

## 科学研究費助成事業 研究成果報告書

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研究課題名(和文) 高効率・高耐久性SOFC/SOEC電極のための結晶粒界構造と元素組成の最適化

研究課題名(英文) Optimization of grain boundary architecture and chemistry for efficient, durable SOFC/SOEC electrodes

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研究成果の概要(和文)：SOFCの高効率化には、速い交換反応をもたらす結晶粒界の働きと構造の関係を明確にする必要がある

これらを明らかにするため、混合伝導体表面での酸素交換反応速度に対する結晶粒界を含むナノ構造の役割に関して評価を行った。PLD法で作製されたSr(Ti,Fe)O<sub>3-x</sub>膜の成長温度を上げると、結晶化度、結晶性、粒径、表面粗さ、酸素含有率が向上し、表面状態が改質された。膜の酸素表面交換反応速度(k)を連続的なIn situ光吸収法にて評価し、結晶性の高い膜が大きいkを示す事を明らかにした

交換速度kとその経時劣化については、表面構造の変化と相関があり、粒界の局所的なドーピングがkを改善しないことを明らかにした

研究成果の概要(英文)：The role of nanostructure, including grain boundaries, on oxygen surface exchange kinetics of a mixed conductor were studied, in order to identify optimal structure and grain boundary chemistry for rapid exchange kinetics and therefore high SOFC/SOEC efficiency. Sr(Ti,Fe)O<sub>3-x</sub> films with different nanostructures were fabricated by pulsed laser deposition. Higher growth temperatures led to increased crystallinity and crystalline quality, larger grains, higher surface roughness, higher oxygen content, and modified surface chemistry. An in situ optical absorption relaxation approach was used to evaluate the films' oxygen surface exchange kinetics (k). Faster kinetics were seen for crystalline films compared to amorphous films. In situ crystallization resulted in ultra-fast k. k and its degradation over time correlated with changes in surface chemistry. Local doping of grain boundaries did not improve k. [More results to be added later after publication.]

研究分野：Materials Science &amp; Engineering

キーワード：solid oxide fuel cell electrode optical absorption oxygen exchange surface chemistry thin films pulsed laser deposition efficiency

### 1. 研究開始当初の背景

The slow rate at which oxygen is transferred from the gaseous molecular state to oxide ions within a ceramic lattice at an oxygen electrode surface (the so-called “oxygen surface exchange” process) dominates efficiency losses in many solid oxide fuel/electrolysis cells. In order to increase the oxygen surface exchange rate, previous research in the community has focused on how the bulk chemistry (and defect chemistry), surface chemistry, and electronic structure impact the oxygen surface exchange coefficient,  $k$ . However not as much work focused on the role of microstructure. Since real electrodes are not perfect single crystals, it is vitally important to understand how their long range defects, such as grain boundaries, impact the surface exchange kinetics. In particular, very few studies (if any) have been performed on model geometry systems to systematically study the impact of grain boundaries in good mixed conducting electrodes (as opposed to pure electronic conductors or pure ionic conductors).

### 2. 研究の目的

This research sought to answer 3 questions:

- 1) What is the relationship between processing conditions and electrode nanostructure (including: crystallinity, grain size, grain orientation, oxygen content, surface chemistry)?
- 2) What is the impact of nanostructure, including grain boundaries, on surface exchange kinetics in a good mixed ionic and electronic conductor?
- 3) What is the impact of tailoring the local grain boundary chemistry on the surface exchange kinetics?

By answering these questions, an understanding of optimal microstructure and grain boundary chemistry in mixed conducting electrodes could be developed, in order to maximize the surface exchange kinetics and improve solid oxide cell efficiency.

### 3. 研究の方法

The research involved a) sample fabrication, b) structural characterization, c) measurement of surface exchange kinetics, and d) measurement of degradation of surface exchange kinetics over time.

A) Fabrication: Dense thin films of  $\text{Sr}(\text{Ti,Fe})\text{O}_{3-x}$  with well-controlled surface

areas and grain boundary densities were grown at different temperatures on transparent substrates by pulsed laser deposition from a ceramic target. Grain boundary doping was achieved by depositing a surface layer of another oxide and annealing to produce in-diffusion along the grain boundaries, followed by etching to remove the residual surface oxide.

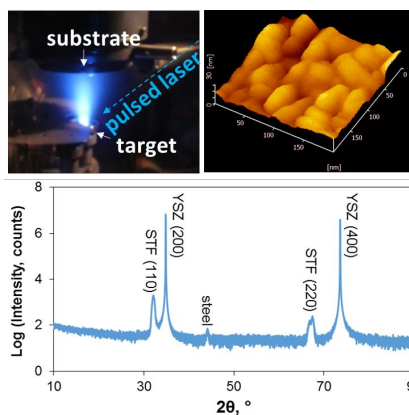


Fig. 1: PLD fabrication of columnar-grained, oriented  $\text{Sr}(\text{Ti,Fe})\text{O}_{3-x}$  thin films [5]

B) Structural characterization: Crystallinity, grain orientation, grain size, crystalline quality, degree of oxidation, and surface chemistry were characterized by X-ray diffraction (coupled scans and rocking curves), atomic force microscopy, scanning electron microscopy, transmission electron microscopy, UV-vis spectroscopy, and angle-resolved X-ray photoelectron spectroscopy.

C) Measurement of Surface Exchange Kinetics: A novel optical transmission relaxation approach was applied for the first time on this composition in thin film form to determine the surface exchange kinetics. The technique is based on the relationship between optical absorption and oxygen content in the films, which was confirmed through density functional theory calculations. Surface exchange kinetics of pristine films were measured as a function of temperature during gas changes from 0.21 to 0.04 atm  $\text{O}_2$  by fitting the optical transmission relaxation to a surface-exchange limited kinetics equation. Advantages of the optical transmission relaxation approach are that it is *in situ*, requires no metallic current collectors and therefore surveys native surface behavior, and that it allows continuous measurements for long times under realistic operating conditions.

D) Measurement of Degradation:

Surface exchange kinetics were measured as a function of time at 500 °C continuously in the optical transmission relaxation setup in order to evaluate the aging behavior of the electrodes and relate it to their nanostructures.

#### 4 . 研究成果

First, the relationship between film growth temperature and its structure was determined. Higher growth temperatures led to increased crystallinity, larger grains, better crystalline quality (grain alignment), increasing oxidation, and increased Sr surface concentrations. Films grown below ~ 550 °C were largely amorphous. Sr(Ti,Fe)O<sub>3-x</sub> films grown at higher temperatures on (100)-oriented Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> exhibited a single (110) out-of-plane orientation with columnar grains having multiple in-plane orientations, while those grown on SrTiO<sub>3</sub> (100)-oriented substrates exhibited only the (100) out-of-plane orientation and were epitaxial.

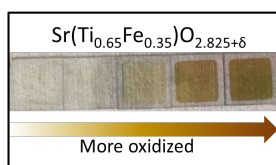


Fig. 2: Films grown at higher temperatures were more oxidized, as seen in the increasing optical absorption and coloration [4].

Second, the relationship between structure and the chemical surface exchange coefficient ( $k_{chem}$ ) of pristine films was uncovered. The main results are highlighted here:

I) Amorphous thin films did not exhibit visible oxygen exchange, but highly crystalline films showed reasonable  $k_{chem}$ . Films grown at high temperatures (800 °C) having the highest crystalline quality did not show the fastest exchange kinetics, which was attributed to the increased Sr surface segregation in films grown at high temperatures.

II) The highest  $k_{chem}$  was found for films grown at intermediate temperatures or for previously amorphous thin films after crystallizing at 550 °C. *In situ* crystallization of previously amorphous films led to a dynamic nanostructuring of the films, opening up more pristine surface area for the exchange reaction, and resulting in orders of magnitude increases in  $k_{chem}$ .

III) Neither grain boundaries nor thin film orientation caused observable changes in surface exchange kinetics in this composition. In other words, the columnar

nano-grained films and epitaxial films showed almost identical  $k_{chem}$  for the as-grown films. This result may be related to a) the significant effect of Sr surface segregation in films grown at high temperatures, b) the small grain boundary widths expected for high Fe concentrations in this composition, and c) the good mixed conducting properties of the grains themselves.

IV) Degradation of  $k_{chem}$  over time occurred most significantly in the first 30 h of operation. Lower  $k_{chem}$  values as a result of thermal treatment were correlated to higher Sr surface concentrations by angle resolved XPS. Chemical etching of the surfaces to remove the Sr excess recovered the  $k_{chem}$  values (i.e., removed the degradation effect).

V) Taken together, the results suggest that optimizing  $k_{chem}$  requires crystallinity (a high growth temperature property) and minimal Sr surface segregation (a low growth temperature property).

Third, the effect of locally changing grain boundary chemistry was studied. To date, each local grain boundary substituent (Ni, Ce, etc.) has not improved the surface exchange kinetics but in some cases modified the degradation behavior.

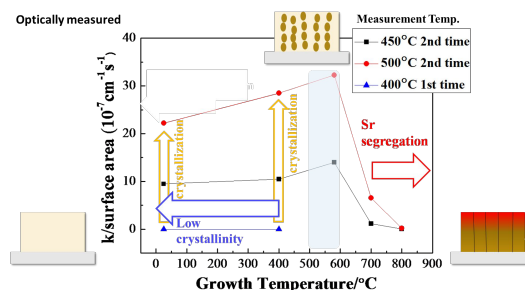


Fig. 3: Area-normalized  $k_{chem}$  as a function of film growth temperature, showing highest values for films grown at intermediate temperatures (just crystallizing) or previously-amorphous films post-annealed at intermediate temperatures (also just crystallizing) [4]

#### 5 . 主な発表論文等

{ 雑誌論文 } ( 計 3 + 2 submitted/in preparation 件 )

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[2] T. Chen, G.F. Harrington, K. Sasaki, and N.H. Perry, “Relating microstructure to surface exchange kinetics using in situ optical absorption relaxation” *ECS Transactions* 75 [43] (2017) 23-31

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N.H. Perry, “Development of design principles for electro-chemo-mechanically active oxides,” Materials Science & Engineering Special Seminar (2017/1/26), University of Illinois at Urbana-Champaign [invited]

N.H. Perry, “Electro-chemo-mechanics of SOFC/SOEC air electrodes based on  $\text{Sr}(\text{Ti},\text{M})\text{O}_3$ ,” International Congress on Ceramics (ICC-6), (2016/8/23), Dresden [invited]

N.H. Perry, “Understanding and controlling chemo-mechanical coupling in perovskite oxides,” 229<sup>th</sup> Electrochemical Society (ECS) Conference (2016/5/31), San Diego [invited]

N.H. Perry, “In situ, non-contact studies of oxygen exchange kinetics in thin film mixed conducting electrodes,” Electrochemical Society (ECS) PRiME Conference (2016/10/2-7), Honolulu

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〔図書〕(計 1 book + 1 chapter 件)

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〔産業財産権〕

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