論文 / 著書情報
Article / Book Information

題目(和文)	吸着種領域モデル及び反応サイトイメージングによる固体酸化物型燃料電池多孔質電極における反応動力学に関する研究
Title(English)	Reaction Kinetics and Dynamics on Solid Oxide Fuel Cell Porous Electrodes through Species Territory Adsorption Model and Active Sites Imaging
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出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10789号, 授与年月日:2018年3月26日, 学位の種別:課程博士, 審査員:花村 克悟,佐藤 勲,平井 秀一郎,山中 一郎,伏信 一慶
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10789号, Conferred date:2018/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	機械制御システム　　専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of　（　工学　）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

The thesis entitled as "Reaction Kinetics and Dynamics on Solid Oxide Fuel Cell Porous Electrodes through Species Territory Adsorption Model and Active Sites Imaging" consists of six chapters.

In Chapter 1 "Introduction", background and current status of solid oxide fuel cell (SOFC), which is a promising energy conversion technology with high efficiency, are reviewed and the main specific targets of the thesis are raised. For state-of-the-art SOFCs, porous composite electrodes are widely used such as Ni/yttria-stabilized zirconia (YSZ) for anodes or strontium-doped lanthanum manganite (LSM)/YSZ for cathodes. These electrodes have micro/nano-scale complex structures consisting of electron conductors, oxide ion conductors, and pore phases, where chemical species are transported and accompanied by electrochemical reactions at the triple phase boundary (TPB). The accurate understanding and description of the electrochemical reactions on porous electrodes are key issues for further development of materials and structural design to enhance electrodes performance and stability. In this thesis, toward construction of the detailed kinetics and dynamics on SOFC porous electrodes, analytical reaction model is constructed and imaging technique of active sites is developed.

In Chapter 2 "Species territory adsorption model for hydrogen oxidation in SOFC anode", analytical model for hydrogen oxidation in the TPB of Ni/oxide ion conductor cermet anode, named as species territory adsorption model, is constructed. It is assumed that the chemical species are adsorbed within a finite narrow area on Ni or oxide ion conductor around the TPB. The reaction rate in the anode is controlled by the surface reaction between the adsorbed hydrogen and adsorbed oxygen; all other reactions take place under chemical equilibrium. Based on the reaction model, analytical expressions of the current density with respect to oxygen activity and the anode overpotential with respect to current density can be obtained. The latter can combine the anode overpotential at low- and high-current-density regions, which are conventionally expressed independently. Moreover, it is clarified that the current density asymptotes the limiting value as the oxygen coverage around the TPB approaches unity. The theoretical limitation of current density given here is determined by the rate constants of surface reactions and the coverage of adsorbed hydrogen on Ni.

In Chapter 3 "Comprehensive analysis of Ni/YSZ anode using species territory adsorption model", the quantitative validation of the species territory adsorption model for Ni/YSZ anode is discussed based on the comparison to measured and reported experimental results. By introducing referenced thermodynamic and kinetic parameters predicted by density functional theory calculations, the model can predict anode overpotential using unknown values of quantities of state for oxygen migration process in YSZ near a TPB, frequency factor for hydrogen oxidation, and effective anode thickness. The former two are determined through careful fitting process between the model and experimental results of Ni/YSZ cermet and Ni-patterned anodes. This makes it possible to estimate effective anode thickness based on the model, which shows a positive correlation with temperature in six kinds of Ni/YSZ anodes used in this study and references. In addition, the comparison between the model and published numerical simulation indicates that the model can predict more precise dependence of anode overpotential on steam partial pressure than that by Butler-Volmer equation with empirical exchange current density.

In Chapter 4 "Imaging of microstructure-scaled active sites in porous composite cathode", imaging technique of active reaction sites in porous electrodes is developed in microstructure scale. A power generation equipment with a nozzle for direct helium gas impinging jet to the cell is newly prepared to quench an SOFC reaction. The quench performance test shows that the temperature of YSZ electrolyte can be decreased from 830 to 150 °C within 1.5 sec, which is in good agreement with analytical results based on the average Nusselt number of impinging jet heat transfer. Using constructed quench system and oxygen isotope labeling, active sites for oxygen reduction reaction in LSM/ScSZ porous cathode are visualized at 800 °C. From the ^{18}O concentration mappings of the quenched cathode obtained by secondary ion mass spectroscopy (SIMS) with a spatial resolution of 50 nm, enhanced ^{18}O diffusion into LSM, which is promoted by overpotential, is observed only near the cathode/electrolyte interface. This result indicates that reaction sites near the cathode/electrolyte interface are more electrochemically active than those at other regions.

In Chapter 5 "Analysis method of oxide ion flux at cathode/electrolyte interface through oxygen isotope labeling", SOFC power generation in $^{18}O_2$ and quench experiment is conducted at 700 °C using the methodology developed in Chapter 4. From the analysis of ^{18}O diffusion profiles in YSZ electrolyte, quantitative oxide ion flux incorporated from the cathode/electrolyte interface is estimated. The results indicate that 22~31% of the overall electrochemical reaction occurs at the cathode/electrolyte interface, while the remaining 69~78% of those proceeds inside the porous cathode.

In Chapter 6 "Conclusions", the key findings and contributions are summarized and future perspective is presented.