{+}-β\textsuperscript{″}-alumina. A silver film of 500 Å thickness was evaporated onto the opposite side as reversible electrode. Voltages up to 1.6 V were applied to the cell by a potentiostat/galvanostat (Jaissle, IMP 83). The current was recorded by a Keithley 195 A multimeter. It took about one day to achieve an equilibrium value. Pure Ar gas, purified by an oxisorb device (filled with argon, Messer Griesheim) was applied as inert atmosphere to avoid oxygen exchange. The operating temperature was between 180–200 °C. The arrangement is shown in Figure 1.

Results

Figure 2 shows the steady state current vs. the applied voltage. In the lower voltage range from 0 to about 0.6 V, the current shows a plateau. However, when the voltage is above 0.7 V, the current begins to increase quickly. In accordance with (15), when \( \exp(\frac{Uq}{kT}) \gg 1 \), the current increases exponentially. From the plateau value and by extrapolation from the beginning of the exponential increase, assuming a theoretical slope of \( \frac{q}{kT} \), to the current axis, the conductivity of the electrons is found to be \( 4.5 \times 10^{-8} \Omega^{-1} \text{cm}^{-1} \) at 200 °C, and the conductivity of the holes is 7 orders of magnitude lower (\( 5 \times 10^{-15} \Omega^{-1} \text{cm}^{-1} \)) at this temperature.

Fig. 2. Wagner polarization method. The steady-state current as a function of the applied voltage at 200 °C. The difference between the currents obtained for increasing and decreasing voltages is due to the change in the oxygen stoichiometry.

Fig. 3. The time dependence of the current after applying a voltage at 200 °C.

Fig. 4. log \( I [\text{A}] \) as a function of time at 200 °C after applying a voltage of 0.3 V.
A typical equilibration curve of the current is shown in Fig. 3, indicating a period of at least 4 hours to observe a steady state current. But, after one cycle of voltage variation, the equilibrium is achieved more quickly. In Fig. 4, the diffusion coefficient of the electrons in Ag⁺-β⁺-alumina at 200 °C was deduced to be about $10^{-7}$ cm²/sec from the slope of the log $l - t$ curve using the data evaluation as described previously [5].

Discussion

The observed conductivities of both electrons and holes are compared in Tables 1 and 2 with previous results reported in the literature. It may be seen that the present data are in agreement with those of MgO-doped Na⁺-β⁺-alumina but are quite different from results on Ag⁺-β⁺-alumina extrapolated from the temperature range 550–790 °C to 200 °C, which indicates an electronic conductivity of the order of $10^{-13}$ Ω⁻¹ cm⁻¹. In addition to the error from the extrapolation, differences may be due to the application of single crystal sample as compared to ceramic materials used in the present investigation and the application of high oxygen partial pressure in the reference work. In addition, degradation of the electrolyte may be caused by the applied voltages at the higher temperature, which may result in a thin layer of insulator. Al₂O₃ may have possibly been formed as a product of degradation.

Figure 5 shows the relation between the conductivity and the silver (or sodium) activity. The data at $a = 1$ are based on the experimental results and literature data. The straight lines are an extrapolation of the measured values at $a_{Ag} = 1$ assuming the theoretical slopes of

$$\frac{d \log \sigma_e}{d \log a_{Ag}} = \frac{1}{2} \quad \text{and} \quad \frac{d \log \sigma_h}{d \log a_{Ag}} = -\frac{1}{2}.$$ 

Accordingly, a p-n junction occurs in Ag⁺-β⁺-alumina at a silver activity of $10^{-7}$ at 200 °C. For comparison, the available literature data on the electronic conductivity of pure and doped Na⁺-β⁺-alumina are drawn. There is an agreement within a few orders of magnitude between the different materials.

The following conclusions may be drawn:

1. Comparison of the present and previous results on β/β⁺-alumina materials containing different con-
Table 1. Compilation of data from the literature and this work on the partial electronic conductivity of $\beta^-$ and $\beta^+$-aluminas. The conductivity is given for the activity of the mobile component as fixed by the reversible reference electrode.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Material and cell</th>
<th>$T$ [°C]</th>
<th>$\sigma_e$ [$\Omega^{-1} \text{cm}^{-1}$]</th>
<th>$E$ [eV]</th>
<th>$t_e$ [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[7]</td>
<td>Na/Na$^+$-$\beta$-Al$_2$O$_3$/Fe+</td>
<td>120</td>
<td>&lt;3 $\times 10^{-8}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaFe$<em>{5.5}$Al$</em>{1.5}$O$_7$</td>
<td>120</td>
<td>6.7 $\times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[6]</td>
<td>Na/Na$^+$-$\beta$-Al$_2$O$_3$/S+C</td>
<td>125–350</td>
<td>2 $\times 10^{-9}$ (120 °C)</td>
<td>0.552</td>
<td>$1.1 \times 10^{-8}$ (25 °C)</td>
</tr>
<tr>
<td></td>
<td>2.5 wt% MgO</td>
<td></td>
<td>1.8 $\times 10^{-8}$ (180 °C)</td>
<td>10$^{-1}$ (100 °C)</td>
<td></td>
</tr>
<tr>
<td>This work</td>
<td>Ag/Ag$^+$-$\beta$-Al$_2$O$_3$/Pt</td>
<td>180</td>
<td>1.76 $\times 10^{-8}$ (Ag)$_p$</td>
<td>3.4 $\times 10^{-6}$</td>
<td>7 $\times 10^{-6}$</td>
</tr>
<tr>
<td>[8]</td>
<td>Na$<em>{x}$TiS$<em>2$/Na$</em>{1-x}$Fe$</em>{5/2}$Al$<em>{11/2}$O$</em>{17.1}$/Au+</td>
<td>25–52</td>
<td>10 wt% Fe 5.61 $\times 10^{-8}$</td>
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<td></td>
<td>40 wt% Fe 1.04 $\times 10^{-2}$</td>
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<tr>
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<td>Ag/Ag$^+$-$\beta$-Al$_2$O$_3$/Pt+</td>
<td>550–790</td>
<td>$10^{-5}$ (800 °C)</td>
<td>1.32</td>
<td>$10^{-5}$ (800 °C)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$10^{-5}$ (800 °C)</td>
<td></td>
<td>$10^{-5}$ (800 °C)</td>
</tr>
<tr>
<td>[9]</td>
<td>Ca/Ca$^{++}$-$\beta$-Al$_2$O$_3$/Au+</td>
<td>635–746</td>
<td>$10^{-5.7}$ (635 °C)$_e$</td>
<td>1.88</td>
<td>$10^{-4}$ (635 °C)</td>
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<td>$10^{-1.6}$ (635 °C)$_h$</td>
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<td>$10^{-3}$</td>
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<tr>
<td>[10]</td>
<td>Ag, In$_x$WO/In-$\beta$-Al$_2$O$_3$/Au+</td>
<td>450–800</td>
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<td>$10^{-3}$</td>
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<td>$10^{-7}$ (800 °C)$_h$</td>
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<td>$10^{-8}$ (450 °C)$_h$</td>
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<td>[11]</td>
<td>Cu/Cu$^{++}$-$\beta$-Al$_2$O$_3$/Au+</td>
<td>850</td>
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<td>7 $\times 10^{-7}$ (Cu)$_h$</td>
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<td>$6 \times 10^{-6}$ (Cu)$_h$</td>
<td></td>
<td>$7 \times 10^{-7}$ (Cu)$_h$</td>
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* Data which were extrapolated from reference papers.

Table 2. Partial electronic conductivity as a function of the metal activity.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>$T$ [°C]</th>
<th>$a_m$</th>
<th>$\sigma_e$ [$\Omega^{-1} \text{cm}^{-1}$]</th>
<th>$\sigma_h$ [$\Omega^{-1} \text{cm}^{-1}$]</th>
<th>$\Delta E_a$ [eV]</th>
<th>Materials</th>
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<td>This work</td>
<td>200</td>
<td>1</td>
<td>$4.5 \times 10^{-8}$</td>
<td>$5 \times 10^{-15}$</td>
<td>Ag$^+$-$\beta^+$-alumina</td>
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<tr>
<td>[8]</td>
<td>180</td>
<td>1</td>
<td>$1.76 \times 10^{-8}$</td>
<td></td>
<td>Na$<em>{1.5}$Fe$</em>{1.5}$Al$<em>{2}$O$</em>{17.1}$</td>
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<tr>
<td></td>
<td>25</td>
<td>$10^{-28}$</td>
<td>$3 \times 10^{-7}$</td>
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<td>[7]</td>
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<td>1</td>
<td>$&lt;3 \times 10^{-8}$</td>
<td>$6.7 \times 10^{-4}$</td>
<td>$-$Na/Na$^-$$\beta$-alumina/Fe+</td>
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<td></td>
<td>NaFe$<em>{5.5}$Al$</em>{1.5}$O$_7$</td>
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<td>[6]</td>
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<td>$3 \times 10^{-13}$</td>
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<td>150</td>
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<td>$&lt;10^{-8}$</td>
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<td>$&lt;10^{-9}$</td>
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<td>[9]</td>
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<td>$E_e = 1.88$</td>
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<td>1</td>
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<td>$10^{-16}$</td>
<td>$E_h = 1.83$</td>
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<td></td>
<td>200 *</td>
<td>1</td>
<td>$5.77 \times 10^{-16}$</td>
<td>$5.58 \times 10^{-26}$</td>
<td></td>
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</tr>
<tr>
<td>[11]</td>
<td>850</td>
<td>1</td>
<td>$7 \times 10^{-7}$</td>
<td>$6 \times 10^{-6}$</td>
<td>$E_e = 3.35$</td>
<td></td>
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<tr>
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<td>727</td>
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<td>$1.3 \times 10^{-7}$</td>
<td>$1.6 \times 10^{-8}$</td>
<td>$E_h = 3.17$</td>
<td></td>
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<tr>
<td></td>
<td>200 *</td>
<td>1</td>
<td>$1.94 \times 10^{-26}$</td>
<td>$2.57 \times 10^{-26}$</td>
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<td></td>
</tr>
</tbody>
</table>

* Data which were extrapolated from reference papers.
ducting species, shows a big difference between the observed electronic conductivities for the high and low temperature.

2. The applied atmosphere (i.e., the $O_2$ pressure) may have an influence on the electronic concentration in addition to the variation of the silver activity.

When the sample is exposed to low oxygen partial pressure, the silver activity in the $\beta'$-alumina will increase because of Duhem-Margules’ equation. This will only happen in oxygen gas atmosphere, but because the blocking electrode was covered by epoxy resin in the present work, this processes was inhibited or reduced, since the experimental arrangement is favorable to keep a high silver activity.

3. Compared to the ionic conductivity, the electronic conductivity of Ag$^{+}$-$\beta'$-alumina may be considered to be negligibly small over the entire range of thermodynamic stability.