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A Study of Anode Functional Layer for Protonic Solid Oxide Electrolysis Cells
(プロトン固体酸化物電解セルに対するアノード機能層の研究)

Carbon neutrality is the goals set by countries around the world for 2050. One of the key measures is decarbonizing the production of hydrogen, resulting in “green” hydrogen. Instead of a “gray” hydrogen process based on steam methane reforming, a renewable energy grid integrated water electrolysis system makes carbon-free, green hydrogen production feasible. Steam electrolysis with solid oxide electrolyte cells has some advantages in comparison to room temperature water electrolysis based on the thermodynamic aspects of the water splitting reaction. Protonic solid oxide electrolysis cells (P-SOECs) comprising $\text{Ba}(\text{Zr,Ce,M})\text{O}_{3-\delta}$ ($\text{M} = \text{Y, Yb, etc.}$) proton-conducting electrolytes are promising for steam electrolyzer because they can directly produce a pure hydrogen without separation and the high operation temperature can promote electrode reaction at a reasonable rate without a use of precious metal catalysts. Major issues of P-SOECs are the relatively high anode reaction resistance with the cell using thermodynamically stable Zr-rich side $\text{Ba}(\text{Zr,Ce,M})\text{O}_{3-\delta}$ and the low Faradaic efficiency by formation of hole minor carriers. The proton-accessible anode reaction areas are limited near the gas-anode-electrolyte triple-phase boundary (TPB) in P-SOECs owing to the mismatch of primary ionic carries between anode and electrolyte materials. $\text{Ba}(\text{Zr,Ce,M})\text{O}_{3-\delta}$ electrolyte involves hole carries through the vacancy–gas association in relatively high oxygen partial pressures and the migration of the holes thus formed decrease the Faradaic efficiency. $\text{Ba}(\text{Zr,Ce,M})\text{O}_{3-\delta}$ electrolytes with Zr-rich side composition are thermodynamically stable in high humidified condition and suitable for steam electrolysis applications. Meanwhile $\text{Ba}(\text{Zr,Ce,M})\text{O}_{3-\delta}$ electrolytes tend to show high grain boundary resistance and large hole concentration in air atmosphere with increasing Zr contents because of the thermodynamic properties. Hence, it is a great challenge to improve the cell resistances and Faradaic efficiency of the P-SOECs with high Zr content $\text{Ba}(\text{Zr,Ce,M})\text{O}_{3-\delta}$ electrolyte. The reaction kinetics in the sites near TPB must be crucial to the overall anode reaction resistances in P-SOECs, and the hole injection into $\text{Ba}(\text{Zr,Ce,M})\text{O}_{3-\delta}$ electrolytes normally occurs near the anode/electrolyte interfaces. Therefore, it is highly motivated to modify the interfaces by functional oxide thin films in order to increase the electrochemically active sites in TPB and depress the hole carriers in the underlayer of the anode. This thesis demonstrates that the implementation of anode functional layer (AFL) at electrolyte/anode interface is an efficient way to improve simultaneously the anode reaction resistance and Faradaic efficiency of P-SOECs based on high Zr-content electrolyte. Various thin films with different structures and transport properties were employed to AFL and the material optimization was carried out in terms of the electrolysis current and efficiency of the corresponding cells. The functionality of AFL was clarified by means of electrochemical measurements with homemade high temperature steam electrolyzer test station. Finally, a robust guidance to design optimal AFL were dedicated.

This thesis consists of 6 chapters. Chapter 1 summarized the recent advances and major issues of P-SOECs. The motivation to design the anode/electrolyte interface and objectives to develop AFL were described.

Chapter 2 gave the experimental methods for material synthesis, cell fabrication and deposition of AFL. The measurement setup of electrochemical analysis and efficiency evaluation was also introduced.

In chapter 3, $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ (LSC) thin film (~90 nm) was applied as AFL in P-SOECs based on Zr-rich side $\text{BaZr}_{0.6}\text{Ce}_{0.2}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb6211) and Ce-rich side $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb1711) electrolytes, respectively. The LSC AFL was found to significantly increase the electrolysis current of BZCYYb6211 cell with decreasing both ohmic and polarization resistances. Hence the BZCYYb6211 cell exhibited the similar current density as BZCYYb1711 cells (1.22 vs 1.13 A cm^{-2}) at 600 °C in 1.3 V with AFL. Faradaic efficiency of about 70% was achieved by BZCYYb6211 cell at 500 °C near 1.3 V. The decreased ohmic resistance indicated that the conduction paths near anode/electrolyte interface were increased by AFL.

In chapter 4, various oxides with double (O^{2-}/e^-) or triple ($\text{H}^+/\text{O}^{2-}/\text{e}^-$) conductivity were employed as AFL on BZCYYb6211 electrolyte cells with a conventional anode of double conducting $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF). Material survey was conducted in terms of electrolysis current density and open circuit voltage (OCV). Consequently, triple conducting $\text{Ba}_{0.95}\text{La}_{0.05}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (BLFZ) showed high OCV and electrolysis currents than the cell without AFL (NoAFL). The electrochemical impedance analysis confirmed that BLFZ could decrease ohmic resistance for bulk proton transport, which could be attributed to the extension of proton-accessible electrochemical areas near the TPB, attributed to the excellent proton conductivity. Distribution of relaxation time (DRT) analysis proved that anode reaction was boosted without long range surface diffusion of oxygen species over LSCF anode because of the significantly extended reaction areas over BLFZ AFL. The cells with BLFZ AFL achieved the electrolysis current of 0.57 A cm^{-2} at 1.3 V at 600 °C, which was higher than the previous reports for the cells with LSCF or other double conductor anodes. Furthermore, the Faradaic efficiency increased from 46% to 75% with a use of BLFZ at 500 °C. These results proved that BLFZ AFL could set the water and oxygen partial pressure at a relatively high and low level in the AFL/electrolyte interface probably due to the high proton and low oxide ion conductivity. Such chemical potentials were favorable to decrease the hole carrier concentrations in the BZCYYb electrolyte. Hence, the corresponding cells showed relatively high OCV and high efficiency.

In chapter 5, it was demonstrated that the combination of BLFZ AFL and $\text{H}^+/\text{O}^{2-}/\text{e}^-$ triple conducting $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF) anode is beneficial to increase significantly both the electrolysis current and conversion efficiency of P-SOECs. The thickness of BLFZ AFL was optimized in terms of electrolysis current, proving that the cell with 150 nm-thick AFL yielded the highest current of 0.83 A cm^{-2} at 600 °C in 1.3 V. The cell exhibited very high Faradaic efficiency of 71% in 0.74 A cm^{-2} at 600 °C and 82% in 0.22 A cm^{-2} at 500 °C, which are superior to other reports on P-SOECs using high Zr-content electrolytes. DRT analysis revealed that BLFZ AFL reduces the resistance related to water adsorption due to the excellent hydration capability whereas PBSCF anode sufficiently decrease the resistance related to charge transfers. The cell with BLFZ AFL showed excellent long-term stability over 100 h with an electrolysis current of 1 A cm^{-2} at 600 °C under high steam condition.

Chapter 6 gave the summary and conclusion of this thesis. In this thesis, the author demonstrated that modification of anode/electrolyte interface with functional oxide interlayer is an alternative way to develop highly efficient P-SOECs with Zr-rich electrolyte. The AFL can tune the hole carrier concentration in electrolyte and increase proton-accessible reaction areas near the TPB. The preceding results demonstrated that the oxides combining high hydration capability and relatively low oxide ion conductivity were promising candidate for AFL of P-SOECs with high energy efficiency and durability.