ELECTROCHEMICAL IMPEDANCE CHARACTERISTICS OF SOME MEDIUM TEMPERATURE SEMICELLS FOR SOFC

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ABSTRACT

Electrochemical characteristics of the semicells $\text{Ce}_{0.83}\text{Gd}_{0.17}\text{O}_{1.91}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{2.5}$; $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.91}$ and $\text{Ce}_{0.83}\text{Gd}_{0.17}\text{O}_{1.91}$, $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{2.5}$-Ag clusters have been studied by electrochemical impedance and chronoamperometric methods at various electrode polarisations $\Delta E$ and temperatures $T$. The polarisation resistance values, depending on $\Delta E$ and $T$, have been established from the electrochemical impedance data. The activation energy has been found to decrease slightly with the increase of $|\Delta E|$. The cathode reaction charge transfer coefficient $\alpha_c = 1.0$ has been obtained from the Tafel-like overvoltage $\eta$, log$i$-plots at $T>823\text{K}$, indicating the mass transfer limited process in the cathode material. The $Z''$-plots have a complicated shape, and at least two time-constant values (two limiting stages) can be obtained. Thus, the kinetically mixed process, characterised by the slow transfer of electron to $\text{O}_{\text{ads}}$ and the diffusion-like step of $\text{O}_{\text{ads}}$ in the cathode material, is possible.

INTRODUCTION

Solid oxide fuel cells (SOFCs) are the promising energy production systems for the 21st century because of their high total (heat+electricity) efficiency, environmental friendliness, and utilisation of a variety of fuel resources (1-5). Most typical SOFCs, using traditional yttria-stabilised zirconia (YSZ) as an electrolyte, are operated at 900° to 1000°C. Recently, SOFCs for a low-temperature operation (600°-700°C) have been the focus of several groups (1,4-10) because for the distributed heat-power cogeneration applications of SOFCs, an operating temperature lower than 700-750°C is highly attractive for cost-effectiveness. The lower operation temperature makes it possible to replace expensive structural material(s) for less-expensive stainless steel (1-3). Additionally a wide variety of fabrication methods for stainless steel enables a complicated structural design. However, at low temperatures, the traditional cathode materials, for example $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ (LSMO), do not provide satisfactory performance (6,9,10). One probable candidate cathode material for low-temperature SOFCs is a perovskite-type complex oxide $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ (LSCO). LSCO has very high electronic and high oxide ion conductivities in a wide temperature range (9-14). According to (15), the main problem of LSCO is the high reactivity with a zirconia-based electrolyte at $T \geq 900°C$ and its high thermal expansion coefficient. It is assumed that these compatibility problems will not be as important when a ceria-based oxide electrolyte ($\text{Ce}_{1-x}\text{Gd}_x\text{O}_2$; $\text{Ce}_{1-x}\text{Sm}_x\text{O}_2$) is used (16). It is believed that the LSCO cathode in
combination with a ceria-based electrolyte can be used in SOFC if \( T \leq 700^\circ C \). However, the low-temperature operation requires the LSCO cathode material for SOFC to be carefully prepared so that sufficient performance can be achieved. It was found that doping Co-site of LSCO with \( \text{Fe}^{3+} \) can reduce the thermal expansion coefficient (17), but this procedure reduces the ionic conductivity of LSCO (9,10). The addition of doped ceria electrolyte powder to the \( \text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3\) cathode material can decrease the total thermal expansion coefficient and maintain reasonable ionic conductivity of oxygen ions (18). Steel and Bae (19) established that for the cathode material with thickness \( l \leq 100 \, \mu m \) the rate-determining step in the reaction mechanism is most probably the surface exchange process, and the diffusion of the oxygen ions through the cathode material is fast.

The overall reaction of oxygen electroreduction at the SOFC cathode can be expressed as

\[ 0.5\text{O}_2(g) + 2e^- + \text{V}^{\text{cr}}_0 \rightarrow \text{O}^\text{cr} \]

where \( \text{O}_2(g) \), \( \text{V}^{\text{cr}}_0 \) and \( \text{O}^\text{cr} \) represent an oxygen molecule in a gas phase, oxygen vacancy, and an oxygen ion at a regular oxygen site, respectively. If we, to a first approximation, assume that the relationship between the current density \( i \) and the overpotential across the interface \( (\eta = E^w-E_{\text{OCV}}, \text{where } E^w \text{ is the working electrode potential and } E_{\text{OCV}} \text{ is the open-circuit potential}) \), can be described by the usual Butler-Volmer equation (20):

\[ i = i_0 \left[ \exp(\alpha_s F\eta/RT) - \exp(-\alpha_c F\eta/RT) \right] \]

where \( i_0 \) is the exchange current density, \( F \) is the Faraday's constant, \( R \) is the universal gas constant, \( T \) is the absolute temperature, and \( \alpha_s \) and \( \alpha_c \) are the charge transfer coefficients of the anode and cathode reactions, then the polarisation resistance \( R_p \) can be approximated as

\[ R_p = \left( \frac{\partial \eta}{\partial i} \right) = \frac{RT}{F} \left( \frac{1}{\alpha_s + \alpha_c} \right) \frac{1}{i_0} \]

The exchange current density at these conditions is given

\[ i_0 = \frac{RT}{F} \left( \frac{1}{\alpha_s + \alpha_c} \right) \frac{1}{R_p} \]

At very high cathodic overpotentials \((|\eta_c| \gg 0)\) Eq. [2] simplifies to

\[ i = -i_0 \exp\left( -\frac{\alpha_c F\eta_c}{RT} \right) \]

and

\[ \alpha_c = -\frac{RT}{\eta_c F} \ln\left| \frac{i}{i_0} \right| \]

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It should be noted that the Butler-Volmer equation can be used for the study of the electroreduction of oxygen under certain conditions, but this analysis gives no adequate information about the microscopic details of the reaction. For this reason, various models have been developed (1-10, 21-27). According to these models the electroreduction of O₂ at porous Pt can take place only at the three-phase boundary (TPB), while both the TPB and surface of La₁ₓSrₓMnO₃₋₈ can be active at the high overpotential values (21,22,27). According to (6,10,21-24), there are still considerable discrepancies in the reaction mechanism (steps) and rate determining steps of the O₂ reduction at various cathode materials (LSMO, LSCFO etc.), and therefore more information is needed for the detailed analysis of O₂ electroreduction at porous LSCO.

In the present study, we investigated the electrochemical behaviour of the following semi-elements: Ce₀.₈₃Gd₀.₁₇O₁.₉₁La₀.₆Sr₀.₄CoO₃.₈ (Sys 1); Ce₀.₈₃Sm₀.₂₀O₁.₉₁La₀.₆Sr₀.₄CoO₃.₈ (Sys 2), and Ce₀.₈₃Gd₀.₁₇O₁.₉₁La₀.₆Sr₀.₄CoO₃.₈—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 versus Pt|porous Pt|O₂ reference electrode.

EXPERIMENTAL

Preparation of Cathode Materials and Electrolytes

The La₀.₆Sr₀.₄CoO₃.₈ powder was prepared by the conventional solid state reaction technique (4,14,16,26) from commercially available powders of La₂O₃ (99.99%), SrCO₃ (99.9%), Co₃O₄ (99.9%). Powders with the stoichiometric compositions were ball-milled with a zirconia mill container and zirconia grinding balls in H₂O for 3 h (4) and after drying calcined at 1473 K for 10 h to form a perovskite phase. The perovskite (trigonal R-3c) phase was crushed and ball-milled for 3 h using the same ZrO₂ system. The X-ray diffraction (XRD) measurements indicate the formation of the single-phase perovskite structure.

The Ce₀.₈Sm₀.₂O₁.₉ (CSO) and Ce₀.₈₃Gd₀.₁₇O₁.₉ (CGO) electrolytes were prepared from the corresponding oxides CeO₂ (99.9%), Gd₂O₃ (99.9%) and Sm₂O₃ (99.8%), using conventional solid state reaction technique (7,8). Powders with the stoichiometric compositions were ball-milled for 3 h and calcined at 1473K in air for 10 h. The formed electrolyte materials (cubic Fm-3m structure; established by XRD method) were crushed and ball-milled in ethanol and, after adding an organic binder, were pressed into pellets with a diameter of 2 cm and thickness of 0.6 mm at the pressure p = 20 kN cm⁻² for 0.5 min and sintered at 1473 K for 10 h.

A three-electrode assembly (4,6) was used to study the electrochemical properties of the electrodes. LSCO paste, which was prepared by mixing the LSCO powder (synthesised and characterised before) with an appropriate amount of organic binder (ethyl cellulose) and solvent (turpentine oil), was screen-printed on one side of the CGO or CSO electrolyte as a working electrode with the surface area Sₑ = 0.5 cm². The working electrodes were fired at 1473 K in air for 8 h and characterised by XRD and SEM methods before application of the counter and reference electrodes. In some cases, the cathode material was activated by the Ag-nanoparticles, and for that the cathode material was impregnated with the AgNO₃ solution, followed by decomposition and firing at 1073
K for 3 h (16). The Pt counter and reference electrodes were prepared by screen-printing
the Pt-paste (Engelhard) on the other side of the electrolyte (4), followed by sintering at
1223 K for 2 h. The areas of the Pt counter and reference electrodes were 0.5 and 0.4
cm², respectively. The anode | electrolyte | cathode assembly was placed in an
appropriately designed reactor and cathode, reference electrode and anode were exposed
to air. Pt grids were attached and pressed with the isolated springs on the working and
counter electrodes as current collectors. Three Pt wires were connected to the working,
counter and reference electrodes and led to a potentiostat/galvanostat (type 1287,
Solartron), frequency response analyser (type 1260, Solatron). The frequency f was
changed from 3 MHz to 0.01 Hz. The ac voltage amplitude was 5 mV. The spectra were
recorded at 10 points per decade. The ohmic series resistance of the system (electrolyte +
contact and Pt wire resistances) was determined from the impedance data at high
frequency (ω = 2πf → ∞) at ΔE = 0.

Complex Plane (Nyquist) Plots and Activation Energy

Figures 1 and 2 show the complex plane (Z" Z') plots for the Sys 1 and Sys 2 semicells
at different temperatures in open circuit conditions. The Z",Z' plots display an inductive
tail at very high frequencies (not shown in figures) and a capacitive behaviour at high to
medium frequencies from 10 kHz to 0.01 Hz. The presence of the inductive tail at
f >100 kHz can be ascribed to the inductance of the measurement leads. In the region
from 10 kHz to 0.01 Hz, at least two arcs, corresponding to two time constants, were
observed at lower temperatures (T < 873K). At T = 773K, the high-frequency arc (arc 1)
is noticeably smaller than the low-frequency arc (arc 2). The shape of the high-frequency
arc depends only slightly on T, and the time constant decreases with T and probably
describes the ionisation of adsorbed Oads at the cathode surface. The time constant of
arc 1 depends somewhat on the electrolyte composition and thus on TPB
characteristics.

![Figure 1. Nyquist plots for La₅₀Sr₅₀CoO₃Ce₄₅₃Gd₉₄Gd₉₁₇O₁₉ semicell at AE=0 and
temperatures (K) noted. Inset is equivalent circuit for fitting Z', Z" plots, where R₁
is high-frequency resistance (R₁=Z' (ω→∞)); CPE₁, R₂, CPE₂ and R₃ are the so-called
high- and low-frequency constant phase elements (Z_CPE= A₀(ω)⁻α, A₀ is the CPE
column and α is fractional exponent) and charge transfer resistances, respectively.](image)

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Figure 2. Nyquist plots for $\text{La}_{0.8}\text{Sr}_{0.4}\text{CoO}_3|\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ semicell at $\Delta E=0$ and temperatures (K) noted. Inset is the equivalent circuit used for fitting the Nyquist plots, where $R_1 = Z'(\omega \to \infty)$, $C_1$ and $R_2$ are the high-frequency capacitance and charge transfer resistance, $C_2$ and $R_3$ are the low-frequency capacitance and charge transfer resistance, and $Z_W$ is the Warburg-like diffusion impedance.

The decrease in the phase angle $|\delta|$ with temperature (Figure 3) at $T>823$K indicates that the "true" charge transfer process is the rate-determining step at $f>10$ Hz ($\delta = -2^\circ$ at $T\geq873$ K). With increasing $T$, the so-called medium frequency arc 1 disappears.

Figure 3. Dependence of phase angle on frequency for $\text{Sr}_{0.4}\text{CoO}_3|\text{Ce}_{0.83}\text{Gd}_{0.17}\text{O}_{1.9}$ interface ($\Delta E=0$) at temperatures (K) noted.
The shape of low-frequency arc 2 depends noticeably on $T$ and $\Delta E$, and arc 2 becomes more depressed with increasing $T$, which can be explained by the more resistive behaviour of the cathode|solid electrolyte interface at higher temperatures. The low-frequency 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 time-constant values for arc 2 ($\tau_2$) are independent of the electrolyte composition at fixed $T$ and $\Delta E$ and characterise mainly the properties and process in LSCO. The $\tau_2$ noticeably decreases with the increase of $T$ at fixed $\Delta E$ and of negative polarisation at fixed $T$.

The data in Figures 1 and 2, at first approximation, can be simulated by the equivalent circuit in Figure 1, where $R_1$ is the total high-frequency series resistance of the system $Z_1(\omega \to \infty)$; CPE$_1$, $R_2$, CPE$_2$ and $R_3$ are the so-called high- and low-frequency constant phase element and charge transfer resistance values, respectively. For fitting the $Z^*, Z'$-plots, the Zview 2.2 software has been used (28). The fractional exponent $\alpha_1 = 1.0$ and very low values of $R_2$ for arc 1 (Figure 4) indicate that the "true" charge transfer process is the rate-determining step at $f > 10$ Hz and $T > 823$K. The fractal exponent values $\alpha_2 < 0.5$ for arc 2 of Sys 1 and Sys 2 indicate that CPE$_2$ behaves as a Warburg-type diffusion impedance. Thus, the CPE$_2$ in Figures 1 and 2 can be exchanged for the generalised finite Warburg element (GFW) for a short circuit terminus model expressed as

\[ Z_{GFW} = R_D \tanh \left( \frac{L^2 \omega D}{D} \right)^{\alpha_w} \]

where $R_D$ (Figure 4) is the limiting diffusion resistance, $L$ is the effective diffusion layer thickness, $D$ is the effective diffusion coefficient of a particle, and $\alpha_w$ (Figure 4) is a fractional exponent (28-32). The very small chi-square function values $\chi^2 < 2 \times 10^{-5}$ and weighted sum of squares $\Delta^2 < 0.05$ have been established using the equivalent circuit in

![Figure 4. Charge transfer resistance $R_2$, diffusion resistance $R_D$, and fractional exponent versus temperature dependence for La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ semicell.](image)

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Figure 2. Therefore, it seems that the second arc characterises the kinetically mixed charge transfer and diffusion-like limited processes ($\delta<15^\circ$), but the diffusion-like resistance and $\alpha_w$ decrease with increasing $T$.

The capacitive parts of the impedance spectra ($Z''$, $Z'$) were used to determine the polarisation resistance ($R_p$) from the difference between the intercepts of the low and high-medium frequency parts of the spectra with the $Z'$-axis of Nyquist plots. $R_p$ allows quantification of the total potential loss of the overall cathodic (reduction) processes, taking into account the ohmic and activation polarisations as well as the mass transport characteristics. Including the medium temperature arc 1 and low-frequency arc 2, the total cathode polarisation resistance $R_p$ is less than 5 $\Omega$ cm$^2$ at $T = 1073$ K, and about 2500 $\Omega$ cm$^2$ at $T = 773$ K for Sys 1. Noticeably smaller $R_p$ values have been obtained for Sys 2 at the same temperatures. On the other hand, the fitting data can be used for obtaining the polarisation resistance values for the high-frequency process (arc 1), $R_{p1}$, and low-frequency process, $R_{p2}$, at fixed $\Delta E$. The $R_p$, $R_{p1}$ and $R_{p2}$ have been used for calculating the cathode reaction conductivity $\sigma$ (obtained from total $R_p$), $\sigma_1$ ($R_{p1}$) and $\sigma_2$ ($R_{p2}$) values. The linear dependencies of $\log\sigma$ on ($T$)$^{-1}$ (so-called Arrhenius plots) as well as the Arrhenius plots for arc 1 ($\sigma_1$) and arc 2 ($\sigma_2$) at fixed $\Delta E$ have been used for calculating the values of activation energy. At $\Delta E = -0.1$ V, $A_1 = 127$; $A_2 = 129$; and $A_2 = 123$ kJ mol$^{-1}$ (where $A_1$, $A_2$, and $A_2$ are the activation energies of the total polarisation and high- and low-frequency processes, respectively), decreasing with the increase in negative polarisation of LSCO. Somewhat higher $A_1$, $A_2$, and $A_2$ values have been obtained for Sys 2. The values of $A_1$, $A_2$, and $A_2$ are in reasonable agreement with the data obtained for the LSCF|CGO + Ag semicell (26).

**Current Relaxation Plots and Charge Transfer Coefficient**

Some typical current relaxation ($i,t$-) curves are given in Figure 4, when the cathode (working) electrode (LSCO and others) was stepped to a potential $\Delta E = -0.05$, -0.1, -0.2, -0.3, -0.5, and -1.0 V with respect to a Pt|porous PtO$_2$ reference electrode, respectively. The dependencies of cathodic current ($i_c$) on time ($t$) at $\Delta E =$ const. given in Figure 5 indicate that the shape of the $i_c,t$-curves depends on $T$. The $i_c$ decreases with time at lower $T$ ($T < 823$K) but increases with time at $T \geq 823$K. The shape of $i_c,t$-plots depends slightly on the chemical composition of the solid electrolyte. At $\Delta E =$ const, the $i_c$ versus $t$ dependence is more pronounced for the CSO|LSCO semicell than for the CGO|LSCO semicell, and at lower $T$ the current density values are noticeably higher for CSO electrolyte, indicating that the TPB characteristics noticeably influence the $i_c$ values at $T < 823$K. At $T > 873$K, there is a very weak dependence of $i_c$ on the electrolyte material. Thus, at lower values of $T$, the oxygen reduction is probably limited by the TPB reaction, and the LSCO|gas interface reaction does not contribute significantly to the overall reaction. Thus, the oxygen reaction at $T < 823$K is limited by the TPB at the moment when the cathodic potential is applied to the interface. At higher temperatures, the reaction is probably controlled by the rate of transfer of the partially reduced oxygen species (i.e., O$_{ads}$ transfer) (24), and the active region is not limited only by the TPB area properties. The increase in concentration of the oxygen vacancies will improve the diffusion of the charged species, leading to an increase in catalytic activity. The same mechanism has been established for the La$_{0.9}$Sr$_{0.1}$MnO$_3$|YSZ semicells (27).
Figure 5. Chronoamperometric curves for the Ce$_{0.83}$Gd$_{0.17}$O$_{1.9}$|La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ (1) and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$|La$_{0.6}$Sr$_{0.4}$CoO$_{3-δ}$ (2) semicells at $ΔE = -0.1$ V and at temperatures noted in the figure. These results are in a good agreement with the values of the charge transfer coefficient, obtained from the Tafel-like $η_{c, logi}$-curves (presented in Figure 6; calculated from the $i$-$t$-curves at $t ≥ 100$ s, where the stable values of $i$ have been established at fixed $ΔE$. $ΔE$ values have been corrected by the ohmic potential drop to obtain $η_{c}$). According to these calculations, $α_{c} = 0.63$ and $α_{c} = 1.05$ have been established for the LSCO|CGO interface at $T < 823$ K and $T ≥ 823$ K. Thus, the O$_{ads}$ diffusion seems to be the rate-determining step at higher $T$, and the electroreduction reaction (O$_{ads}$ + e$^- →$ O$_{ads}$) is the rate-determining step at $T < 823$ K. The values of the exchange current density, obtained from the Tafel plots, increase with temperature and are higher for Sys 2 than for Sys 1.

Figure 6. Tafel plots for the La$_{0.6}$Sr$_{0.4}$CoO$_3$ | Ce$_{0.83}$Gd$_{0.17}$O$_{1.9}$ interface at different temperatures (K) noted in the figure.
The decrease of $i_c$ with $t$ at lower $T$ indicates that the extension of the active region for oxygen reduction is unlikely for LSCO supported on CGO and CSO electrolytes at $T<823 \text{ K}$. Comparison of our data with that for the LaSrMnO$_3$|Y$_2$O$_3$-ZrO$_2$ and LaSrMnO$_3$|LaSrGaMnO$_3$ (LSGMO) interfaces (27) shows the drastic influence of the chemical composition of the cathode and electrolyte on the shape of the $i_c$, $E$-plots. These data indicate that the oxygen reduction at LSCO|CGO and LSCO|CSO interface at $T<873 \text{ K}$ (as for LSMO | YSZ interface (24,27)) is primarily limited by the TPB reaction, and the reduction reaction at the cathode surface|gas phase interface does not contribute significantly to the overall cathodic reaction. However, the fitting data of the $Z''$,Z'-plots show that the oxygen reduction at LSCO|CGO and LSLO|CSO interface is mainly limited by the mixed kinetics, i.e., charge transfer and diffusion-like steps, in the porous cathode material when the cathodic potential is applied to the interface.

CONCLUSIONS

The kinetically mixed process (slow mass transport and electron transfer stages) seems to take place at the Ce$_{0.83}$Gd$_{0.17}$O$_{1.9}$La$_{0.6}$Sr$_{0.4}$MnO$_{3.5}$ and Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$La$_{0.6}$Sr$_{0.4}$MnO$_{3.5}$ interfaces in air at $773 \leq T \leq 1173 \text{ K}$. The values of activation energy, decreasing with increasingly negative polarisation, and of the charge transfer coefficient $\alpha_e = 1.05$ at $T>823 \text{ K}$ indicate that the O$_{ads}$ mass transfer process in solid cathode material can probably be the rate-determining step in agreement with the fitting results of the Nyquist plots.

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