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研究課題名（和文）Frequency Domain Characterization of Optically Controlled Processes in Perovskite Materials

研究課題名（英文）Frequency Domain Characterization of Optically Controlled Processes in Perovskite Materials

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研究成果の概要（和文）：結果の一部は、ペロブスカイト太陽電池のインピーダンス応答をデコンボリューションする詳細な視点を確立することでした。プロジェクトの他の部分は、ペロブスカイト材料などのイオン伝導体の粒界で発生する光イオン効果の発見でした。この部分の実験は、3%GdドープCeO2（GDC）で実行されました。
多結晶材料の粒界のイオン伝導性を大幅に向上させますが、これは、技術材料のイオン伝導の主な欠点の1つです。空間電荷領域とそれらによって引き起こされるポテンシャル障壁は、バンドギャップの上の光によって軽減できることを示します。光生成された電子正孔対は、空間電荷を補償しますが、電子伝導性にはつながりません。

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

研究成果の概要（英文）：In this project, we focused on light interaction of perovskite materials. One part of the results was establishing a detailed perspective that deconvoluted the impedance response of perovskite solar cells. The other part of the project was the discovery of an opto-ionic effect happening at grain boundaries of ionic conductors, such as perovskite materials. The experiments for this part were performed on 3%Gd-dopedCeO2 (GDC, one of the most prominent ionic conductors and model material for ionic conduction). The new opto-ionic effect immensely increases the ionic conductivity of the grain boundaries of polycrystalline materials, one of the major drawbacks for ionic conduction in technical materials. It could be shown that the space-charge region and the potential barrier caused by those can be mitigated by light above the bandgap. Photogenerated electron-hole pairs compensate the space-charges but do not lead to electronic conductivity.

研究分野：fuel cells

キーワード：opto-ionics　ionic conductivity　light effect　grain boundaries　impedance

１．研究開始当初の背景

In recent years, perovskite materials have gained a lot of attraction for various purposes in materials science. These materials have the chemical structure ABX_3 and exhibit many advantageous characteristics, such as the option to combine materials and substitute materials on the A- and B-side to tailor the characteristics of the resulting material. Electronic and ionic conductivity, together with good catalytic properties have made perovskites the state-of-the-art choice for the oxygen electrode for high temperature fuel cells and electrolyzers (solid oxide fuel cells/electrolyzers, SOFC/SOEC, or combined as solid oxide cells, SOC).

More recently, perovskites have been discovered to also show very beneficial electro-optical properties, which made them an attractive choice as absorber material for solar cells. That research branch has seen a lot of attention in the last years and is considered a “hot topic”. Again, the beneficial properties of being able to tailor the characteristics of the material by choice of material, and by substitutions on A-, B-, and in the case of perovskite materials for solar applications, even the X-side.

These benefits come along with some drawbacks that mainly concern the stability of the materials. That is a major drawback for the commercialization of perovskite solar cells but also still a problem for fuel cell electrode materials. In case of the former, (photo-enhanced) ionic migration and photo-decomposition are of major concern. Given that the materials in SOC research consist of the same structure, research in this field can look back at several decades of research. Based on this immense knowledge, model materials can be chosen to investigate optical effects for the material class of perovskites in general.

For this project, collaboration in the field of high temperature perovskite materials for fuel cell applications was planned with the group of Prof. Tuller at MIT (Cambridge, USA) who is a visiting professor at Kyushu University. Collaboration in the field of perovskite materials for solar cell applications was planned with the group of Prof. Adachi at Kyushu University.

２．研究の目的

In this study, the main goal was to add understanding of the opto-electronic processes in perovskite materials using advanced measurement technology. Goal was to find answers to the fundamental questions about stability and how to tailor the materials to optimize their efficiency while maintaining robustness against temperature and (UV-) light illumination.

For this purpose, (generalized) impedance measurements are a good option because those can be used to investigate the materials in operando. However, impedance measurements including optical excitation and optical response such as dynamic absorption properties are relatively new and require increased attention in order to establish standard techniques for the characterization and understanding of the processes in these materials under various conditions, which even includes the interactions of different materials, such has electron/hole transport layers or other barrier layers in multi-layered structures.

That is why, the goals in this study concerned the development of measurement methods and characterization strategies for the photo-electrochemical processes in perovskite materials as well as providing new insights and a better understanding of those.

３．研究の方法

This project had a strong focus on measurement technology and the development of new measurement techniques. That is why, a flexible setup with precise voltage and current measurement plus a controllable light source and fast light sensors were installed and used. The setup was controlled via a Solartron 1260 frequency response analyzer and a Zurich Instruments MFIA impedance analyzer, which offer flexibility in terms of the controlled, evaluated and correlated signals.

The samples were thin film samples with inter-digitated electrodes (IDE) that enable electronic measurement as well as light illumination and penetration for absorption measurements.

In the first phase of the project, different perovskite materials were investigated. Thin films of $(MA,FA)Pb(I,Br)_3$ films (perovskite solar cell absorber material, ratio between I and Br was varied) were produced. Apart from that, $SrTiO_3$ (in crystalline and amorphous form), a model perovskite material for fuel cell and sensor applications, was tested.

In a second phase, the impedance response of full perovskite solar cells was investigated. Full cells were tested under light and the relevant processes were analyzed and compared with the common understanding as documented in the recent literature.

For the main purposes of this project, the materials relevant for solar cells and SOC showed quite a significant electronic photoconductivity or electronic conductivity, respectively, which accounts for much larger values than the ionic effects that should be investigated here. Doping variation did not lead to consistent new insights because the electronic conductivity of samples with different doping and substitution amounts showed significantly altered electronic properties, such that a systematic study did not seem conclusive.

That is why, another material was chosen for the evaluation of the ionic effects: Gd-doped CeO_2 (GDC). GDC is one of the most prominent oxygen ion conductors and well-documented in the related literature. It does not crystalize in a perovskite structure but a fluorite structure, but the mechanisms under light are supposed to be of comparable nature and thin films could be reproducibly manufactured, and their stability was adequate for the planned experiments.

Thin films with 3% Gd-doping were produced. The rather unusually low doping concentration was chosen because of its well-defined grain boundaries that were supposed to play a major role in the ionic conductivity under light. Both polycrystalline and epitaxial films, with and without grain boundaries, were produced in order to enable a direct comparison of the role of the grain boundaries for the conduction mechanisms and the opto-ionic effects. IDEs were applied as well and conductivity measurements were conducted in the dark and under light with a UV-LED (375nm wavelength, with a photon energy slightly above the band-gap of GDC) in a temperature range between 250°C and 450°C.

Apart from those conductivity measurements, intensity-modulated photocurrent spectroscopy (IMPS) was applied for the first time non-photoactive samples, investigating the dynamics of the opto-ionic effect. Single-frequency impedance transients (SFIT), continuous impedance measurements at a single frequency during changes of measurement conditions (in this case light on/off), were also conducted and correlated to the IMPS measurements.

４．研究成果

In this project, we focused on the light interaction of perovskite materials. One part of the results was establishing a detailed perspective that deconvoluted the impedance response of perovskite solar cells.

The other part of the project was the discovery of an opto-ionic effect happening at grain boundaries of ionic conductors, such as perovskite materials. The experiments for this part were performed on 3%Gd-dopedCeO_2., which is a model material that should behave analogous upon illumination as a perovskite material. The new opto-ionic effect immensely increases the ionic conductivity of the grain boundaries of polycrystalline materials, one of the major drawbacks for ionic conduction in technical materials. It could be shown that the space-charge region and the potential barrier caused by those can be mitigated by light above the band-gap. Photogenerated electron-hole pairs compensate the space-charges but do not lead to electronic conductivity. Temperature changes and photo-decomposition could be excluded to play a part in the observed effects.

Collaborative work with the group of Prof. Adachi at Kyushu University was conducted. The group provided thin films of perovskite solar cell absorber materials and full solar cells. The collaboration with MIT consisted only of remote meetings due to the pandemic.

５．主な発表論文等

〔雑誌論文〕　計0件

〔学会発表〕　計3件（うち招待講演　0件／うち国際学会　1件）

１．発表者名 T. Defferriere, D. Klotz, J. C. Gonzales Rosillo, H. L. Tuller, J. L. M. Rupp
２．発表標題 Photo-enhanced grain boundary ionic conductivity in gadolinium doped ceria solid electrolytes
３．学会等名 Electroceramics XVII,Darmstadt, Germany（国際学会）
４．発表年 2020年～2021年

１．発表者名 D. Klotz, T. Defferriere, J. C. Gonzalez-Rosillo, J. L. M. Rupp, H. L. Tuller
２．発表標題 Photo-Enhanced Grain Boundary Ionic Conductivity in Gadolinium Doped Ceria
３．学会等名 PRiME 2020 (Digital Meeting)
４．発表年 2020年～2021年

１．発表者名 D. Klotz, T. Defferriere, G. F. Harrington, J. L. M. Rupp, H. L. Tuller
２．発表標題 Analyzing the Grain Boundary Resistance in Oxygen Ion Conductors By Static and Dynamic Impedance Measurements
３．学会等名 PRiME 2020 (Digital Meeting)
４．発表年 2020年～2021年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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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