Impedance spectroscopy of reduced monoclinic zirconia

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Zirconia doped with low-valent cations (e.g. Y3+ or Ca2+) exhibits an exceptionally high ionic conductivity, making them ideal candidates for various electrochemical applications including solid oxide fuel cells (SOFC) and oxygen sensors. It is nevertheless important to study the undoped, monoclinic ZrO2 as a model system to construct a comprehensive picture of the electric behaviour. In pure zirconia a residual number of anion vacancies remains because of contaminants in the material as well as the thermodynamic disorder equilibrium, but electronic conduction may also contribute to the observed conductivity. Reduction of zirconia in hydrogen leads to the adsorption of hydrogen and to the formation of oxygen vacancies, with their concentration affected by various parameters (e.g., reduction temperature and time, surface area, and water vapour pressure). However, there is still little known about the reactivities of defect species and their effect on the ionic and electronic conduction. Thus, we applied electrochemical impedance spectroscopy to investigate the electric performance of pure monoclinic zirconia with different surface areas in both oxidizing and reducing atmospheres. A novel equivalent circuit model including parallel ionic and electronic conduction has previously been developed for titania and is used herein to decouple the conduction processes. The concentration of defects and their formation energies were measured using volumetric oxygen titration and temperature programmed oxidation/desorption.

Introduction

Oxide ceramics are gaining more widespread use as refractory structural and functional materials in a wide range of dielectric and electronic applications.1 Zirconium dioxide (ZrO2), especially when doped with Y2O3, CaO or MgO, combines its high ionic conductivity with a high mechanical and chemical resistance2–5 and thus is currently considered the most promising material for use as a solid electrolyte in gas sensors (λ-probes6–9) and solid oxide fuel cells (SOFC)10–12. Within the last decade, zirconia based materials have also gained technological and scientific interest in the field of heterogeneous catalysis.13–17 The use of zirconia and sulfated zirconia as a constituent in mixed oxides in catalysts has been discussed intensively.18–20 Active sites on the surface of such species are most likely electronic or structural defects that lower the bonding strength of adsorbed molecules, thereby favouring subsequent reactions. Because of structural and chemical properties similar to titania, zirconia may behave like titania when it is used as a support for noble metal catalysts. Currently, there is much interest in undoped zirconia for its role in solid solutions (e.g. with CeO2) and its influence on catalysis21,22. Unlike stabilised tetragonal or cubic zirconia, undoped ZrO2 with monoclinic equilibrium structure is not suitable for electrical applications, as it undergoes a 5–9% volume shrinkage due to the monoclinic-to-tetragonal phase transition at 1350 K.23 Nevertheless, it is important to study the undoped, monoclinic ZrO2 as a model system to obtain a comprehensive picture of the electrical behaviour. Furthermore, any data of electronic conduction obtained for the undoped monoclinic zirconia may also be valid for stabilised tetragonal or cubic zirconia (e.g. YSZ), thereby improving our understanding of the electrochemical processes in SOFC and gas sensors. Since the working temperatures of catalysts generally remain well below temperatures needed for the monoclinic-to-tetragonal phase transition, the study of undoped monoclinic zirconia is of purely catalytic interest as well.

Zirconia is a stable oxide that tends to lose surface oxygen only after thermal treatment under high vacuum above 973 K.2,24 Nevertheless, theoretical studies have predicted the presence of defect sites (anion vacancies) at significantly lower temperatures when zirconia is exposed to a reducing atmosphere.25–30 FTIR and EPR studies focused on the chemisorption of CO and H2/O2 on pure zirconia and suggested the formation of oxygen deficient surface sites.24,30,33 Previously, we were the first to verify the formation of oxygen vacancies and to measure their quantity in hydrogen treated monoclinic zirconia using volumetric oxygen titration.34 Based on FTIR and EPR observations,24,35 we postulated the formation of a Zr3+/e– pair similar to that of oxygen vacancies in TiO2.36,37

When zirconia is treated in hydrogen at temperatures below 873 K, surface oxygen vacancies are formed with an activation energy of 20 kJ mol–1 (0.22 eV), whereas the vacancies formed...
at higher temperatures need significantly higher activation energies of 120 kJ mol\(^{-1}\) (1.25 eV). Presumably, this higher activation energy originates from the diffusion of oxygen vacancies into the bulk of zirconia. The additional energy for oxygen diffusion of 1 eV was also measured in zirconia by tracer diffusion and impedance spectroscopy studies.\(^{38,39}\)

The deviation from stoichiometry also affects the electrical behaviour of semi-conducting oxides like CeO\(_{2-x}\)^{5,40–42} or TiO\(_{2-x}\)^{5,43,44} Most studies of zirconia have been carried out on doped and stabilised zirconia samples, where the conductivity can be exclusively attributed to high ionic conductivity due to oxygen vacancies formed extrinsically by doping with low-valent cations.\(^{4,5,45}\) However, hydrogen treatment can cause an additional conduction mechanism as described by Levy et al., who proposed a model for the electrical conductivity of electrochemically reduced stabilised zirconia with two different conduction processes (ionic and electronic) depending on the deviation from stoichiometry.\(^{46}\) In a previous paper, we developed an alternative conduction model for substoichiometric titania using electrochemical impedance spectroscopy.\(^{47}\)

Some authors reported higher electrical conductivities in zirconia at grain boundaries.\(^{5,48–50}\) This raises the question whether the introduction of interfaces by nanostructurisation will contribute to a further enhancement of the electrical conductivity. However, until now undoped monoclinic zirconia has been rarely discussed.

Therefore, the aim of this work was to study the electric properties of undoped monoclinic zirconia in oxidizing and reducing atmospheres under various conditions including surface area, reduction temperature and oxygen partial pressure. This was done with electrochemical impedance spectroscopy on nanocrystalline as well as on coarse-grained zirconia samples with controlled stoichiometry.

**Experimental**

**Materials**

The zirconium(iv) oxide used in this work was prepared by low temperature drying of a solution of zirconia-aquat (a suspension of 20% ZrO\(_2\) in water, 0.1 \(\mu\)m particle size, supplied by Alfa Aesar). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis revealed a content of 1.09% of Hf and 168 ppm of iron. Before use the zirconia was calcined and sintered in air at various temperatures, leading to a systematically controlled surface area.\(^{34}\) The surface area of the samples was determined by adsorption of nitrogen at 77 K according to BET (Fig. 1). The structure of the samples during thermal and vacuum treatment was investigated by X-ray diffraction (XRD) and Raman spectroscopy.

The nanocrystalline “fresh” sample (n-ZrO\(_2\)) crystallizes in the monoclinic structure with an average crystallite size of 5 nm, as revealed by X-ray line broadening. It has a BET surface area of 115–120 m\(^2\) g\(^{-1}\) and is thermally stable up to 723 K, above which the zirconia starts to sinter. Upon sintering the specific surface area decreases continuously with increasing calcination temperature leading to a value of 13 m\(^2\) g\(^{-1}\) after calcination at 1273 K (Fig. 1). This latter sample still exhibits the monoclinic structure with a crystallite size of 20 nm. Thus, the subsequent data were obtained with two different zirconia samples: the nanocrystalline sample (calcined at 673 K), which was only used at temperatures below 723 K to avoid sintering, and the fully sintered sample (calcined at 1273 K).

Hydrogen, helium and oxygen were highest grade gases supplied by Messer–Griesheim. Hydrogen was further purified by passing through an oxygen removing purifier, and helium was freed from traces of oxygen with an Anoxy-Cil unit. Condensable contaminants were removed from hydrogen and helium by liquid nitrogen traps, while oxygen was passed through a trap cooled with liquid nitrogen–ethanol.

**Volumetric apparatus**

Volumetric measurements were performed in an all glass apparatus as described previously.\(^{34}\) Zirconia was treated in flowing dry hydrogen at a typical flow rate of 1 ml s\(^{-1}\). In order to control the activity of oxygen, in some experiments the hydrogen was passed through an U-shaped tube whose bottom was covered by H\(_2\)O. Upon cooling to 273 K, the vapour pressure of water in the resulting gas stream was fixed at 6.1 mbar.

**Electrochemical impedance spectroscopy**

An IM6e impedance spectrometer (Zahner-Elektrik) was used to measure the magnitude of the impedance and the phase shift between current and voltage (50 mV a.c.) in a frequency range of 10 mHz to 1 MHz. The impedance spectra were acquired using the 2-pole mode with gold electrodes, as described elsewhere.\(^{47}\)

To retain ready gas access to the zirconia surface, the samples were compressed with low pressure (2000 bar) to produce pellets of about 1 mm thickness and 6 mm diameter. To minimize the contact resistance, thin layers of gold were deposited on both sides of the pellets by high vacuum deposition. The pellets were placed in a quartz glass tube equipped with gold electrodes that were pressed onto the pellet with 1 bar. The apparatus is suitable for different gas treatments.
and is described elsewhere.\textsuperscript{36} Some measurements were performed with a water vapour pressure of 6.1 mbar by passing the gases through a trap in which water was held at 273 K. Samples were heated up to 1073 K with a tubular oven that was controlled by a Ni/NiCr thermocouple, situated in the reactor about 5 mm downstream of the pellet.

**Results**

**Effect of surface area on the number of oxygen vacancies**

In a previous paper we discussed the formation of oxygen vacancies in ZrO\(_2\) and the effect of various parameters including reduction temperature, reduction time, and water vapour pressure.\textsuperscript{34} These studies were done on fully sintered zirconia samples that had been prepared by calcination in air at 1273 K. In contrast, the present work considers the fresh, nanocrystalline ZrO\(_2\) samples (n-ZrO\(_2\)) that had been treated in hydrogen containing 6.1 mbar water vapour at temperatures below 723 K.

Fig. 2 shows the increase in the number of oxygen vacancies as obtained by volumetric oxygen titration with increasing reduction temperature for both the nanocrystalline zirconia (a) and the sintered sample (b). Both samples exhibit a similar behaviour when reduced at temperatures below 723 K. Assuming a partial equilibrium between the gas phase and the surface of zirconia, the van’t Hoff plot revealed an energy of 25 kJ mol\(^{-1}\) (0.26 eV) for both samples, which is assumed to be the energy needed for the formation of oxygen vacancies on the surface of ZrO\(_2\).\textsuperscript{34}

The number of oxygen vacancies on a per-weight basis is higher in the nanocrystalline sample by a factor of about 10. We point out that this is also the ratio of the specific surface areas between the nanocrystalline (\(\sim 120 \text{ m}^2\ \text{g}^{-1}\)) and sintered sample (\(\sim 13 \text{ m}^2\ \text{g}^{-1}\)) as shown in Fig. 1. Thus, relative to the surface area, the concentration of the oxygen vacancies is the same in both samples. This direct relationship between the number of vacancies and the surface area supports our assumption that at least in the given temperature range the oxygen vacancies are concentrated at the surface.

When the reduction temperature is raised above 673 K, the increase in the number of vacancies is significantly different for the two samples. While the number of oxygen vacancies in the nanocrystalline sample continues to increase rapidly with increasing reduction temperature, the formation of oxygen vacancies in the latter seems to be hindered and temperatures above 873 K are needed for a further increase. The activation energy needed for the formation of these vacancies was calculated to be 115 kJ mol\(^{-1}\) (1.2 eV) as obtained from the Arrhenius plots. The relevant processes described by this activation energy include the formation of surface vacancies and their diffusion through the bulk. Thus, the vacancies in nanocrystalline zirconia seem to diffuse from the surface into the bulk at much lower temperatures (673 K) than in sintered zirconia (873 K).

**Impedance spectroscopy of zirconia in oxygen**

(a) **Nanocrystalline zirconia.** Pure zirconia is an insulator at room temperature with capacitive behaviour in the whole frequency range. With increasing temperature zirconia becomes a semiconductor, exhibiting capacitive conduction at high frequencies and a parallel ohmic conduction in the low frequency range (Fig. 3a). The corresponding phase shift changes from \(-90^\circ\) in the high frequency region (capacitive) to \(0^\circ\) in the low frequency region (ohmic). With increasing temperature the low frequency resistance decreases from about 2 G\(\Omega\) at 623 K to about 150 M\(\Omega\) at 723 K. This behaviour is typical for semiconducting materials.\textsuperscript{51}

Beyond 0.1 Hz an additional impedance contribution is observed which increases with decreasing frequency. In this frequency range the phase shifts to negative values again (Fig. 3a). This indicates that an additional capacitive impedance contributes to the total impedance even at this low frequency. The height of the impedance step in this frequency range increases with increasing temperature. We found a similar behaviour for nanocrystalline titania, for which we proposed a mechanism including a parallel pathway.\textsuperscript{42}

(b) **Sintered zirconia.** For comparison, samples of sintered zirconia were treated in flowing oxygen at various temperatures. Fig. 3b shows the corresponding impedance spectra taken at 723 K. The impedance at high frequencies for the sintered sample is similar to that of the nanocrystalline sample; however, it is significantly different at low frequencies, with...
higher values in the sintered sample. Below 0.1 Hz the impedance increases again and the phase shift to negative values is even more pronounced and now seems to reach $-45^\circ$, which is typical for diffusion controlled conduction processes.\textsuperscript{51}

**Effect of gas treatments**

(a) **Treatment in oxygen and in ambient air.** To study the effect of oxygen partial pressure the nanocrystalline zirconia sample was treated in flowing dry oxygen as well as in ambient air. The Nyquist spectrum for zirconia in flowing dry oxygen in Fig. 4b was measured at 1073 K and shows a slightly depressed semicircle in the high frequency region, similar to the spectrum of nanocrystalline zirconia at lower temperatures. The time constant for this process was calculated from the impedance data to be 76 $\mu$s. At low frequencies, a linear increase with a 45° slope indicates a diffusion-limited process, which is also present (but less evident) at lower temperatures.

When zirconia is treated in ambient air an additional semicircle appears, leading to a higher overall impedance compared to the oxygen treated sample (Fig. 4a). The first semi-circle at high frequencies is almost not suppressed and corresponds to a process with a time constant of 40 $\mu$s. In both samples, this rather fast process is probably due to electronic transport.\textsuperscript{51} The well separated second semi-circle describes a much slower process with a time constant of 0.2 s.

(b) **Treatment in hydrogen.** The impedance of zirconia treated in hydrogen containing 6.1 mbar water at room temperature is similar to the corresponding value of oxygen treated zirconia, even after long treatments. With increasing reduction temperature, the low frequency impedance of hydrogen treated zirconia decreases with increasing reduction temperature from 240 M$\Omega$ at 573 K to 45 M$\Omega$ at 713 K. We found that sintering of zirconia occurred at lower temperatures when exposed to hydrogen than to oxygen (713 K vs. >723 K). Thus, the reduction temperature for the nanocrystalline sample was always kept below 713 K to avoid further sintering.\textsuperscript{34} The corresponding Nyquist spectra consists of only one, slightly suppressed semicircle (Fig. 5) and no signs of a second conduction pathway in the low frequency region were found.

**Discussion**

**Mechanism of conduction**

Zirconia doped by low-valent cations like Y$^{3+}$ or Ca$^{2+}$ are prime examples of ionic conductors. In pure zirconia a residual number of anion vacancies remains due to contaminants in the material and thermodynamic disorder equilibrium, but electronic conduction may also contribute to the observed finite conductivity.

Thus, we applied an equivalent circuit model, combining both ionic and electronic conduction, that was recently developed for titania.\textsuperscript{47} Considering all contributions to the overall impedance, we propose the following scheme for the conduction mechanism, occurring (i) via pathway A by electronic conduction and (ii) via pathway B by ionic transport. The serial contributions of pathway A describe the electron transport from the electrode to the oxide (ct), electronic conduction through the oxide (b), and electron transport between the oxide grains (gb) and are each characterised by an ohmic resistor in parallel to a capacitor.

In pathway B the ionic conduction is characterised by an ohmic resistor ($R_i$). Since the ionic motion may be impeded by diffusion limitations, especially at low frequencies, a simple distributive impedance element, the Warburg impedance element ($W$), was added to the circuit diagram. At the limit of low frequencies the impedance of pathway B increases and the phase shift changes to negative values. The reason for this breakdown of the surface conduction may arise from ion blocking by grain boundaries perpendicular to the charge flow, or by ion blocking at the interface to the gold electrode. In both cases this blocking is characterised by a capacitor ($C_w$) in series to the resistor $R_i$. The resulting equivalent circuit diagram is shown in Fig. 6.

In order to prove the validity of the proposed mechanism we compared the experimentally obtained impedance spectra (data points), depicted as Nyquist diagrams, with the impedance simulated from the circuit diagram (continuous line).
part of the conductivity in the high surface material occurs near the surface area of zirconia. Additionally, the proportional effect of the surface area on the number of oxygen vacancies indicates that the electrons introduced during the reduction are located near the surface of zirconia. Thus, we assume that part of the electronic conduction occurs near the surface of the zirconia particles.

The obtained bulk capacity \( (C_b) \) values were similar for both the fresh and sintered samples. Below 723 K these values were independent of the temperature. The corresponding dielectric constants (between 12 and 13), calculated from this bulk capacitance, agree well with literature data for monoclinic zirconia (12.4 \( ^{31} \)) and therefore support the proposed model.

The contribution of the grain boundaries to the overall electronic impedance leads to a considerably higher capacitance \( (C_{gb}) \) for the high surface sample due to the larger number of grain boundaries to be passed. On the other hand, the ohmic grain boundary resistance \( (R_{gb}) \) of the high surface sample is lower than that of the low surface sample. This apparent discrepancy can be resolved by recognising that during sintering the volume of the particles probably shrinks, leading to an increased mean distance between the grains. As a result, the charge transport between the grains is inhibited, thereby causing a higher overall ohmic resistance, despite the lower number of passages between grain boundaries for the sintered sample.

The resistance of the ionic pathway \( (R_i) \) is also lower for the high surface sample, providing further evidence that the ionic conduction is confined to the surface. The high capacitance that blocks the ionic pathway suggests that the transfer and therefore the discharge of ions at the electrodes is inhibited, presumably due to the low exchange current density of oxygen at the gold electrode.

**Effect of the oxygen partial pressure.** The ohmic resistance of the air treated sample (at 1073 K) is higher by a factor of about 1.7 compared to the treatment in pure hydrogen (Fig. 4). This result indicates that at least at those high temperatures charge carriers may be formed during the reduction of \( \text{Zr}^{4+} \) via the equation:

\[
\text{Zr}^{4+} + \frac{1}{2}\text{O}_2 \rightarrow \text{V}_\text{O} + e^- + \text{Zr}^{3+} + \frac{1}{2}\text{O}_2
\]

In equilibrium reactions the surface oxygen vacancies and the \( \text{Zr}^{3+} \) ions may also form a surface complex, following

\[
\text{Zr}^{3+} + \text{V}_\text{O} \rightarrow + \text{Zr}^{3+}-\text{V}_\text{O}
\]
Furthermore, one has to consider that the electrons may be captured by an oxygen vacancy or by a \( \text{Zr}^{3+} - \text{V}_\text{O} \) complex to form surface \( F \) centers, with the electrons presumably occupying donor sites in the bulk of the zirconia.

The number of defects, which are formed independently due to the release of an oxygen atom, can be estimated by the effect of oxygen pressure on the impedance. This is assuming that the electronic conduction at any given temperature is proportional to the number of electrons formed and independent of whether they are bound to oxygen vacancies or to donor sites. The law of mass action then gives the equation

\[
K = p_{\text{O}_2}^{1/2} 
\]

where \( x \) is the concentration of the electrons and \( n \) is the number of independently formed defects. According to this relation the electronic conductivity, and hence the number of independently formed defects. Thus, we have to assume that \( \text{Zr}^{3+} \) and oxygen vacancies indeed form a surface complex and that approximately half of the electrons are bound to that complex while the other half of the electrons occupy independent sites.

**Hydrogen treated samples**

When zirconia was treated in hydrogen the low frequency impedance of both samples decreased by a factor of 3–4 (Fig. 8 and 9). This effect is much smaller in zirconia than in titania, where the conductance between the hydrogen and oxygen treated samples differs by a factor as high as \( 10^6 \). Nevertheless the mechanism for this hydrogen effect may be the same as in titania, according to the equation

\[
\text{O}_2^2- + \text{H}_2 \text{g} \leftrightarrow \text{V}_\text{s} + 2e^- + \text{H}_2\text{O}_\text{g} 
\]

The extent of reduction, however, is much smaller in zirconia and the electrons are probably confined to the surface \( (V_\text{s}) \). According to this equation, the vapour pressure of water significantly affects the equilibrium of the reaction and thus was maintained at 6.1 mbar (water vapour pressure at 0°C).

The experimental data (data points) agree very well with the simulated impedance values upon applying the proposed equivalent circuit (continuous line). Due to the enhanced electronic conduction the ionic contribution now becomes negligible resulting in scattered parameters for ionic conduction in the data fit. Thus, for the analysis of the hydrogen data, the pathway \( B \) in the equivalent circuit was omitted.

Table 2 shows the fitting parameters for the electronic conduction obtained for different temperatures. The bulk capacitance slightly increases with increasing temperature, and the calculated values for the dielectric constant (11–13) are similar to those of zirconia treated in oxygen.

Generally, the ohmic resistances decrease with increasing temperature indicating activated processes. An Arrhenius analysis of the overall conductivity data taken at 1.3 Hz (Fig. 10) reveals two regimes characterised by different activation energies. Below 673 K, the sum of all resistive contributions results in an apparent activation energy of 25 kJ mol \(^{-1}\) (0.26 eV). Above 673 K the electronic conduction along the surface is characterised by an apparent activation energy of 100 kJ mol \(^{-1}\) (1.04 eV), the energy barrier for electronic conduction across the grain boundaries is 125 kJ mol \(^{-1}\) (1.3 eV) and the transfer of electrons to the gold electrode needs 65 kJ mol \(^{-1}\) (0.67 eV). Therefore, we conclude that the electronic transport along the zirconia surface is again the main contribution to the ohmic resistance in pathway \( A \).

**Energy level of the donor sites**

The apparent activation energy for electronic conduction arises from the effect of temperature on the number of charge carriers as well as the energy needed to enable the promotion of electrons from the donor sites to the conduction band.

### Table 2. Calculated equivalent data (only path A) of nanocrystalline ZrO\(_2\) treated in hydrogen containing 6.1 mbar water at various temperatures.

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<th>( T/\text{K} )</th>
<th>( R_\text{gb}/\text{M}\Omega )</th>
<th>( C_\text{gb}/\text{pF} )</th>
<th>( R_\text{gb}/\text{M}\Omega )</th>
<th>( C_\text{gb}/\text{pF} )</th>
<th>( R_\text{gb}/\text{M}\Omega )</th>
<th>( C_\text{gb}/\text{nF} )</th>
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Hydrogen treatment leads to an oxygen surface vacancy along with two free electrons (eqn (3)), or one free electron and a Zr$^{3+}$ ion, if some fractions of these electrons are localised at the zirconium ions. The energy needed for this process is 25 kJ mol$^{-1}$ (0.26 eV) when reduction was carried out at temperatures below 873 K. For this temperature range it could be shown that oxygen vacancies are formed at the surface of the oxide, and that their number is directly proportional to the specific surface area. As a result, both electrons and vacancies are confined to the surface. The energy needed for the formation of these electrons is 25 kJ mol$^{-1}$ of 0.27 eV.

The apparent activation energy for electronic conduction after treatment in hydrogen in the temperature range between 673 K and 873 K is 1.04 eV. After subtracting the energy needed for the formation of electrons (0.26 eV), the remaining apparent activation energy (0.78 eV) is consistent with the energy needed to promote the electrons from their intergap to the conduction band. This result is in reasonable agreement with recent calculations by Shluger et al., who proposed that the formation of F$^{2-}$ centres in hydrogen treated monoclinic zirconia occurs at 1 eV below the conduction band. This suggests that further to the oxygen vacancies the electrons are also localised at the surface or grain boundaries, as proposed from the proportionality between oxygen vacancies and specific surface area. Furthermore, these results support the assumption that the electrons move along the surface rather than through the bulk of the grains.

However, a different situation is found at temperatures below 653 K, where the activation energy for bulk conduction in the oxygen treated low-surface sample is 0.26 eV, indicating a different conduction mechanism. Most likely, extrinsic dopants like iron ions form charge carriers, their number being independent of temperature. The measured apparent activation energy for electronic conduction is therefore expected to be equal to the energy needed for activation alone. If that is the case these electrons would occupy donor sites 0.26 eV below the conduction band.

For comparison, zirconia treated in oxygen exhibits a stronger temperature dependence with an activation energy of 150 kJ mol$^{-1}$ (1.55 eV). The activation energy for oxygen diffusion is generally greater than 200 kJ mol$^{-1}$ (2 eV), which seems to exclude this mechanism of conduction. However, it could be shown that doping of zirconia with Ca$^{2+}$ or Y$^{3+}$ ions, typically used in SOFC, reduces the energy needed for oxygen diffusion to approximately 120 kJ mol$^{-1}$ (1.24 eV). In this sample, the iron content may reduce the activation energy in a similar way.

**Conclusions**

The partial reduction of monoclinic zirconia (ZrO$_2$) in hydrogen and its effect on the electric performance was investigated using volumetric oxygen titration, temperature programmed oxidation/desorption and electrochemical impedance spectroscopy. Hydrogen treatment below 873 K leads to the formation of oxygen vacancies at the surface (apparent activation energy ~25 kJ mol$^{-1}$), while at higher temperatures the vacancies were able to diffuse into the bulk (~115 kJ mol$^{-1}$). The formation of these vacancies is accompanied by the release of electrons, their number being directly proportional to the specific surface area. These electrons were found to be confined to the surface and need 0.78 eV to be raised to the conduction band.

**References**


