Solid oxide fuel cells (SOFCs) are considered as one of the most promising systems for energy conversion in the near future due to their very high electrical efficiency and the possibility to operate with lower or zero emissions. However, wider use of SOFC technology is restrained by high material costs and long-term durability problems. Both of these challenges have been addressed quite successfully over recent years by the introduction of the so-called intermediate-temperature SOFC (IT-SOFC) concept. IT-SOFCs make use of low-temperature ionic conductors, such as gadolinia-doped ceria \( \text{Gd}_{0.2} \text{CeO}_2 \) (CGO) or samaria-doped ceria \( \text{Sm}_{0.2} \text{CeO}_2 \) instead of the traditional yttria-stabilized zirconia, thus allowing reducing the operating temperature of the cell to below 800°C. Such a temperature reduction greatly enhances the long-term stability of the fuel cell, as the rate of electrochemical corrosion of construction details and current collectors decreases exponentially with temperature. Equally important, lower operating temperatures allow cheaper materials, such as various stainless steels, to be employed as potential construction and current collector steels. Additionally, the issue of finding suitable sealing materials becomes less severe through fewer restrictions on the thermal expansion properties imposed.

One of the key issues in IT-SOFC research is the development of cathode materials that would possess high electrochemical activity toward the oxygen electroreduction process at operation temperature. \( \text{La}_0.6 \text{Sr}_0.4 \text{CoO}_3 \) (LSCO) is a mixed ionic and electronic conductor of \( \text{ABO}_3 \) perovskite structure. As can be seen from Table I, the electronic conductivity of LSCO is much higher than that for Sr-doped \( \text{LaMnO}_3 \), the cathode material most commonly used in high-temperature SOFCs. The main concerns regarding the wider use of LSCO are the large thermal expansion mismatch with the CGO electrolyte, as well as the relatively low tolerance toward reducing environments.

Numerous papers on LSCO have been published over the recent years, but a large scatter is present in the results published by different groups. Moreover, of the papers that do investigate the effect of cathode geometry on the reliability of the determination of electrochemical parameters, only some provide experimental data to validate the conclusions reached by mathematical modeling. Oxygen electroreduction kinetics at mixed ionic/electronic conductors has been studied by Adler et al., and the effect of cathode chemical composition, overpotential, and cell geometry has been analyzed in detail. The importance of the chemical potential gradient inside the solid porous cathode phase on the charge-transfer kinetics and the mechanism for various electrochemical processes has been analyzed as well.

In this paper, a different approach has been chosen. A comparison of experimentally obtained results for Pt/CGO cathode and \( \text{La}_0.6 \text{Sr}_0.4 \text{CoO}_3 \) cathode half-cells and Ni/CGO cathode half-cells on the effect of cathode and electrolyte temperatures has been analyzed.

**Experimental**

Preparation of LSCO.—The cathode powders were prepared by the nitrate solution thermal combustion method, using \( \text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}, \text{Sr(NO}_3)_2 \) (both Aldrich, 99.9%) and \( \text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O} \) (98%, Riedel-de Haën) as precursors and glycine (99%, Sigma-Aldrich) as the reducing and complex-forming agent. A detailed description of the experimental procedure has been given elsewhere, and only a short overview is given here. \( \text{La(NO}_3)_3 \cdot 6\text{H}_2\text{O}, \text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}, \text{and } \text{Sr(NO}_3)_2 \) were dissolved in Millipore water and thereafter the calculated amount of glycine as a reducing agent, dissolved in Millipore water, was slowly added under moderate stirring. The resulting solution was heated on a hot plate to form a viscous solution and thereafter added dropwise into a Pt beaker that was preheated to the temperature range 575–675 K. The solvent was quickly evaporated and the corresponding systems reacted autothermally to form the fine-size structural complex oxide nanopowder. Additional sintering of the material was carried out at \( T \geq 1373 \text{ K } \) for homogenization of the complex oxide composition and better time stability of the cathodes prepared from powder. The resulting powders demonstrated an exceptionally high Brunauer–Emmett–Teller (BET) surface area (\( S_{\text{BET}} > 100 \text{ m}^2/\text{g} \)) and a distinct peak at 1.6 nm in the corresponding pore radius distributions.

Half-cell preparation and experimental setup.—The supporting electrolyte pellet was prepared by dry-pressing of the commercial CGO powder (99.9%, NexTech Materials, \( S_{\text{BET}} \approx 19.9 \text{ m}^2/\text{g} \)) at 90 MPa for a period of 10 s, followed by a 15 h sintering cycle at 1723 K. The resulting pellets were 725 ± 10 \( \mu \text{m} \) in thickness, 19.86 ± 0.05 mm in diameter, and 1.469 ± 0.006 g in mass, corresponding to 99.6% of the theoretical density of CGO. Commercial Pt paste (MaTeck) was used for preparation of the counter and reference electrodes (CE and REs), which were then fired at 1373 K for 60 min. A 0.5 cm\(^2\) LSCO cathode was printed onto the other side of the pellet through a 200 mesh screen and sintered at 1423 K for 5 h in air in order to achieve good contact with the supporting electrolyte. \( S_{\text{BET}} \) of ready LSCO cathode was 9.6 ± 0.8 m\(^2\)/g, and the pore size distribution function has a maximum near 27.0 Å. The total pore volume was remarkable (\( V_{\text{total}} \approx 4 \times 10^{-3} \text{ cm}^3/\text{g} \)). A very thin layer of Pt paste was applied onto the cathode material for current collection purposes and fired at 1273 K for 60 min. The cell geometry and experimental setup are shown schematically in Fig. 1. The RE was placed inside a drilled hole at the distance of less than

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* Electrochemical Society Student Member.
** Electrochemical Society Active Member.
† E-mail: enn.lust@ut.ee
10^−2 cm from the working electrode (WE).8–11 The surface area of the Pt counter and Luggin REs were 3 and 0.04 cm², respectively. The assembly was placed inside a vertical furnace (Carbolite VST 12/400) and exposed to air. Thus, the experimental construction of the three-electrode cell was very similar to that analyzed by Adler (details are given in Fig. 8a in Ref. 20).

**Single-cell preparation and experimental setup.**—The preparation route for the electrolyte pellet as well as for the cathode was identical to that of the half-cell. The anode was built up in two layers: an anode active layer of finer microstructure, prepared from a mixture of commercial NiO and CGO with S_{BET} = 70.8 m²/g, and a coarse and more porous anode diffusion layer, prepared from commercial NiO/CGO with S_{BET} = 6.5 m²/g into which 1 wt % of carbonaceous pore former (carbon acetylene black) was added.

The anode layers were deposited onto the electrolyte by applying the paste through a 200 mesh screen. The choice of the sintering temperature of 1623 K was based on the results of previous studies.11,18,24 The exact temperature near the pellets was registered with process temperature control rings (PTCR-MTH, 1340–1520 °C, Degussa). The sintered anode had a surface area of 1.65 cm² and a thickness of approximately 30 μm. The cathode was prepared so as to have a geometric surface area identical to that of the anode (so-called symmetric cell design) to allow truthful electrochemical measurements to be conducted.16–18 The cathode thickness was found to be approximately 20 μm. A thin layer of Pt paste (MatTek) was applied on both electrodes in order to ensure a very good electrical contact without contributing to the electrochemical processes. The absence of the influence of the Pt current collector on oxygen electroreduction was verified by the half-cell construction, where the cathode was prepared using Pt paste (all other components were the same), and the oxygen electroreduction rate was over 100 times lower than that for the porous LSCO cathode [CGO] Pt-anode half-cell, discussed in this work.

The cell geometry and experimental setup are shown in Fig. 2. The sample was fixed between two alumina tubes. A gold ring (NexTech Materials) was used to seal the anode compartment from the cathode side. Fiber-free high-temperature sealing (Microtherm) was used on the cathode side for softer contact between the tube and the sample, and for additional sealing. Electrical contact with the cell was achieved via a platinum wire that was wrapped around a platinum mesh. The setup was placed inside an additional alumina tube to provide greater mechanical stability and positioned horizontally inside a tube furnace (Carbolite MTF12/38/400). The sample temperature was monitored online with a NiCr thermocouple (Amarell) located on the anode side of the cell in the closest vicinity of the sample. The flow rate and ratio of hydrogen and argon to the anode were controlled with mass flow controllers by Aalborg.18,24 Prior to entering the furnace, the gases were humidified using a room-temperature bubbler containing Milli Q+ water. The oxidant gas flow was controlled by a calibrated air pump (for air) or by a digital mass flow controller by Aalborg (for pure oxygen).

All electrochemical measurements reported in this study were carried out using a Solartron 1260 frequency response analyzer in conjunction with a Solartron 1287A potentiostat/galvanostat electrochemical interface.

**Results and Discussion**

**Half-cell measurements.**—The configuration shown in Fig. 1 is essentially an application of the three-electrode configuration used in aqueous electrochemistry to the solid-state systems.8–12,24,25 By placing the RE in a drilled hole as close to the WE as possible, the ohmic drop caused by the electrolyte is minimized and the applied electric potential, to a first very rough approximation, corresponds to the potential at the WE vs PtO₂ RE, i.e., the setup allows the po-

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**Table I. Comparison of some properties of La_{0.6}Sr_{0.4}MnO_{3−δ} and La_{0.6}Sr_{0.4}CoO_{3−δ}**

<table>
<thead>
<tr>
<th>Property</th>
<th>La_{0.6}Sr_{0.4}MnO_{3−δ}</th>
<th>La_{0.6}Sr_{0.4}CoO_{3−δ}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline structure</td>
<td>Rhombohedral perovskite</td>
<td>Rhombohedral perovskite</td>
</tr>
<tr>
<td>Electronic conductivity</td>
<td>280 S/cm (1273 K)</td>
<td>&gt;10⁻² S/cm (873 K)</td>
</tr>
<tr>
<td>Decomposition pO₂</td>
<td>10⁻¹ atm (1273 K)</td>
<td>&gt;10⁻² atm (1273 K)</td>
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<tr>
<td>CTE</td>
<td>12.6 × 10⁻⁶ K (308–1273 K)</td>
<td>20.5 × 10⁻⁶ K (303–1273 K)</td>
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</tbody>
</table>

---

**Figure 1.** Setup used for electrochemical testing of half-cells: (a) schematic drawing of the experimental setup: WE, RE, CE; (b) cell geometry; (c) surface scanning electron microscopy (SEM) micrograph of the LSCO cathode; and (d) surface SEM micrograph of the porous Pt counter electrode (both at 2000× magnification).

**Figure 2.** (Color online) Setup used for electrochemical testing of single cells: (a) schematic drawing of the experimental setup, (b) cell geometry, (c) cross-sectional SEM micrograph of the LSCO cathode, and (d) cross-sectional SEM micrograph of the two-layer Ni/CGO anode (both at 2000× magnification).
tential at the WE to be measured directly. By increasing the surface area of the porous Pt CE, one guarantees that the capacitance of the CE does not contribute to the overall capacitance measured.\textsuperscript{18,20,24-26} Along with many others, Chung et al.\textsuperscript{16} and Adler\textsuperscript{19-22} showed that such cell geometry minimizes the polarization contribution of the CE and thus is suitable for fundamental research of the electrochemical properties of SOFC cathode materials at different electrode potentials.

The complex Nyquist and Bode plots\textsuperscript{25-31} for two identically prepared Pt\textsubscript{CGO}/La\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3−δ} half-cells: Pt[CGO]/LSCO I and [CGO]/LSCO II are shown in Fig. 3a and b for 873 K in ambient air and zero-potential conditions. The influence of the cathode potential $\Delta E$ on the oxygen electroreduction kinetics is very well visible in Fig. 3c and d, where the total polarization resistance of $\mathrm{O}_2$ electroreduction and negative value of the phase angle decrease noticeably with $\Delta E$ applied. The characteristic frequency of the oxygen electroreduction process is practically independent of $\Delta E$ applied, as well as of high-frequency series resistance $R_s(f \to \infty)$ values obtained. The independence of $R_s(f \to \infty)$ on the cathode potential $\Delta E$ indicates that there is no big problem with the experimental setup used. The overall impedance response was modeled with an equivalent circuit of formula $L(R(C,P_1)(R(C,P_2))$, where $L$ stands for high-frequency inductance, $R_s(f \to \infty)$ is the very high-frequency series resistance, $R_1$ the polarization resistance of the higher-frequency process (arc I), $C_1$ the double-layer capacitance of the higher-frequency process, $R_2$ the polarization resistance of the low-frequency process (arc II), and $C_2$ a coefficient of a constant phase element (CPE\textsubscript{2}) that describes the complicated capacitive-resistive behavior of the low-frequency process (i.e., dissolution of the adsorption energy, geometrical, and energetical inhomogeneity of the surface,\textsuperscript{26,34}) etc.). Very low values were obtained for the goodness-of-fit parameter ($\chi^2 < 6 \times 10^{-5}$) in the modulus data weighting mode.\textsuperscript{26} The higher-frequency semicircle (characteristic relaxation frequency $f_{\text{max}} = 10 \ldots 30$ Hz, arc I) showed Arrhenius-type exponential temperature dependence but negligible dependence on the applied negative potential (Fig. 4a) inherent to slow mass-transfer processes that do not involve charged species. Based on the reaction mechanisms proposed in the literature,\textsuperscript{18,23} the dissociative adsorption of molecular oxygen\textsuperscript{8-11} can be considered as the most probable process to give rise to such a response.\textsuperscript{28,29} The low-frequency depressed semicircle ($f_{\text{max}} = 0.7 \ldots 0.9$ Hz, arc II) exhibited an exponential temperature dependence (Fig. 4b) as well as a significant potential dependence (Fig. 3) and was thus assigned to a slow charge-transfer process involving partially reduced oxygen species.\textsuperscript{8-11} The values of 0.87 and 0.88 were obtained for the CPE\textsubscript{2} fractional exponent, $\alpha_{\text{CPE}}$ (Fig. 5b) [CPE impedance $Z_{\text{CPE}} = Q^{-1}(j\omega)^{\alpha_{\text{CPE}}}$ where $Q^{-1}$ (Fig. 5a) is the CPE coefficient\textsuperscript{30,31}], suggesting that the reaction is spatially not limited to the LSCO/CGO/air interface [the so-called three-phase boundary (TPB) interface], in which case $\alpha_{\text{CPE}}$ would be equal to unity, but extends somewhat inside the porous cathode bulk.\textsuperscript{8,11,28,32} At $\Delta E \neq 0$, the medium-frequency part of the $Z' - Z''$-plot is not separable from the low-frequency arc of the semicells studied (Fig. 3c). The phase angle $\varphi$ vs log $f$ plots (Fig. 3d) indicate that there is only one mixed kinetic rate-limiting step at $\Delta E \neq 0$. The magnitude of the area-specific polarization resistance varies somewhat from cell to cell (Fig. 3a and b). It is thought that the experimental setup shown in Fig. 1 amplifies even the slightest of variations in the electrolyte thickness [i.e., determines the dependence of $R_s(f \to \infty)$ on the electrolyte thickness] and cathode microstructure (mainly contact resistance component at the cathode/electrolyte interface) as, in this half-cell geometry, the thin surface contact layer of the cathode is electrochemically active and contributes mainly to the overall impedance response.\textsuperscript{28,29,32} The noticeable difference between half-cell parameters has been established by other authors as well and has been explained by similar problems.\textsuperscript{23,34} Should one of the cells possess microscopic defects in the screen-printed cathode layer and areas of poor contact between the cathode and the electrolyte (the
existence of which is impossible to avoid with conventional screen-printing techniques, such a cell is likely to exhibit significantly higher values of area-specific polarization resistance, as well as high-frequency series resistance, contact resistance, and very high-frequency series resistance values observed in Fig. 3 and 4.

The surface diffusion process may be influenced by driving over-potential (i.e., cathode potential applied) as well, because driving surface chemical as well as potential gradients is influenced by the rate at which the species are removed from the regions of charge transfer.19-22 The very high values of CPE 2 coefficient $Q_2$ at $f < 10$ Hz obtained using fitting procedure given in Fig. 5a show the accumulation of partially reduced oxygen species into the nanoporous LSCO cathode and therefore the noticeable role of so-called chemical capacitance, discussed by Adler et al.19-22 and Jamnik and Bauman et al.28,29

The data in Fig. 3 can be classified as the time-invariant impedance spectra according to the classification by Jensen et al.,33 because $\omega_{0y} = 1/2\pi f_{max}$ is independent of cathode potential and temperature applied as well as on the cathode microstructure (LSCO I or LSCO II). Based on the analysis of the literature data,33 this effect could be related with the TPB length of the cathode, as the capacitance ($C_1$) and low-frequency resistance ($R_2$) in CPE2 (Fig. 4b) is proportional to the TPB length.

**Figure 4.** Potential dependence (a) and temperature dependence (b) of resistive components of two identically prepared half-cells (filled symbols—Pt(CGO)LSCO I, open symbols—Pt(CGO)LSCO II) at 873 K. Triangular symbols stand for the higher frequency resistance, $R_1$, rectangular symbols for the lower frequency resistance, $R_2$. Regression lines have been added to (b) along with the corresponding Arrhenius activation energy values.

**Figure 5.** Potential dependence of capacitative components $C_1$ and $Q_2$ (a) and fractional exponent of the low-frequency CPE of two identically prepared half-cells (filled symbols—Pt(CGO)LSCO I, open symbols—Pt(CGO)LSCO II) at 873 K. Triangular symbols stand for the higher frequency capacitance, $C_1$, rectangular symbols for the lower-frequency capacitative component, $Q_2$ in CPE2.

**Single-cell measurements.** — In contrast, the electrochemical impedance spectra for the Ni(Ce$_{0.9}$Gd$_{0.1}$O$_2$)$_x$LSCO$_{1-x}$ (denoted as Ni(CGO)LSCO I and Ni(CGO)LSCO II) shown in Fig. 6 are much more coherent. Based on the comparison of best-fit values for the $x^2$ parameter as well as by Randles interpretive plot analysis,25,26,30,31 the higher-frequency process ($f_{max} = 5 \ldots 11$ Hz, denoted as III) was fitted using a Randles-type subcircuit.11,24,25,31
polarization resistance decreases with increasing potential.

Based on the experimental data, the frequency range for which the magnitude of $|Z|$ is affected upon switching from hydrogen and argon fuel mixture to pure hydrogen (under constant oxidant flow) corresponds to the frequency dependence of the anodic process. Similarly, by changing the oxygen partial pressure in the cathode compartment, one can identify the cathodic, i.e., electroreduction reaction contribution to the real part $Z'$ of the single cell.32,33 The $\Delta Z'$ vs log $f$ plots for Ni/CGO/LSCO I and Ni/CGO/LSCO II (shown in Fig. 7a and b) suggest that based on the fuel composition variation and oxygen or air variation experiments for semicircles (Fig. 7c) and our previous data,31 the process of highest characteristic frequency corresponds to an anodic (i.e., fuel oxidation) process, whereas the lower frequency process can be assigned to the electroreduction of $O_2$.8,11,18 Based on the analysis of a simple equivalent circuit consisting of a high-frequency electrolyte series resistance $R_s$ in series with a charge-transfer resistance $R_t$, the real part of an impedance is given as

$$Z'(\omega) = \frac{R_s + R_t + \frac{R_t R_s^2 C_2^2 \omega^2}{1 + R_s^2 C_2^2 \omega^2}}{1}$$

The corresponding derivative of $Z'(\omega)$ with respect to log $\omega$ is given by

$$\frac{\partial Z'(\omega)}{\partial \log \omega} = \frac{2\omega R_t R_s C_2^2}{(1 + R_s^2 C_2^2 \omega^2)^2}$$

Analysis of more complicated circuits is given in the paper by Jensen et al.31 Analysis of Eq. 2 shows that $\partial Z'(\omega)/\partial \log \omega$ approximates to zero as $\omega \to 0$ or $\omega \to \infty$ and has maximum values at characteristic frequency $f_{\text{max}}$ (Fig. 7c). Thus, the data in Fig. 7 are in good agreement with these mathematical conclusions.33 Therefore the differences of corresponding derivatives characterize the oxidation and reduction processes with different characteristic relaxation time constants, respectively. Furthermore, the values of the characteristic relaxation frequency for the two cells obtained by equivalent circuit modeling are in excellent agreement with the characteristic relaxation frequency values obtained by the $\Delta Z'$, log $f$ plot analysis (Fig. 7a-c).

In Fig. 7d the $\Delta Z'$ vs log $f$ plots for the Ni/CGO/LSCO I single cell have been given calculated at different cell potentials with respect to open-circuit potential ($E_{\text{OCV}} = 0.91$ V), i.e.,

$$\Delta Z' = \frac{\partial Z'(E_{\text{OCV}})}{\partial \log f} - \frac{\partial Z'(E_{\text{fix}})}{\partial \log f}$$

at constant fuel and oxidant composition. As can be seen from Fig. 7d, the influence of cell potential is very well visible, mainly at lower frequency ($f < 1.0$ Hz), where electroreduction of $O_2$ is the main limiting step. The influence of the cell potential on the fuel oxidation process is small.

Temperature variation experiments allowed the Arrhenius activation energy values for the cathodic process to be determined as 1.36 eV (Fig. 8). The values calculated are in very good agreement with our previous results,8,11,18 as well as with the results of Horita et al.,32 who observed a value of 1.32 eV for charge-transfer limitation in the $La_{0.8}Sr_{0.2}CoO_3La_{0.8}Sr_0.2Ga0.8Mg0.2O_2.8$ (cathode|electrolyte) system under comparable experimental conditions. Moreover, the experimentally observed apparent reaction or
suggests the low-frequency process can be assigned to a slow charge-transfer step at the TPBs of the cathode.

Experimentally observed activation energy values of 0.93 and 1.22 eV for the anodic charge-transfer resistance, $R_3$, and the Warburg-type diffusion resistance, $R_W$, respectively, suggest that the anodic contribution is due to slow charge-transfer processes at the TPB, coupled probably by surface diffusion of adsorbed hydrogen species. The results of calculations by Williford et al. imply that for a $1 \mu m$ spherical Ni particle at 800°C, the time required for surface diffusion to transport an H atom along the Ni surface to the TPB reaction site is about $10^{-5}$ s, whereas the residence time of chemisorbed species at the TPB reaction zone is estimated to be on the order of $10^{-9}$ s, and thus, the possibility of surface diffusion limitation seems to be substantiated. The fact that $R_W$ was found to be practically independent of applied cell potential provides further support for the involvement of noncharged intermediate species in the anodic electro-oxidation process of hydrogen fuel.

Figure 7. $\Delta Z'$ vs log$f$ plots for Ni/CGO(LSCO) I (a) and Ni/CGO(LSCO) II (b) upon gas composition variation: closed symbols—$\Delta Z'$ for a shift from 10% $H_2 + 87$% Ar + 3% $H_2O$ to 97% $H_2 + 3$% $H_2O$ on the anode side at a constant air flow of 100 mL/min; open symbols—$\Delta Z'$ for a shift from air to pure oxygen on the cathode side at constant 97% $H_2 + 3$% $H_2O$ flow of 100 mL/min. All measurements were conducted in open-circuit conditions at 873 K. The data have been averaged over a period of three points for smoothness. (c) $\Delta Z'$ vs log$f$ plots for Pt/CGO(LSCO) I half-cell upon oxidant variation conditions from pure oxygen to air at different electrode potentials, noted in figure. (d) $\Delta Z'$ vs log$f$ plots (calculated according to Eq. 3 in text) for Ni/CGO(LSCO) I at different fixed cell potentials at constant fuel (10% $H_2 + 87$% Ar + 3% $H_2O$; flow 100 mL min$^{-1}$) and oxidant (air, 100 mL min$^{-1}$) compositions.

Figure 8. Arrhenius-type activation energy plots (a) and resistive components ($R_2; R_W; R_3$) (b) vs cell potential plots of two identically prepared Ni(Ce$_0.9$Gd$_{0.1}$O$_{2.95}$)(Ce$_0.9$Gd$_{0.1}$O$_{2.95}$)La$_0.6$Sr$_0.4$CoO$_{3-x}$ single cells: filled symbols—with LSCO I, open symbols—with LSCO II. Circular symbols stand for $R_3$, triangular symbols for $R_W$, and rectangular symbols for $R_2$. Regression lines have been added to (a) along with the corresponding Arrhenius activation energy values.
in NiCe0.9Gd0.1O2−[Ce0.9Gd0.1O2−]La0.8Sr0.2CoO4− single cells. However, the surface diffusion can be influenced by the fuel oxidation reaction overpotential because chemical and electrode potential gradients could be influenced by the rate at which fuel oxidation reaction products and intermediates are removed from the reaction sites. However, very weak dependence of $R_{\text{f}}$ on $E$ applied indicates that this process is not significant at the Ni/porous CGO anode.

The very low-frequency semicircle (Fig. 6b) was found to be highly dependent on the hydrogen partial pressure but showed negligible temperature dependence, and thus can be interpreted as a characteristic of the anode concentration polarization or as an experimental artifact.

Experimental artifact. This very low frequency semicircle can be characteristic of the anode concentration polarization or as an experimental artifact. This very low frequency semicircle can be observed only for some single cells completed and therefore, the very detailed studies of single cells with variously prepared anodes (variations on porosity, pore size distribution, specific surface area, ratio of micro/mesopores) are inevitable. The occurrence of such disturbances further elucidates the importance of an experimental approach to the issue of the possible effects of cell geometry and microstructure of the electrodes on the properties of electrochemical systems.

The dependence of capacitive components for single cells on the cell potential is shown in Fig. 9a and the values of $\alpha_{\text{CPE}}$ for fuel oxidation in Fig. 9b. Thus, the single-cell setup provides experimental conditions that are rather similar to the real conditions in a working SOFC and thus, should give a better estimate of the qualities of the chemical composition of the cathode material (specific surface area, porosity, pore size distribution, ratio of micro- and mesopore volumes, etc.) for larger scale application.

Comparison of results.— Table II summarizes the results of equivalent circuit modeling of two half-cells and two single cells tested for the purposes of this study. Based on the results of temperature and potential variation experiments, it is assumed that arcs denoted as II correspond to the same slow oxygen electroreduction process in both experimental setups tested. The magnitude of the respective charge-transfer resistance, $R_{\text{f}}$, as well as capacitive components and the fractional exponent ($\alpha_{\text{CPE}}$), differs somewhat for the two-cell configurations probably because the microstructures of the cathode in the half-cell setup and in the single-cell setup are slightly different and therefore, the differences in electrode polarization effects (mass transfer, charge transfer), thickness of the electrolyte, and contact resistance at the cathode/electrolyte interface, etc., influence the results obtained. Another apparent discrepancy lies in the difference in corresponding activation energy values (Fig. 4 and 8). However, by plotting the $E_{\alpha}$ values against the applied potential (Fig. 9a), one notices that the activation energy at 0 V clearly deviates from the rest with a significantly higher value. By fitting a regression line through the rest of the points and extrapolating it to zero applied potential conditions, a much better agreement ($E_{\alpha} = 1.29$ eV) can be obtained. Based on the complex impedance plane (Nyquist) plot and Bode plot analysis, the rate-limiting step of the total cathodic reaction changes from a mixed kinetics process toward charge-transfer limitation with increasing negative potential, and this effect probably causes the half-cell setup to overestimate the thermal activation energy values at zero-potential conditions.

Arc I, assigned to slow dissociative adsorption of molecular oxygen in the half-cell, is not identified in the spectra of the single cells, probably due to intense overlapping of arcs in the impedance spectra at higher frequency. However, the data in the $\Delta \log Z''$ vs $\log f$ plots (Fig. 7) indicate that the overall cell response depends on the oxygen partial pressure in the cathode compartment at frequencies that coincide with the $f_{\text{max}}$ obtained.

Conclusion

A comparative study of two experimental setups for electrochemical impedance spectroscopy measurements has been carried out in this study. It was found that the so-called half-cell setup provides a higher resolution for the determination of rate-limiting cathode processes. Furthermore, due to the large surface area of the Pt counter (anode) electrode, the polarization contribution originates solely from the working electrode (the LSCO cathode), and therefore, such cell geometry can be considered as suitable for fundamental research of the electrochemical properties of SOFC cathode materials.

However, it was found that in order to obtain an estimate of how these cathode materials behave in real operating conditions, the single-cell experimental setup should be considered as well. By using the method of $\Delta \log Z''$ vs $\log f$ plots combined with fuel and oxidation composition variation experiments, the impedance spectra of a
Table II. Results of the equivalent circuit modeling of systems studied.

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<th>ID</th>
<th>Setup</th>
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<th>Arc II</th>
<th>Arc III</th>
<th>Arc IV</th>
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<tbody>
<tr>
<td>Pt(CGO)LSCO I</td>
<td>Half-cell</td>
<td>$(R_C \bar{C})$</td>
<td>$(R_C \bar{Q})$, $\sigma_{CPE} = 0.87$</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Pt(CGO)LSCO II</td>
<td>Half-cell</td>
<td>$(R_C \bar{C})$</td>
<td>$(R_C \bar{Q})$, $\sigma_{CPE} = 0.88$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ni(CGO)CGO</td>
<td>Single cell</td>
<td>—</td>
<td>$(R_C \bar{Q})$, $(C_R \bar{W})$</td>
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<td>—</td>
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<tr>
<td>Ni(CGO)CGO</td>
<td>Single cell</td>
<td>—</td>
<td>$(R_C \bar{Q})$, $(C_R \bar{W})$</td>
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</tr>
<tr>
<td>Potential dependence</td>
<td>Low</td>
<td>Low</td>
<td>Significant</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>$1/R \sim P_{O_2}$</td>
<td>Unknown</td>
<td>0.22</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>$1/R \sim P_{H_2}$</td>
<td>None</td>
<td>0.25 ... 0.33</td>
<td>Only visible</td>
<td>when</td>
<td>pH$_2 &lt; 0.2$ atm</td>
</tr>
</tbody>
</table>

**Interpretation:** Dissociative adsorption

**Oxygen reduction**

**$H_2$ diffusion**

**TPB**

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**References**


**Acknowledgments**

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**Figure 10.** Arrhenius activation energy vs applied cathode potential for Pt(CGO)LSCO I (filled symbols) and Pt(CGO)LSCO II (open symbols). Solid lines stand for the corresponding regression fits for the cathode potential range from 0.05 to 0.2 V.