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Oxygen exchange kinetics of epitaxial $\text{PrBaCo}_2\text{O}_{5+\delta}$ thin films

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The oxygen exchange kinetics of thin films of the oxygen-deficient double perovskite $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) have been determined by electrical conductivity relaxation (ECR) and by oxygen-isotope exchange and depth profiling (IEDP). Microstructural studies indicate that the PBCO films, prepared by pulsed laser deposition, have excellent single-crystal quality and epitaxial nature. The ECR and IEDP measurements reveal that the PBCO films have high electronic conductivity and rapid surface exchange kinetics, although the ECR data indicate the presence of two distinct kinetic pathways. The rapid surface kinetics compared with those of other perovskites suggest the application of PBCO as a cathode material in intermediate-temperature solid oxide fuel cells. © 2006 American Institute of Physics. [DOI: 10.1063/1.2163257]

Solid oxide fuel cells (SOFCs) generate electrical power with high efficiency and are nonpolluting.¹ For commercialization, operation of SOFCs at intermediate temperatures (500–700 °C) is desirable in order to permit the use of metallic interconnects and to reduce costs.^{2,3} At lower temperatures, the cathode resistance becomes the limiting factor in determining the overall cell performance and consequently new improved cathode materials are needed.⁴ Current efforts are aimed at finding oxides that are electrolyte compatible and which have the required high oxygen diffusion and surface exchange kinetics necessary for low electrode resistance.^{1,3,5} Recently, using electrical conductivity relaxation (ECR) and thermogravimetric analysis on bulk ceramic materials, we have found that $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) has unusually rapid oxygen transport kinetics at low temperatures (300–500 °C), suggesting its application as a cathode in SOFCs.⁶ Similar results have been reported recently for $\text{GdBaCo}_2\text{O}_{5.5+\delta}$.⁷

To study electrode behavior, most of the previous studies have used porous electrodes, where uncertainties in the microstructure can lead to difficulties in interpretation of experimental results.⁸ The use of dense thin films with well-defined microstructures and geometry is one approach to avoid the complex issues of porous electrodes.^{9–12} In this work, we have synthesized highly epitaxial PBCO thin films by using pulsed laser deposition (PLD) and have systematically studied their oxygen transport kinetics by electrical conductivity relaxation (ECR) and by isotope exchange and depth profiling (IEDP).

PBCO has an oxygen-deficient double perovskite structure (Fig. 1) with space group $Pmmm$. PBCO powder was made by the Pechini method.¹³ Stoichiometric amounts of Pr_6O_{11} , barium, and cobalt nitrates were dissolved in dilute nitric acid. Ethylene glycol and citric acid were added to the solution and the mixture was stirred at 150 °C until it

formed a dry foamed resin. Further heating at 300 °C and then at 600 °C for 24 h periods decomposed the dry foam containing residual organic components. A pellet of 1 in. diameter was pressed from the powder and then sintered in air at 1100 °C for 10 h to serve as the target for PLD. The pellet was shown to be single phase by powder x-ray diffraction and the cell parameters were determined by Rietveld refinement using the GSAS program to be $a=3.9084(1)$ Å, $b=3.9052(1)$ Å, and $c=7.6343(1)$ Å. Thin films of PBCO were deposited on rectangular (001) oriented SrTiO_3 (STO) single-crystal substrates (10 mm × 3 mm) because of the excellent lattice match. The typical PBCO film thickness is ~1950 Å.

FIG. 1. The structure of $\text{PrBaCo}_2\text{O}_{5+\delta}$: oxygen, barium, cobalt, and praseodymium atoms are shown as partially shaded, shaded, filled, and gray circles, respectively. The partially occupied oxygen atom sites are shown as cross-hatched circles.

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FIG. 2. Grazing incidence diffraction scans along the substrate's [200] direction for different scattering depths. The curves are shifted for clarity. Labeling of the PBCO peaks is according to the $Pmmn$ structure. The asterisk marks an (unknown) interfacial phase.

The PBCO films were characterized by x-ray diffraction using the z -axis diffractometer at the NSLS beamline X22C with a wavelength of 1.5406 Å. In the grazing incidence geometry, the incident angle was selected by rotating the diffractometer against the incoming beam and the exit angle was defined to be the same as the incident angle by a pair of slits. Radial scans along the STO [200] in-plane direction using different scattering depths Λ are shown in Fig. 2. In addition to the PBCO (004) reflection ($c_{\text{PBCO}}=7.727$ Å), the PBCO (200) ($a_{\text{PBCO}}=3.908$ Å) peak is superimposed on the STO (200) ($a_{\text{STO}}=3.905$ Å). The rocking curve (width in θ) of the PBCO (002) reflection has a full width at half-maximum of only 0.1° , compared to a resolution-limited width of the STO (002) of 0.007° , indicating that the PBCO thin films on (001) STO have excellent single crystallinity and are epitaxial. Upon increasing Λ , an interfacial peak at $2\theta=41.2^\circ$ becomes visible. This interfacial phase exhibits a much smaller coherence length (140 Å) than the remainder of the film. The interface relationship was determined from this scan and corresponding out-of-plane scans to be $[001]_{\text{PBCO}} \parallel [100]_{\text{STO}}$, and $[010]_{\text{PBCO}} \parallel [001]_{\text{STO}}$.

The electrical conductivities of PBCO films on STO substrates in air were measured to determine the high-temperature transport properties. As the temperature is increased, the conductivity first increases due to thermal activation and then falls as the film starts to lose oxygen with an accompanying decrease in the hole concentration (Fig. 3). The transition point is near 645 K. It is important to note that the PBCO films on (001) STO have excellent electrical conductivity ($\sim 10^2$ S/cm²) over a very broad temperature range from 300 to 1000 K. Compared with the traditional electrode materials such as (La,Sr)MnO₃ or (La,Sr)(Co,Fe)O₃, PBCO thin films have much better electrical conductivity, especially in the low-temperature region.

The oxygen transport kinetics in the PBCO films were determined by electrical conductivity relaxation and isotope exchange and depth profiling in various oxygen environments. Both techniques measure only the ionic contribution to the transport kinetics. In ECR experiments, the sample is first held at equilibrium at an initial oxygen partial pressure. At constant temperature, the gas atmosphere is then changed

FIG. 3. Conductivity of a PBCO film in air. Diamond and cross symbols correspond to measurements made on increasing and decreasing temperature, respectively.

abruptly to a new oxygen pressure. The change in the conductivity of the sample, which reflects the change in the oxygen content, is recorded until the new equilibrium is established. By analyzing the normalized conductivity,

$$g(t) = (\sigma_t - \sigma_0) / (\sigma_\infty - \sigma_0),$$

where σ_0 and σ_∞ are the initial and final conductivity, respectively, the chemical diffusion coefficient $\tilde{D}$ and the chemical surface exchange coefficient k_{chem} can be obtained directly. Since the as-grown PBCO film is very thin (<2000 Å), it is reasonable to assume that the oxygen transport is controlled by the surface exchange rate.¹⁴ For a single surface reaction, the normalized conductivity of a plate sample is $g(t) = 1 - \exp(-t/\tau)$, where τ is the time constant. The experimental data are not well described by this simple model, but a good fit can be obtained using two independent time constants according to

$$g(t) = 1 - A_1 \exp(-t/\tau_1) - A_2 \exp(-t/\tau_2),$$

where $A_1 + A_2 = 1$ and τ_1 and τ_2 are the time constants. This kinetic model implies that the PBCO film consists of two independent regions with different exchange rates that could correspond to two different film microstructures or two reactions on the highly epitaxial film and surface step terrace-induced antiphase domain boundaries.^{15,16} The good agreement confirms the assumption that the kinetics are surface controlled. The surface exchange coefficients were calculated from the two time constants ($k_{\text{chem},n} = l/\tau_n$, where l is the thickness of the film). As we can see from Fig. 4, $k_{\text{chem},1}$ is one order of magnitude higher than $k_{\text{chem},2}$. In both regions, oxidation (low pressure to high pressure) is faster than reduction (high pressure to low pressure), as is usually observed for the surface exchange reactions.¹³

The surface exchange rate was determined for a PBCO/STO film sample by ¹⁸O IEDP. The sample was first equilibrated in oxygen (0.2 atm) with normal isotopic abundance for 1 h at 500 °C and then exposed to ¹⁸O (99% isotopic abundance, 0.2 atm) for 300 s and rapidly quenched. The resulting ¹⁸O profile was determined using imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS IV). A dual-beam technique was used: sputtering with 20 keV Cs⁺ (2100 $\mu\text{m} \times 200 \mu\text{m}$ crater) and analysis with 25 keV ⁶⁹Ga⁺ (40 $\mu\text{m} \times 40 \mu\text{m}$ central region). This assured that the ¹⁶O

FIG. 4. The surface exchange coefficients measured for PBCO/STO. The symbols $\bullet$ $\blacksquare$ correspond to a gas switch from 0.02 to 0.1 atm and the symbols $\blacktriangle$ $\blacktriangledown$ from 0.1 to 0.02 atm. The symbol $\blacklozenge$ is the IEDP measurement.

ion signal was not saturated while achieving acceptable sputtering rates. A flat ^{18}O profile in the film confirms that the oxygen diffusion in the film is too fast to influence the ECR results ($D_{\text{O}} > 3 \times 10^{-8} \text{ cm}^2/\text{s}$). SIMS ^{18}O images (resolution 100 nm) did not reveal any lateral heterogeneity. The SIMS from a thin (<10 nm) interfacial region shows indications of the extra phase identified by x-ray diffraction. The IEDP result is in reasonable agreement with k_{chem2} from ECR (Fig. 4). The relationship between the surface exchange coefficient determined by the two techniques is $k_{\text{chem}}(\text{ECR})/\Gamma = k_{\text{O}}(\text{IEDP})$, where Γ is the thermodynamic factor [$\Gamma = d \ln(\mu_{\text{O}})/d \ln(c_{\text{O}})$], where μ_{O} and c_{O} are the oxygen atom chemical potential and concentration, respectively]. In Fig. 4, we have used the values for Γ previously measured for bulk polycrystalline PBCO⁶ to make the comparison.

In summary, the oxygen surface exchange kinetics of PBCO were measured using the electrical conductivity relaxation technique and verified by an independent IEDP measurement. The ECR data indicate the presence of two distinct kinetic pathways, whereas the IEDP experiment gives an average value. The surface exchange is much faster than we previously reported for thin films of the disordered perovskite $\text{LaSrCo}_2\text{O}_{6-x}$ on LaAlO_3 .¹⁷ As-synthesized LSCO films have comparable crystallinity to PBCO/STO with a (200) rocking curve full width at half-maximum of 0.1° . The surface exchange rate is much slower than observed for PBCO. When the LSCO film is annealed at 900°C , the crystalline quality decreases, as indicated by a broadening of the (200) peak from 0.1° to 0.3° , and the surface exchange rate increases significantly but is still lower than observed for

PBCO. The very fast surface exchange for PBCO may be associated with the film's c axis being aligned in the film plane, thereby increasing the number of surface oxygen vacancies. The value of the c -axis parameter ($c=7.727 \text{ \AA}$) is slightly larger (1.2%) compared to the ceramic target, which indicates a higher vacancy concentration in the film. The microstructural origin of the two different oxygen exchange rates observed by ECR requires further investigation. The high electronic conductivity, rapid surface exchange kinetics, and the high oxygen diffusivity measured for bulk samples suggest the application of PBCO as a cathode material in intermediate-temperature solid oxide fuel cells.

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