

ELECTROCHEMICAL IMPEDANCE CHARACTERISTICS OF SOME MEDIUM TEMPERATURE SEMICELLS FOR SOFC

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Solid oxide fuel cells (SOFC-s) are the promising energy production systems for the 21st century because of their high total efficiency, environmental friendliness and utilisation of a variety of the fuel resources (1). Recently, the SOFC with a low-temperature operation (600÷700°C) was focused on by several groups. One probable cathode material for low-temperature SOFC is a perovskite-type complex oxide $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSCO), having high electronic and oxide ion conductivities in a wide temperature range (1-3).

In the present study, the electrochemical behaviour of following semielements $\text{Ce}_{0.83}\text{Gd}_{0.17}\text{O}_{1.9} | \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (Sys 1); $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9} | \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (Sys 2) and $\text{Ce}_{0.83}\text{Gd}_{0.17}\text{O}_{1.9} | \text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}\text{-Ag}$ (Sys 3) at $773 \leq T \leq 1173$ K and at fixed cathodic polarisations $\Delta E = 0; -0.05; -0.1; -0.3; -0.5$ and -1.0 V vs. Pt | porous Pt | O_2 reference electrode has been studied. The $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ cathode material and the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (CSO) and $\text{Ce}_{0.83}\text{Gd}_{0.17}\text{O}_{1.9}$ (CGO) electrolytes were prepared by the conventional solid state reaction technique (1-3). A three-electrode assembly was used to study the electrochemical properties of the electrodes.

The complex plane (Z'' , Z') plots at different T and ΔE (from 0 to -1 V) have been measured in the range of ac frequency $0.01 \text{ Hz} \leq f \leq 100 \text{ kHz}$ at $773 \leq T \leq 1173$ K. In the region $0.01 \text{ Hz} \leq f \leq 10 \text{ kHz}$, at least two arcs, corresponding to two time constants, were observed at $T \leq 873$ K and the high-frequency arc (arc 1) is noticeably smaller than the low-frequency arc (arc 2). The shape of the arc 1 depends only slightly on T and the time constant τ_1 decreases with T and probably describes the ionisation of adsorbed O_{ads} at the cathode surface. τ_1 depends somewhat on the electrolyte composition, thus, on the TPB characteristics. The decrease in the phase angle δ with T at $T > 823$ K indicates that the "true" charge transfer process is the rate-determining step at $f > 10$ Hz ($\delta \approx 0$ at $T \geq 873$ K). With increasing T , the arc 1 disappears.

The shape of the arc 2 depends noticeably on T and ΔE , and becomes more depressed with increasing T , which can be explained by the more resistive behaviour of the cathode | solid electrolyte interface at higher T . The Z'' , Z' -plots can be simulated by the equivalent circuit, where R_1 is the high-frequency series resistance of the system; CPE_1 , R_2 , CPE_2 and R_3 are the so-called high-frequency and low-frequency constant phase elements and charge transfer resistances, respectively. The fractional exponent $\alpha_1 \approx 1.0$ and very low values of R_2 for arc 1 indicate that the "true" charge transfer process is the rate-determining step at $f > 10$ Hz and $T < 823$ K. $\alpha_2 \leq 0.5$ for arc 2 of Sys 1 and Sys 2 indicates that CPE_2 behaves as a Warburg-type diffusion impedance (4). Thus, CPE_2 can be exchanged to the generalised finite Warburg element for a short circuit terminus model. τ_2 for the arc 2 is independent of the electrolyte composition at fixed T and ΔE , and characterises mainly the properties and processes in LSCO. τ_2 noticeably decreases with the increase of T at fixed ΔE , and of negative polarisation at fixed T . Thus, the arc 2 probably characterises the exchange reaction of oxygen from the gas phase into the solid (i.e. electroreduction of O_{ads} to O_{ads}^-) and the slow diffusion of O_{ads}^- to TPB in the solid cathode material.

The polarisation resistance values, depending on ΔE , T and electrolyte, have been established. The activation energy calculated decreases slightly with the increase of $|\Delta E|$. The activation energy is higher for Sys 2 than for Sys 1. The charge transfer coefficient of the cathode reaction $\alpha_c \approx 1.0$ has been obtained from the Tafel-like overvoltage η_c , $\log i$ -plots at $T > 823$ K, indicating the mass transfer limited process in the cathode material. The exchange current density, depending on the system studied, increases with T .

References

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