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 ceria-type complex oxide La$_{1-x}$Sr$_x$CoO$_{1.5}$ (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 Ce$_{0.83}$Gd$_{0.17}$O$_1$| L$_{0.8}$Sr$_{0.2}$CoO$_{3.5}$ (Sys 1); Ce$_{0.83}$Sm$_{0.2}$O$_1$| L$_{0.8}$Sr$_{0.2}$CoO$_{3.5}$ (Sys 2) and Ce$_{0.83}$Gd$_{0.17}$O$_1$| L$_{0.8}$Sr$_{0.2}$CoO$_{3.5}$| Ag (Sys 3) at 773 ≤ T ≤ 1173 K and at fixed cathodic polarisations ΔE = 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 L$_{0.8}$Sr$_{0.2}$CoO$_{3.5}$ cathode material and the Ce$_{0.83}$Sm$_{0.2}$O$_1$ (CSO) and Ce$_{0.83}$Gd$_{0.17}$O$_1$ (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 Hz ≤ f ≤ 100 kHz at 773 ≤ T ≤ 1173 K. In the region 0.01 Hz ≤ f ≤ 10 kHz, at least two arcs, corresponding to two time constants, were observed at T ≤ 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 depends on T and probably describes the ionisation of adsorbed O$_{ads}$ at the cathode surface. τ 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 (δ = 0 at T ≥ 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$_1$, 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 $\alpha = 1.0$ 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. $\alpha = 0.5$ 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 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 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$_{ads2}$) and the slow diffusion of O$_{ads2}$ 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 |ΔE|. The activation energy is higher for Sys 2 than for Sys 1. The charge transfer coefficient of the cathode reaction $\alpha = 1.0$ has been obtained from the Tafel-like overvoltage $\eta$, logi-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