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論 文 内 容 要 旨

1. Introduction

Solid Oxide Fuel Cell (SOFC) is a device that can convert the chemical energy into electrical energy directly without any combustion. SOFC has been commercialized since last decade ago as one of the alternavite energy converter. SOFC operate at high temperature and it has several important component such as anode, electrolyte, cathode and interconnector. Among the SOFC component, the cathode part has large resistance which restrict the performance of SOFC. Many researcher and worker focus on the cathode part since it has large overpotential and the oxygen reduction at the cathode is difficult reaction to be activated.

A cathode material for SOFC should meet various requirements such as described in the following:

1) High electronic conductivity,
2) High catalytic activity for oxygen reduction,
3) The chemical stability under the SOFC operating condition or cell preparation condition,
4) Has high morphological stability,
5) The thermal expansion coefficient that matches with an electrolyte.

For cathode material, it is preferred that materials with the electronic conductivity exhibits higher than c.a. 100 S/cm at SOFC operating atmosphere. Under these conditions, several spinel perovskite oxides with 3d metal transition can be selected.

The material selection becomes important to obtain a high electronic and ionic cathode. Several states the art of the cathode SOFC is Co-based perovskite oxide, such as: $La_{1-x}Sr_xCoO_{3-\delta}$ (LSC), and

$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF). However, these materials has large thermal expansion coefficient mismatch with the ionic conducting oxide despite shows high performance electrochemical properties. In the case of the SOFC cathde, the B-site of the perovskite structure is strongly connected with the oxygen as BO_6 octahedron and mainly determines the character of the perovskite-type oxide. So far, The Ni in the B-site of perovskite-type structure rarely studied. The $LaNiO_{3-\delta}$ is one of the "mother" composition for several cathode such as: $La(Ni,Fe)O_{3-\delta}$, and $La(Ni,Co)O_{3-\delta}$ which is rarely studied although it may have better performance.

Numerous studies on these materials so far concerned only the performance, and just a few did the mechanism of the oxygen reduction process. Thus, the electrochemical kinetics on this electrode material is not clear yet. In this study, electrochemical oxygen reduction process on a $LaNi_{1-x}Fe_xO_{3-\delta}$ and $LaNi_{1-x}Co_xO_{3-\delta}$ electrode was investigated to determine the reaction mechanism in order to improve its performance.

2. Basic Properties of $LaNi_{1-x}M_xO_{3-\delta}$ (M = Fe, Co and x = 0.2, 0.4, 0.6, 0.8)

The electrochemical performance of solid oxide fuel cell cathode depends on their ability to reduce and transport the oxygen through their bulk or surface. This ability corresponds to their oxygen vacancy concentration and transport properties. Thus, it is important to understand the properties as an aid for further research. So far, the basic properties of Ni-based perovskite oxide haven't been studied yet. In order to understand the factor limiting of their electrochemical performance, it is necessary to understand their basic properties.

At first, the the electronic conduction mechanism and defect chemical model were determined by the electronic conductivity measurement and high temperature gravimetry, respectively. From electronic conductivity measurement, the $LaNi_xFe_{1-x}O_{3-\delta}$ has a hopping or semiconductor conduction mechanism. Meanwhile, the $LaN_xCo_{1-x}O_{3-\delta}$ has metal-like conduction mechanism. The small polaron model where the $Ni^{3+} + Fe^{4+} \rightarrow Ni^{2+} + Fe^{4+}$ is considered as the disproportionation of the B-site transition, which is well-fitted to $LaNi_xFe_{1-x}O_{3-\delta}$. The delocalized model defect chemical model is well-fitted with the experimental data for $LaNi_{0.6}Co_{0.4}O_{3-\delta}$.

In other side, the diffusivity, D^*, and surface oxygen exchange kinetics, k^*, has been determined by isotope exchange by isotope exchange technique and secondary ion mass spectrometry. From the $\vartheta \ln k^* / \vartheta \ln D^*$ classification, the $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ fall into electron rich conductor. Meanwhile, the

$LaNi_{0.6}Feo_{0.4}O_{3-\delta}$ fall in the range of poor to rich electron conductor. It suggest that the $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ will have better electrode performance compared to the $LaNi_{0.6}Feo_{0.4}O_{3-\delta}$.

The result of oxygen nonstoichiometry at high $p(O_2)$ ($1 - 10^{-4}$ bar) was in good agreement with the lattice expansion which was almost independent over the $p(O_2)$ for $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, $LaNi_{0.6}Co_{0.4}O_{3-\delta}$, and $LaNiO_{3-\delta}$ as well. The secondary phase didn't observe for $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$. On the side, the secondary phase, NiO, was observed for the $LaNiO_{3-\delta}$ sample. The thermal expansion of LNC is higher than the LNF. However, the LNF and LNC could be considered to have good compatibility with Zirconia or Ceria-based electrolyte.

3. Determination of Rate Limiting Step on $LaNi_{0.6}M_{0.4}O_{3-\delta}$ film Electrode (M = Fe, Co)

Electrochemical properties of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ film electrodes were measured by electrochemical impedance spectroscopy as functions of temperature, *T*, oxygen partial pressure, $P(O_2)$, and thickness of the film electrode to determine the rate determining step of oxygen reduction process. From its chemical capacitance, the oxygen reduction process was limited on the surface, which had good agreement with the isotope exchange depth profile measurement. In the isotope diffusion profile, The reaction barrier of the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ film electrodes can be divided into three parts: surface, subsurface, and bulk dense film electrode. However, the contribution of subsurface and diffusion is less than 1% of total resistance barrier of $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ dense film electrode.

4. Reaction Mechanism of $LaNi_{0.6}M_{0.4}O_{3-\delta}$ Porous Electrode (M = Fe, Co)

$LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ porous electrode was measured as a function of temperature (923~1153K) and oxygen partial pressure (10^{-3}~1 bar) by impedance spectroscopy. Analysis of the electrode kinetics using appropriate equivalent circuits that the origins of electrochemical processes were separately identified yields value for area specific conductivity and chemical capacitance. Based on the capacitance, the effective reaction length (ERL) was estimated for the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ porous electrode. The ERL was near the triple phase boundary indicates that it has a slow bulk diffusion. Another method by Adler-Lane-Steele model was conducted to give another insight on ERL on $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ porous electrode. The model also showed that ERL is near the triple phase boundary.

5. The Effect of $Ce_{0.9}Gd_{0.1}O_{1.95}$ Coexistence on the Oxygen Exchange Kinetics on Perovskite Oxide Electrodes

The composite electrode between mixed ionic and electronic conductor and ionic conducting oxide has been studied in order to get better performance of solid oxide fuel cell cathode. The contact area between electronic and ionic conducting part is believed as the reason that electrode performance enhances drastically compared to the single phase porous electrode. The question has been rising on the reason of enhancement of composite electrode. In the composite electrode, the effective reaction length, the length of the oxygen reduction reaction takes place, should be increased due to the increasing the contacting area between electronic and ionic conducting part. However, in our study on $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ – $Ce_{0.9}Gd_{0.1}O_{1.95}$ and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ – $Ce_{0.9}Gd_{0.1}O_{1.95}$ composite electrode, the effective reaction length was not enhances despite the electrochemical performance increased drastically. There is another factor as the reason of the enhancement on the composite electrode.

The first experiment was on the $Ce_{0.9}Gd_{0.1}O_{1.95}$ existence on the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ film electrode. The effect of $Ce_{0.9}Gd_{0.1}O_{1.95}$ loading on $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ electrode has been demonstrated by an experiment with a comparison of two different samples. From our study, $Ce_{0.9}Gd_{0.1}O_{1.95}$ porous layer existence of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ film surface enhances the oxygen surface exchange which is demonstrated by the electrochemical impedance and the depth profile method.

The second experiment was on the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ bulk sample which coated by $Ce_{0.9}Gd_{0.1}O_{1.95}$. The isotope exchange treatment and secondary ion mass spectroscopy were utilized to determine the surface oxygen exchange kinetics (k^*) of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ coated with $Ce_{0.9}Gd_{0.1}O_{1.95}$. The k^* of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ coated with $Ce_{0.9}Gd_{0.1}O_{1.95}$ enhanced compared to the bare $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ due to the formation of the triple phase boundary between $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, $Ce_{0.9}Gd_{0.1}O_{1.95}$, and gas phase of oxygen. The $Ce_{0.9}Gd_{0.1}O_{1.95}$ only affects the k^*, while the diffusivity (D^*) is no clear dependence of the $Ce_{0.9}Gd_{0.1}O_{1.95}$ existence. The role of $Ce_{0.9}Gd_{0.1}O_{1.95}$ at $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ surface involved in the oxygen reduction can be to serve the incorporation site for the adsorbed and dissociated oxygen at the $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ surface.

The third experiment was on the powder sample which measured by pulsed isotope exchange. Three different samples, $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$, $Ce_{0.9}Gd_{0.1}O_{1.95}$, and $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ - $Ce_{0.9}Gd_{0.1}O_{1.95}$ were measured their oxygen surface exchange at 573 – 673 K at 10^{-2} bar $p(O_2)$. The profile of oxygen 32, 34, and 36 has different characteristic especially on the oxygen 34. It appears that 34 is the result of the slow reaction at the surface as the incorporation is the limiting step. In the case of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ it appeared the 34 as a

slow incorporation process, and adding $Ce_{0.9}Gd_{0.1}O_{1.95}$ enhanced the incorporation process as the 34 didn't observe at $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ - $Ce_{0.9}Gd_{0.1}O_{1.95}$. The PIE result was compared to the isotope exchange experiments which both of measurement have different agreements on activation energy.

To give another insight, the high ionic conductivity cathode of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ has been investigated so far. Several experiments on $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ - $Ce_{0.9}Gd_{0.1}O_{1.95}$ composite electrode was performed. The surface exchange kinetics of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ didn't enhance due to the $Ce_{0.9}Gd_{0.1}O_{1.95}$ existence. It is due to the electronic conducting path of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ was blocked by the $Ce_{0.9}Gd_{0.1}O_{1.95}$ existence. Moreover, the diffusivity of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ and $Ce_{0.9}Gd_{0.1}O_{1.95}$ is close each other which indicates the additional ionic conducting path wasn't needed by $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ to make faster oxygen reduction process.

6. Hetero-Structured Electrode of Ni-based Perovskite Electrode

The dissimilar structure between the two oxides attracts the attention since it could enhance the cathode performance significantly. This strategy has been used to develop a hetero-structure electrode which could has a higher performance than a single phase electrode. In this study the hetero-structure of $LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ (Perovskite oxide) film electrode and $La_2NiO_{4-\pm}$ (Rudlesden-popper) porous electrode was studied. The enhancement of the cathode performance was observed and the reaction mechanism in the hetero-structure was studied in this part. Moreover, the hetero-junction of two mixed conductors was also studied in the form of the composite electrode.

7. Exploring New Cathode Material of Ni-Based Perovskite Structure

$LaNi_{0.6}Fe_{0.4}O_{3-\delta}$ and $LaNi_{0.6}Co_{0.4}O_{3-\delta}$ is cathode solid oxide fuel cell which Strontium-free. One of the ways to enhance the cathode performance is to enhance the amount of oxygen vacancy concentration. When an aliovalent dopant (dopant which has different valence) is doped to the A-site perovskite oxide, the oxidation state of the substitution ion would be different from the host ions. As the effect, to compensate the formation of oppositely charged defects, the electroneutrality would be needed. Thus, the oxygen vacancy is expected to generate in this state and enhance the ionic conductivity of the cathode.

（別紙）

論文審査結果の要旨及びその担当者

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論文審査結果の要旨

化石燃料の利用は人類社会の発展にとって重要な要素となってきたが，資源量には限りがあり，地球温暖化ガスの排出も問題となっている。このため，化石燃料をより効率よく利用する技術として，固体酸化物形燃料電池（Solid Oxide Fuel Cell: SOFC）が注目され，家庭用コジェネレーションシステムをはじめとして，より本格的な普及に向けた開発が進められている。SOFC の性能を左右する空気極材料には，希土類，アルカリ土類および遷移金属からなるペロブスカイト型複合酸化物が用いられる。Ni を遷移金属サイトに含むペロブスカイトでは，Ni は 3 価に相当する異常原子価をとることが知られており，Fe や Co との共存により安定化することで，高性能な電極材料の候補とされるが，その物性や電極としての挙動には不明な点が多く，その解明が重要な課題となっている。本論文は，ニッケル系ペロブスカイト型酸化物の，酸素不定比性，輸送特性，および電気化学特性を明らかにし，高性能電極の設計指針を提示することを目的としたものであり，全編８章からなる。

第１章は緒論であり，本研究の背景と目的を述べている。

第２章では，$LaNi_{1-x}M_xO_{3-\delta}$ (M=Fe,Co)を取り上げ，酸素空孔濃度の酸素分圧依存性を熱微重量天秤法およびクーロン滴定法によって定量化し，その欠陥平衡モデルを構築して，酸素の部分モルエンタルピー，部分モルエントロピーを算出している。さらに，同位体交換と二次イオン質量分析とを組み合わせた手法によって測定した酸素の同位体拡散係数，および，高温粉末 X 線回折によって得られた格子定数の温度・酸素分圧依存性を，先の欠陥平衡式をもとに解析し，後の章で行う電極反応の解析のための基礎データとしている。

第３章では，電極反応解析のためのモデル試料として，$LaNi_{1-x}M_xO_{3-\delta}$ (M=Fe,Co)の緻密膜電極を作製し，その電気化学的な挙動を，温度と酸素分圧をパラメータとする交流インピーダンス測定によって解析している。電極内の酸素空孔の生成・消滅に基づく化学容量が，インピーダンスの周波数依存性を決定している事を明らかにし，その膜厚依存性およびバイアス依存性から，電極反応の律速過程が表面およびその近傍での反応・輸送過程であることを解明するとともに，これを同位体交換法により検証している。

第４章では $LaNi_{1-x}M_xO_{3-\delta}$ (M=Fe,Co)の多孔質電極を作製し，その電気化学的挙動を交流インピーダンス法によって解析している。前章までに得られた基礎データをもとに，Adler-Lane-Steele モデルを適用して有効電極反応場の空間的な広がりを見積もるとともに，これをインピーダンスの緩和時間から実測した値と比較することで，この系では電極反応場が予想よりも短く，電極／電解質界面のごく近傍での酸素の吸着・解離過程が特性を決定する因子であるとの結論を導き出している。

第５章では, $LaNi_{1-x}M_xO_{3-\delta}$ (M=Fe,Co)の電極反応速度を向上させるために, 酸化物イオン導電体である $Ce_{0.9}Gd_{0.1}O_{1.95}$（GDC）粒子を混合する方法を提案している。緻密 $LaNi_{1-x}Fe_xO_{3-\delta}$ 表面を多孔質 GDC 粒子で修飾したモデル系のインピーダンスおよび同位体交換速度を測定し，GDC 粒子の共存が表面の触媒活性にも影響を与える事を見出している。さらに，パルス同位体交換法によって，$LaNi_{1-x}Fe_xO_{3-\delta}$粒子表面では，解離・吸着した酸素がバルクに取り込まれる過程が反応障壁として存在すること， GDC 粒子が介在する事でこの過程の速度が促進される事を見出している。さらには, $LaNi_{1-x}Fe_xO_{3-\delta}$に対して Rudlsden-Popper 相である La_2NiO_4粒子を共存させた場合にも同様の促進効果があることを見出し，高性能電極材料の設計に有益な指針を与えるものとなっている。

第７章では, $LaNiO_3$に対して La サイトに Sr などの低価数イオンを固溶させることで電気化学反応速度を向上させることを試みており，より高性能な電極を探索するための方向性を提示している。

第８章は結論であり，本論文を総括している。

以上要するに，本論文は，SOFC の高性能電極の設計に関する基礎的な知見を与えるものであり，この技術の普及による化石燃料の使用量低減に貢献するとともに，環境科学分野の学術の発展に寄与するところが少なくない。

よって，本論文は博士（学術）の学位論文として合格と認める。