様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科研費 KAKENHI

科学研究費助成事業　　研究成果報告書

令和　４ 年　 ６ 月　 ８ 日現在

機関番号：１７１０２
研究種目：若手研究
研究期間：2018～2021
課題番号：１８Ｋ１３９９３

研究課題名（和文）Opto-Electrical Analysis of the Oxygen Reduction Reaction at Solid-Gas Interfaces

研究課題名（英文）Opto-Electrical Analysis of the Oxygen Reduction Reaction at Solid-Gas Interfaces

研究代表者

Ｋｌｏｔｚ　Ｄｉｎｏ（Klotz, Dino）

九州大学・カーボンニュートラル・エネルギー国際研究所・助教

研究者番号：００８１４８４９

交付決定額（研究期間全体）：（直接経費）　　3,200,000円

研究成果の概要（和文）：このプロジェクトでは、光と固体-気体界面との相互作用を分析しました。3%GdドープCeO_2（GDC、電解質および複合電極の一部としてSOFCで使用するための最も有力な材料の1つ）の薄膜を使用したさまざまな実験を行いました。特に粒界での電子構造は、バンドギャップ上の光によって基本的に影響を受けることがわかりました。また、イオン伝導度は光によって増加し、これは、混合イオン電子伝導電極（MIEC）の重要なパラメーターとなります。MITとのコラボレーションが行われたが。イオン伝導度の増加について見出された結果は非常に優れていたため、この光イオン効果にさらに焦点が当てられました。

研究成果の学術的意義や社会的意義
The newly discovered new light effect could be beneficial for fuel cells, batteries, sensors and other devices that rely on ionic conductivity. Overall, it will potentially lead to higher efficiency of these devices which will decrease energy demand and help meeting carbon emission reduction goals.

研究成果の概要（英文）：In this project, the interaction of light with solid-gas interfaces was analyzed. Various experiments with thin films of 3%Gd-dopedCeO_2 (GDC, one of the most prominent materials for use in SOFC as electrolyte and part of composite electrodes). It was found out that the electronic structure, especially at the grain boundaries, is fundamentally affected by light above the bandgap. Also, the ionic conductivity is increased by the light, which is an important parameter for mixed ionic electronic conducting electrodes (MIEC). Collaboration with MIT was conducted. Due to the pandemic, only remote meetings were held. The results found for the increase in ionic conductivity were so outstanding, that further focus was laid on this opto-ionic effect.

研究分野：fuel cells

キーワード：oxygen evolution　thin films　ionic conductivity　impedance measurements

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

The background of the study was previous work by the group of Prof. Tuller at MIT (Cambridge, USA), who is a collaborator and visiting professor at the International Institute for Carbon-Neutral Energy Research (I^2CNER) at Kyushu University.

In his group, it had been demonstrated that it is possible, for a model material, to track the oxidation state of a specific atom in the electrode material by the absorption properties. In concrete, the model material is Pr-doped CeO_2. In this material, Ce can change its oxidation state depending on the oxygen partial pressure. In turn, Pr adjusts to this and can be present as Pr^{3+} and as Pr^{4+}. The beneficial aspect of this valence change is that Pr^{4+} has a much larger optical absorption than Pr^{3+}, which can also be seen with the bare eye because a thin film will turn from transparent to orange.

That is a helpful tool for further understanding the oxygen reduction reaction, one of the most important reactions for electrochemical energy conversion, essential for fuel cells, electrolysis and solar water splitting. For the reaction of hydrogen and oxygen reacting to water and vice versa, it is the half-reaction that causes most losses in the respective devices. Further improvement of understanding and corresponding tailoring of materials and structures promise improved efficiency of those devices, which will play a key role in a renewable energy scenario.

The previous work had already been conducted in the course of a collaboration between MIT and Kyushu University, with researchers at both institutions collaborating and having regular exchange. Test facilities are available at both institutions

２．研究の目的

The oxygen reduction reaction comes along with an incorporation and excorporation of oxygen ions in the crystal lattice of the electrode material. More detailed knowledge of the respective reaction steps, including the change in oxidation state of the electrode material, will provide new insights of the reaction itself and how it can be improved.

This is part of a larger project, followed by many research groups all over the world, to investigate the exact mechanisms and reaction steps of the oxygen reduction and oxidation reactions. On the one hand, these reactions are essential for many applications concerning renewable energies and non-fossil fuels (such as solar fuels), but on the other hand, it is one of the most complex electrochemical reactions because it features the transfer of four electrons for each oxygen molecule to be converted.

Scientists have been struggling with explaining the reaction steps, but this knowledge is necessary to design efficient electrode materials and structures for renewable energy sources.

The approach that is conducted here is beneficial in many senses, because it is experimental and in ambient air, which means the conditions are close to actual working conditions of the respective materials, plus it is a relatively cheap approach that does not require any complicated techniques such as measurements in vacuum or in a synchrotron facility, as many other approaches with similar goals do.

３．研究の方法

This study planned to use frequency domain techniques, namely a generalized impedance spectroscopy approach, to analyze the dynamics of the reaction steps, namely, to look at the dynamics of voltage change (a measure for the chemical potential or the oxygen concentration) and the change in oxidation state of the electrode material. This is done with a thin film of Pr-doped CeO_2, the model material with which the group of Prof. Tuller had conducted the ground-laying work.

Thin films have been produced at Kyushu University and the existing infrastructure has been used to perform measurements. The thin films were contacted electronically and placed in a furnace with a through-hole where light can penetrate. The light transmission was monitored with a light sensor on the other side of the furnace. The voltage and current signals were then correlated with the signal of the light sensor. A Solartron 1260 frequency response analyzer was used for this purpose because it possesses the option to have an additional channel and calculate the impedance, or more general, the transfer function, between the main channels (voltage and current) and the additional or auxiliary channel. Most other instruments do not allow for such advanced measurement settings.

４．研究成果

The project could successfully demonstrate the proposed methods. Frequency domain measurements (generalized impedance measurements) were successfully conducted, and parameter dependencies of the obtained spectra were analyzed. That is mainly the time constant of the process that changes the light transmission, which is again directly proportionate to the oxidation state of the thin film material. The light signal could be easily calibrated to the oxidation state by measurements in equilibrium, where no external voltage bias was applied. Then the oxidation state is determined by the ambient conditions. The final measurements were done in air but with an applied voltage bias that represented the potential gradient as determined by a concentration gradient of the oxygen partial pressure that is adjusted on the surface of the thin film. Those measurements were all in good agreement and the new method was presented at the EMRS conference in Strasbourg in 2018, where it got a lot of positive feedback and won the poster prize.

However, it was found out that although, it is possible to determine the dynamics of the change in oxidation state, the process is limited by the surface exchange of the thin film and of the counter electrode and has therefore limited significance for the dynamics of the oxygen incorporation itself. New electrode designs needed to be developed together with collaboration partners to get rid of the limiting factor of the surface exchange. Due to the pandemic, this has not been possible to do. The setup was upgraded to achieve higher sensitivity by implementing a laser diode as light source instead of an LED for a higher signal-to-noise ratio, the electrode design has been discussed and planned, but samples could not be produced, and no further experiments could be conducted.

However, the experiments of light interacting with thin films had another outcome which was of high relevance and was further investigated. Since the interaction of light with solid-gas interfaces had planned to be analyzed, various experiments with thin films of 3%Gd-doped CeO_2 (GDC, one of the most prominent materials for use in solid oxide fuel cells, SOFC, as electrolyte and part of composite electrodes) had also been conducted. In these experiments, it was found out that the electronic structure, especially at the grain boundaries, is fundamentally affected by light above the bandgap.

This led to a major discovery. In essence, the ionic conductivity is increased by the light, which is an important parameter for mixed ionic electronic conducting electrodes (MIEC). Photoconductivity is a well-known concept but in the documented research, it is almost exclusively (set aside perovskite absorber materials for solar cells) an electronic effect. Light creates additional charge carriers, electrons and holes, that contribute to the conductivity. In our case, light could remove, to a significant extent, the potential barrier for ionic conductivity without changing other parameters of the material such as temperature, number of charge carriers, or photo-decomposition.

Collaboration with MIT was conducted. Due to the pandemic, only remote meetings were held. The results found for the increase in ionic conductivity were so outstanding, that further focus was laid on this opto-ionic effect.

５．主な発表論文等

〔雑誌論文〕　計1件（うち査読付論文　1件／うち国際共著　1件／うちオープンアクセス　1件）

１．著者名 Dino Klotz	４．巻 98
２．論文標題 Negative capacitance or inductive loop? - A general assessment of a common low frequency impedance feature	５．発行年 2019年
３．雑誌名 Electrochemistry Communications	６．最初と最後の頁 58-62
掲載論文のDOI（デジタルオブジェクト識別子） 10.1016/j.elecom.2018.11.017	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 該当する

〔学会発表〕　計9件（うち招待講演　3件／うち国際学会　9件）

１．発表者名 Dino Klotz
２．発表標題 Photoconductivity Analyzed in the Frequency Domain - An Introductory Case Study of Strontium Titanate
３．学会等名 International Conference on Electroceramics（招待講演）（国際学会）
４．発表年 2019年～2020年

１．発表者名 Dino Klotz, Thomas Defferriere, Jennifer L. M. Rupp, Harry L. Tuller
２．発表標題 Frequency Domain Photoconductivity Measurements - Overview, Examples and Recent Advances
３．学会等名 22nd International Conference on Solid State Ionics（国際学会）
４．発表年 2019年～2020年

１．発表者名 Dino Klotz
２．発表標題 Generalized Electrochemical Impedance Spectroscopy (GEIS) in Solid State Ionics
３．学会等名 European MRS（国際学会）
４．発表年 2018年

１．発表者名
Dino Klotz

２．発表標題
Generalized Electrochemical Impedance Spectroscopy (GEIS) in Solid State Ionics

３．学会等名
Electroceramics XVI（国際学会）

４．発表年
2018年

１．発表者名
Dino Klotz, Nicola H. Perry, Harry L. Tuller

２．発表標題
Analyzing the Oxygen Reduction Reaction at Solid-Gas Interfaces by Optical Impedance Spectroscopy

３．学会等名
Electroceramics XVI（国際学会）

４．発表年
2018年

１．発表者名
Dino Klotz

２．発表標題
Generalized Electrochemical Impedance Spectroscopy - Analyzing Solid-Gas Interfaces Optically

３．学会等名
International Workshop on Impedance Spectroscopy（招待講演）（国際学会）

４．発表年
2018年

１．発表者名
Dino Klotz, Thomas Defferriere, Harry L. Tuller

２．発表標題
Photoconductivity Analyzed in the Frequency Domain - An Introductory Case Study of Strontium Titanate

３．学会等名
Nonstoichiometric Compounds VII（国際学会）

４．発表年
2018年

1．発表者名 Dino Klotz, Thomas Defferriere, Jennifer L. M. Rupp, Harry L. Tuller
2．発表標題 Frequency Domain Photoconductivity Measurements - Overview, Examples and Recent Advances
3．学会等名 Solid State Ionics 22（国際学会）
4．発表年 2019年

1．発表者名 Dino Klotz
2．発表標題 Photoconductivity Analyzed in the Frequency Domain - An Introductory Case Study of Strontium Titanate
3．学会等名 9th International Conference on Electroceramics（招待講演）（国際学会）
4．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

－

6．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

7．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

8．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関