様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科研費 KAKENHI

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研究課題名（和文）Environmental Degradation of Perovskite Electrode Surfaces in Solid Oxide Fuel Cells

研究課題名（英文）Environmental Degradation of Perovskite Electrode Surfaces in Solid Oxide Fuel Cells

研究代表者

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研究者番号：８０６１３２３１

交付決定額（研究期間全体）：（直接経費）　　3,400,000円

研究成果の概要（和文）：固体酸化物形燃料電池（SOFC, Solid Oxide Fuel Cell）は、固体電解質形燃料電池とも呼ばれ、動作温度は700-1,000℃を必要とするので高耐熱性の材料が必要となる。また、起動・停止時間も長い。今回の研究では、ガスによる個体酸化物燃料電池のペロブスカイト電極の劣化を調査しました。また、CO2、H2O、O2の共吸着を調査し、H2Oが炭酸塩の形成を遅らせることを発見しました。

研究成果の学術的意義や社会的意義
Our results were the first to explain the H2O and CO2 competition on the perovskite electrodes surfaces. We have concluded that humidified air can suppress the formation of carbonate phase and as a result extend the electrodes' durability.

研究成果の概要（英文）：The project addressed the problem of environmental degradation of SOFCs electrodes operating in air conditions. Air consists of N2, O2, CO2, H2O and other molecules. While N2 is mostly inert, CO2 and H2O can be significant competitors for adsorption sites on the electrode surface. We have investigated the co-adsorption of H2O and CO2 with O2. We understood that H2O has promoting effect for oxygen exchange while CO2 leads to the formation of carbonate phase that blocks the electrode surface. H2O and CO2 are natural competitors and H2O on the surface can significantly delay or suppress the carbonate phase formation. At low air humidity the carbonate phase is formed, at high air humidity the carbonate phase is suppressed. Our theoretical results were verified by experimental observation of wet and dry CO2 interacting with the electrode surface. We have compared theoretical and experimental IR spectra and we monitored the formation of the carbonate. Results are published: J. Mater. Chem. A

研究分野：materials science

キーワード：SOFC　electrochemistry　electrode reactions　perovskites　DFT

様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９（共通）

１．研究開始当初の背景

The project addressed the problem of environmental degradation of SOFCs electrodes operating in air conditions. Air consists of N2, O2, CO2, H2O and other molecules. While N2 is mostly inert, CO2 and H2O can be significant competitors for adsorption sites on the electrode surface. We have investigated the co-adsorption of H2O and CO2 with O2. We understood that H2O has promoting effect for oxygen exchange while CO2 leads to the formation of carbonate phase that blocks the electrode surface. H2O and CO2 are natural competitors and H2O on the surface can significantly delay or suppress the carbonate phase formation. At low air humidity the carbonate phase is formed, at high air humidity the carbonate phase is suppressed. Our theoretical results were verified by experimental observation of wet and dry CO2 interacting with the electrode surface. We have compared theoretical and experimental IR spectra and we monitored the formation of the carbonate. Results are published: J. Mater. Chem. A, 2018,6, 22662-22672.

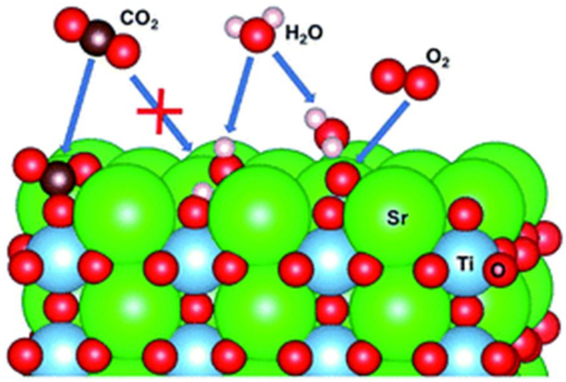

Figure 1. Competative coadsorption of O2, CO2 and H2O on SrTiO3 surface.

２．研究の目的

Our purpose was to investigate and understand the mechanism of electrode surface degradation in air. Our results have shown that the formation of carbonate leads to low oxygen exchange rates. On the other hand, surface water can promote oxygen exchange. We investigated the interplay between O2, CO2, and H2O on the perovskite surface.

３．研究の方法

In this study Periodic, plane wave DFT calculations and first principle molecular dynamics were performed with the Vienna Ab initio Software Package (VASP). The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional was applied using projector augmented wave pseudopotentials. Electron energies were converged to 10−5 eV using the tetrahedron smearing method with Bloch correction for bulk systems and Gaussian smearing for surfaces. The calculations were performed with 400 eV cut-off energy and Monkhorst–Pack k-points mesh of 6 × 6 × 4 for the bulk systems and 6 × 6 × 1 for the slab systems. Geometry optimization was performed using the conjugated gradient algorithm. For bulk systems relaxation was performed of the cell volume, cell shape, and atomic positions. For slab models, relaxation was performed for the atomic positions only. Slabs were constructed using 8 alternating layers of SrO and TiO2 in the [0 0 1] crystallographic directions. The coordinates of the atoms in the bottom four layers (two SrO and two TiO2) were fixed, while the coordinates of the four layers (two SrO and two TiO2) at each surface were fully relaxed. The relaxation was performed until the forces converged to values bellow 0.03 eV Å−2. Activation barriers for various reaction mechanisms were obtained using the nudged elastic band method (NEB) combined with the climbing nudged elastic band method (cNEB). In the process of NEB calculations five images were used between the starting and ending geometries. Starting geometries for the surface species were obtained using the computational annealing technique with first-principle molecular dynamics.

4．研究成果

Based on the Langmuir adsorption theory we have built a thermodinamic model for the CO2 and H2O competition for surface sites on the SrTiO3 electrode.
The CO2 occupied sites are given with the following equaiton where K are equilibrium cnbstats and P is partial pressure.

$$\theta_{CO_2}=\frac{K'_{CO_2}P_{CO_2}}{1+K'_{CO_2}P_{CO_2}+K_{H_2O}P_{H_2O}}+\left(1-\frac{K'_{CO_2}P_{CO_2}}{1+K'_{CO_2}P_{CO_2}+K_{H_2O}P_{H_2O}}-\frac{K_{H_2O}P_{H_2O}}{1+K'_{CO_2}P_{CO_2}+K_{H_2O}P_{H_2O}}\right)\left(\frac{K_{CO_2}P_{CO_2}}{1+K_{CO_2}P_{CO_2}+K_{H_2O}P_{H_2O}}\right)$$

The H2O occupied sites are given with the following equaiton where K are equilibrium cnbstats and P is partial pressure.

$$\theta_{H_2O}=\frac{K_{H_2O}P_{H_2O}}{1+K'_{CO_2}P_{CO_2}+K_{H_2O}P_{H_2O}}$$

Based on the equlibrium conatant computed with DFT activation energies and selected pressures we estimated the following surface covarage for the CO2 and H2O.

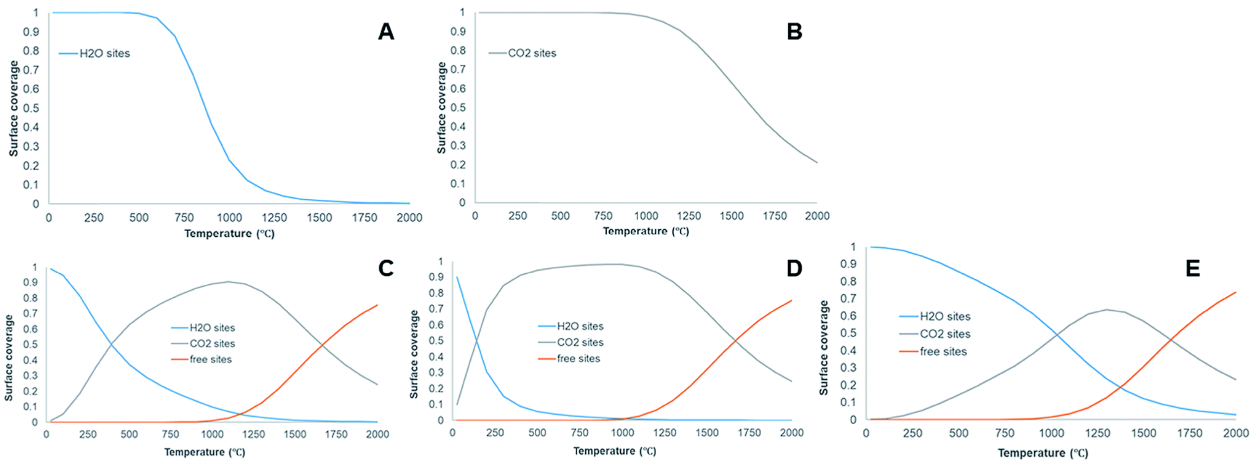

Figure 2. Surface coverage of CO_2 and H_2O. (A) P H_2O = 10−5 in absence of CO_2; (B) P CO_2 = 3.9 × 10−4 in absence of H_2O; (C) P H_2O = 10−5 and P CO_2 = 3.9 × 10−4; (D) P H_2O = 10−6 and P CO_2 = 3.9 × 10−4; (E) P H_2O = 10−4 and P CO_2 = 3.9 × 10−4.

We should note that in this work we limit our research to several abundant molecules in the atmosphere: O_2, CO_2, and H_2O. However, depending on the geographical location, the atmospheric air may contain other molecules which can affect the surface composition, chemical properties and operation of devices with perovskite electrodes. Various NO_x and SO_x compounds can be found in the air close to sites with volcanic activity and large cities with thermal power plants and intensive automobile traffic and their effect on perovskite surfaces remain unclear.

５．主な発表論文等

〔雑誌論文〕　計2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　0件）

１．著者名 Yoonyoung Kim, Motonori Watanabe, Junko Matsuda, Aleksandar Staykov, Hajime Kusaba, Atsushi Takagaki, Taner Akbay, Tatsumi Ishihara	４．巻 8
２．論文標題 Chemo-mechanical strain effects on band engineering of the TiO2 photocatalyst for increasing the water splitting activity	５．発行年 2020年
３．雑誌名 Journal of Materials Chemistry A	６．最初と最後の頁 1335-1346
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/C9TA11048H	査読の有無 無
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 -

１．著者名 Staykov Aleksandar、Fukumori Shun、Yoshizawa Kazunari、Sato Kenta、Ishihara Tatsumi、Kilner John	４．巻 6
２．論文標題 Interaction of SrO-terminated SrTiO3 surface with oxygen, carbon dioxide, and water	５．発行年 2018年
３．雑誌名 Journal of Materials Chemistry A	６．最初と最後の頁 22662～22672
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/C8TA05177A	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕　計3件（うち招待講演　2件／うち国際学会　2件）

１．発表者名 Aleksandar Staykov
２．発表標題 Interaction of O2, CO2 and H2O with perovskite surface. Insights from the theory
３．学会等名 SSI-22（招待講演）（国際学会）
４．発表年 2019年

１．発表者名 Aleksandar Staykov
２．発表標題 Interaction of O2, CO2 and H2O with perovskite surface. Insights from the theory
３．学会等名 SOIFIT workshop Royal Society London（招待講演）
４．発表年 2020年

１．発表者名 Aleksandar Staykov, Tatsumi Ishihara, John Kilner
２．発表標題 Interaction of O2, CO2 and H2O with perovskite surface. Insights from the theory
３．学会等名 PACRIM13（国際学会）
４．発表年 2019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