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Mapping electrochemically driven gas exchange of mixed conducting $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{1.9}$ thin films by ^{18}O tracer incorporation under reducing atmosphere

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ABSTRACT

Thermally and electrochemically driven ^{18}O tracer exchange experiments in $H_2/H_2{}^{18}O$ atmosphere were performed on $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ thin films on single crystalline YSZ substrates. Noble metal current collectors were deposited on both films and electrochemically polarized during the exchange experiment. The resulting tracer distribution was analyzed by spatially resolved secondary ion mass spectrometry. Increased tracer fraction near the current collectors was found under cathodic polarization and decreased tracer fraction under anodic polarization. High cathodic bias leads to enhanced n-type electronic conductivity, which increases the extent of the electrochemically active zone.

1. Introduction

Mixed ionic and electronic conduction (MIEC) is widely investigated for intermediate-temperature solid oxide fuel cell (SOFC) cathodes [1–3] and there is also strongly growing interest in applying reduction stable MIECs as SOFC anodes [4–10]. Studies on some perovskite-type porous anodes demonstrated low area specific resistance and high stability for redox cycling [4–7]. For ceria-based anode materials also mechanistic investigations on geometrically well-defined thin films have been performed [8–10]. However, details on the surface exchange rate and ionic or electronic conductivity are still scarce for most oxide electrodes in reducing atmosphere. Additional measurements, also employing new analysis methods, are therefore of high relevance for a better understanding of the properties of mixed conducting anodes and the search for new materials.

It has been demonstrated that isotope exchange with subsequent SIMS analysis is a very powerful tool to monitor the surface reaction kinetics and the bulk diffusion of oxygen in SOFC electrode and electrolyte materials under both equilibrium and polarized conditions [11–18]. Moreover, because of the relatively high lateral and depth resolution of SIMS, the electrochemically active regions of the electrodes can be visualized. This has already been shown for cathode materials [14,17], while in reducing atmosphere imaging of oxygen incorporation zones by voltage driven ^{18}O tracer exchange is rarely employed.

In the present study, we analyze the distribution of ^{18}O in polarized and non-polarized thin films of $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ (STFO) and $Ce_{0.8}Gd_{0.2}O_{2-\delta}$ (GDC) on yttria stabilized zirconia (YSZ) substrates. By comparison of the tracer distribution after thermally driven oxygen exchange and after experiments with cathodic and anodic bias, the width of the electrochemically active region and the factors governing the oxygen exchange could be visualized.

2. Experimental

2.1. Sample preparation

The GDC target ($Ce_{0.8}Gd_{0.2}O_{2-\delta}$) for pulsed laser deposition was prepared from powder (Treibacher, Austria) by isostatical pressing and subsequent sintering at 1550 °C for 5 h. The STFO ($SrTi_{0.7}Fe_{0.3}O_{3-\delta}$) powder was prepared by solid state reaction from $SrCO_3$ (99.99% pure, Sigma-Aldrich), TiO_2 (99.99% pure, Sigma Aldrich), and Fe_2O_3 (99.98% pure, Sigma Aldrich). The educts were thoroughly mixed, calcined at 800 °C, ground, again calcined at 1000 °C, and—after a further grinding step—isostatically pressed and sintered at 1250 °C. The phase purity of both targets was confirmed by X-ray diffraction. STFO and GDC thin films were deposited on (100)-oriented yttria stabilized zirconia single crystals (YSZ, 9.5 mol% Y_2O_3 in ZrO_2, supplier: CrysTec, Germany) by pulsed

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laser deposition (PLD) using a KrF excimer-laser (Lambda COMPexPro 201 F, 248 nm wavelength). The deposition of 200 nm thin films was carried out in 4×10^{-2} mbar of pure oxygen with a pulse repetition rate of 5 Hz and a nominal pulse energy of 400 mJ. The substrate temperature during the deposition was controlled by a pyrometer (Heitronics, Germany) and was 650 °C.

2.2. Electrode design

Acceptor-doped mixed conductors are often very good electronic p-type conductors in oxidizing atmosphere. For such materials, an electric contact with a metallic tip is typically sufficient for a homogeneous polarization of a small thin film electrode [19]. In reducing atmosphere, however, the p-type conductivity decreases by several orders of magnitude. Despite acceptor doping $SrTi_{0.7}Fe_{0.3}O_{3-\delta}$ (STFO) and $Ce_{0.8}Gd_{0.2}O_{1.9}$ (GDC) are even weak n-type conductors in reducing atmosphere at the ^{18}O exchange temperature [20–23]. Due to the much lower electronic conductivity compared to oxidizing conditions, the electrochemically active region is expected to be limited to a small area around the electric contact. In order to investigate the width of this active region, rectangular (160 μm × 400 μm) noble metal current collectors were sputter deposited (MCS 020, BAL-TEC AG, Germany) in two steps: on top of the YSZ substrate (prior to MIEC deposition) and on top of the deposited MIEC layer. The sample design is sketched in Fig. 1a; bottom and top current collectors and one large counter-electrode were placed on one and the same sample. The bottom current collectors (5 nm Ti/100 nm Pt) were structured from a thin film by ion beam etching, the top electrodes (5 nm Cr/100 nm Au) were produced by a lift-off method. For the buried current collectors platinum was chosen, since it is sufficiently stable during subsequent PLD deposition of the oxide. For the top electrodes Au was used owing to its poor catalytic activity to avoid three phase boundary activity. For the sake of clarity, the electrode regions with contacting noble metal collectors are named as electrodes with top current collectors (ET) and electrodes with bottom current collectors (EB), and abbreviations ET and EB are used throughout the text.

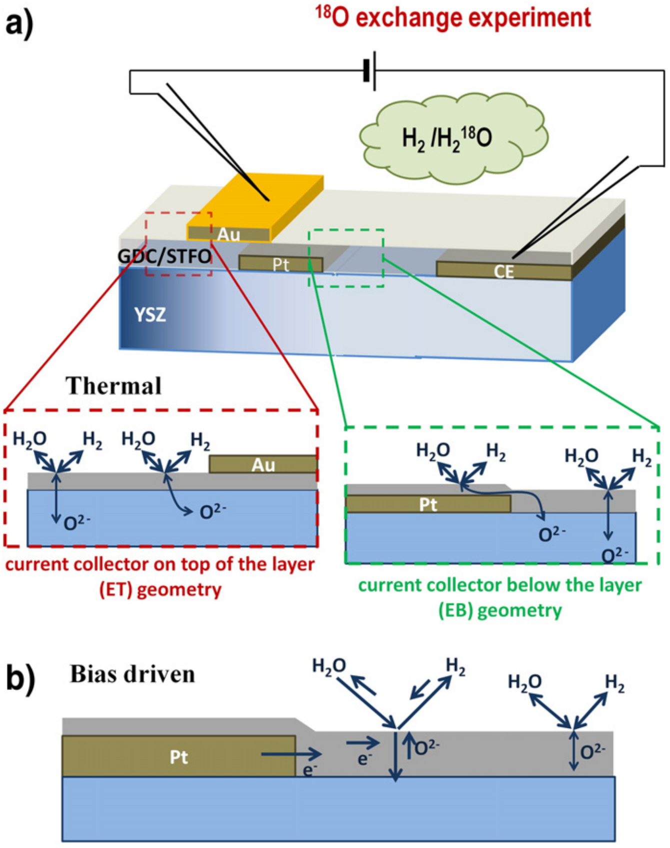

Fig. 1. (a) Noble metal electrodes, which provide an electrical contact and block oxygen diffusion were prepared below (EB geometry) and on top (ET geometry) of the GDC or STFO layer. The oxygen diffusion pathways under equilibrium conditions are sketched for ET and EB current collectors. Working and counter electrodes were contacted and polarized in the tracer exchange chamber. (b) Increased oxygen incorporation rate caused by cathodic bias near an EB current collector; in some distance from the current collector edge only thermally driven tracer exchange remains due to limited electronic conductivity within the MIEC thin film.

2.3. Procedure of the isotope exchange experiments

A mixture of hydrogen and ^{18}O tracer enriched water was used to carry out the experiments in a thermodynamically defined, reducing atmosphere. This atmosphere was produced by mixing diluted hydrogen (2.5% H_2 in Ar, Alphagaz ARCAL 10, Air Liquide) with a defined amount of $^{18}O_2$ (97% isotopic enrichment, 0.625% O_2 in the mixture) and feeding this mixture through a platinum sponge at 500 °C to form a gas containing equal amounts of water and hydrogen. The formation of tracer-enriched water with a tracer fraction of 60–70% was monitored by a mass spectrometer (Pfeiffer, OmniStar GSD 320). Probably the (porous) quartz supported Pt catalyst, which is present in the reaction chamber, is a source of oxygen exchange and therefore reduces the tracer content in the resulting atmosphere. In this reducing, tracer containing atmosphere, the samples were heated from room temperature to 410 ± 10 °C for 10 min and were subsequently quenched to freeze the distribution of ^{18}O (the corresponding oxygen partial pressure in the mentioned humid hydrogen atmosphere at 410 °C can be calculated to be 8.4×10^{-30} bar [24]). The heating and cooling rate was 150 °C/min, so the time of sample heating and cooling was short compared to the exchange experiments. During the exchange process, on each sample one ET and one EB current collector were simultaneously polarized against the counter electrode—cf. Fig. 1a. Current flow and out of equilibrium reaction for ET polarization are sketched in Fig. 1b in more detail. In this manner, the tracer distribution can be monitored in the MIEC above the electrolyte, above the EB current collectors and beneath ET current collectors for the case of pure thermal diffusion as well as for different dc polarization on the same sample.

The resulting ^{18}O distribution in the thin films was subsequently investigated by means of time-of-flight secondary ion mass spectrometry (ToF-SIMS). These measurements were done on a ToF-SIMS 5 machine (ION-TOF GmbH, Germany) in collimated burst alignment (CBA) mode, which allows accurate determination of ^{18}O concentration in oxides [25, 26]. As primary ions Bi_3^{++} were used (25 kV accelerating voltage). Negative secondary ions were analyzed in areas of 50 μm × 50 μm and 160 μm × 160 μm, using a raster of 512 × 512 and 1024 × 1024 pixels, respectively. For the sputtering of material Cs^+ ions (1 kV accelerating voltage) were used with a sputter crater of 500 μm × 500 μm and a sputtering ion current of 70 nA. The charging of the surface was compensated with an electron flood gun and partly by additional argon flooding if the electron flood gun was not sufficient. The isotope fraction (f_{18O}) was obtained by normalizing integrated intensities (I) via $f_{18O} = I_{18O}/(I_{18O} + I_{16O})$.

In Fig. 1a, the different locations of the SIMS analysis and the pathways of thermally driven gas exchange are sketched. The metal layers are supposed to be sufficiently blocking for oxygen, which was experimentally confirmed by measuring a tracer fraction close to natural abundance beneath the EB current collector as well as beneath the ET collectors (see Section 3). The remaining slight tracer enrichment beneath the Au current collectors (ET), which is nearly two orders of magnitude lower than without a metal layer, may be due to some grain boundary diffusion of oxygen through the metal layer [13]. Nonetheless, the amount of tracer beneath the current collectors is sufficiently small to assume blocking metal layers in the discussion. In order to compare the lateral isotope distribution of different electrodes, the current