Subsurface segregation of yttria in yttria stabilized zirconia

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I. INTRODUCTION

Yttria stabilized zirconia (YSZ) owes its success as an electrolyte in fuel cell technology mainly to its high ionic conductivity. Both the external surface and the grain-boundary network play an important role in this application; the former in the uptake of oxygen molecules and their conversion to oxygen ions, the latter in the diffusion process through the electrolyte. It is believed that the oxygen exchange at the surface is the rate-limiting factor in the solid oxide fuel cell (SOFC). In order to understand the role of the external YSZ surface in this process, its composition should be known.

The electrolyte is exposed to high temperatures both during the fabrication process and during the operation of the SOFC. Calcination temperatures in excess of 1200 °C are not uncommon and the working temperature of the SOFC lies around 1000 °C. After exposure to these temperatures the YSZ surface composition differs from that of the bulk composition. Yttria segregation to the external surface has been observed for YSZ containing an Y2O3 doping between 2 and 19 mol %. The process of segregation is driven by the reduction of the surface free energy of the electrolyte. Strain relaxation and the formation of a space-charge region associated with defects and aloivalent cations are considered to be the main contributions in the reduction. The surface structure of the YSZ surface is reported to change due to the increased Y2O3 concentration. For YSZ stabilized in the tetragonal phase, separation into large Y enriched cubic and small Y depleted tetragonal grains is observed. For YSZ stabilized in the cubic phase, the possible existence of a pyrochlore type cubic phase of Y2Zr2O7 at 33 mol % Y2O3 with a unit size nearly twice that of the fluorite type phase has been reported.

Impurities are always present in oxides. In the case of YSZ, the main contaminants are the oxides of Na, Si, Al, Ca, Fe, and Hf. These impurities (except maybe Hf) segregate to the surface at similar temperatures to that of Y2O3. It has, therefore, been suggested that the impurities, especially Si, influence the segregation behavior of Y2O3. It has been found that Si increases the Y segregation, although others contradict this. The formation of a compound between Y2O3 and SiO2 has been reported. The composition and structure of the Y silicate depend on the bulk impurity content and the atmosphere in which the samples have been calcined. Increasing the calcination temperature changes the morphology of the impurity phase from a thin film wetting the complete surface around 1350 °C to an accumulation in large isolated pockets along the grain boundaries and in triple points at temperatures above 1450 °C.

The segregation behavior is, however, still very controversial. It is, therefore, the aim of this study to increase the insight in the complex segregation behavior of Y2O3 in ZrO2 and to determine the accompanying change in surface free energy. We used low-energy ion scattering (LEIS) for this...
study, since it can, in contrast to more common techniques like x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary-ion mass spectroscopy (SIMS), be used to selectively probe the outermost surface layer and to quantify its composition; thus, precisely the layer which is so important in the uptake of oxygen.

II. EXPERIMENT

Five samples are used: 3 and 10 mol % $Y_2O_3$ doped $^{94}ZrO_2$ (3 and 10 iYSZ) and the reference samples 10 mol % $Y_2O_3$ doped $ZrO_2$ (10YSZ), $Y_2O_3$ and $^{94}ZrO_2$. LEIS measurements on all samples are done on the setup called NODUS.\textsuperscript{11,12} time-of-flight (TOF)-LEIS measurements on $Y_2O_3$ and $^{94}ZrO_2$ are done on CALIPSO.\textsuperscript{13,14}

A. Samples

3 and 10 iYSZ are synthesized using the following low-temperature precipitation method. As starting materials $^{94}ZrO_2$ (>99% chemically pure, 93.4% isotopically pure, see Table I) and $YCl_3$, $6H_2O$ (99.999% chemically pure), purchased from Pennwood Chemicals Inc., USA and Aldrich, Germany, respectively, are used. The $^{94}ZrO_2$ powder is decomposed by heating with NaHSO\textsubscript{4} and $H_2SO_4$. The sulfuric acid is added to fully dissolve the $^{94}ZrO_2$ powder. Subsequently, the reaction product $Zr(SO_4)_2$ and the YCl\textsubscript{3} are dissolved in deionized water to form a solution with the desired $Y/Zr$ ratio. This is dripped into an ammonia solution of 25 ml NH\textsubscript{4}OH and 200 ml deionized water under continuous stirring. The precipitation is filtered out, rinsed several times with a solution of 5 ml NH\textsubscript{4}OH in 40 ml deionized water until the filtrate solution is free of SO\textsubscript{4}\textsuperscript{2-}. Finally, the mixture is filtered, rinsed with absolute ethanol and dried. Afterward, the powder is pressed uniaxially at 350 MPa to samples of 6 mm in diameter and 1.4 mm in height. Accordingly, the samples are calcined in a continuous O\textsubscript{2} flow at 1 bar in a conventional tube oven. The heating rate is 3°/min. The 10YSZ sample is calcined at temperatures ranging from 300 °C to 1600 °C, the 3YSZ sample, at temperatures ranging from 300 °C to 1200 °C. The samples are kept at each calcination temperature for 5 h. The cooling rate is determined by the thermal inertia of the tube oven and the O\textsubscript{2}, which is kept flowing until the samples have cooled down to a temperature below 50 °C. This way, the samples cool down to half their initial calcination temperature within 90 min. After reaching a temperature around 50 °C, the samples are taken out of the tube oven. The 10YSZ powder (TOSOH Co.) is pressed into a pellet (Ø 10 mm and 1.5 mm thick).

$Y_2O_3$ (Johnson Matthey, chemical purity 99.999%) and $^{94}ZrO_2$ powders are compacted in copper cups (Ø 2 mm and depth 0.6 mm).

Cleaning sample surfaces in NODUS is done by a combination of annealing at 300 °C and oxidation with atomic oxygen.\textsuperscript{15} In CALIPSO, this is done by calcination in 200 mbar O\textsubscript{2} at 300 °C for 20 min, followed by sputtering with $5 \text{keV}^{40}Ar^+$ ions ($2.5 \times 10^{15} \text{ions/cm}^2$).

B. Low-energy ion scattering measurements

The (normal) LEIS measurements on 3YSZ and 10YSZ are done with $3 \text{keV}^{4He^+}$ ions (to determine impurity segregation) and $5 \text{keV}^{40}Ar^+$ ions (to determine $Y_2O_3$ segregation). With $^{4He^+}$ ions, we can detect the impurities Na, Si, and Ca. The ion dose needed to measure one spectrum is about $1 \times 10^{14} \text{He}^+ \text{ions/cm}^2$. With $5 \text{keV}^{40}Ar^+$ ions, the largest possible separation of the Y and Zr peaks is obtained. The $^{40}Ar^+$ ion dose needed to measure one spectrum is about $5 \times 10^{13} \text{ions/cm}^2$. After calcination (see Sec. II A), a first spectrum is measured using $^{4He^+}$ ions, followed by measuring a sputter profile with $^{40}Ar^+$ ions. After the sputter profile, again, a LEIS spectrum is measured with $^{4He^+}$ ions. To prevent the samples from charging their surfaces, they are flooded with low-energy electrons. In standard YSZ samples, Y with mass 89 amu and all five natural isotopes of Zr with masses ranging from 90 to 96 amu are present. Since even for $5 \text{keV}^{40}Ar^+$ ions, the mass resolution of NODUS is not sufficient to separate the LEIS peaks of these elements, Y and Zr will be observed as one combined peak. As an example, the LEIS spectrum of 10YSZ is given in Fig. 1 (a). The asymmetry of the peak is caused by the presence of the five Zr isotopes. In principle, it is possible to quantify this spectrum using reference samples. However, data analysis is made simpler and more reliable if the Y and Zr peaks can be separated in the LEIS spectrum. This is established by using samples mainly having the $^{94}Zr$ isotope. Practical reasons prohibit the use of the $^{96}Zr$ isotope, although an even better separation of the Y and Zr LEIS peaks will be obtained. The result of a LEIS measurement on 10YSZ is given in Fig. 1 (b). The $^{89}Y$ and $^{94}Zr$ peaks are now clearly separated. LEIS measurements on $Y_2O_3$ and $^{94}ZrO_2$ are done with $5 \text{keV}^{40}Ar^+$.

C. Time-of-flight-low-energy ion scattering measurements

TOF-LEIS measurements are done to get a better understanding of the shape of the Y and Zr LEIS peaks and back-

<table>
<thead>
<tr>
<th>Isotope</th>
<th>$^{90}Zr$</th>
<th>$^{91}Zr$</th>
<th>$^{92}Zr$</th>
<th>$^{94}Zr$</th>
<th>$^{96}Zr$</th>
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<tr>
<td>Content (wt %)</td>
<td>3.59</td>
<td>1.06</td>
<td>1.63</td>
<td>93.5 ± 0.4</td>
<td>0.22</td>
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<table>
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<tr>
<th>Contaminant</th>
<th>Na</th>
<th>Ti</th>
<th>Fe</th>
<th>Al</th>
<th>Si</th>
<th>Sn</th>
<th>Hf</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt %)</td>
<td>0.008</td>
<td>0.011</td>
<td>0.005</td>
<td>0.006</td>
<td>0.014</td>
<td>0.11</td>
<td>0.5</td>
<td>0.012</td>
</tr>
</tbody>
</table>
background in Fig. 1 (b). In a conventional LEIS experiment, no distinction is made between scattered ions \((^{40}\text{Ar}^+)\) and sputtered ions \((\gamma^+, \text{Zr}^+, \text{YO}^+, \text{ZrO}^+\), etc.). All ions with a certain energy (independent of mass) contribute to the intensity in the LEIS spectrum at that particular energy, giving the result as depicted in Fig. 1 (b). TOF-LEIS measurements are identical to conventional LEIS measurements, but with the difference that the incoming ion beam is now pulsed and only the scattered (or sputtered) ions that pass the analyzer within a certain time window are detected. So, it is possible to measure LEIS spectra of particles with a certain mass only.

The conventional LEIS spectra are measured with 5 keV \(^{40}\text{Ar}^+\) ions and an ion-beam current of 0.17 nA. The ion dose used to measure one spectrum equals \(5 \times 10^{12}\) ions/cm\(^2\). The TOF-LEIS measurements are done with a 5 keV \(^{40}\text{Ar}^+\) pulsed ion-beam (pulse duration of 300 ns, repetition frequency of 110 kHz) and an ion-beam current of 5 nA. The used dose to measure one TOF-LEIS spectrum is also \(5 \times 10^{12}\) ions/cm\(^2\) making a direct comparison between LEIS and TOF-LEIS spectra possible. The available time window for particle detection is 10 \(\mu\)s. This window is divided into three parts to detect particles with mass lower, equal, and higher than 40 amu. To prevent the samples from charging their surfaces are flooded with low-energy electrons.

The results of the (TOF-)LEIS measurements on \(^{94}\text{ZrO}_2\) are given in Fig. 2. Similar results are obtained on \(\text{Y}_2\text{O}_3\). The solid curve in Fig. 2 shows the conventional LEIS spectrum. The broken curve shows the TOF-LEIS spectrum for the scattered particles. The high intensity of the background at low energies is now reduced considerably. The remaining background is partly caused by a combination of multiple scattering and reionization of \(^{40}\text{Ar}\) at the surface. If this would be the only contribution, the background should decrease for lower energies until it disappears at the threshold energy for reionization, which is not the case. Therefore, the background is partly caused by sputtered particles. The open circles in Fig. 2 show the spectrum obtained from particles with mass lower than 40 amu, while the closed circles show the spectrum obtained from particles with mass higher than 40 amu. It is clear that sputtered ions heavier than \(^{40}\text{Ar}^+\) dominate the background. The open squares in Fig. 2 show the spectrum after summation of the signals from the three separate contributions (mass lower, equal, and higher than 40 amu). This summed spectrum is practically identical to the conventional LEIS spectrum, confirming that there are no other significant contributions to that LEIS spectrum.

### III. RESULTS

#### A. Impurity segregation

The segregation of impurities affects the surface concentrations of Y and Zr. This is clearly shown in the LEIS spectra after calcination to 600 \(^\circ\)C and 1200 \(^\circ\)C (Fig. 3). At 600 \(^\circ\)C, only an O and an (Y,Zr) peak are visible in the \(^{4}\text{He}^+\) LEIS spectra. At 1200 \(^\circ\)C, the surface is completely covered by impurity oxides, as can be concluded from the presence of the Na, Si, Ca, and O peaks and the absence of the (Y,Zr) peak. The LEIS spectra do show a step in the background at the position where the (Y,Zr) peak should be, indicating scattering from Y or Zr from layers below the outermost surface. The results of the He measurements on the 10/YSZ sample after each calcination temperature are given in Fig. 4. A similar result is found for the 3/YSZ sample. Below 950 \(^\circ\)C, no impurities are observed and the spectra look similar to that of Fig. 3 at 600 \(^\circ\)C. For temperatures of 1000 \(^\circ\)C and higher, the surface is completely covered by the oxides of Na, Si, and Ca. The LEIS spectra now look similar to that of Fig. 3 at 1200 \(^\circ\)C. The surface O concentration seems to have increased slightly when the surface becomes covered by the impurity oxides. The relative surface coverages of these three oxides on 3 and 10/YSZ hardly change for tempera-
FIG. 3. LEIS spectra (3 keV $^4$He$^+$) of the 10/YSZ sample measured after calcination at 600 °C and 1200 °C. The Y and Zr peaks can not be separated with 3 keV $^4$He$^+$ and show up as one combined (YZr) peak. The LEIS spectrum measured after calcination at 600 °C only shows an O and an (YZr) peak. After calcination at 1200 °C, impurities (Na, Si, and Ca) cover the complete YSZ surface.

FIG. 4. Influence of the calcination temperature on the surface composition of the 10/YSZ sample. The sample is calcined in O$_2$ for 5 h at temperatures between 300 °C and 1600 °C. The LEIS spectra are measured with 3 keV $^4$He$^+$. The (YZr) signals are divided by 10. The large spread in the signal intensities is caused by the fact that the LEIS signals are determined from only one LEIS spectrum, so further measurements could be done on a practically unaltered surface.

tutes of 1000 °C and higher and are given in Table II. The impurities neither come from the tube oven, in which the samples are calcined, nor are they a consequence of the cleaning method.

B. Yttria segregation

1. Data analysis

The ratio of the elemental surface compositions $n_Y/n_{Zr}$ can be calculated from the LEIS surface peak area ratio $S_Y/S_{Zr}$ according to

$$
\frac{n_Y}{n_{Zr}} = \frac{S_Y(E_i) T(E_f) \varepsilon(E_f) \frac{d\sigma_Y(E_i)}{d\Omega} P_Y^+(E_i)}{S_{Zr}(E_i) T(E_f) \varepsilon(E_f) \frac{d\sigma_{Zr}(E_i)}{d\Omega} P_{Zr}^+(E_i)}.
$$

Here, $E_i$ is the ion energy before collision, $E_f$ is the ion energy after collision, $T(E_f)$ is the analyzer transmission, $\varepsilon(E_f)$ is the detector efficiency, $d\sigma(E_i)/d\Omega$ is the differential cross section, and $P_Y^+(E_i)$ is the ion fraction of the scattered particles.

The Y and Zr surface peak areas are determined by the integration of analytical functions representing the binary surface peaks as deduced from the TOF-LEIS measurements (see Fig. 2). The binary collision peak can be clearly of Gaussian shape, although a slight asymmetry is observed toward the low-energy side of the peak. The peak can, therefore, be represented by an asymmetrical Gaussian function according to Creemers et al.$^{16}$ Five parameters are needed to describe such a function. Four of them, the peak position, the peak width, the exponential factor of the asymmetrical contribution, and the ratio of the symmetric to asymmetric part at the position of the peak maximum, are determined from fitting the Zr peak of the $^{94}$ZrO$_2$ sample and are taken as constants for the fits of the Zr peaks in the Y/YSZ spectra. Only the fifth parameter, the intensity, is allowed to vary in order to obtain best possible fits. The background can be described by an exponential function in the energy range (400–1200 eV) used for fitting.

The LEIS spectrum of Y$_2$O$_3$ can also be fitted with an asymmetrical Gaussian function for the Y peak and an exponentially decaying function for the background. The background functions for both Y$_2$O$_3$ and $^{94}$ZrO$_2$ spectra have similar decay constants. The Y/YSZ spectra can, therefore, be fitted with two asymmetrical Gaussian functions and one exponentially decaying function for the background.

The major part of the LEIS measurements have been done on NODUS, while the TOF-LEIS measurements are done on CALIPSO. Although the setups are different, their scattering geometries are practically the same [incoming ion beam perpendicular to the sample surface and scattering angles of 142° (NODUS) and 145° (CALIPSO)]. Therefore, the Y$_2$O$_3$ and $^{94}$ZrO$_2$ samples are also measured on NODUS. The spectra are fitted with the same functions as deduced from the TOF-LEIS results, but with slightly different values for the fit parameters. This modification is needed to satisfy the differences in the analyzers characteristics. An example of a fit is given in Fig. 1 (b). Excellent agreement is obtained between fit and measured spectrum.

<table>
<thead>
<tr>
<th>Impurity (%)</th>
<th>3/YSZ</th>
<th>10/YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na (Na$_2$O)</td>
<td>23±10</td>
<td>10±9</td>
</tr>
<tr>
<td>Si (SiO$_2$)</td>
<td>68±7</td>
<td>74±6</td>
</tr>
<tr>
<td>Ca (CaO)</td>
<td>9±3</td>
<td>16±3</td>
</tr>
</tbody>
</table>
The determination of the detector efficiency function, the analyzer transmission, and the ion fraction has been described in detail by Cortenraad et al. Following these procedures, the ion fractions for scattering by Y and Zr are both found to be 0.10 ± 0.05 as determined for 5 keV $^{40}$Ar$^+$ scattering on Y$_2$O$_3$, $^{94}$ZrO$_2$, and 10i/YSZ. The ion fraction ratio used in Eq. (1) is thus equal to one, irrespective of the chemical composition of the target. The differential cross sections are calculated using the Molière approximation to the Thomas–Fermi potential. Corrections for $e$, $T$, $P^*$, and $d\sigma/d\Omega$ have been done after determining the surface peak area although they are all slightly energy dependent. The difference between corrections made before or after peak fitting is less than 1%.

2. Sputter profiles

Typical results of sputter profiles from 3 and 10i/YSZ samples are given in Figs. 5 (a) and 5 (b), respectively. The open symbols in Figs. 5 (a) and 5 (b) show Y and Zr LEIS signals after the determination of the surface peak areas and corrections for the various factors as reported in Sec. III B.1. For the 3i/YSZ sample, the Zr signal increases sharply with sputter dose until $2.5 \times 10^{15}$ ions/cm$^2$ after which it increases gradually until it stays constant for doses between 6.5 and $12 \times 10^{15}$ ions/cm$^2$. The Y signal on the other hand increases until $1 \times 10^{15}$ ions/cm$^2$, decreases subsequently until about $6.5 \times 10^{15}$ ions/cm$^2$ after which it stays constant. These profiles can be understood easily when two effects are taken into account: The removal of impurities and the presence of a thin subsurface Y signal, which is higher than the bulk value. The removal of impurities exposes the layer beneath it, causing an increase of the measured Y signal [indicated by 1 in Fig. 5 (a)]. The increase of the Y signal will continue until all impurities are removed from the surface and the Y signal becomes constant. The segregation of Y$_2$O$_3$ to the subsurface results in a subsurface Y signal, which is higher than the bulk value. Continued sputtering will decrease the Y signal [indicated by 2 in Fig. 5 (a)] until it becomes constant. As both processes occur simultaneously, the Y signal in the sputter profile first increases and then decreases until it remains constant at high ion dose. The Zr signal increases by both the removal of impurities as well as the removal of the segregated Y$_2$O$_3$. The sharp increase of the Zr signal with increasing sputter dose [indicated by 1* in Fig. 5 (a)] is caused by the removal of impurities and Y$_2$O$_3$, while the more gradual increase [indicated by 2* in Fig. 5 (a)] is mainly due to sputtering of segregated Y$_2$O$_3$. The Y and Zr signals in the sputter profile of the 10i/YSZ sample [Fig. 5 (b)] develop similar to that of the 3i/YSZ sample. Although the same two processes as in case of the 3i/YSZ sample play a role here, the difference in the profile of the Y signal versus the sputter dose is caused by the smaller segregation factor of Y$_2$O$_3$.

For 1000 °C and higher, all sputter profiles for 3i/YSZ look similar to that of Fig. 5 (a), while those for 10i/YSZ look similar to that of Fig. 5 (b). Below 1000 °C, the sputter profiles look different from that of Fig. 5. Below 1000 °C, less segregation of impurities is observed to the outermost layer compared to the situation above 1000 °C. Therefore, the sharp increase of the Y signal at low dose, as seen in Fig. 5, is not observed in these sputter profiles. Due to the low calcination temperatures only a small Y enrichment is found at the surface. Therefore, the Y signal decreases only slightly with increasing dose until it becomes constant. The Zr signal shows the reverse picture.

In all sputter profiles, both Y and Zr signals reach constant values. For 3i/YSZ, the measured Y/Zr ratio is in all cases 0.06, for 10i/YSZ, the Y/Zr ratio is 0.22. These values are equal to the Y/Zr ratios calculated from the nominal composition of the starting materials. Because preferential sputtering of one of the components (Y, Zr, and O) compared to the others is found negligible for the sputter doses used, the constant Y and Zr LEIS signals represent their oxide concentrations in the absence of segregation (bulk composition). The found relation between LEIS signal and oxide concen-
Arrhenius plot for the segregation of Y$_2$O$_3$ in the 94 ZrO$_2$ matrix.

For calcination temperatures below 1000 °C, the Y$_2$O$_3$ surface concentration can be determined directly from the sputter profiles. For calcination temperatures of 1000 °C and higher, this is not possible due to the presence of the impurities. Therefore, a sputter model is used to determine the Y$_2$O$_3$ concentration in the first (or outermost) and second (or subsurface) layer for all calcination temperatures. In this model, the particles are sputtered at random from the various surface layers. The O concentration is taken the same for all layers and possible preferential sputtering is neglected. The accumulation of impurities is restricted to the outermost layer (concluded from the direct increase of the Y and Zr signals in the sputter profiles like Fig. 5). No distinction is made between the different impurities. The accumulation of Y$_2$O$_3$ is restricted to the outermost layer for calcination temperatures below 1000 °C and restricted to the subsurface layer for calcination temperatures of 1000 °C and higher. The ratio between Y$_2$O$_3$ and ZrO$_2$ in the enriched Y$_2$O$_3$ layer is allowed to vary in the model, in order to obtain the best possible fits for the sputter profiles. For deeper layers, the composition is taken equal to the bulk composition. The sputter rates of the different particles are allowed to vary in the model. The best results, however, are obtained when all sputter rates are taken equal. Typical results of the simulations for the Y and Zr sputter profiles are given by the solid (Y) and broken (Zr) curves in Figs. 5 (a) and 5 (b). The subsurface layer of the 3YSZ sample calcined at 1150 °C [Fig. 5(a)] is composed of 30 mol % YO$_{1.5}$ (=18 mol % Y$_2$O$_3$) and 70 mol % ZrO$_2$, the subsurface layer of the 10YSZ sample calcined at 1400 °C consists of 45 mol % YO$_{1.5}$ (=29 mol % Y$_2$O$_3$) and 55 mol % ZrO$_2$. Figure 6 gives the surface and subsurface Y$_2$O$_3$ concentrations for all calcination temperatures. Below 850 °C, the Y$_2$O$_3$ surface concentration is used to calculate the (sub)surface Y$_2$O$_3$ and ZrO$_2$ concentrations.

3. Interfacial free energy

For calcination temperatures below 1000 °C, the Y$_2$O$_3$ surface concentration can be determined directly from the sputter profiles. For calcination temperatures of 1000 °C and higher, this is not possible due to the presence of the impurities. Therefore, a sputter model is used to determine the Y$_2$O$_3$ concentration in the first (or outermost) and second (or subsurface) layer for all calcination temperatures. In this model, the particles are sputtered at random from the various surface layers. The O concentration is taken the same for all layers and possible preferential sputtering is neglected. The accumulation of impurities is restricted to the outermost layer (concluded from the direct increase of the Y and Zr signals in the sputter profiles like Fig. 5). No distinction is made between the different impurities. The accumulation of Y$_2$O$_3$ is restricted to the outermost layer for calcination temperatures below 1000 °C and restricted to the subsurface layer for calcination temperatures of 1000 °C and higher. The ratio between Y$_2$O$_3$ and ZrO$_2$ in the enriched Y$_2$O$_3$ layer is allowed to vary in the model, in order to obtain the best possible fits for the sputter profiles. For deeper layers, the composition is taken equal to the bulk composition. The sputter rates of the different particles are allowed to vary in the model. The best results, however, are obtained when all sputter rates are taken equal. Typical results of the simulations for the Y and Zr sputter profiles are given by the solid (Y) and broken (Zr) curves in Figs. 5 (a) and 5 (b). The subsurface layer of the 3YSZ sample calcined at 1150 °C [Fig. 5(a)] is composed of 30 mol % YO$_{1.5}$ (=18 mol % Y$_2$O$_3$) and 70 mol % ZrO$_2$, the subsurface layer of the 10YSZ sample calcined at 1400 °C consists of 45 mol % YO$_{1.5}$ (=29 mol % Y$_2$O$_3$) and 55 mol % ZrO$_2$. Figure 6 gives the surface and subsurface Y$_2$O$_3$ concentrations for all calcination temperatures. Below 850 °C, the Y$_2$O$_3$ surface concentration is used to calculate the (sub)surface Y$_2$O$_3$ and ZrO$_2$ concentrations.

The ratio between Y$_2$O$_3$ and ZrO$_2$ in the enriched Y$_2$O$_3$ layer for calcination temperatures of 1000 °C and higher. The Y$_2$O$_3$ subsurface concentrations are 3 and 10 mol % for all calcination temperatures below 950 °C. From the sharp increase that follows and the leveling off at 1000 °C, it is concluded that within 5 h, thermodynamic equilibrium has not been reached within the calcination time of 5 h.

The difference in interfacial free energies ($\Delta F$) between Y$_2$O$_3$ and ZrO$_2$ can be determined in analogy to surface segregation using

$$\frac{n_Y}{n_{Zr}}_{\text{int}} = \frac{n_Y}{n_{Zr}}_{\text{b}} \exp \left( -\frac{\Delta F}{RT} \right).$$

Here, int represents the interface or in this case the subsurface layer, b is the bulk, R is the gas constant, and T is the absolute temperature. The Arrhenius plot is given in Fig. 7. For $T \rightarrow \infty$, the subsurface Y/Zr ratio must be equal to the bulk Y/Zr ratio, independent of the sign and magnitude of $\Delta F$. Equation (2) only holds for thermodynamic equilibrium, which in our case is reached for $T \approx 1000$ °C. The difference in the interfacial free energy ($\Delta F$) is determined to be $-21 \pm 3$ kJ/mol for both 3 and 10YSZ samples, which points to a similar segregation process for both samples.
IV. DISCUSSION

A. Impurities

The high impurity concentrations at the external surface are a consequence of a strong segregation from the bulk. The total molar bulk content of these impurities is about 800 ppm (see Table I, after correction for the atomic weights), which is a quite normal value for oxides. Similar strong segregation of impurities is also observed for many other standard (not isotopically enriched) YSZ samples. The oxygen exchange at the electrolyte surface, which is essential to the operation of the SOFC, involves a kind of Mars–van Krevelen process and needs multivalent cations at the surface. The observed impurities, however, all have a single valency and will, therefore, form a barrier layer for the oxygen exchange. This will have a detrimental effect on the performance of the SOFC. The segregation behavior to the external surface (grains neighboring the gas phase) is also representative for the segregation to the internal grain-boundary network.3,4,20 This means that not only the surface exchange, but also the bulk and grain-boundary diffusion will be influenced by the impurity segregation.

As both the impurities and $Y_2O_3$ seem to segregate to the surface at about the same temperature, a relation between these two has been suggested by Hughes et al.9,21,22 and by Ingo and Padeletti.10 They identify two different chemical bonds with Y for the segregated regions with XPS: An Y-oxide and an Y-silicate bond. Our study shows that the impurities are confined to the outermost layer and $Y_2O_3$ segregates to the layer directly beneath it. It is unavoidable that Si---O---Y bonds are formed in this situation. If an Y silicate is present at the surface, the chemical composition can be determined from the Si/Y ratio.8,9,23 In our study, an average Si/Y ratio of 1.5 is found using the Si concentration in the outermost layer and the $Y_2O_3$ concentration from the subsurface layer. The same ratio is found by Hughes9 for a 10YSZ sample calcined between 1200 °C and 1700 °C. Furthermore, he suggests that the formed compound is a dimeric ion silicate. The difference in the surface free energies between surfactants (all impurities combined) and ZrO$_2$ can be calculated to be at least $-100$ kJ/mol, using Eq. (2). This high value for $\Delta F$ can not be explained from the known values of the surface free energies of the impurities (like SiO$_2$) and YSZ, not even in the inconceivable situation that YSZ becomes completely reduced and the impurities remain fully oxidized.19,24,25 This means that the factors involved in the interaction between surfactants and YSZ have to be taken into account.

Due to the possible relation between $Y_2O_3$ and impurities, it is likely, but unknown, that a different segregation of $Y_2O_3$ would be observed if the total impurity concentration had been reduced below 10 ppm. In that case, the surface of the used samples can not be covered completely by an impurity layer anymore. Theunissen et al.3 claim to observe the same segregation of Y$_2$O$_3$ in pure and SiO$_2$ doped YSZ samples. The pure samples have a Si content of 0.01–0.04 wt %,4 which is comparable to our situation. This means the Si content present in the sample is high enough to cover the surface completely with SiO$_2$, and will do so. The doped samples have an impurity level of 0.5–1 wt % SiO$_2$, which is observed as a surface concentration of only 3 at. % with XPS. In spite of the relatively high Si bulk content, segregation will stop when the driving force, the lowering of the surface free energy, is gone. This point is reached when one monolayer of SiO$_2$ covers the surface. It is therefore not surprising that no different segregation behavior was found between the “pure” and doped YSZ samples.

B. Yttria

1. Fit procedure

In general, quantitative LEIS analysis is based on calibration against reference samples with known surface concentrations. When iYSZ and reference samples ($Y_2O_3$ and $^{94}ZrO_2$) are measured under identical experimental conditions, Eq. (1) reduces to

$$n_i^{YSZ} = \frac{S_i^{YSZ}}{S_i^{reference}} n_i^{reference},$$

with $k \in \{Y,Zr\}$. The problem of this method lies in the fact that, in contrast to Eq. (1), differences in surface structure and density between iYSZ and the reference samples have to be taken into account. Bulk structures of the samples involved26–29 are known, in contrast to their exact surface structures. The density of the iYSZ samples increases after each calcination treatment, caused by the fact that the samples were not treated at high temperature during preparation in order to study the compositional changes during sintering. A rough estimate of the increase in density is obtained by measuring the mass and dimensions of the sample after each calcination treatment. Between room temperature and 1200 °C, the density of the 10iYSZ sample increases by 20%, while the density of the 3iYSZ sample increases even by 96%. Such large increases in the density of YSZ, due to the sintering of the sample, are also encountered in literature.30 Also, the Zr peak of the 10iYSZ sample annealed to 600 °C was already 25% more intense than the corresponding peak of the $^{94}ZrO_2$ sample (used in the TOF-LEIS measurements).

Binary peaks in the LEIS spectra are usually fitted with symmetrical functions like Gaussians31 or Lorentzians.32–34 This finds its origin on empirical grounds32 or on the assumption that the energy distribution of the ion source is Gaussian shaped and all other broadenings are symmetrical.35 If the Y and Zr peaks are fitted with normal Gaussian functions, the $Y/Zr$ ratio would be overestimated by at least 10%, mainly caused by the fact that the Y peak lies on the low-energy tail of the Zr peak. Only after the use of TOF-LEIS, it could be concluded that the asymmetry is an inherent feature of the LEIS peaks and, consequently, that symmetric functions can not be used. The asymmetry of the Zr peak is, however, exaggerated as the used ZrO$_2$ powder is not 100% pure $^{94}ZrO_2$ (see Table I). Strictly speaking, the presence of the five Zr isotopes requires that the Zr peak is fitted with five asymmetrical Gaussian functions. However, a fit with only one peak is preferred. This last situation is justified by the small difference (less than 1%) in surface peak areas as determined by fitting the Zr peak with one or five
asymmetrical Gaussian functions. The background is often approximated by a linear or Shirley-type function. Such a background refers to backscattered $^{40}$Ar$^+$ ions. This is only a small part of the total background, as can be added to the TOF-LEIS spectrum of sputtered particles with mass higher than 40 amu. Calcinating the YSZ samples at temperatures in excess of 950 °C results in a surface that is covered by impurities. This means that besides ions containing only Y, Zr, and O, ions also containing Si, Na, and/or Ca can be expected to contribute to the background intensity. A difference in the overall shape of the background is, however, not observed and it can still be described by the same exponentially decaying function.

2. Segregation

The driving force for impurity segregation should be the lowering of surface or interfacial energy. The segregation of Y$_2$O$_3$ to the subsurface layer might be a combination of strain relaxation and a different bonding for the Y$_2$O$_3$ particle (it might be energetically favorable for Y$_2$O$_3$ to bind with SiO$_2$ instead of ZrO$_2$). For 3YSZ samples calcined at 1000 °C, an Y$_2$O$_3$ surface concentration of 7.5 mol % is generally reported in literature. Only Theunissen$^2$ found a concentration of 18 mol % Y$_2$O$_3$. For 10YSZ samples, the literature value is 18 mol %. The absolute concentrations found in this study are 18 and 30 mol % for the 3 and 10YYSZ samples, respectively, and thus a factor 2.4 and 1.7 higher than the values reported in literature. This is related to the much higher surface sensitivity of LEIS with respect to techniques like AES and XPS, but also to the fact that an impurity layer covers the YSZ surface. The thickness of the Y$_2$O$_3$ enriched layer is at most 5 Å or one ZrO$_2$ unit cell (impurities not included), in contrast to values reported in literature ranging from 20 to 60 Å.$^{38,42}$

Although there are several models describing the segregation of Y$_2$O$_3$ in ZrO$_2$,$^{44,45,47}$ only Hughes$^{45}$ has actually tried to determine the segregation enthalpy. However, the large probing depth of XPS and the presence of a large quantity of carbon at the surface, besides the impurities Si, Na, and Fe, cloud his results.

It is interesting to note that the difference in surface segregation enthalpies of Y$_2$O$_3$ and ZrO$_2$ can be calculated to be $\sim 12.3$ kJ/mol, based on an interfacial energy contribution, a binary interaction term and a solute strain contribution.$^{45}$ This value corresponds both in sign and order of magnitude with the value found in our work.

V. CONCLUSIONS

The YSZ surface is completely covered by the oxides of the impurities Na, Si, and Ca after calcination to 1000 °C or higher. This strong segregation of impurities is a general phenomenon in YSZ. The impurities are restricted to the outermost surface layer, which supports the use of LEIS in these studies. Due to the stability of the impurity oxides, a barrier for oxygen exchange is formed. It is estimated that a total bulk impurity level of 10 ppm will still poison more than half of the YSZ surface. Since the impurities will also segregate to the grain boundaries, they will also influence the grain-boundary diffusion coefficient of the oxygen ions. This will have detrimental consequences for the performance of the SOFC. Y$_2$O$_3$ accumulates in the subsurface layer for calcination temperatures in excess of 1000 °C. Above 1000 °C, the Y$_2$O$_3$ concentration in the subsurface layer is about 18 and 30 mol % for the 3 and 10 mol % YSZ samples, respectively. This is a factor of 2.4, respectively, 1.7 higher than values reported in literature, where it is assumed that yttria segregates to the outermost surface layer. From the Arrhenius plot, a difference in interfacial free energies between Y$_2$O$_3$ and ZrO$_2$ of $\sim 21$±3 kJ/mol has been determined.

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