Electrical Properties in Yttria Stabilized Zirconia Investigated by Impedance Spectroscopy

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Yttria Stabilized Zirconia (YSZ) is an important solid electrolyte with applications in solid oxide fuel cells (SOFC) and oxygen separators, due to its good electrical and mechanical properties. This work aims at a deeper insight into the complicated factors influencing the conductivity of YSZ with the help of the Impedance Spectroscopy. The impedance data analysis is performed by the recently developed new structural approach called Differential Impedance Analysis (DIA) [1-8]. It eliminates the need of an initial hypothesis about the system, extracting the impedance model directly from the experimental data.

The high ionic conductivity of cubic stabilized zyrconia is realized via the addition of a large concentration of the acceptor dopant Y_2O_3. For charge compensation oxygen vacancies are formed. It is known that the ionic conductivity of YSZ takes place by a vacancy mechanism. There is an experimental evidence for the elimination of the contribution of cations, as well as of protonic and electronic transport. The high concentration of the dopant Y_2O_3 aids the formation of associates $(Y'_{Zr}V^{\cdot\cdot}_{O})^{\cdot}$ and $(2Y'_{Zr}V^{\cdot\cdot}_{O})^{x}$ [9], which serve as vacancy trapping centres and thus a very small part of the oxygen vacancies take active part in the conductivity process. What is not well known is the mobility and concentration of the free vacancies able to take part in the mass transport and their temperature dependence. It is supposed that the defect complexes bring to the formation of vacancy ordered phases (microdomains) with different temperature stability.

The conductivity of YSZ can be affected by its complicated microstructure. Some problems may arrise from secondary microstructural changes in the bulk such as formation of cubic tetragonal interfaces, internal microcracking and disintegration, which may increase the resistance of the bulk material. The grain boundaries are a serious source for conductivity changes. In principle pure boundaries in fast ion conducting solids show a low boundary resistance. The presence of depletion space charge layers at the boundaries, i.e. depletion of oxygen vacancies is a reason for the grain boundary blocking effect. In some cases the “spillover” effect might be also taken into account for the explanation of YSZ conductivity behaviour [10].

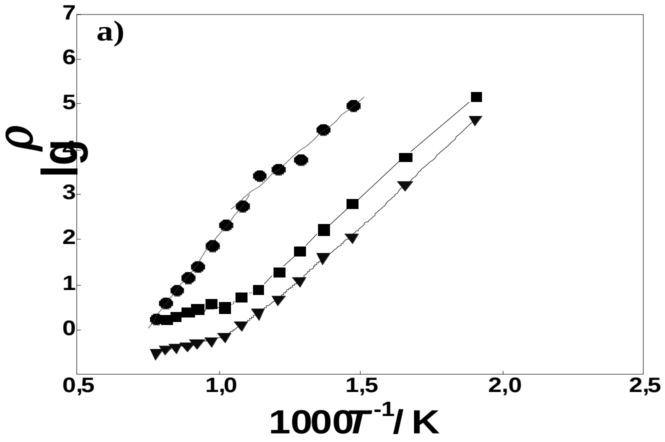
The modeling of the electrode reaction follows the classical electrochemical concept for the charge-transfer process occurring at the three-phase boundary interface (TPB) [11]. Although the publications regarding this process are numerous, a simultaneous observation of the electrolyte conductivity and electrode reaction is not done before.

YSZ samples produced by ESCETF Single Crystal Technology B.V. were investigated. The single crystal with <100> orientation comprised 9,5 mol% yttrium oxide, while the polycrystalline material contained 8.5 mol %. The impedance measurements were done on

Solartron 1260 FRA over the frequency ranges 13 MHz - 0,1Hz with density 9 points per decade. The experiments included in this study were carried at amplitude 300 mV and variation of the temperature in the interval from 200 to 950 ^{o}C. The samples were covered with porous platinum electrodes. A procedure for corrections of the parasitic inductance of the cell and of the cabling was done before the DIA analysis.

Our first experiments show that Arrhenius plots built for the two materials have a kink at 650 ^{0}C for the single crystal and at 600 ^{0}C for the polycrystalline sample [12]. The calculated activation energies (E_a) coincide - of about 0.3-0.4 eV for temperatures below the kink and of about 1.14 eV above the kink. These results show that the grain boundaries of the polycrystalline sample are clean and do not have a blocking effect.

The following activation energies for electrode reaction were obtained from the Arrhenius plots (Fig. 1a): E_a = 0.52 eV for the temperature interval 500-600^{0}C and E_a = 1.62 eV for temperatures above 600^{0}C. They follow the same tendency as the single crystal sample (Fig. 1b), where E_a = 0.66 eV for temperatures 550-650^{0}C and E_a = 1.62 eV for temperatures above 650^{0}C. The higher activation energy at higher temperatures could be explained with a change in the rate limiting stage of the electrode reaction. We can suppose transport (diffusion) limitation for the low temperature interval up to 650^{o} C. At higher temperatures an increased surface accumulation of oxygen species is observed. It indicates a slower dissociation in relation to the bulk incorporation, which is in agreement with the conclusions in [13].



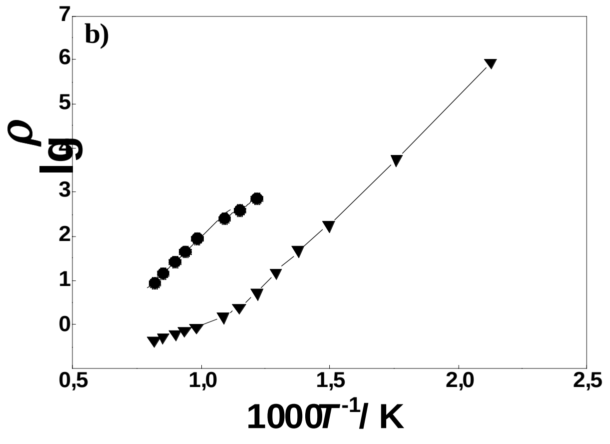


Fig. 1. Arrhenius plots of polycrystalline YSZ (a) and YSZ single crystal (b) for bulk (_), grain boundaries (_) and electrode reaction (●)

It is interesting to note that the activation energy of the electrode reaction for polycrystalline and single crystal YSZ at lower temperatures is the same, while above the kink that of the polycrystalline material is higher. This result shows that the grain boundaries do not influence the transport mechanism, which is the rate limiting stage at lower temperatures, while at higher temperatures they hamper the bulk incorporation.

It should be mentioned that the kink in the Arrhenius plots for the bulk and for the grain boundaries appears at the same temperature at which it is observed for the electrode reaction. It confirms the hypothesis for internal relation between the conductivity of the sample and the electrode reaction behaviour.

Obviously the quantitative evaluation of YSZ conductivity and oxygen transfer are of great importance for elucidating the knowledge about this material and thus about the methods for its predictable optimization. A prolongation of this impedance study by the new and powerful techniques as IRSR and ESCA will give a possibility for correlating structure characteristics with chemical and physical properties of the material.

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