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| Author(s) | 汪, 寧 |
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学位論文内容の要旨

博士の専攻分野の名称 博士（工学） 氏名 Ning Wang

学位論文題名

Development of Proton Oxide-Ion Electron Triple Conducting Electrodes for Protonic Ceramic Cells
(プロトンセラミックセルに用いるプロトン-酸化物イオン-電子混合伝導性電極の開発)

It is a great challenge to address global energy and climate change crises by new clean energy devices utilizing renewable energy sources (*e.g.*, solar, wind, geothermal, biofuels). Protonic ceramic cells (PCCs) based on the proton conducting $\text{Ba}(\text{Zr,Ce})\text{O}_3$ solid electrolytes are a highly efficient storage device of natural energy with, because they can produce hydrogen by steam electrolysis with a use of electrical powers originating from natural energy (EC mode) and conduct power generation with the hydrogen products (FC mode). Nevertheless, the performances of the current devices lag far behind those expected from the electrolyte resistances at the temperatures below 600°C . A major reason for the reduced performance at lower temperatures is the occurrence of the considerable interfacial polarization at air electrodes in both FC and EC modes. The well-known air electrode materials, such as $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF), $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC) and so on are oxide ion conductors; there is a mismatch of main ionic carriers between the air electrode and the electrolyte, which limits the efficient area for air electrodes' reaction to the air electrode-electrolyte-gas triple phase boundaries (TPB). The materials having efficient proton conductivity together with electron and oxide ion conductivity, if available, is expected to extend the effective reaction area to the overall surface of the electrode, and thus decreases the interfacial polarization resistances. Such $\text{H}^+/\text{O}^{2-}/\text{e}^-$ triple conducting materials could be derived from the oxides having the pronounced hydration capability at intermediate temperatures. The main objective of this thesis is to explore the triple perovskite type oxides with high hydration capability at intermediate temperatures, and figure out the hydration mechanism to lead a robust guideline for the material design. Finally, the excellent cell performances were demonstrated with the PCCs using triple conducting air electrodes.

In chapter 1, the general background of energy conversion devices based on protonic ceramic cells was firstly described. Then the progresses on PCCs were summarized for the comprehensive understanding of proton-conducting oxide cells. The issues of PCCs was analyzed and the aims of this thesis were proposed.

In chapter 2, experimental and theoretical techniques used in this thesis were surveyed.

In chapter 3, $\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{1-x}\text{Ni}_x\text{O}_{3\delta}$ (LSCN; $x=0-0.3$) families were found to undergo the thermochemical hydration and take favorably proton defects in the concentration of 0.06–0.15 mole fraction at around 400°C by exposed to water pressure of 0.023 atm. Hence LSCN electrodes could efficiently reduce the polarization resistances regarding to the water formation and dissociation reactions on protonic ceramic fuel cells (PCFCs)

and protonic ceramic electrolysis cells (PCECs), respectively, attributed to the mixed $H^+/e^-/O^{2-}$ triple phase conductivity. The thin-film cells based on Zr-rich $BaZr_{0.4}Ce_{0.4}Y_{0.2}O_3$ electrolyte yielded the peak power density of 0.88 W cm^{-2} in FC mode and electrolysis current of 1.09 A cm^{-2} at 1.3 V in EC mode at 600°C , respectively, which are superior to the well-known $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ electrodes under the same conditions. The XANES measurements proved that the hydration did not involve the valence change of O and metal atoms.

The chapter 4 reported on the massive uptake of proton carriers in cubic perovskite type $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ at intermediate temperatures through the hydration reaction triggered by the charge disproportionation between oxygen and manganese redox. $La_{0.7}Sr_{0.3}MnO_{3-\delta}$ underwent the decline of antibonding O $2p$ states hybridized with Mn $3d$ orbitals together with oxidation of Mn^{3+} to Mn^{4+} by hydration, and thus, retained bulk protons in the concentration of 0.14 mole fraction in wet air at around 420°C , which was corresponding to the concentration of the well-known protonic conductor $BaZr_xCe_{0.8-x}Y_{0.2}O_{3-\delta}$. These results offered a general concept to design mixed $H^+/O^{2-}/e^-$ triple conductors operating in air conditions, namely, that transition metal oxides possessing holes on O $2p$ states together with oxygen vacancies could be promising candidates.

In chapter 5, it was also demonstrated that a cubic-type $La_{0.7}Sr_{0.3}Mn_{0.7}Ni_{0.3}O_{3-\delta}$ (C-LSMN7373) perovskite was promising for intermediate-temperature PCFCs because of the sufficient $H^+/e^-/O^{2-}$ triple conductivity. The oxides could be hydrated by gaining 0.1 mole fraction H_2O under wet air at 415°C , as confirmed by thermogravimetry analysis. An *in situ* extended X-ray absorption fine structure (EXAFS) analysis revealed that the hydration reaction took place via the association between H_2O and oxygen vacancy, coupled with the charge disproportionation between Mn and O atoms. Rhombohedral-type $La_{0.7}Sr_{0.3}Mn_{1-x}Ni_xO_{3-\delta}$ could not undergo hydration because the oxygen vacancy concentration required for water association was lower than the cubic phase concentration. The cathode performances of various PCFCs were examined by fabricating thin-film cells based on a $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})O_3$ electrolyte. The peak power density of the PCFCs with cubic-type LSMN7373 cathode was 386 mW cm^{-2} at 600°C , which was much higher than the reported values for the Zr-rich side electrolytes. Moreover, the cathodic polarization resistance was lower than that of the cell with the widely used $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode below 550°C .

The chapter 6 is the summary of this thesis. The hydration enthalpy of $La_{0.8}Sr_{0.2}Co_{0.7}Ni_{0.3}O_{3-\delta}$ and C- $La_{0.7}Sr_{0.3}Mn_{0.7}Ni_{0.3}O_{3-\delta}$ were about -110 kJ mol^{-1} as calculated from the dehydration temperatures under water pressure of 0.023 atm. Therefore, these oxides must retain sufficient amount of water even in the temperature range of the PCC's operation, i.e. $500\text{--}600^\circ\text{C}$ under water partial pressure of 0.1 atm. The performances of PCECs and PCFCs with cubic-type $La_{0.7}Sr_{0.3}Mn_{0.7}Ni_{0.3}O_{3-\delta}$ air electrodes were superior to those reported for the corresponding cells with O^{2-}/e^- double conductors at 500 and 600°C , because the interfacial polarization resistances of the formers were significantly lower than those of the later. It was concluded that the hydrated oxides could extend the reaction areas for the water formation or splitting reactions on the proton conducting solid electrolytes due to the $H^+/O^{2-}/e^-$ triple conductivity and thus, were promising air electrodes for the intermediate temperature PCCs.