

## 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)フェルミ準位のコントロールによる燃料電池電極表面現象の改善

研究課題名(英文)Enhancement of fuel cell electrode kinetics by control of Fermi level

研究代表者

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研究成果の概要(和文)：固体酸化物形燃料電池(SOFC)はクリーンで効率的なエネルギー変換が可能であるが、変換効率と耐久性向上によるコスト削減が必要である。本研究に於いて、SOFC用カソード電極の迅速な酸素取込み改善で性能理解と改善を試みた。モデル電極材料 $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-x}$ にLa(材料への電子供与性"ドナー"元素)を混入し、カソード電極の電子濃度増加が酸素表面交換率を向上するという仮説を検証した。実験より、本過程での電子発生量を示す「欠陥化学的モデル」を開発した。異なるLa濃度で緻密薄膜電極を作製し、濃度が効率に与えた影響を見る「光伝送緩和」等の新技術により、表面交換比率を究明した。化学機械的耐久性も調べた。

研究成果の概要(英文)：Solid oxide fuel cells (SOFCs) offer clean, efficient energy conversion, but their cost needs to be lowered by increasing their efficiency and durability. In this work I sought to understand and improve the efficiency of the SOFC cathode, by modifying how rapidly it could incorporate oxygen from the gas. I tested the hypothesis that increasing the electron concentration of the cathode could improve its oxygen surface exchange rate by starting with the model cathode material  $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-x}$  and introducing "donor" elements like La which can donate electrons to the material. From several experiments I developed a "defect chemical model" showing how many electrons were generated by this process. I fabricated dense thin film cathodes with different La concentrations and determined their surface exchange rate by new techniques, including "optical transmission relaxation" to see how the La concentration impacted their efficiency. The chemo-mechanical durability was also investigated.

研究分野：Materials Science &amp; Engineering / Ceramics

キーワード：SOFC electrode thin film surface oxygen exchange defect chemistry doping electronic structure

## 1. 研究開始当初の背景

(1) Solid oxide fuel cells (SOFCs) convert fuel directly to electricity, with high efficiency, reduced emissions, fuel flexibility, and potential for heat and power co-generation. Lower operating temperatures ( $< 600^{\circ}\text{C}$ ) of SOFCs could overcome materials durability and therefore cost issues. A key barrier to use of SOFCs at low temperatures is the high resistance of oxygen incorporation at the cathode. In order to improve cathode performance for low temperature operation, the mechanisms controlling the oxygen surface exchange rate must be clarified and subsequently engineered.

(2) Recent work by collaborators Tuller *et al.* showed the activation energy of the cathode  $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-x}$  correlates with the energy difference between the conduction band minimum and the Fermi level, implying that the transfer of electrons from the cathode to the adsorbed oxygen is the rate-limiting step. Therefore increasing the Fermi level, towards the conduction band minimum, was expected to enhance the electron transfer process, improving the surface oxygen exchange rate and ultimately the low temperature cathode performance.

## 2. 研究の目的

Better understanding and possible improvement of oxygen exchange kinetics in solid oxide fuel cell cathodes was investigated with a new approach: increasing the Fermi level, which could potentially overcome the hypothesized rate-limiting barrier of electron transfer to the adsorbed oxygen.  $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-\delta}$  cathodes were engineered to raise the Fermi level, by 1) donor doping, and 2) *in situ* light illumination, with the aim of enabling high efficiency, low temperature operation, and increasing understanding of the rate-limiting defects and processes. Particular questions that the work addressed were:

- (1) What is the impact of Fermi level, varying over a wide range, on oxygen surface exchange kinetics in an advanced SOFC cathode material,  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$  (STF)?
- (2) To what extent can Fermi level be controlled by donor doping in p-type perovskites? Can a p-to-n transition be engineered?
- (3) What is the impact of donor doping on cathode performance?

## 3. 研究の方法

(1) Sample fabrication.

Both bulk ceramics and dense thin film cathodes were prepared with 5 different donor doping concentrations. Bulk ceramics (for electrical conductivity measurements and pulsed laser deposition targets) were fabricated by Pechini and solid state approaches with high temperature sintering. Dense thin film cathodes were fabricated by pulsed laser deposition on a variety of substrates.

(2) Development of new technique.

In this work an optical transmission setup was built to enable *in situ*, contact-free characterization of native thin film cathode surface exchange kinetics by the new “optical transmission relaxation” technique, with collaborators. The technique was applied to study both equilibrium and kinetic properties of  $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-x}$  cathodes for the first time and  $(\text{Ce},\text{Pr})\text{O}_{2-x}$  cathodes (as a model system) in this work.

(3) Performance characterization.

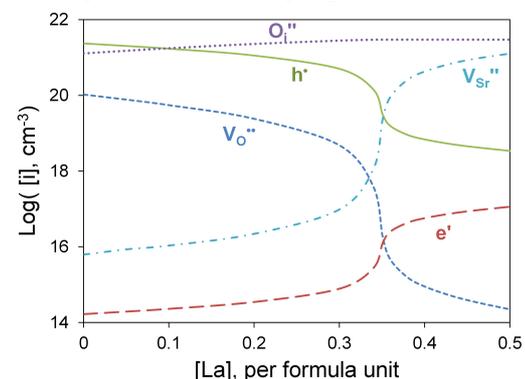
Important fuel cell cathode performance metrics, such as electrical conductivity, surface exchange kinetics, equilibrium defect concentrations, and thermal and chemical expansion coefficients were measured *in situ* over a range of temperatures and oxygen partial pressures to develop a comprehensive understanding of the relationship between electron concentration / defect chemistry and performance. Approaches included optical transmission, ac impedance spectroscopy, dilatometry, and thermogravimetric analysis.

(4) Defect modeling.

Based on the experimentally measured properties (e.g., electrical conductivity) and defect concentrations, a thermodynamic defect chemical model was developed by fitting the data using mass action equations and charge neutrality.

## 4. 研究成果

(1) Impact of donor doping on electron and



point defect concentrations in p-type  $\text{Sr}(\text{Ti,Fe})\text{O}_{3-x}$ :

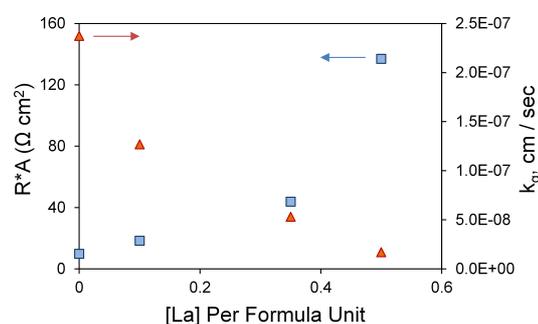
**Figure 1: Defect concentrations [4]**

Using bulk and thin film electrical conductivity, optical absorption, and prior thermogravimetric analysis measurements as data, a thermodynamic defect chemical model describing the impact of donor doping with La on  $\text{SrTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$  was developed. This knowledge is useful to the broader community for explaining point defect concentrations and Fermi level in perovskites containing both acceptor and donor dopants. Furthermore, it highlighted that addition of a donor in this p-type cathode impacted the defect chemistry in a complex way. At low donor concentrations ( $[\text{La}] < [\text{Fe}]$ ), the oxygen vacancy and hole concentrations decreased significantly to compensate for the donors. The electron concentration and Fermi level were raised only slightly. At higher donor concentrations ( $[\text{La}] > [\text{Fe}]$ ), the oxygen sublattice became saturated with oxygen, and so compensation of the donors by cation vacancy formation began. Owing to the presence of cation vacancies, once again, the electron concentration and Fermi level were raised only slightly. Measurements demonstrated that the material remained p-type even for very high donor dopant concentrations: cation vacancies act like a p-type defense mechanism, resisting electron formation. However, the defect model suggests that under reducing conditions, in equilibrium, donors would be compensated much more by electrons rather than cation vacancies. Therefore, in currently ongoing work, the fabrication of STF cathodes under such conditions is being pursued to generate much higher electron concentrations and potentially switch the material from p-type to n-type and generate a much larger change in Fermi level.

(2) Impact of donor doping (raising the Fermi level) on oxygen surface exchange rate in  $\text{Sr}(\text{Ti,Fe})\text{O}_{3-x}$ :

Surface exchange kinetics of dense STF thin films were measured by ac-impedance spectroscopy and optical transmission relaxation over a range of donor concentrations. The results demonstrated that donor doping at small concentrations had little effect on the surface exchange rate, but that large donor concentrations were detrimental. In other words, the exchange kinetics did not scale with Fermi level. Such results, in combination with the new defect chemical model discussed above,

suggest that in these donor doped compositions, electron transfer is no longer rate-limiting. Instead, the low oxygen vacancy and hole concentrations are expected to limit the performance. The work implies that other methods that raise the Fermi level without deleteriously impacting other key defect populations are needed to potentially improve the performance. The results also suggest that the rate-limiting step may change in a given system with slight changes in composition. Finally, the importance of precisely controlling cathode thermal history and gas impurity content for measurements of surface exchange was realized in this study.



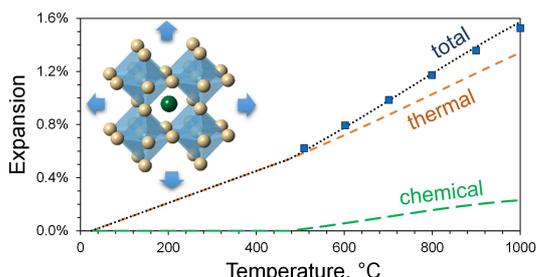
**Figure 2: Area-specific resistance (left) and surface exchange coefficient (right) measured by ac impedance spectroscopy on thin film La-doped STF [4]**

(3) Application of new “optical transmission relaxation” technique to study thin film cathode kinetics:

The optical transmission relaxation (OTR) technique was applied to measure STF surface oxygen exchange kinetics for the first time, but in order to initially demonstrate the viability of the technique, it was also applied to a well-characterized “model” cathode system,  $(\text{Pr,Ce})\text{O}_{2-x}$  (PCO), with collaborator Sean Bishop. In this work, OTR was applied to quantify the degradation rate of PCO surface exchange for the first time and additionally to demonstrate that the surface exchange kinetics could be fully recovered, after aging, by application of reactive surface additives including  $\text{La}_2\text{O}_3$  and  $\text{Sm}_2\text{O}_3$ . Uncovering such approaches towards impurity tolerance is vital for developing cathodes that remain efficient for long lifetimes in real fuel cell conditions, where many impurities are present in the stack materials, gases, and environment. Importantly the work demonstrated the viability of using the OTR technique to enable studies of native cathode surface behavior without the need for any metal

current collectors which may obscure the true performance. In ongoing work the OTR technique is being applied to STF in comprehensive studies of surface exchange kinetics under different operating conditions.

(4) Evaluation of chemo-mechanical stability of  $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-x}$  cathodes:



**Figure 3: Data and fit by new model of thermochemical expansion in STF, with separate chemical and thermal expansion contributions shown [3]**

In order to apply new cathode materials such as STF in real, operating fuel cells, one must ensure not only high electrochemical performance as discussed above, but also chemo-mechanical stability. Cathodes must exhibit good thermal expansion coefficient matching to the adjacent electrolyte and additionally, low chemical expansion coefficients. This is because chemical expansion of cathodes owing to loss of oxygen from their lattice can cause delamination and cracking, dramatically impacting cell performance. In this work both the isothermal chemical expansion coefficients and iso-stoichiometric thermal expansion coefficients were determined in STF for the first time over a range of temperatures and oxygen partial pressures. The measurements (by dilatometry and thermogravimetric analysis) enabled development of a model describing complete thermo-chemical expansion of STF upon heating as would be experienced in an operating cell during start-up. The work also demonstrated the beneficial role of increasing Fe content in STF: this change not only increases electrical conductivity and surface exchange kinetics (previously shown by others), but also lowers the chemical expansion coefficient, presumably by charge delocalization. The chemo-mechanical studies were further extended to provide a more generalized picture of chemical expansion in perovskites through development of computational modeling and a new empirical model.

## 5 . 主な発表論文等

(研究代表者、研究分担者及び連携研究者には下線)

〔雑誌論文〕(計 5 件)

1. L. Zhao, N.H. Perry, T. Daio, K. Sasaki, S.R. Bishop, "Improving the Si impurity tolerance of  $\text{Pr}_{0.1}\text{Ce}_{0.9}\text{O}_{2-δ}$  SOFC electrodes with reactive surface additives," *Chemistry of Materials* (2015, Online) DOI: 10.1021/acs.chemmater/5b00501. Refereed.
2. D. Marrocchelli\*, N.H. Perry\* (\* = equal contribution), and S.R. Bishop, "Understanding chemical expansion in perovskite-structured oxides," *Physical Chemistry Chemical Physics* (2015, Online) DOI: 10.1039/C4CP05885B. Refereed.
3. N.H. Perry, J.J. Kim, S.R. Bishop, and H.L. Tuller, "Strongly coupled thermal and chemical expansion in the perovskite oxide system  $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-α}$ ," *Journal of Materials Chemistry A* 3 (2015) 3602-3611, DOI: 10.1039/C4TA05247A. Refereed.
4. N.H. Perry, D. Pergolesi, S.R. Bishop, and H.L. Tuller, "Defect chemistry and surface oxygen exchange kinetics of La-doped  $\text{Sr}(\text{Ti},\text{Fe})\text{O}_{3-α}$  in oxygen-rich atmospheres," *Solid State Ionics* 273 (2015) 18-24, DOI: 10.1016/j.ssi.2014.09.013. Refereed.
5. N.H. Perry, D. Pergolesi, K. Sasaki, S.R. Bishop, and H.L. Tuller, "Influence of Donor Doping on Cathode Performance:  $(\text{La},\text{Sr})(\text{Ti},\text{Fe})\text{O}_{3-δ}$  Case Study," *ECS Transactions*, 57 [1] (2013) 1719-1723, DOI:10.1149/05701.1719ecst. Refereed.

〔学会発表〕(計 11 件)

Invited Talks:

1. N.H. Perry, "In situ Electro-Optical Characterization of Thin Films for Energy Applications" 5th PHOENICS International Symposium, Kumamoto University, Japan (February 27, 2015) Invited.
2. N.H. Perry, "Tailoring Chemo-Mechanical Coupling to Enhance Durability of Mixed Conducting Perovskite Electrodes," 39th International Conference and Exposition on Advanced Ceramics and Composites (ICACC), Daytona Beach, U.S.A. (January 29, 2015) Invited.
3. N.H. Perry, "Influence of Electronic Structure on Oxygen Incorporation Kinetics and Related Chemical Expansion," Nagasaki University, Japan (June 6, 2014) Invited.
4. N.H. Perry, "Oxygen incorporation, transport, and related chemical expansion

in solid oxide fuel cell materials” Swiss Federal Institute of Technology (ETH), Zürich, Switzerland (June 2, 2014) Invited.  
5. N.H. Perry, J.J. Kim, M. Kuhn, J.W. Druce, T. Daio, S.R. Bishop, and H.L. Tuller, “Investigating the Role of Electronic Structure in Oxygen Exchange Kinetics Using Model Thin Film (Sr,Ba,La)(Ti,Fe)O<sub>3-α</sub> Fuel Cell Cathodes” European Materials Research Society Spring Meeting, Lille, France (May 26-30, 2014) Invited.

Contributed Talks:

6. J.J. Kim, S.R. Bishop, D. Chen, N.H. Perry (presenter), and H.L. Tuller, “Defect equilibria and reaction kinetics of Pr doped ceria thin films by simultaneous in situ optical absorption and impedance measurements,” 39th International Conference and Exposition on Advanced Ceramics and Composites (ICACC), Daytona Beach, U.S.A. (2015), Talk

7. N.H. Perry, D. Marrocchelli, J.J. Kim, S.R. Bishop, and H.L. Tuller, “Towards Chemo-Mechanically Durable SOFC/SOEC Electrodes: Factors Influencing Chemical Expansion in Perovskites,” MRS Fall Meeting and Exhibit, Boston, U.S.A. (November 30-December 5, 2014), Talk

8. N.H. Perry, J.E. Thomas, D. Marrocchelli, L. Zhao, J.J. Kim, S.R. Bishop, and H.L. Tuller, “Chemical Expansion of Mixed Ionic and Electronic Conducting Perovskites,” Spring Electrochemical Society (ECS) 225th Meeting, Orlando, U.S.A. (May 11-15, 2014), Talk

9. N.H. Perry, T. Daio, J.W. Druce, S.R. Bishop, and H.L. Tuller, “Fundamental Studies of Oxygen Surface Exchange on Model Thin Film (Sr,La)(Ti,Fe)O<sub>3-α</sub> SOFC Cathodes: Role of Bulk and Surface Chemistry,” Materials Research Society (MRS) Spring Meeting, San Francisco, U.S.A. (2014), Talk

10. N.H. Perry, J.W. Druce, D. Pergolesi, J.A. Kilner, S.R. Bishop, and H.L. Tuller, “Donor Doping of a P-Type SOFC Cathode: Influence of La on Sr(Ti,Fe)O<sub>3-δ</sub> Defect Chemistry and Performance” 38th International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach, U.S.A. (2014), Talk

11. N.H. Perry, D. Pergolesi, K. Sasaki, S.R. Bishop, and H.L. Tuller, “Influence of Donor Doping on Cathode Performance: (La,Sr)(Ti,Fe)O<sub>3-δ</sub> Case Study,” SOFC-XIII in Okinawa, Japan (2013), Talk

〔図書〕(計 0 件)

〔産業財産権〕  
出願状況(計 0 件)

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発明者：  
権利者：  
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番号：  
出願年月日：  
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発明者：  
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