Thermoelectric Material Ca₃Co₄O₉ as a Cathode Electrode for IT-SOFCs

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Intermediate Temperature Solid Oxide Fuel Cells (IT-SOFCs)¹⁾ have expected to generate efficiently at 600-800 $^{\circ}$ C due to the utilization of the alloy interconnecter (e.g Fe-Cr²⁾). Along with this, SOFC cathode materials have desired properties of low polarization resistance, thermal and chemical compatibility for electrolyte and long time durability at lower temperature.

As one of the candidates of SOFC cathode materials has well known $La_{1-x}Sr_xMnO_3$ (LSM)³⁾, which is shown its high thermal and chemical stability. However, the cathode characteristics of LSM have drawbacks of rapidly deterioration below 800 °C. In the meanwhile, cobalt oxide for the cathode materials such as $Sm_{1-x}Sr_xCoO_3$ (SSC), $La_{1-x}Sr_xCoO_3$ (LSCF) or $Ba_{1-x}Sr_xCo_{1-x}Fe_xO_3$ (BSCF) have interested in which exhibit higher performance as the mixed ionic and electronic conductor (MIEC) at IT region.

Calcium cobalt oxide $Ca_3Co_4O_9$ (hereafter Ca349) is the compound that has studied heretofore for candidate of thermoelectric material due to the high seebeck coefficient and electrical conductivity and the low thermal conductivity⁴). The peculiar aspect of this compound is that its crystal structure consists of 2D misfit layer between CoO_2 (CdI₂ type) and Ca₂CoO₃ (NaCl type) sublattices⁵ differ from 3D perovskite structure for the most of SOFC cathode materials. The aim of this work is that it determines the thermal, chemical and electrochemical properties of Ca349 as IT-SOFC cathode material.

Polycrystalline Ca349 was prepared using solid-state reaction at 880 °C for 24 h from CaCO₃ and Co₃O₄ powders. Ca349 powder was carried out the chemical reaction tests with Ce_{0.9}Gd_{0.1}O_{1.95} (CGO) electrolyte and XRD measurements. Ca349 pellets ware measured thermal expansion coefficient (TEC). Electrode slurry was made from powder Ca349 and organic additives, and deposited on CGO pellets, then, heat-treated at 700 °C. These pellets ware performed the impedance measurements and SEM observations. In addition, SOFC single cell generation tests using Ca₃Co₄O₉ cathode, which included the open circuit voltage, the I-V characterization and the impedance measurements ware carried out.

No chemical reaction between Ca349 electrode and CGO electrolyte at 750 °C was observed. SEM observation of the cross section is shown in Fig. 1. It was observed the good adherence between the electrode and the electrolyte. Furthermore, it was found that TEC value of Ca349



Fig. 1. SEM image of cross section of the Ca349-CGO pellet.

electrode approximates to that of CGO electrolyte. The area specific resistance (ASR) was calculated from the total polarization resistance R_p and electrode surface area *S* using the following: ASR=($R_p \times S$)/2. In ambient air, the resulting ASR values ware 4.0 Ω cm² at 700 °C (Fig. 2). The single cells using Ca349 cathode ware confirmed the SOFC generation by open circuit voltage measurements. These results indicate that the Ca349 has the enough capability to candidate of novel cathode material for IT-SOFC⁶).



Fig. 2. Temperature dependence of impedance spectra of Ca349 cathode in air.

References

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