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Influence of Microstructural Parameters of LSC Cathodes on the Oxygen Reduction Reaction Parameters

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The solid oxide fuel cell single cells with porous cathodes prepared at various sintering temperatures, having remarkable differences in micro/meso porosity, were studied using impedance, cyclic voltammetry and chronoamperometry measurement methods. Atomic force microscopy, scanning electron microscopy, focused ion beam–scanning electron microscopy, Brunauer-Emmett-Teller and X-ray diffraction methods were used to describe the cathode material physical and porosity characteristics. It was demonstrated that the porosity and surface area of a cathode strongly depend on the cathode sintering temperature. Influence of single cell working temperature, electrode polarization and oxidant and or fuel partial pressure onto the single cell electrochemical behavior, has been analyzed. Power density vs. current density plots show that the electrical power of single cells depend noticeably on the cathode porosity, O₂ partial pressure in the cathode as well as on H₂ partial pressure in the anode compartment. Impedance data were analyzed in detail, using equivalent circuit fitting as well as difference derivative impedance vs. log frequency plots method. It was concluded that the characteristic time constants for the cathode and anode processes are very similar and the exact separation of the anode and cathode processes characteristics is complicated.

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The single cells were placed into the ProboStat measurement system for detailed analysis of electrochemical and electrical properties. The cathode compartment was tightened with gold ring. The impedance spectra were recorded in a two electrode setup within the frequency range from 1 MHz to 0.01 Hz and within the potential range from open circuit potential (OCV) to cell potential ΔE = 0.7 V. For electrochemical studies, the Solartron 1260 frequency response analyzer in conjunction with a Solartron 1287A potentiostat/galvanostat, completed with electrochemical interface, has been used. The ac voltage amplitude was 5 mV. The Zview 2.2 software was applied for fitting the impedance data.

The gas atmosphere was controlled by using the gas flow meters (Bronkhorst type F-201C). The fuel used contained H₂ and Ar and oxidant was a mixture of O₂ and N₂. Usually O₂ + N₂ gas flow was three time faster than the fuel mixture (H₂ + Ar) flow in an anode compartment to avoid the problems with H₂ leakage (mass transfer diffusion) into the cathode compartment. The anode was reduced in 50% H₂ + 50% Ar mixture at 1073 K until the stable OCV from 1.010 to 1.062 V was established. In fuel cell tests the oxygen concentration was varied from 20 to 100%. Also the same gas concentration range was varied in the anode side for H₂ + Ar mixture.

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Preparation of Single Cells and Experimental Setup

Ni/yttrium stabilized zirconia (Ni-YSZ) cermet as a support and anode with thickness dₐ = 600 μm, ytrria-stabilized zirconia (Zr₀.₈₄Y₀.₁₆O₂₋₃) and gadolinia-doped ceria (Ce₀.₉Gd₀.₁O₂₋₃) as a bimodal electrolyte (thickness of both layers is nearly dₑ = 15 μm) have been screen printed on top of each other. The anode and electrolyte layers have been co-sintered at 1623 K for 3h. The micro-mesoporous La₀.₆Sr₀.₄CoO₃₋δ (LSC) as a cathode (thickness is nearly dₑ = 30 μm and geometrical area Sₑ = 1.77 cm²) was screen printed onto the electrolyte (Ce₀.₉Gd₀.₁O₂₋₃) layer. The raw cathode powder was synthesized using the nitrate solution thermal decomposition method. Organic solvents, ethyl cellulose as a binder and terpineol as a dispersant were used for preparation of raw cathode paste. The single cells were placed into the ProboStat measurement system for detailed analysis of electrochemical and electrical properties. The cathode compartment was tightened with gold ring. The impedance spectra were recorded in a two electrode setup within the frequency range from 1 MHz to 0.01 Hz and within the potential range from open circuit potential (OCV) to cell potential ΔE = 0.7 V. For electrochemical studies, the Solartron 1260 frequency response analyzer in conjunction with a Solartron 1287A potentiostat/galvanostat, completed with electrochemical interface, has been used. The ac voltage amplitude was 5 mV. The Zview 2.2 software was applied for fitting the impedance data.

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Analysis of Experimental Results

The Fig. 1 (single cell cross-section images) shows the micro-mesoporous cathodes studied and there is no remarkable delamination of the cathode after electrochemical testing of single cells under various electrochemical conditions. The conductivity for different single cells, obtained from the very high ac frequency data, disclosed later, confirms that there is a very good contact between electrolyte and cathode. The electrolyte layers appear almost as fully dense phases and contain only some isolated closed pores, but pinholes or cracks

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have not been observed. Mesopores (diameter from 2–50 nm) and macro pores (wider than 50 nm) have been observed in a cathode microstructure. Based on data in Refs. 4,6,10-12 the macropores act like transport pores increasing the gas permeability (oxidant and fuel diffusion) on the reaction sites and also water can escape as steam from reaction center of the anode side. The anode structure has been optimized in detail in our previous papers.10-12 It should be noted that water concentration in anode side affects strongly the anode performance.13

The focused ion beam scanning electron microscopy (FIB-SEM) data, reconstructed using information obtained using FIB method (80 slices with medium thickness ~0.1 μm) and calculation software Visage Imaging Amirae and given in Fig. 2, show that the porosity and tortuosity of a cathode depends noticeably on $T_{\text{Sint}}$ applied. The calculated total porosities are 66.5%, 60.0% and 33.4%, for cells sintered at 1323 K, 1373 K and 1423 K, respectively. The calculated specific surface area $S_{\text{FIB}}$ for cathodes were 0.95, 0.79 and 0.32 m²/g for 1-3, respectively, decreasing with increasing the sintering temperature from 1323 to 1423 K. $S_{\text{FIB}}$ values are in a reasonable agreement with $S_{\text{BET}}$ values, given in Fig. 3. The pore size distribution function data show that the pore size increases with the rise of $T_{\text{Sint}}$ applied. However, the pore size distribution function depends on the gas (N₂ or Kr) used and more detailed data will be published later after exhaustive theoretical analysis of experimental and modeling data. Influence of increased meso-macro porosity and specific surface area of the cathodes on the electrochemical data (discussed later) is remarkable especially for the cell with cathode sintered at 1323 K.

The data in Fig. 4 show that the crystallinity of the cathode material depends significantly on the cathode sintering temperature. The as-prepared LSC powder (synthesized at $T = 673$–773 K and having very high specific surface area, $S_{\text{BET}} = 5.2$ m²g⁻¹), shows very weak crystallinity of the perovskite phase. The combustion of metal nitrates and organic compounds was incomplete and some foreign phases (for example some carbonates) in raw powders have been observed. After heating the raw powders up to 1273 K, no unwanted structures have been detected any more. Much better crystallinity was observed for cathodes prepared at higher sintering temperatures (1323 to 1423 K).

All studied cathode electrodes prepared at $T_{\text{Sint}} \geq 1323$ K have been crystallized in single perovskite phase with trigonal structure, characterized with spacegroup R-3c. The cathode particle crystallite sizes, obtained by using Lorentzian fitting method, varying from 0.6 to 2.0 μm ($T_{\text{Sint}}$ from 1323 to 1423 K), are in a good correlation with the AFM and SEM data. Thus, the particle medium size increases with $T_{\text{Sint}}$ from 1323 to 1423 K.

The AFM data in Fig. 5 show that the particle size distribution, porosity, surface roughness, and root mean squared height (RMS) depend noticeably on the sintering temperature. The amount of free volume (i.e. porosity) in the cathode matrix depends on the particle medium size varying from 0.7 to 1.5 μm for cathodes sintered at 1323 and 1423 K, respectively, as well as on the size distribution of the particles in the raw powder.10-12,14-15 The surface roughness factor $R = S_{\text{real}}/S_{\text{geom}}$ values weakly decrease and RMS values increase with $T_{\text{Sint}}$ applied ($S_{\text{real}}$ is surface area calculated from AFM data and $S_{\text{geom}}$ is geometrical so-called flat cross section surface area).10-12

Electrochemical Results and Discussion

Figs. 6 and 7 demonstrate the complex plane impedance (Nyquist) and Bode (phase angle, log frequency) plots for single cells tested. The semicircles represent the electrode electrical response, and therefore the semicircle at very high frequency area $f > 20$ KHz describes mainly the impedance response at the electrolyte grain boundaries.4-6,10,13-15 The comparatively high very high frequency resistance values are caused by the co-sintering of anode, yttria-stabilized zirconia and gadolinia-doped ceria at moderate sintering temperature $T = 1623$ K for 3h. Usually, higher sintering temperatures (1823 K) have been used for good sintering homogenisation to achieve good ionic conductivity of gadolinia-doped ceria electrolytes.10-12,17-19 In addition, taking into account the meso/macro porous nature of the cathode (Fig. 1) and also anode the contact resistance between electrolyte and cathode is somewhat higher than that for microporous cathode, contacting better with well sintered Ce₀.9Gd₀.1O₂−δ electrolyte. However, the

Figure 2. FIB-SEM analysis of cathode electrodes 1 (a), 2 (b) and 3 (c) sintered at $T_{\text{Sint}} = 1323$ K, 1373 K and 1423 K, respectively. The length of edge is 8 μm for each cube on graph.
higher co-sintering temperatures initiate the degradation of meso-macro porous anode structure. The high-frequency ($500 \, \text{Hz} < f < 20 \, \text{kHz}$), medium frequency ($50 < f < 500 \, \text{Hz}$) (however not very well separable for our systems (Figs. 6 and 7)) and low frequency ($f < 50 \, \text{Hz}$) depressed semicircles characterize the electrochemical processes in cathode and anode electrodes at open surface area, meso-

Figure 5. AFM data for cathodes of single cells: 1 (a) and 3 (b). Explanations are given in text.

Figure 6. Nyquist plots (a) and phase angle vs. frequency plots (b) for cells 1, 2 and 3 at working temperature 873 K (sintering temperatures and $\text{H}_2$ and $\text{O}_2$ concentrations are noted in figure). Solid line – fitting using equivalent circuit, given in Fig. 13a; dots – experimental data.

Figure 7. Nyquist plots for cells 1, 2 and 3 at open circuit potential and at working temperature (a) $T_{\text{work}} = 773 \, \text{K}$ and (b) $T_{\text{work}} = 1073 \, \text{K}$ (cathode sintering temperatures and $\text{O}_2$ and $\text{H}_2$ concentrations are noted in figure). Solid lines – fitting using EC given in Fig. 13a, and dots – experimental points.

Data in Fig. 6 show that the highest total polarization resistance ($R_p$) values have been measured for single cell completed with cathode, sintered at highest sintering temperature ($T_{\text{Sint}} = 1423 \, \text{K}$), however, demonstrating the smallest pores and micropores, respectively.\textsuperscript{10–12,17–19}
Data in Figs. 8 and 9 show that the low frequency polarization resistance (as nearly linear part in $Z'$ data) decreases at working temperatures above 873 K (Figs. 6a, 7a, 7b). It should be noticed that the shape of Nyquist and Bode plots (a and b) for single cell 2, at OCV and working temperature 873 K and for various oxygen and fuel concentrations, given in figure.

Nyquist plots for single cell 2 at OCV and working temperature 973 K and for various oxygen and fuel concentrations, given in figure.

Surprisingly, at lower working temperatures ($T \leq 773$ K), the width of the high-medium frequency semicircle (20 kHz – 50 Hz) is slightly lower for single cells with cathode sintered at higher temperature (Fig. 7a). Impedance data measured within this frequency area, probably describe the processes at more open surface areas, responsible for oxygen reduction reaction on cathode side. However, the ratio between limiting stages depends on the sintering temperature of the cathode, especially in the low frequency region ($f < 50$ Hz), the polarization resistance $R_{p,low}$ increased with increasing the sintering temperature from 1323 K to 1423 K of the cathode (Figs. 6–8) and the characteristic frequency for low frequency processes ($f_{low}$) is smaller (characteristic time constant $\tau_{ch} = 1/f_{low}$ is longer) for materials prepared at higher cathode sintering temperatures. However, $f_{high}$ increases with the rise of $T_{sint}$ and $f_{high}$ depends mainly on $p_{O_2}$, but not on $p_{H_2}$. Thus, it seems that the high-frequency region at the Nyquist plots is mainly influenced by the cathode processes. At higher working temperatures, $T > 973$ K, the high- and medium-frequency processes are mainly limited by the rate of charge transfer step(s) ($\theta = -3^\circ$) and there are no wide high frequency semicircles in the Nyquist plots (Fig. 7b).

In our earlier papers, high-medium frequency series resistance and lowest high series resistance ($R_{ch} = Z'(\omega \to \infty)$) at $f > 20$ kHz. Thus, the contact resistance value for electrolyte / cathode interface $R_{ch}$ is lower (and the total contact surface area for particles at the cathode / electrolyte interface is bigger) and therefore the grain boundary resistance is smaller for cells sintered at higher temperatures. The high-medium frequency semicircle, weakly separable and visible in Figs. 6a and 7a, but nicely visible in Fig. 7b, (as nearly linear part in $Z'$, $Z''$ plot) characterizes mainly the charge transfer and mass transfer steps at more open anode and cathode surface areas. The Nyquist (Fig. 6a, 7a, 7b and especially Fig. 9) and phase angle ($\theta$) vs. log $f$ plots (Fig. 6b) show that the high and medium frequency processes cannot be clearly separated without using Fourier analysis. However, Fourier analysis seems to be somewhat artificial for our single cells due to the strong overlapping of the anode and cathode processes (demonstrated and discussed later by differential derivative impedance modulus analysis method). From the physical and application points of view, the exact separation of the anode and cathode processes is not very important. The exact separation can be made after collecting three electrode data for anode and cathode processes, using so-called half-cell testing method. Increasing the sintering temperature of cathode causes the increase in the low frequency semicircle polarization resistance ($R_{p,low}$) ($R_{p,low}$ is determined as a width of low–frequency semicircle), but high frequency semicircle (i.e. $R_{h}$, high–medium resistance) decreases at working temperatures above 873 K (Figs. 6a, 7a, 7b).

Connections with the Nyquist and Bode plots in Figs. 6–9 indicates that the anode and cathode processes are coinciding, because the time constants for fuel oxidation and oxygen electroreduction reaction are very similar as it was established already in Refs. 10–12. In our earlier papers, Bardford et al.24 and Jensen et al.21 papers, it was shown that by changing step by step the fuel $H_2$ (at fixed $O_2$ concentration) or $O_2$ concentration (at fixed fuel concentration) in working anode and cathode compartments respectively, it is possible to analyze the limiting anode or cathode processes.

Measurements at different $T$ indicate that the high-medium frequency processes (from 5000 – 50 Hz) and low frequency processes ($f < 50$ Hz) are thermally activated.8 The semi-circles were found to be noticeably depressed, indicating the multi step activation energy controlled processes. The processes in the high frequency region have mainly mixed kinetic limitation, where the charge transfer processes are more important as the experimental phase angle values from 0 to ~12° have been obtained, ($\theta = 0^\circ$ is characteristic of the charge transfer and $\theta = 45^\circ$ of diffusion of oxygen ions at the cathode/electrolyte interface). Within the low frequency region ($f < 50$ Hz), the polarization resistance $R_{p,low}$ increased with increasing the sintering temperature from 1323 K to 1423 K of the cathode (Figs. 6–8) and the characteristic frequency for low frequency processes ($f_{low}$) is smaller (characteristic time constant $\tau_{ch} = 1/f_{low}$ is longer) for materials prepared at higher cathode sintering temperatures. However, $f_{high}$ increases with the rise of $T_{sint}$ and $f_{high}$ depends mainly on $p_{O_2}$, but not on $p_{H_2}$. Thus, it seems that the high-frequency region at the Nyquist plots is mainly influenced by the cathode processes.
adsorption, charge transfer and mass transport limitations. It can be seen in Figs. 8 and 9, that the \( \text{O}_2 \) concentration in the cathode compartment is important mainly only for the low–frequency processes. The total \( R_c \), but mainly \( R_{\text{low}} \), decreases with increasing the fuel or oxygen partial pressure. The very high–frequency and high–frequency resistances weakly depend on \( p_{\text{O}_2} \) and \( p_{\text{H}_2} \), indicating that it is impossible to separate correctly the time constants and charge transfer parameters for the anode and cathode within these frequency regions. For the correct separation of the experimental parameters at the anode and cathode processes, the data for three electrode cells will be obtained and discussed in our future publication.

Barfod et al.,20 Jensen et al.21 and Kungas et al.,10–12 used difference derivative impedance modulus plots to separate the anode and cathode processes contributions and the \( \Delta Z \) response over frequency range studied helps to understand the influence of a parameter changed (\( p_{\text{O}_2}, p_{\text{H}_2}, \Delta E, \) etc.). As the anode composition and structure does not change in all single cells 1-3 studied, and the \( \text{H}_2 + \text{Ar} \) mixture in anode compartment has been fixed during one experiment, the impedance modulus (Fig. 10) and impedance real part (Fig. 11a, 11b) distribution show only the effects connected with the cathode compartment reaction (to a first approximation). At working temperature 873 K, the influence of the cell potential on the cell 2 behavior is illustrated in Fig. 10 and the \( \Delta Z \), log \( f \) curves have been calculated with respect to impedance value measured at \( \text{OCV} \). With decreasing the cell potential (given in figure) the decrease of the cathodic polarization resistance (i.e. \( \Delta Z \)) has been established compared with reference curve measured at \( \text{OCV} \). The characteristic frequency is independent of the cell potential applied (Fig. 10), indicating that the time constant (i.e. reaction limiting steps) does not depend on \( \Delta E \) applied, but the value of \( \Delta Z \) decreases. For more compact cathodes (the cathode sintering temperature is higher), the low–frequency characteristic time constant increases (the characteristic frequency decreases) and the values of \( \Delta Z \) increase (\( \Delta Z \) values were calculated with respect of \( Z \) measured for cathode at \( T_{\text{Sint}} = 1323 \) K). Surprisingly, the high–frequency region (900 < \( f \) < 20 kHz) and low–frequency (\( f < 900 \) Hz) region responses are in an opposite direction (Figs. 11a and 11b). Therefore, the high-frequency medium polarization resistance values decrease with increasing the sintering temperature of the cathode. Same conclusions are valid at higher working temperature for difference derivative impedance real part \( \Delta Z' \), log \( f \) plots (Fig. 11a). Fig. 11c demonstrates influence of \( p_{\text{O}_2} \) on the \( \Delta Z' \), log \( f \) dependence (\( \Delta Z' \) values were calculated with respect of \( Z \) data measured at \( p_{\text{H}_2} = 0.2 \) atm). As it can be seen with the rise of \( p_{\text{O}_2} \), \( \Delta Z' \) decreases. However, \( f_{\text{low}} \) value decreases, which is caused by the activation of the more microporous cathode areas (with longer mass transfer (diffusion) length) with the rise of \( p_{\text{O}_2} \). Data in Fig. 11d show that only at \( T_{\text{Sint}} = 1423 \) K and at higher working temperatures (\( T > 973 \) K), the low–frequency cathode and anode processes probably can be separated and the characteristic frequency for low–frequency anode process seems to be somewhat higher (\( f_{\text{low, anode}} = 10 \) Hz) compared with that for cathode \( f_{\text{low, cathode}} = 1 \) Hz processes. Thus, as it can be seen later from modeling data, the mass transfer (diffusion) processes are quite complicated and do not obey correctly the simple semi-infinite diffusion models.22–27

**Figure 10.** Difference of derivative of the impedance modulus \( \Delta \delta Z \) plots at various cell potentials with respect of \( \text{OCV} \), noted in figure.

**Figure 11.** Difference of derivative of the real part of impedance \( \Delta \delta Z' \) plots (a, b), for various cathodes sintered at temperatures, noted in figure, (with respect of \( T_{\text{Sint}} = 1323 \) K) at working temperatures 973 (a) and 873 K (b). Difference derivative impedance modulus \( \Delta Z \) plots (c and d) sintered at temperatures 1373 K (c) and 1413 K (d) and oxygen and fuel concentrations, noted in figure.
The calculated power density vs. current density plots show the noticeable influence of the cathode sintering temperature (Fig. 12a), oxygen and hydrogen partial pressure (Fig. 12b) and working temperature (Fig. 12a) on the power density $P$ of cells. Comparatively high values of power have been achieved at $T = 923$ K for single cell 1, based on cathode sintered at 1323 K. Taking into account the limiting character of the electrolyte series resistance $R_{el}$ (i.e. the high $iR_{el}$ drop of the very thick (thickness 30 μm) and not very well sintered electrolyte due to low co-sintering temperature applied), the $P$ values for the cells 2 and 3 are moderate. However, in agreement with impedance data analysis, the power density depends on the oxygen as well as fuel partial pressures (Figures 6–12), and the value of $P$ increases noticeably with the increase of $p_{O_2}$ and $p_{H_2}$.

Modeling of Experimental Data

The remarkably depressed semicircles in Nyquist plots (Figs. 6–9) indicate that a quite detailed model is required and multiple peaks provide clear indication that more than one time constant is required to describe the high–medium– and low–frequency processes. All impedance spectra for studied single cells have been modeled with the equivalent circuit (EC) presented in Fig. 13a, where $R_1 = R_{el} = Z_{(\omega \to \infty)}$ is very high-frequency (electrolyte + phase boundaries) resistance, $C_1$ and $R_2$ are high-frequency (including medium frequency data for simplicity) capacitance and charge transfer resistance values, respectively, $C_2$ and $R_3$ are the low-frequency capacitance and charge transfer resistance values and $Z_W$ is the Warburg-like diffusion impedance. The chi-square function $\chi^2 \leq 10^{-3}$ and weighted sum of squares $\Delta \chi^2 < 0.1$ are quite small for all impedance spectra, measured at different $T$ and fitted using EC in Fig. 13a. However, there is only a small systematic deviation of $\Delta\text{real}$ or $\Delta\text{imag}$ (up to 1%, $\Delta\text{real}$ and $\Delta\text{imag}$ are the relative residuals for real and imaginary part of impedance, respectively) at higher temperatures ($T \geq 873$ K), especially for imaginary part of the impedance (Fig. 13c).
The high–frequency capacitance $C_1$ value is in a same magnitude as $C_2 (10^{-3} - 10^{-4} \text{ Fcm}^{-2})$, which is characteristic of the surface adsorption limited processes (adsorbed species like $\text{O}_2^{\text{ads}}$, $\text{O}^{2-}$). The high–frequency resistance $R_2$ and $C_1$ depend weakly on the cell potential as well as on the partial pressures of oxygen and hydrogen. $R_2$ obtained from the high–frequency semicircle, decreases, with increasing the cathode sintering temperature, especially at higher working temperatures ($T \geq 1500 \text{ K}$).

Conclusions

Co-fired at $T = 1323 \text{ K}$ for 3h electrolyte ($\text{Zr}_{1-x}\text{Y}_2\text{O}_{12-y} - \text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-y}$) and Ni-cermet anode based systems were completed with cathodes sintered at different temperatures from 1323 to 1423 K. The sintering temperature determines the porous structure of the cathode and, hence, has a very strong influence on the total polarization resistance, capacitive adsorption of intermediates and mass transfer characteristics for the cathode. At higher working temperatures ($T > 1500 \text{ K}$) at least two semicircles with different time constants have been observed in impedance spectra. At lower working temperatures ($T \leq 773 \text{ K}$) the situation is more complicated and more than two time constants can be calculated. However, the width of a high–frequency depressed semicircle, characterizing the high–frequency processes at more open surface areas, decreases with increasing the sintering temperature conversely to that for depressed semicircles observed in low–frequency region. Non-linear least squared fitting data indicate that the very complicated finite-length mass transfer processes (solid state diffusion, migration, surface diffusion, diffusion in gas phase and probably Knudsen-like diffusion) occur in intermediate temperature SOFC cathodes. The oxygen and hydrogen partial pressures have noticeable influence on the high–, medium– and also low–frequency charge transfer time constant values. At sintering temperatures $T_{\text{sint}} \geq 1323 \text{ K}$, the total polarization resistance increases with decreasing $p_{\text{O}_2}$. The analysis of the differential derivative of the impedance modulus and impedance real part plots shows that the time constants for anode and cathode processes are partially overlapping in time scale and therefore anode and cathode processes cannot be separated correctly without using the three electrode (so-called half-cell) measurement data.

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References


Figure 14. Dependence of the series resistance $R_1$ on the working temperature for cathodes sintered at different temperatures, noted in figure.