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論文内容要旨

Reducing carbon footprints by replacing fossil fuels with eco-friendly and sustainable energy has been a worldwide goal since global climate change emerged as a serious problem. Solid oxide fuel cells (SOFC) transform chemical energy of fuels into electrical energy through electrochemical reactions. SOFC is a promising energy device for the next generation because of its high power density, energy conversion efficiency, and fuel flexibility. However, the elevated temperatures of over 750°C required for SOFC operation present several disadvantages such as high cost of materials, particularly for interconnects, and rapid degradation of the cell, which is why researchers are attempting to develop IT-SOFCs that can operate at lower temperatures (500°C ~ 700°C). The cathode material is the most crucial part to consider in IT-SOFCs because oxygen reduction reaction (ORR) that occurs at the cathode has the highest activation energy of all the reactions.

Oxygen separation membranes are another prospective electrochemical device for the production of hydrogen which is considered a future fuel. Compared to the conventional steam reforming method, CH₄ reforming via partial oxidation using an oxygen separation membrane is advantageous due to its speedy operation, compact size and an ability to manufacture highly purified H₂. Not only as a fuel reformer, but the membranes can be also used to produce pure O₂ which improves the production efficiency of various combustion systems.

Mixed ionic electronic conductors (MIECs) are now at the center of attention as a cathode material for IT-SOFCs as well as an oxygen separation membrane because both its ionic and electronic conduction allow oxygen reduction reaction (ORR) to occur on the entire surface. Among many MIECs, Co-based perovskite-type oxides are state-of-the-art. For instance, over 1 W/cm² of peak power was demonstrated at 600°C in a cell with Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) as the cathode [1]. However, other factors in addition to electrochemical activity should be considered for device application. Co-based perovskite-type oxides are regarded as less appropriate than Co-free and Fe-based

perovskite-type oxides in terms of mechanical properties, cost, and thermal stability. Thus, the motivation of this study is to search for Co-free and Fe-based perovskite-type mixed conducting oxides with performance comparable to Co-based perovskite-type oxides.

Perovskite-type strontium ferrite, $\text{SrFeO}_{3-\delta}$, has been focused of many studies because of its high oxygen nonstoichiometry (δ) and mixed conductivity. However, due to the oxygen vacancy order-disorder transition from cubic perovskite to brownmillerite makes it hard to be applied for devices [2]. In this study, bismuth-doped strontium ferrites were focused on from the fact that the substitution of trivalent cation for divalent strontium showed an increase in structural stability. Moreover, the nature of the $6s^2$ lone pair in Bi^{3+} allows it to easily make the bonds with $2p$ orbit electrons in O^{2-} resulting in local structure distortion that decreases barrier energy for oxide ion transport, resulting high ionic conductivity according to reports of Bi-containing oxides such as stabilized Bi_2O_3 [3,4,5].

There are a few previous studies focusing on electrochemical properties of Bi-Sr-Fe-based perovskite-type oxides. Brinkman *et al.* proved the mixed conductivity of this material system, especially relatively high ionic conductivity through oxygen permeation experiments [6]. According to a report by Niu group, $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (BSF55) showed the lowest electrode resistance among Co-free perovskite-type oxides [7]. Regardless of its potential as a solid-state ionic material, details on defect equilibrium including oxygen nonstoichiometry and factors affecting cathode properties, such as electrode thickness and a change in defect equilibrium through doping have not been reported so far.

Therefore, the purpose of this study is to investigate defect equilibrium and oxygen nonstoichiometry of Bi-Sr-Fe-based perovskite-type oxides in detail. In addition, two applications, IT-SOFC cathode and oxygen separation membrane, are considered for the material system.

In this thesis, chapter 3 deals with crystal structure, defect equilibrium, and oxygen nonstoichiometry of Bi-Sr-Fe-based perovskite-type oxides. In chapter 4, the relationship between cathode properties and factors, such as electrode thickness, dopant and composition are thoroughly discussed. Finally, the fabrication of porous body-supported thin film membrane and its oxygen permeation characteristics are described in chapter 5.

Based on both oxygen nonstoichiometry and electrical conductivity as a function of oxygen partial pressure, $P(\text{O}_2)$, it was confirmed that strontium acceptors were mostly charge-compensated by oxygen vacancy ($\text{V}_{\text{O}}^{\bullet\bullet}$) formation through 50 mol% of Sr doping. Therefore, the relation between the charge defect concentrations of Bi-Sr-Fe-based perovskite-type oxides would be $[\text{Sr}_{\text{Bi}}] \approx [\text{V}_{\text{O}}^{\bullet\bullet}] \gg [\text{Fe}_{\text{Fe}}]$ for a wide range of temperature and $P(\text{O}_2)$, which is apparently different that of Co-based perovskite-type oxides. Nonetheless, mixed conductivity was clearly revealed at $P(\text{O}_2) > 10^{-6}$ atm and the decomposition $P(\text{O}_2)$ of $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ (BSF55) was lower than the equilibrium $P(\text{O}_2)$ of Bi/ Bi_2O_3 from a temperature range of 650 to 750°C. Taking into account both defect equilibrium and thermal

stability, Bi-Sr-Fe-based perovskite-type oxides fulfill the requirements to be a IT-SOFC cathode. In addition, conductivity and oxygen nonstoichiometry measurements showed that La doping resulted in a change in defect equilibrium, increase in electron hole concentration, and decrease in oxygen vacancy concentration. Also, Mn-doped BSFs will probably show the same trend of defect equilibrium, based on the conductivity measurements.

Regarding cathode properties in chapter 4, the estimated effective thickness of BSF55 porous electrode in this study was between 12 μm ~ 24 μm , based on fitting done using the Gerischer impedance model. From the $P(\text{O}_2)$ dependence, it is suggested that reaction limiting step of the ORR at BSF55 electrode is oxygen dissociation from 600°C to 650°C and above 700°C is charge transfer reaction and oxygen adsorption. In the case of La-doped $\text{Bi}_{0.7}\text{Sr}_{0.3}\text{FeO}_{3-\delta}$ (BSF73) electrodes, resistance for ORR decreases with increasing La doping by 30 mol% and from 30 mol%, it starts to increase with further La doping. Combined with the oxygen permeation result that show the maximum permeation flux at 30 mol% of La doping, electronic defect concentration partially affects the surface exchange reaction in Bi-Sr-Fe-Based perovskite-type oxides, which have poor electronic conductivities as a cathode. The addition of $\text{PrBaCo}_2\text{O}_{5+\delta}$ (PBCO) up to 30 mol% lowered the activation energy and affected $P(\text{O}_2)$ dependence. This can be interpreted as the electrode reaction mechanism changed through the addition of PBCO. From the results that Bi-Sr-Fe-based perovskite-type oxide electrodes showed both lower activation energy and thermal expansion coefficient than other famous Co-based perovskite-type oxide electrode, except for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF) as shown in Fig. 1, it is highly possible of this material system to be applied as a cathode for IT-SOFCs.

In Chapter 5, BSF55 porous body-supported BSF55 thin membrane was successfully fabricated by the spin-coating method. Fabricated thin BSF55 membranes with thicknesses between 12 μm and 15 μm were dense enough to separate oxygen from air. As shown in Fig. 2, oxygen permeation results suggested that not only the porous body but also the porous layer on the opposite side is important ($j(\text{O}_2)_{\text{ox}} = j(\text{O}_2)_{\text{red}} = j(\text{O}_2)_{\text{bulk}}$ at steady state). In the case of BSF55, $j(\text{O}_2)$ seemed to be limited by the

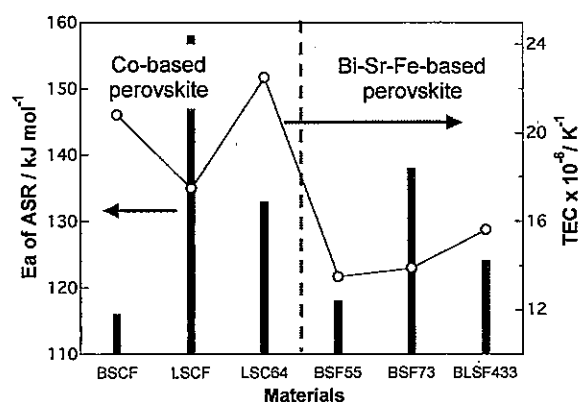


Figure 1. Activation energy of electrode reaction and thermal expansion coefficient of Co-based perovskite oxides and Bi-Sr-Fe-based perovskite oxides.

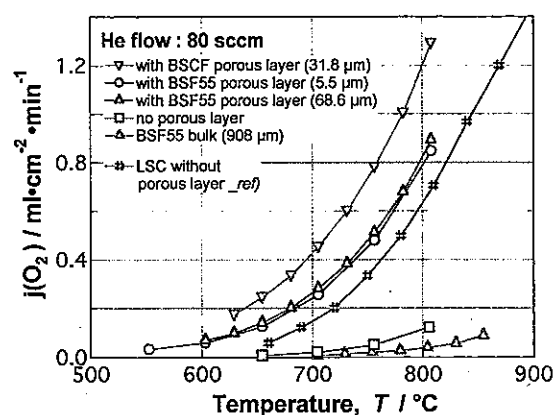


Figure 2. Oxygen permeation rate of various types of BSF55 membranes under 80 sccm of He flow.

oxidation reaction of oxygen, in other words, the faster surface exchange reaction of oxygen occurs at the porous body rather than the porous layer on the opposite side of membrane.

In conclusion, Bi-Sr-Fe-based perovskite-type oxides show a defect equilibrium condition of $[Sr_{Bi}] \approx [V_{O}^{\bullet\bullet}] \gg [Fe_{Fe}^{\bullet}]$ for a wide range of temperature and $P(O_2)$, which is quite different from Co-based perovskite-type oxides. When electrode thicknesses and electronic defect concentration are taken into account, this material system is able to replace other Co-based perovskite-type oxides as an electrode. Finally, it was found that porous body-supported thin membrane of Bi-Sr-Fe-based perovskite-type oxides could have oxygen permeability comparable to that of Co-based perovskite-type oxides by enhancing the surface area of both the porous body and the porous layer.

References

- [1] Z. Shao *et al.*, *Nature* **431** (2004) 171.
- [2] J. Mizusaki *et al.*, *J. Solid State Chem.*, **99** (1992) 166-172.
- [3] R. Seshadri *et al.*, *Chemistry of Materials*, **13** (2001) 2892~2899.
- [4] J.B. Goodenough, *Solid State Ionics*, **94** (1997) 21.
- [5] E.D. Wachsman *et al.*, *Science* **334** (2011) 935.
- [6] K. Brinkman, *et al.*, *Solid State Ionics*, **181** (2010) 58.
- [7] Y. Niu *et al.*, *J. Mater. Chem.*, **20** (2010) 9621.

論文審査結果の要旨

酸化物イオン・電子混合導電体は、固体酸化物形燃料電池(SOFC)の正極材料や酸素透過膜への応用が期待される材料である。Co を含有するペロブスカイト型酸化物が、優れた酸化物イオン・電子混合導電性を有するためこれまで広く研究されてきたが、熱膨張係数が固体電解質材料に比べて著しく大きい、機械的強度が低い、さらに価格が高い等の欠点があり、Co を含まずに同等の混合導電性を発現する材料の開発が期待されている。そこで、Co を含有しない Bi-Sr-Fe 系ペロブスカイト型酸化物に着目し、その合成、混合導電性を支配する酸素不定比性と欠陥平衡の解明、SOFC の正極材料ならびに酸素透過膜としての応用を検討した。本論文はこれらの研究成果をまとめたものであり、全編 6 章から構成される。

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、本論文で用いられた実験方法を作製と評価に分けて詳細に記述している。合成には目的に応じて固相反応法とペチニ法が用いられた。酸素不定比性はヨウ素滴定法と電量滴定法により決定された。電気伝導度の温度・酸素分圧依存性、電極特性、酸素透過特性の評価方法も確立された。

第 3 章では、Bi-Sr-Fe 系ペロブスカイト型酸化物が作製され、その酸素不定性と欠陥平衡を明らかにした。Bi サイトが Sr で 30~50 mol% 置換された場合、立方晶ペロブスカイト型酸化物が単相として得られた。同時に La 置換、Mn 置換試料も固溶体として合成された。酸素不定比性の測定から、Bi-Sr-Fe 系ペロブスカイト型酸化物において、アクセプターの Sr はほぼ全て酸素空孔の生成で補償されることが示された。同時に、La や Mn 置換した試料では、補償機構が電子的補償(正孔の生成)に移行することを見出し、本系材料の欠陥平衡を明らかにした。さらに、本系材料が 850°C において 0.78 S/cm と Co 基ペロブスカイト型酸化物に匹敵する高い酸化物イオン伝導度と正極材料や酸素透過膜として応用可能な耐還元性を有していることを明らかにした。

第 4 章では、Bi-Sr-Fe 系ペロブスカイト型酸化物の SOFC 正極材料としての特性を明らかにした。本系材料と化学的両立性を示す Sm 置換 CeO₂ 薄膜を電解質としたセルに、多孔質電極として Bi-Sr-Fe 系ペロブスカイト型酸化物を成膜し、複素インピーダンス解析が行なわれた。電極の有効厚さは 12~24 μm 程度であり、電極反応の律速過程は酸素分子のかい離反応と示唆された。高い電子伝導性を示す 30 mol%La 置換試料では電極抵抗の低減が達成された。さらに、不足する電子伝導性を補う目的で、Bi-Sr-Fe 系ペロブスカイト型酸化物と Pr-Ba-Co 系ダブルペロブスカイト型酸化物との複合体電極が作製され、30 vol%の Pr-Ba-Co 系酸化物を添加することで、電極抵抗ならびにその活性化エネルギーが最小となった。

第 5 章では、Bi-Sr-Fe 系ペロブスカイト型酸化物のもう一つの電気化学デバイスへの応用として酸素透過膜が検討された。50 mol%Sr 置換試料を同組成の多孔体上に厚さ 12~15 μm の緻密膜として形成する技術を確認し、表面修飾を施すことで厚さ 1mm 程度のバルク体に比較して 34 倍の酸素透過速度を実現した。

第 6 章は本論文を総括した結論である。

以上要するに本論文は、Bi-Sr-Fe 系ペロブスカイト型酸化物なる新規な混合導電性酸化物を合成し、電気伝導性を支配する欠陥平衡を解明するとともに、電気化学デバイスとしての固体酸化物形燃料電池や酸素透過膜に応用可能であることを示したものであり、固体イオニクス材料の発展に寄与するところ少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。