

# Investigation of CeO<sub>2</sub> doped with multi-valent cations for mixed ionic and electronic conducting solid oxide fuel cell electrodes

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論文題名 : Investigation of CeO<sub>2</sub> doped with multi-valent cations for mixed ionic and electronic conducting solid oxide fuel cell electrodes  
(固体酸化物形燃料電池用の多価元素添加セリア系の混合導電性電極材料に関する研究)

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## 論 文 内 容 の 要 旨

Solid oxide fuel cells (SOFCs) have been attracting great attentions because they promise to provide clean, environmentally compatible power generator by directly converting chemical energy into electrical energy with high energy conversion efficiency and high fuel flexibility. The key challenges to commercialization for SOFCs is to lower the operating temperature. However, reducing the operating temperature decreases the conductivity of electrolyte and the electrode kinetics resulting in a large ohmic and polarization resistances. By using thin film electrolyte, the ohmic resistance can be reduced significantly. Therefore, the overall cell performance is determined by the polarization losses of the electrochemical reactions at anodes and cathodes, and the key technical challenge is how to minimize electrode polarization losses at lower operating temperatures. By using mixed ionic electronic conductor (MIEC) the polarization resistance of the electrode materials can be decreased. Therefore, Mn, Fe or Eu doped ceria were investigated for mixed ionic and electronic conducting solid oxide fuel cell electrodes. The long-term durability of electrode performance is as important as initial performance. Impurities in the operating environment (e.g. in feed gases or in the cell materials) are well known to contribute to long-term degradation in performance of SOFCs, therefore, in part, hindering widespread SOFC commercialization. Therefore, we investigated the long term durability of oxygen exchange rate of Pr-CeO<sub>2</sub> which is a potential cathode material for SOFC.

This thesis is divided into seven chapters.

Chapter 1 reviewed the principle of SOFC current status of materials of SOFC. Defect diagram of pure and doped ceria were discussed. Techniques for study of defect equilibria and transport, the key challenge of SOFC materials and approach in this thesis are introduced.

Chapter 2 describes the experimental techniques used in this work including sample preparation method and material characterization techniques (SEM, XRD, Raman and XPS and electrochemical measurement methods and methods of thermogravimetric Analysis (TGA) and optical transmission relaxation (OTR) measurement.

In Chapter 3, the electrical conductivity of 20 mol% Eu-doped ceria (Ce<sub>0.8</sub>Eu<sub>0.2</sub>O<sub>2-δ</sub>) was measured by using impedance spectroscopy. 20 mol% Eu-doped ceria showed a similar conductivity as a function of pO<sub>2</sub> and activation energy for electrical conductivity in reducing conditions to Gd-doped ceria reported in the literature. No evidence for multivalency of Eu was observed in electrical

conductivity measurements over the studied range. Either the electron mobility of Eu small polarons is too low or Eu is not displaying multivalency in the studied range.

In Chapter 4,  $x$  mol% Mn-CeO<sub>2</sub> and  $x$  mol% Fe-CeO<sub>2</sub> ( $x=3-50$ ) powders were synthesized and characterized by XRD and Raman. Raman spectroscopy and lattice parameter analysis revealed that the solubility limit of Mn or Fe in CeO<sub>2</sub> is lower than 3 mol% for the present preparation conditions. The solubility of Mn was increased by co-doping La into Mn-CeO<sub>2</sub>. By calculating the change of lattice parameter, for 10 mol% Mn-CeO<sub>2</sub>, the Mn solubility was increased to 2.9 mol% by 10mol% La dopant. Conductivity of 20mol%-CeO<sub>2</sub> was measured by impedance spectroscopy and showed a pure ceria like  $pO_2$  dependence at higher temperature and a doped ceria like one at lower temperature. Additionally, it agrees with reduction enthalpy derived from conductivity. Activation energy calculated from Arrhenius plot of conductivity is 1.1 eV. According the activation energy data versus composition for the different dopants, the Mn solubility can be estimated to be about 0.1~1mol% which agrees with XRD and Raman results.

In Chapter 5, oxygen exchange kinetics of Pr-CeO<sub>2</sub> (PCO) was measured by optical transmission relaxation (OTR). A significant degradation in kinetics found after aging and identified to arise from accumulation of a siliceous phase on the PCO film surface. Deposition of La oxide or Sm oxide on the aged film surface was found to fully recover oxygen exchange kinetics in aged films and a film intentionally coated with siliceous phase. Surface treatments with other oxides (Nb, Al, Ti, and Zn) were not found to recover oxygen exchange kinetics. La and Sm likely react with Si to form a porous silicate layer allowing gas transfer to the PCO surface, whereas other studied materials are unlikely to form silicates. La oxide was also deposited on aged SrTi<sub>0.65</sub>Fe<sub>0.35</sub>O<sub>3- $\delta$</sub> , prone to degradation via Sr segregation (as opposed to siliceous phases), and no improvement was found, further indicating La reacts with Si and is not leading to a significant catalytic effect.

Chapter 6 and 7 are conclusion and future section. It summarizes the results in this thesis, and discusses future work.