

MANGANESE OXIDE BASE ELECTROCATALYSTS FOR PROTON-CONDUCTING CERAMIC CELLS

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There has been a strong interest in clean and renewable energy sources due to finite fossil fuel sources, increasing oil prices and environmental concerns. Hydrogen is regarded as the leading candidate fuel, because it releases only H₂O during combustion and it is compatible to use in high efficiency fuel system. Steam reforming of hydrocarbon gas is currently the main way to produce hydrogen but still relies on fossil fuel consumption. On the contrary, water electrolysis using electric power generated by renewable energy is attracted as sustainable hydrogen production method. Especially, steam electrolysis using solid electrolyte cells is promising for efficient hydrogen production because high-temperature heat partly offers the energy for water electrolysis, leading favorable kinetics and thermodynamics. Hence, it is motivated to investigate on solid oxide electrolysis cell (SOEC) using proton-conducting ceramics to achieve highly efficient conversion from electrical power into chemical fuel gas directly. However, sufficient performance has not been achieved yet in the current system because large overpotential is needed for oxygen evolution reaction at anode owing to the relatively slow kinetics and the limited active zone in the anode/electrolyte interfaces due to the mismatch of ionic carries. Accordingly, it is a great challenge to develop high performance oxygen electrode with efficient electrocatalytic ability for 4 electron transfer oxygen evolution reaction.

Recently, it is reported that high valence state metal oxide reveal superior electrocatalytic activity for water oxidation s because the energy levels between the occupied metal orbital and the O 2p orbital are very close, causing a strong hybridization and facilitating o-o bond formation. Herein, we examined electrocatalytic performance of high valence state Mn(V) oxide Ba₃(MnO₄)₂ as an anode for SOEC This oxide has been reported to be very stable at elevated temperatures in oxidative conditions. Proton-conducting BaZr_{0.4}Ce_{0.4}Y_{0.2}O_{3-δ} (BZCY) was used as proton conducting electrolyte. Bulk electrolyte cell were constructed with a BZCY disc which were prepared by solid state reactive sintering (SSRS) method. The electrolyte precursor powder was prepared by mixing proper amount of BaCO₃, CeO₂, ZrO₂, and Y₂O₃ according to the desired stoichiometry with the addition of 1.0wt.% NiO as a sintering aid. This mixture was ball-milled for 48 h and uniaxially pressed under 20 MPa for 1 min and then cold-isostatic-pressed under 100 MPa for 1 min. Finally, green pellets were calcined at 1500°C for 10 h so as to obtain dense electrolyte disc (2 mm d, 9 mm φ) Pt paste was applied at one side of the surface as a cathode. LSCF or LSCF/Ba₃(MnO₄)₂ mixed ink were screen-printed at the other side of the surface as anode materials. Samples are evaluated by XRD and XAS. The electrochemical impedance spectroscopy and I-V measurements were carried out to evaluate the SOEC properties.

Two kinds of anode materials were examined in this research, namely, the cell-1: Pt | BZCY | LSCF and cell-2: Ba₃(MnO₄)₂/LSCF mixed anode cell. The cell-2 showed superior steam electrolytic performance compared to cell-1. The current density of steam electrolysis of cell-2 was 145 mA cm⁻² meanwhile cell-1 was 145 mA cm⁻² in bias voltage of 1.5 V at 600°C. Impedance spectroscopy was conducted to evaluate the anodic polarization resistance. LSCF anode gives 6 Ω cm², however, the Ba₃(MnO₄)₂/LSCF composite anode gives 3 Ω cm². Furthermore, the spectral features were completely different between both. The spectrum of LSCF anode had three semi-circles: high frequency arc (10x-10y Hz), middle frequency arc (10zz-10zy Hz) and low frequency arc (10zz-10zy Hz). On the other hand, Ba₃(MnO₄)₂/LSCF involves only two semi-circles: high frequency arc (10x-10y Hz) and low frequency arc (10zz-10zy Hz). These results indicate Ba₃(MnO₄)₂ changes the reaction pathway of water oxidation electrode/solid electrolyte interface. The oxygen evolution rate was measured by gas chromatography when electrolysis was performed at a constant current density of 100 mA, 200 mA, and 300 mA. The flux of oxygen from anode side is corresponded to that of calculated from the current density, indicating that the faradaic efficiency was almost 100%. XRD pattern of the sample after electrolysis showed that there were no secondary phases, indicating stability of Ba₃(MnO₄)₂ is enough to use in SOEC anodic condition. The above results suggest the Ba₃(MnO₄)₂ is promising for OER electrocatalysts for SOEC.