Effect of water adsorption on conductivity in epitaxial $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ thin film for micro solid oxide fuel cells applications

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Water adsorption, splitting, and proton liberation were investigated on $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ thin films by scanning probe microscopy. An irreversible volume expansion was observed by applying a positive bias with increased temperature. The volume expansion is also linearly dependent on the relative humidity. A reversible water adsorption process and its effect on the conductivity were also investigated by electrochemical strain microscopy and first order reversal curve under a number of experiment conditions. The presence of a Ce^{3+} along with OH groups, detected by hard x-ray photoemission spectroscopy established a clear correlation between the water incorporation and the valence state of Ce.

Introduction

Recent decade has seen a renewed attention to the well-known doped Ceria compounds due to the presence of possible proton conduction at temperature below 300 °C in these materials, which make them promising candidates for low temperature solid oxide fuel cells membranes.[1-3] Proton conduction depends on the efficient adsorption of water molecules at oxygen vacancy sites,[4] whose concentration can be controlled via doping by trivalent rare-earth elements.[5] Despite a number of independent contributions being reported on the water interaction with the ceria-based materials,[6,7] the adsorption and the proton conduction mechanism are still poorly understood.

In the present work we report on the reactivity and proton transport properties of 10% Sm doped CeO_2 (10% SDC). A comparison between CeO_2 and SDC with different Sm content has been reported previously in ref. [8] Here we additional insight to 10% SDC due to the popularity of the $\text{Ce}_{1-x}\text{Sm}_x\text{O}_2$ system, with its high conductivity and relatively good stability in a reducing atmosphere.[9] This study employed epitaxial films grown on (110) NdGaO_3 (NGO) substrates with a thickness of 300 nm. Therefore, we can rule out the influence of microstructural features, such as grain boundaries,[10] and ensure good reproducibility and unambiguous data interpretation.

We used atomic force microscopy (AFM) to map as a function of air humidity the topographic transformation of the sample surface as a result of irreversible reactions. Then, the reversible electrochemical processes were probed by electrochemical strain

microscopy (ESM) [11] in different humidity and temperature (below 110 °C). We further explored the dynamic properties with regard to the charge carrier transport by studying the behavior of the contact resonance frequency in the first order reversal curve (FORC) mode. [12] This approach is complementary to most of the studies reported in literature performed by Electrochemical Impedance Spectroscopy (EIS) experiments.[13] In fact, ESM can be used at lower temperature to investigate the electrochemical systems, where the ion transfer is crucial, without the drawback of fitting the experimental spectra as in the case of EIS. In addition, it provides a 10-20 nm spatial resolution, surpassing EIS in that by 3 orders of magnitude. The sensitive surface characterization was also complemented with bulk spectroscopic information obtained by hard x-ray photoemission spectroscopy (HAXPES). The whole set of experimental data allowed us to understand the surface reaction and charge carrier mechanisms in 10% SDC film, thus shedding more light on the important and still controversial issue of the origin of the water-dependent proton conduction behavior.

Experimental

10% SDC epitaxial thin films were grown by Pulsed Laser Deposition using an excimer pulsed laser source (KrF, $\lambda = 248$ nm), with an energy density of 5 J/cm², substrate temperature of about 600 °C and oxygen partial pressure of 5 Pa.

The structural properties were investigated by x-ray diffraction using a Rigaku D-max diffractometer with Cu K α radiation in the θ -2 θ and rocking curves mode.

The ESM measurements were performed using a Bruker Multimode 8 equipped with a heating stage to change the sample temperature [14] and an environmental cell connected to an air tank through a humidifier, to change the relative air humidity in the range between 1% to about 80%. A custom LabVIEW/Matlab based Band Excitation software was used for voltage and time spectroscopies [15,16].

The HAXPES measurements were performed at the beamline I09 at the Diamond Light Source, UK using a photon energy of 6.054 keV and an energy resolution of <250 meV obtained by a channel-cut Si (004) crystal in addition to the primary double crystal monochromator. The photoelectrons were detected with a EW4000 photoelectron analyzer (VG Scienta, Uppsala, Sweden) mounted in the polarization direction of the photon beam. Photoemission measurements were performed at 400 K, the binding energy scale was calibrated to the Fermi edge cutoff of an Au reference sample.

Results and discussion

The surface topography by AFM reported in Figure 1 (a) shows that the surface is essentially featureless and the root mean square roughness is less than 1 nm, thus allowing scanning probe microscopy measurements unaffected by topography crosstalk. XRD pattern and rocking curve of the 10% SDC/NGO film are shown in Figure 1 (b) and (d), respectively. It can be seen that the film is (00 l) oriented following the same crystallographic orientation of the NGO substrate in pseudocubic notation. No spurious phases or other orientations are present. The epitaxial relationship between the SDC and the pseudocubic cell of NGO substrate is shown in the Figure 1 (c). The SDC film grows with a 45° in plane rotation of the cubic crystallographic axes relative to the orientation of NGO substrate. The good epitaxial growth and crystal quality are confirmed by the small value (about 0.1°) of the full width at half maximum of the rocking curve measured across the (002) reflection. From the XRD data we obtain a lattice parameter of 0.542 nm in agreement with the bulk value reported in literature.

Figure 1. (a) AFM topography of the 10% SDC film. (b) θ -2 θ XRD pattern. (c) A schematic of the structural relationship between SDC and NGO substrate. (d) Rocking curve for the (002) film reflection.

In order to establish the reactivity of the 10% SDC, first the effect of humidity was investigated by biasing samples with the AFM tip. The sample surface was poled with +35 V DC bias applied to the tip at a scanning rate of 0.2 sec/lin. A gradual volume expansion of a few nanometers was observed as the relative humidity (RH) of the air gas increased from 10 to 50%. However, the expansion occurred only above 80 °C as shown in Figure 2 for RH = 10-50%. This finding can be considered a direct proof of the water incorporation, which is fully consistent with the water-mediated electrochemical mechanism observed on pure CeO₂.^[17] However, while for pure CeO₂ film the expansion is observed already at room temperature (RT), a higher temperature is required for the 10% SDC film, indicating that 10% of doping with Sm in SDC inhibits the efficiency of this process.

Figure 2. Plot of the average volume expansion as a function of RH = 10%, 25% and 50%, together with the corresponding AFM deflection images. The measurements were performed at T = 80 °C and +35 V applied to the tip. c)

Having described the irreversible electrochemical behavior of 10% SDC, we now turn our attention to the reversible electrochemical regime, which can be probed by ESM. Note that this technique is much sensitive than the current-based electrochemical methods[18] Therefore, it allows us to study low temperature electrochemical reactions and their effects on the transport process. ESM is developed to study the ionic motion and electrochemical reactions at nanoscale depending on the working conditions and the material properties. In fact, when the tip is biased, oxygen vacancies can be created/annihilated by extracting/inserting their spots oxygen ions or hydroxyl groups from/into the lattice. The subsequent oxygen ion or proton motion results in a localized strain under the tip, which can be detected through the dynamic surface displacement by the AFM cantilever. ESM results obtained at RT and different RH levels are presented in Figures 3 (a). The ESM hysteretic behavior arises as a consequence of the difference in the positive and negative nucleation biases required to activate the processes of injection or annihilation of the vacancies and ions. Therefore, the hysteresis loop area is directly proportional to the change in the ion concentration induced by the voltage cycle. As we can see for the 10%SDC, the loop area decreases with increasing humidity. These behaviors can be more clearly seen in Figure 3 (b), which the loop area is plotted as a function of p_{H_2O} in a log-log plot. The dependence is linear, and the positive sign of the slope suggests that 10% SDC can be considered as a prevalently proton conductor.[19]

We further explored the temperature dependence of the ESM response to extract the activation energy of underlying process.[20] The measurements were performed at various temperatures in air with 50% RH. The ESM hysteresis loop variation reported in Figure 3 (c) shows an increase of the loop area as a function of temperature for both samples. The increase of ESM loop area is due to the thermal activation of ionic and proton mobility, being related to the increase in concentration variation of the prevalent charge carriers type. Therefore, the activation energy for the diffusion process, i.e. the energy that ions and protons need to possess in order to break the inter-atomic bonds and

to jump to the new position, can be obtained from the Arrhenius plot. The estimated local activation energy is about 0.4 eV for 10% SDC (Figure 3 (d)), which is in agreement with macroscopic measurements reported in literature for a typical proton conductor.[21]

Figure 3. (a) Averaged ESM hysteresis loops measured at three different values of relative humidity for 10%SDC (b) Loop area is plotted as a function of relative humidity. (c) Averaged ESM hysteresis loops obtained at three different temperatures for 10% SDC and (d) Arrhenius plot of the loop area. Loops were recorded over a square grid of 10×10 points (corresponding to a $1 \times 1 \mu\text{m}^2$ sample area) for each sample and averaging was performed over all pixels (i.e. 100 individual curves).

To study the on-site transport mechanism of the electrochemical reaction-diffusion process and its voltage dependence, we used the first order reversal curves (FORC) method, which allows systematic tracing of the loop evolution.[22] The measurements were performed at two different humidity levels, namely, in dry air and wet air (50% RH) at room temperature.[23] The FORC ESM results obtained for 10% SDC are reported in Figure 4. The spectral response (cantilever oscillation vs. excitation frequency) during measurements was obtained in Band Excitation mode for each material, using the same AFM tip, as shown in in Figure 4 (a) and (b) for dry and 50% RH air, respectively. The resonance frequency depends on the changes in mechanical properties of the tip-surface junction.[24-26] It can be observed that the resonance frequency increases from about 350 kHz in dry, up to about 385 kHz in 50% RH, which can be explained in terms of good hydrophilic properties..

Figure 4. FORC-type ESM measurements on the 10% SDC film: 2D plot of the amplitude spectra of the cantilever resonance response in dry (a) and 50% RH atmosphere (b) as a function of the DC bias waveform reported in the same graph (white line). Average loops over a square grid of 10×10 points (on a $1 \times 1 \mu\text{m}^2$ sample region) measured in dry air (c) and wet atmosphere (d). The loop areas are reported in the insets with the same axes range.

The loop area is proportional to the ion/proton concentration variation (Δc) which depends linearly on the driving force, and therefore on the maximum excitation bias V_{max} , as shown in the insets of panels (c) and (d) of Figure 4. If we consider $\Delta c = A + B \cdot V_{max}$, the slope B is related to the charge carriers (ion e/o proton) mobility in a non trivial way, while the intercept of the linear behavior of Δc with x-axis $V_c = -A/B$ can be interpreted as the critical voltage needed for the activation of the electrochemical reaction process. (). Water splitting with subsequent injection of liberated protons into the film can be described in Kroger-Vink notation as: $H_2O + 2O_O^\times \rightarrow 2OH_O^\bullet + \frac{1}{2}O_2 + 2e'$. The redox potential of this process is given by Nernst equation: $E_{red} = E_{red}^\circ - 0.059pH - \frac{0.059}{2} \log_{10}[H_2O]$. Thus, since V_c is proportional to E_{red} , one should observe a decrease in V_c moving from dry to wet conditions.[22] It can be seen that V_c decreases from 18 V to 10 V from dry to wet condition, as expected. .

The chemical state of the elemental constituents was obtained by HAXPES measurements. The usage of hard x-rays with a probing depth of about 20 nm allowed diminishing dependence of results on the surface contaminations. The most interesting information was obtained by the O 1s and Ce 3d core level spectra reported in Figure 5. For the fitting procedure, we subtracted Shirley background and used a mixed Gaussian and Lorentzian line shape for each component. For O 1s spectra, three main components can be observed: the hydroxyl (OH) groups (532.5 eV), Ce^{4+} (529.52 eV) and Ce^{3+}/Sm^{3+}

(530.10 eV), where we used a single peak for Sm^{3+} and Ce^{3+} because the separation of the binding energy is not uniquely determined in literature.[19] Using three components for fitting procedure we obtain $[\text{OH}] = 21\%$ and $[\text{Ce}^{3+} \& \text{Sm}^{3+}] = 33\%$. Assuming a nominal concentration of Sm^{3+} (10%), we can estimate the Ce^{3+} concentration being about 23%.

In the case of Ce 3d spectra, we have to consider the spin-orbital splitting of the Ce $3d_{5/2}$ and Ce $3d_{3/2}$ and other splitting that are caused by a redistribution of the entire energy spectrum after a core hole is created.[27] There are four peaks (v_0, v' for $3d_{5/2}$ and u_0, u' for $3d_{3/2}$) that are derived from Ce^{3+} (see Figure 5(b)), and the other six are from the Ce^{4+} valence state.

Using this fitting procedure we obtain a Ce^{3+} concentration around 24%, very close to the estimation by the O1s spectra. Despite the slight discrepancy between the estimations obtained from the O 1s and the Ce 3d core level spectra, the quite high Ce^{3+} content induces the formation of about 12% oxygen vacancies in addition to the 5% already formed by the 10% Sm doping. When Ce is reduced from 4+ to 3+ oxidation state, the mobile electrons favor water adsorption on the film surface. In fact, the adsorbed hydroxyl group can be clearly observed in the O 1s core level in panel (a).

Figure 5. O1s (a) and Ce3d (b) core level HAXPES spectra for 10%SDC. Experimental data (open circles) are compared with the fit results (straight black line), obtained as the envelope of the fit curve components reported in the panels as filled and empty colored panels. In panel (a) [cyan area corresponds to OH, magenta to Ce^{4+} , and green to $\text{Ce}^{3+} \& \text{Sm}^{3+}$. In panel (b) the filled areas indicated by the vertical dashed line correspond to the main contributing component for Ce^{3+} .

It is generally accepted that pristine CeO_2 can be easily reduced to non-stoichiometric CeO_{2-x} . The consequent formation of Ce^{3+} mainly compensates for the formation of positively charged oxygen vacancies. The process of CeO_2 reduction in the Kroger-Vink notation can be written as:

Where $\text{Ce}_{\text{Ce}}^{\times}$ and $\text{O}_{\text{O}}^{\times}$ are the Ce^{4+} and the O^{2-} in the normal lattice, Ce_{Ce}' is the Ce^{3+} having one less positive charge compared to the Ce^{4+} , V_{O}'' is the double positively charged oxygen vacancy and O_2 is the molecular oxygen.

Oxygen vacancies can be introduced in SDC by doping with trivalent metal oxide, using Sm_2O_3 :

where Sm^{3+} is hosted in the Ce^{4+} lattice site with one less positive charge, i.e. Sm'_{Ce} in Kroger-Vink notation. Oxygen vacancies are then formed to compensate for the charge imbalance.

Moreover, reaction (1) can also take place in SDC, where the concomitant Sm doping by reaction (2) will naturally affect the equilibrium of the first reaction. Now let's consider the water adsorption's behavior in 10% SDC. It is known that the surface of CeO_2 oxide is catalytically active and capable of trapping a variety of molecules, including water, can be trapped there.[28] Ce^{3+} and oxygen vacancies are believed to be the active sites in the following hydrogen evolution reaction:[29]

The increase of $[\text{Ce}^{3+}]$, i.e. Ce'_{Ce} in Kroger-Vink notation, will increase the efficiency of this reaction. Assuming no interaction between the various defects, the law of mass action applied to reaction (4) gives:

$$K = \frac{[\text{OH}_\text{o}']P_{\text{H}_2}^{1/2}}{P_{\text{H}_2\text{O}}[\text{Ce}'_{\text{Ce}}][\text{V}_\text{o}'']} \quad (5)$$

In the air atmosphere and at high partial pressure of water vapor and therefore high concentration of OH_o' , one may assume that the majority defects is OH_o' thus we can get:

$$\text{OH}_\text{o}' \propto P_{\text{H}_2\text{O}} \quad (6)$$

This is what we observe in the Figure 2.

In summary, we observed local electrochemical transformation of 10% SDC, which is strongly dependent on the relative humidity. The volume expansion can be associated with the water adsorption on the film surface. The transport mechanism for 10% SDC film was studied by ESM revealing that the hysteresis loop area increases with the water partial pressure, thus demonstrating that the prevalent charge carrier type is the proton. The FORC-type ESM measured was performed to separate the on-site electrochemical reaction and transport process. We observed an increase of the resonance frequency moving from dry to wet air. This can be associated with the higher proton exchange reaction rate. This faster movement of the proton through the film is accompanied by a lower activation energy i.e. a lower energy needed to activate the surface electrochemical reaction.

It has been reported that the water adsorption process at the surface of CeO_2 is energetically favored when Ce^{3+} is present.[30] As a consequence, water can be trapped in the sample, due to the presence of the active Ce^{3+} and oxygen vacancies. Water partially dissociates yielding hydroxyl groups, which fill some of the oxygen vacancies. This is supported by HAXPES measurements at the O1s core level of Figure 5, showing the presence of hydroxyls. Hydroxyl groups can be localized or give rise to proton conduction by hopping between oxygen sites. Finally, our combined study sheds more light on the important and still controversial issue of the origin of water-dependent proton conduction.

Acknowledgments

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