Solid oxide fuel cells (SOFC) are promising energy conversion systems due to their high electrical efficiency (up to 60%), fuel flexibility and environmental friendliness.1,2 Traditional materials, like Ni-YSZ anode envisaged already four decades ago, continue to dominate as the anode material for SOFC due to the issues and problems associated with the newly discovered materials for SOFC systems, for instance lower electrochemical activity, relatively small thickness of the anode, and unknown degradation and time stability.3–12 However, the main disadvantage of Ni-YSZ anode is severe deactivation in hydrocarbon and hydrocarbon derived synthetic fuels due to the carbon formation/deposition on the Ni surfaces and sulfur poisoning from the drocarbon and hydrocarbon derived synthetic fuels due to the carbon formation/deposition on the Ni surfaces and sulfur poisoning from the 

In this paper the stability of the electrochemical performance of SOFC single cell, consisting of LSV-SDC anode and LSC-SDC cathode, was examined. Due to the structural changes the degradation processes in the electrodes were analyzed using secondary ion mass spectrometry focusing on the movement of the anode and cathode components (La, Sr, Co and V) within the single cell.

Experimental

The electrochemical cells analyzed in this study were prepared in a similar manner as in our previous studies6–32 using the infiltration method. 120 μm thick dense Ce0.8Sm0.2O2–δ (SDC) electrolyte layer was sandwiched between two 50 μm thick porous SDC layers into which electrocatalytically active materials were infiltrated. The wafers were fabricated by laminating of the four green tapes (porous-dense-dense-porous layers) using isostatic press (Isostatic laminating system Ilis 46, Keko Equipment) and followed by high temperature calcination at 1500 °C for 5 h. After the calcination the diameter of the dense SDC part was 2.08 cm and the area of the porous SDC matrix was 0.79 cm².

The tapes used in this study were cast from the slurry based on the organic solvents. For the dense electrolyte layer, the tape-casting slurry was prepared by mixing SDC powder (NexTech), mixture of solvents (ethanol and xylene in a weight ratio 17:10) and dispersant (Menhaden fish oil, Sigma) in a weight ratio 2:3:56 and ball-milled for 24 h. The binder (polyvinylbutyral B-98, Sigma-Aldrich) was added into the mixture in a weight ratio 2.27 and homogenized for additional 24 h before adding the plasticizers (ployethylene glycol 400 MW, Aldrich; benzyl butyl phthalate, Merck) in a weight ratio 3.56 and ball-milled for 24 h. The de-airing of the slurry was achieved by very slow rotation of the paste for minimum 24 h. The green tapes were cast onto Teflon tape using a tape-casting system obtained from MTT Corporation (AFA I Automatic Thick Film Coater). The tapes used for the formation of porous electrolyte scaffolds were prepared in a similar manner except that a different ethanol-to-xylene ratio (2.5:10) was used to accommodate the addition of the pore former (graphite powder with particle size distribution 2–15 μm, TIMCAL) and the tapes were cast onto Mylar tape.

Catalytically active ceramic La0.8Sr0.2O2–δ (LSV) anode and La0.8Sr0.2CoO3–δ (LSC) cathode were fabricated by infiltrating the porous SDC scaffolds with corresponding aqueous solutions. The anode solution consisted of La(NO3)3 · 6H2O (99.9%, Alfa Aesar),

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The time stability of solid oxide fuel cell (SOFC) was tested using all ceramic La0.7Sr0.3VO3–δCe0.85Sm0.15O2–δ (SDC) perovskite material as an alternative anode and La0.8Sr0.2CoO3–δ–SDC as a cathode. Both electrodes were prepared using infiltration method. The time stability measurements were carried out for 220 h under 0.6 V cell polarization in H2 fuel and at working temperatures of 600 °C and 700 °C. At both temperatures, the total polarization resistance, Rp, increased in time and the maximal power density values decreased nearly 76% during testing. At the working temperature of 600 °C the RP reached its constant value, 0.50 Ω cm², during the first 12 h of polarization at 0.6 V. At 700 °C noticeable increase in Rp was seen within 100 h operation before the constant Rp value, 0.50 Ω cm², was established. The microstructure and composition of the single cells, including the mobility of Sr within the cell components, before and after time stability measurements, were analyzed using secondary ion mass spectrometry measurement. No degradation of cell components and Sr mobility was observed after the cell preparation process and only minor mobility of elements was seen after 24 h of operation at 600 °C and 700 °C. However, noticeable Sr, V, Co and La mobility was observed after 220 h operation at 600 °C and 700 °C.
Sr(NO3)2 (99.9%, Alfa Aesar) and NH4VO3 (99.9%, Alfa Aesar) in a molar ratio of La: Sr: V = 0.7:0.3:1, and the cathode solution consisted of La(NO3)3 · 6H2O (99.9%, Alfa Aesar), Sr(NO3)2 (99%, Alfa Aesar), and Co(NO3)2 · 6H2O (99%, Aldrich) in a molar ratio of La: Sr: Co = 0.8:0.2:1. Citric acid in a molar 1:1 ratio (metal cations) was used as a complexing agent for both aqueous solutions in order to assist the formation of the perovskite phase at lower synthesis temperatures. After each infiltration step a heat-treatment process at 450 °C for 0.5 h was applied to decompose the nitrates deposited. This procedure was repeated until loadings of 20 wt% (11.5 vol%) LSV and 25 wt% (14 vol%) of LSC were achieved. Thereafter the calcination step for 4 h at 700 °C, respectively, was conducted. It should be noted that the cathode composite was prepared before the anode in all cases under study.

As a final step in cell preparation, ~3 wt% (~1.5 vol%) CeO2 and ~1 wt% (~0.5 vol%) Pd were deposited onto/into the ceramic anode by infiltration of 1 M Ce(NO3)3 (99.9%, Alfa Aesar) and 0.45 M tetraammine palladium(II) nitrate (99.9%, Alfa Aesar) solutions, followed by calcination at 450 °C for 0.5 h.

The electrochemical measurements were carried out in a two electrode system using Gamry Instruments potentiostat Interface 1000. For the current collectors Ag paste (lot no. 1120912, SPI supplies) and Ag wires were used. Prior to the testing the single cell was attached to an alumina tube using a ceramic adhesive (Creambond 552, Aremco, Valley Cottage, NY) and placed horizontally inside a tube furnace (Carbolite MTF12/38/400). The humidified mixture of hydrogen and argon (in a ratio H2: Ar = 1:5, 100 ml min⁻¹) was fed to the anode side through the alumina tube. Systematic analysis of SrV2O6 and La2O3SrO3VO5 phase element with corresponding impedance and R is the parallel total charge transfer resistance of the system.

Cross sections of all the single cells were analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS, PHI TRIFT V nanoTOF) before electrochemical measurements and after the 24 h and 220 h operation at 600 and 700 °C. A primary ion beam applied was positive Ga⁺ and the accelerating voltage was 30 keV. The data were collected within a raster of 200 × 200 μm.

**Results and Discussion**

Relatively high, and well comparable with our previous studies, open circuit voltages (OCV) values, 0.935 V at 600 °C and 0.855 V at 700 °C, were measured for all single cells under study. The obtained OCVs were somewhat lower than the theoretical values (1.077 V and 1.054 V, calculated at 600 and 700 °C), indicating a weak mixed conductivity effect of SDC under reducing conditions at 600 °C and at 700 °C. However, the OCV values were sufficiently high to conclude that the electrolyte was gas leak tight. In addition the measured OCVs did not change remarkably during the first 24 hour operation as well as during the 220 h operation period. It has been reported that in case of Ni-YSZ supported SOFC the decrease of OCV values in long term operation is due to the weakening of the anode-electrolyte interfaces and resulting gas leakage. Therefore, it could be concluded, that the SOFC single cells studied within this paper were gas leak tight during the operation time applied.

During the first 48 h of operation the current density, measured at 0.6 V, decreased approximately 7% at 600 °C before the stable current density, ∼280 mA cm⁻², was achieved (Figure 2). The stable current density values were not achieved for single cells at 700 °C and the total decrease in current density values was up to 7%. Using the cyclic voltammograms (Figure 3) the maximum power density values, Pmax, were calculated at 0.5 V cell potential for both operation temperatures. During the first 24 h operation at 600 °C Pmax decreased 5% from 193 mW cm⁻² to 184 mW cm⁻², and another additional 4% within the rest of 200 h. The decrease in Pmax at 700 °C was more rapid during the first 24 h, from 489 mW cm⁻² to 460 mW cm⁻² (6%). However, after 24 h testing the Pmax stabilized and only 1% decrease was measured for last 200 h. The i-E curves of the single cells measured were not perfectly linear (Figure 3), exhibiting some (more at 700 °C) curvature near OCV region. This demonstrates the occurring the faradic processes within the low electrochemical rate and some influence of iR drop (most likely from the Ag current collector) near the OCV value.

Ohmic resistance values, Ro, and polarization resistance values, RP, were obtained from impedance measurements based on the analysis of Nyquist plots. While operating at 600 °C and 700 °C for 220 h, only very slight increase in Ro was observed (Figure 4a). The corresponding increase at 600 °C at OCV was from 0.68 Ω cm² to 0.70 Ω cm² and at 0.6 V from 0.82 Ω cm² to 0.85 Ω cm². At 700 °C and

**Figure 1.** Equivalent circuits used for the fitting of calculated impedance spectra to the experimental impedance (Nyquist) plots.
Figure 2. Dependence of current density, measured at 0.6 V, on SOFC operation time at 600°C and at 700°C (noted in figure). The humidified mixture of H₂ and Ar in a ratio of 1:5 with a flow rate of 100 ml min⁻¹ has been fed to the anode side.

at OCV, $R_Ω$ changed from 0.24 Ω cm² to 0.26 Ω cm² and at 0.6 V from 0.28 Ω cm² to 0.32 Ω cm². These results indicate that the ionic conductivity of SDC electrolyte somewhat decreased within 220 h due to the electronic conductivity of ceria intermixing movement of the elements in cathode and/or anode of the electrode-electrolyte interconnect. At both tested working temperatures $R_Ω$ as well as $R_p$ were higher at 0.6 V than at OCV conditions. One possible explanation of this phenomena could be that at working conditions (i.e. at potentials lower than OCV) the oxide ion flux through the membrane, formation of water and increase of pO₂ in anode porous matrix influences the Ce³⁺/Ce⁴⁺ balance to direction of Ce⁴⁺ forming and thus reduces the electronic conductivity of ceria matrix. Reduction of electronic conductivity of porous anode matrix or part of anode matrix leads to increase of ohmic resistance as well as reductions of number of active centers i.e. increase of total charge transfer resistance.

Analyzing the impedance spectra, given in Figures 5 and 6, up to three depressed semicircles can be observed (depending on the working temperature and potential applied). Similarly to Kim et al. study no remarkable high frequency semicircle (at frequencies higher than 10⁴ Hz), generally assigned to charge transfer reaction or electrical double layer charging at two phase boundary, has not been seen. It can be also assumed in the case of LSV-SDC anode that the charge transfer reaction on the anode is sufficiently quick and the faradaic reaction contribution to the cell resistance is not significant. Also the non-linearity of i-E curves near the OCV was very minor (Figure 3). Electrode processes in the so called mid-frequency ac range (10⁻¹⁻¹⁰⁴ Hz) are commonly attributed to different gas-solid interactions (adsorption, dissociation, desorption) or surface diffusion of the adsorbed species. The first mid-frequency semicircle, 100–5000 Hz, has been presented at both temperatures (600 and 700°C) and potentials (OCV and 0.6 V) with the relaxation time, $τ_R$, at 600°C and 700°C. At 600°C and at OCV conditions, the resistance of the first semicircle (Figure 7a) increased 8% and 36% at 0.6 V, before reaching the value of 0.31 Ω cm². At 700°C the resistance of the first semicircle did not depend on the cell potential, increasing 29% within 50 h operation before obtaining the constant value of 0.05 Ω cm². It could be said that after 100 h of operation the first mid-frequency semicircle did not depend on the cell potential applied. The absolute phase...
angle values (Figure 7b) within this frequency region were relatively low, 4–8 deg at 600 °C and less than 4 deg at 700 °C, indicating that the rate limiting processes are mainly faradaic charge transfer limited processes (more at 0.6 V than OCV) and only very mildly diffusion limited.

The second mid-frequency semicircle, within 1–100 Hz, has been observed at both temperatures at 0.6 V cell potential. At 0.6 V, $R_2$ was approximately 0.08 Ω cm$^2$ at 600 °C and 0.05 Ω cm$^2$ at 700 °C and it was unable to determine is it there some dependence on time or not. At OCV and at 700 °C the corresponding resistance was less than 0.01 Ω cm$^2$ (absolute phase angle value were the lowest) and did not depend noticeably on time (Figures 7c and 7d).

The low frequency arc with the peak frequency below 1 Hz has been observed for ceramic based SOFC anodes and its origin is not clearly understood. Kim et al. proposed that it could be initiated by the variation in the oxygen nonstoichiometry of the ceramic electrode indicating that the reaction takes place on the two phase boundary rather than at the three phase boundary regions. However, it could originate from the gas phase diffusion or gas conversion as well. In this study the low frequency semicircle only seemed to appear under 0.6 V cell potential and the dependence on the testing time could not be clarified (Figures 7e and 7f). The absolute phase angle values for this semicircle are constant and being 4 deg and 5 deg at 600 °C and 700 °C, respectively.

Based on the impedance detailed analysis it could be conducted that the second mid-frequency semicircle appeared with the increase of working temperature and cell potential and the low frequency (third) semicircle only appeared with the higher cell potential applied. This resulted in the situation where the total polarization of the cell was higher at 0.6 V than at OCV (Figures 5 and 6). Similar by Kim et al. the oxygen nonstoichiometry of the ceramic electrode could have varied and the reactions took mostly place at two phase boundaries resulting the increase of resistance. However based on only the fitted results of the impedance spectra it is not possible to determine the exact processes taking place on the electrodes as well as to separate cathode and anode processes form each other.

TOF-SIMS mass spectrum measured at the sample cross section after 220h operation time is shown in Figure 8 as an example. The TOF-SIMS mass spectra mostly consisted of the element peaks what have been used in cell preparation and only very small amount of impurities, most probably originated from the sample contact with the air, were observed in mass spectra even after long operation times. Figure 9 shows TOF-SIMS Sr distribution maps at the anode/electrolyte/cathode interfaces before and after the electrochemical polarization measurements. Only some small areas contaminated with Sr could be observed inside of the electrolyte phase after the cell
Figure 7. Dependences of (a), (c), (e) resistance values and (b), (d), (f) phase angle values for three semicircles on the testing time at different operation temperatures and cell potentials, noted in figure. Resistance values have been calculated based on the fitting results of calculated impedance spectra to the experimental Nyquist plots.

preparation process. However, slightly more noticeable Sr signal were seen after 24 h operation time due to the slow Sr mobility. Based on TOF-SIMS data a significant amount of Sr have been mass-transfered from both LSV and LSC layers into the SDC electrolyte layer after 220 h of operation time, what may cause Sr depletion in anode and cathode layers as well some structural changes in the electrolyte layer. Surprisingly V, Co and La were also identified inside of the electrolyte phase after 220 h of exploitation (Figure 10), however at a smaller amounts (lower intensities) than Sr. Based on the TOF-SIMS data, V seemed to have quite similar mobility behavior as Sr, but at a lower rates and V penetrated fairly deep into the electrolyte phase. Co as compared to V, had very low mobility even after long operation times and only small amount of Co were found inside of the electrolyte phase. La was mostly located as a thin layer near the electrolyte phase surface, but somewhat La was also observed inside of the electrolyte phase.

Figure 8. TOF-SIMS mass spectrum of the sample cross section after 220h operation of SOFC single cell at 0.6 V.
Figure 9. Sr distribution maps at the anode/electrolyte/cathode interfaces. Locations of LSV, SDC and LSC layers are shown in pictures.

Figure 10. V, Co and La distribution maps after 220h operation of SOFC single cell at 600 °C.

After 220 h polarization higher mobility at 700 °C than at 600 °C has been observed for V, Co and La and these elements were also found at remarkable amounts deep inside of the electrolyte phase.

Based on the electrochemical data and elemental analysis it could be assumed that within the first 50–100 operation hours elements distributed from anode as well from the cathode into the SDC electrolyte phase resulting with the decrease of the cell performance, i.e. decrease of the current density and increase of the total polarization resistance. With the movement of the elements the stoichiometry of elements in the electrodes changed and therefore the concentration of possible reaction sites most likely decreased. However, at 600 °C, the element mobility from the electrodes to the electrolyte slowed down and the electrochemical performance stabilized, while at 700 °C the mobility of the elements continued and the electrochemical performance of the cell decreased.

Conclusions

The time stability of SOFC single cells based on the perovskite structure ceramic anode and cathode was studied in hydrogen atmosphere at temperatures 600 and 700 °C during 220 h operating at 0.6 V. La0.7Sr0.3VO3–δ−Ce0.85Sm0.15O2–δ anode and La0.8Sr0.2CoO3−δ−Ce0.85Sm0.15O2–δ cathode were prepared by infiltrating of the porous Ce0.85Sm0.15O2–δ scaffold with an aqueous solutions of corresponding nitrates. During 220 h operation (at 0.6 V cell potential) the decrease of the maximum power density values calculated at both temperatures were approximately 7%. However, the increases of the polarization resistance values (at both operation temperatures) were somewhat higher. The microstructure and chemical composition of the single cells, including the mobility of Sr and other elements within the cell electrode layers, before and after the time stability measurements, were analyzed using secondary ion mass spectroscopy method. No element mobility was observed during the cell preparation process and only minor mobility of elements was seen after 24 h operation. However, noticeable Sr mass transfer was verified after 220 h operation at 600 °C and 700 °C. Also, some mobility of V, Co and La was identified inside of the electrolyte phase after 220 h of exploitation of cell at 0.6 V.

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