## DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS 85

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# **INDREK KIVI**

Synthesis and electrochemical characterization of porous cathode materials for intermediate temperature solid oxide fuel cells



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# I. LIST OF ORIGINAL PUBLICATIONS

- I. I. Kivi, P. Möller, H. Kurig, S. Kallip, G. Nurk, E. Lust, Development of porous cathode powders for SOFC and influence of cathode structure on the oxygen electroreduction kinetics. Electrochemistry Communications 10 (2008) 1455–1458.
- II. R. Küngas, I. Kivi, K. Lust, G. Nurk, E. Lust, Statistical method to optimize the medium temperature solid oxide fuel cell electrode materials. Journal of Electroanalytical Chemistry, Volume 629, Issues 1–2, 15 April 2009, Pages 94–101.
- III. E. Lust, G. Nurk, P. Möller, I. Kivi, S. Kallip, A. Jänes, H. Kurig, Method for the preparation of a solid oxide fuel cell single cell and the named cell. WO 2008/145145 A1.
- IV. E. Lust, I. Kivi, G. Nurk, P. Möller, S. Kallip, V. Grozovski, H. Kurig, Influence of Cathode Porosity and Potential on Oxygen Reduction Kinetics at Intermediate Temperature SOFCs Cathodes, ECS Transactions, 7 (1) 1071–1080 (2007)
- V. E. Lust, G. Nurk, P. Möller, I. Kivi, S. Kallip, P. Nigu, Influence of Electrode Porosity and Potential of the Oxygen Reduction Kinetics on the Intermediate Temperature SOFCs Cathodes, ESC Transactions, 5 (1) 423– 434 (2007).
- VI. E. Lust, G. Nurk, I. Kivi, R. Küngas, P. Möller, H. Kurig, S. Kallip, Influence of Cathode Porosity on the Characteristics of Medium-Temperature SOFC Single Cells, ECS Transactions, 12 (1) 293–302 (2008).

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# 2. ABBREVIATIONS AND SYMBOLS

constant phase element coefficient
alternating current
area specific resistance
Brunauer, Emmett and Teller method
interfacial oxygen ion vacancy concentration
medium frequency capacitance
low frequency capacitance
capacitance of anode process
capacitance of cathode process
capacitance of diffusion process
grain boundary capacitance
$Ce_{1-x}Gd_xO_{2-\delta}$
complex nonlinear least-squares fitting method
constant phase element for oxydation (anode) process
constant phase element for reduction (cathode) process
high-frequency constant phase element
low- frequency constant phase element
$Ce_{1-x}Sm_xO_{2-\delta}$
diffusion coefficient
particle diameter
electrode potential
activation energy
open-circuit potential
ac frequency
Faraday' constant
fuel cell
Focused Ion Beam – Scanning Electron Microscopy
generalized finite-length Warburg element
$Gd_{1-x}Sr_xCoO_{3-\delta}$
intermediate temperature solid oxide fuel cell
imaginary unit $(\sqrt{-1})$
current density
exchange current density
cathodic current density
effective diffusion layer thickness

$L_{TPB}$	length of free phase boundary
LSCFO	$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$
LSCO	$La_{1-x}Sr_xCoO_{3-\delta}$
LSGMO	$La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$
LSMO	$La_{1-x}Sr_{x}MnO_{3-\delta}$
MIEC	mixed ionic-electronic conductor
n	number of electrons transferred in reaction elementary step
$O^{x}_{o,electrolyte}$	vacancies supplant by oxygen ion in electrolyte
$p_{02}$	oxygen partial pressure
PFA	pore forming agent
PSCO	$Pr_{1-x}Sr_xCoO_{3-\delta}$
R	universal gas constant
$R_1$	high-frequency charge transfer resistance
$R_2$	low- frequency charge transfer resistance
Ran	total resistance of anode process
$R_{an, ct}$	charge transfer resistance for anode process
R <sub>cath</sub>	resistance of cathode process
$R_{\rm D}$	total diffusion resistance
$R_{dif}$	resistance of diffusion-like process
$R_{\rm ex}$	total very high frequency series resistance
$R_{ m gb}$	grain boundary resistance
$R_{ m LF}$	low-frequency polarisation resistance
$R_{ m MF}$	medium-frequency polarisation resistance
$R_{\rm p}$	total polarization resistance
$S_{ m BET}$	specific surface area, obtained by the BET method
S	surface area of electrode
SEM	scanning electron microscopy
SOFC	solid oxide fuel cell
Т	temperature
t	time
TEC	thermal expansion coefficient
TPB	three-phase boundary
$T_{ m W}$	GFW frequency parameter $(T_W = L^2 D^{-1})$
V ", electrolyte	oxygen vacancies in electrolyte
XRD	X-ray diffraction
YSZ	yttria stabilised zirconia
$Z_{W}$	Warburg-like diffusion impedance

Ž	complex impedance
α	CPE fractional exponent
$\alpha_{\rm a}$	transfer coefficient for the anode (oxidation) reaction
$\alpha_{\rm c}$	transfer coefficient for cathode (reduction) reaction
$lpha_{ m w}$	GFW fractional exponent
δ	phase angle
η	overpotential of total reaction
$\eta_{ m c}$	cathodic overpotential
$\theta$	phase difference between voltage and current
μ-SOFC	micro-solid oxide fuel cell
$\Delta^2$	weighted sum of the squares
$\sigma_{ m e}$	electronic conductivity
$\sigma_{\rm ox}$	oxygen ion conductivity
$ au_{ m max}$	characteristic relation time
$\chi^2$	chi-square function
ω	angular frequency (equal to $2\pi f$ )

# **3. INTRODUCTION**

A fuel cell (FC) is an electrochemical conversion device that produces electricity directly from oxidizing a fuel. Fuel cells are characterized by their electrolyte material and, as the name implies, the solid oxide fuel cell (SOFC) has a solid oxide or ceramic electrolyte.

Fuel cells provide many advantages over traditional energy conversion systems, including high electrical efficiency, environmental-friendliness, modularity, fuel adaptability (particularly solid oxide fuel cell), and very low levels of  $NO_x$  and  $SO_x$  emissions. Therefore the SOFCs are very attractive systems taking into account that the various hydrogen containing compounds (natural gas, various alkanes, diesel, gasoline, alcohols, esters, wood gas,  $NH_3$ , even  $H_2S$ , etc.) can be used as fuels [1–7]. In fuel cells, electrical efficiency of up to 60–70% is achievable. Further, when excessive heat from the exothermic process and byproduct gases burning is included, the efficiency of the whole system over 90% can be achieved.

The wider use of SOFC technology is held back by high operating temperature which results in high material costs and long-term durability problems. All of these issues have been addressed quite successfully over the recent years by the introduction of the intermediate temperature (from 750 to 1000 K) solid oxide fuel cell (IT-SOFC) concept. However, at lower temperatures, the traditional materials, for example  $La_{1-x}Sr_xMnO_{3-\delta}$  (LSMO) and  $ZrO_2-Y_2O_3$  (YSZ electrolyte), will not provide a satisfactory peformance. Regardless of problems in redox stability, the ceria based solid solutions ( $Ce_{1-}$  $_{x}Gd_{x}O_{2-\delta}$ , Ce<sub>1-x</sub>Sm<sub>x</sub>O<sub>2-\delta</sub>) have been pointed out as the hopeful electrolytes for intermediate temperature SOFCs, having noticeably higher oxygen ion conductivity, i.e. the lower series resistance values at T < 973 K than YSZ based SOFCs. A convenient candidates for the cathode are the perovskite-type  $Ln_{1-x}Sr_{x}CoO_{3-\delta}$  (Ln = La, Pr, Gd) or  $Ln_{1-x}Sr_{x}Co_{1-\nu}Fe_{\nu}O_{3-\delta}$  materials. These macro-, mesoporous cathode compositions exhibit a very good mixed ionicelectronic conductivity and are collapsible with cerium based electrolytes exhibiting chemical suitability and similar thermal expansion coefficient (TEC). Doped lanthanum cobaltite has no oxygen excess but shows large oxygen deficiency at high temperatures, especially when doped with a lower-valence cation such as strontium.

In a low temperature SOFC, the biggest potential losses take place on the cathode side of FC, where the oxygen electroreduction occurs [8]. For that reason, in this work, the biggest effort has been addressed to optimization of the cathode reaction kinetics. It is well known that gas permeability and electrical conductivity of SOFC cathodes depend strongly on microstructural parameters such as porosity, tortuosity and phase distribution. For this reason, a careful control of the microstructure is crucial for the optimization of the electrochemical performance of the cathode.

The main aim of this work was to improve the cathode quality and activity. The influence of the pore former agent concentration in the screen printing raw paste on the amount and shape of pores inside the fired cathodes has been studied in order to obtain a microstructure of cathodes suitable for SOFCs with high energy and power density. The gas phase, physical and electrochemical measurement results of micro-, meso- and macroporous cathode at different electrode potentials has been analysed. Influence of chemical composition of cathodes on the electroreduction kinetics of molecular oxygen has been analysed.

# 4. LITERATURE OVERVIEW

# 4.1. Design of SOFCs single cells

A lanthanum strontium manganite  $La_{1-x}Sr_xMnO_{3-\delta}$  (LSMO) cathode on yttriastabilized zirconia (ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>, YSZ) electrolyte is currently the state of the art for high-temperature solid oxide material system. Electrochemical behaviour of these materials has been mapped in recent years quite comprehensively. Unfortunately, in literature there is no overwhelming analysis of intermediate SOFCs, especially influence of the cathode microstrucure on the oxygen reduction mechanism and kinetics.

It is also known that  $La_{1-x}Sr_xCoO_{3-\delta}$  (LSCO) exhibits superior cathodic performance to LSMO, e.g. the polarization of a LSCO cathode sputtered on YSZ is very small even at T = 1073 K [9]. On the other hand, LSCO tends to react more rapidly with YSZ electrolyte than LSMO at high temperatures ( $T \ge 1273$  K), and the resulting  $La_2Zr_2O_7$  or SrZrO<sub>3</sub> compounds exhibit very high ohmic resistance. Nonetheless, to our knowledge, there have been only few reports on practical and convenient methods to prepare LSCO cathodes on a YSZ electrolyte without forming any by-products. Currently, the only available method is to use an interlayer on the YSZ electrolyte to prevent unfavorable solid-state reactions between the LSCO cathode and the YSZ electrolyte, however increasing noticeably the series resistance of SOFCs.

LSCO is an excellent ABO3-type perovskite material for fundamental studies because it is reversibly reducible, has high rates of oxygen surface exchange and dif-fusion of oxygen species inside it (diffusion coefficient  $D = 4.9 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$  in compact La<sub>0.7</sub> Sr<sub>0.3</sub>CoO<sub>3-8</sub> at T = 807 K). The interfacial oxygen ion vacancy concentration  $c_0$  is equal to  $2 \times 10^{-4}$  mol cm<sup>-3</sup> and  $c_0$  decreases slightly with increasing temperature [10]. However, the thermal expansion coefficient (TEC) is very high (TEC =  $21.8 \times 10^{-6}$  cm K<sup>-1</sup> for compact  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$  at T = 873 K) and thermal compatibility problems with ceria based electrolytes may arise during thermocycling of the cells. The substitution of the  $Fe^{3+}$  ions into the B site of  $La_{1-x}Sr_xCoO_{3-\delta}$  reduces the TEC values noticeably, but the catalytic activity of La<sub>1-x</sub> Sr<sub>x</sub>Co<sub>1-y</sub>Fe<sub>y</sub>O<sub>3-δ</sub> (LSCFO) is quite low [1-3, 11-13]. Similarly to LSMO (with electronic conductivity  $\sigma_{\rm e} = 200...300 \text{ S cm}^{-1}$  [2]), LSCFO is a very good electronic conductor  $(\sigma_{\rm e} = 230 \text{ Scm}^{-1}, \text{ obtained for } \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \text{ at } T = 1173 \text{ K}), \text{ having}$ very high oxygen diffusion coefficient and the oxygen ion conductivity,  $\sigma_{\text{ox}} \approx 0.2 \text{ S cm}^{-1}$  for La<sub>0.6</sub> Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-8</sub> at T = 1173 K [3, 12, 13]. Thus, the oxide ion conductivity in ferrites / cobaltites  $(La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta})$  is even some orders of magnitude higher than in manganites [2, 4, 11–13], and thus LSCFO is a very good mixed conductor. The TEC value for  $La_{0.6} Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  is 15.3×10<sup>-6</sup> cm K<sup>-1</sup> [12, 13] which is greater than TEC for CGO electrolyte ( $12.5 \times 10^{-6}$  cm K<sup>-1</sup>). Kostogloudis and Ftikos demonstrated

that the A-site deficient  $La_{0.6-z} Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$  based perovskite oxides have somewhat lower TEC values [12] than  $La_{0.6} Sr_{0.4}CoO_{3-\delta}$ , but these materials have comparatively low time stability.

Ringuede and Fouletier [10] established that, in air at moderate temperature T < 803 K, the electrode reaction at La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3-8</sub> was controlled by the oxygen diffusion rate through the dense LSCO layer according to the so-called internal diffusion material model. The activation energy  $E_{act}$  for diffusion process obtained using Warburg diffusion impedance values was nearly 1.08 eV [10, 14, 15].

De Souza and Kilner [14] have shown that the activation energy depends strongly upon the acceptor dopant level and position, varying from ca  $E_{act} =$ 3.1 eV for undoped (in the A-site) LCO material to  $E_{act} \sim 1$  eV for La<sub>0.4</sub>Sr<sub>0.6</sub>CoO<sub>3-6</sub> [14, 15]. It should be noted that the low-frequency polarization resistance ( $R_{LF}$ ) increased with decreasing the oxygen pressure. A noticeable increase of the deviation material from stoichiometry was measured by thermogravimetry, it was assumed that the vacancy diffusion through the dense LSCO is rapid and the gas phase polarization becomes limiting only at low O<sub>2</sub> pressures [15]. Under higher oxygen pressures ( $p_{O_2} > 6 \times 10^{-3}$  bar) at T > 773 K

the low-frequency polarization resistance was proportional to  $p_{O_2}^{-0.5}$ , indicating a dissociative adsorption limiting step [15] in a good agreement with experimental data for 2 µm thick dense LSCO cathode [16].

Also there are some other materials, like  $La_{1-x}Sr_xNi_{1-y}Fe_yO_{3-\delta}$ ,  $LaNi_{1-y}Co_yO_{3-\delta}$  [17] and  $(La_{1-x}Sr_x)_{0.99}Co_{0.6+x}Ni_{0.4-x}O_{3-\delta}$  [18], which have better catalytical properties than manganese containing composition. However, they are more problematic regarding the chemical compatibility [19] with the electrolyte as well as low time stability under reducing condition.

# 4.2. Micro-SOFC concept

In recent years some workgroups are concentrated their attention on the development of the so-called micro solid oxide fuel cell ( $\mu$ -SOFC) conception.  $\mu$ -SOFCs are less capricious due to thin layer construction materials, and have high energy density. High power density of  $\mu$ -SOFC is an enticing target for developers of traditional SOFC conception. Unfortunately, the materials and preparation technology are not enough optimized for high power (P > 1 kW) SOFC device to obtain comparable results with  $\mu$ -SOFC.

Sputtering, lithography and etching processes can be used to design freestanding membranes for  $\mu$ -SOFCs [20–25]. High  $\mu$ -SOFC performances up to 677 mWcm<sup>-2</sup> have been demonstrated at temperatures as low as T = 673 K. The operating temperature of  $\mu$ -SOFCs can be reduced below to T = 873 K, and even down as low as T = 473 K [22]. This can be achieved by reducing the electrolyte layer thickness, i.e. by decreasing the diffusion path length of the oxygen ions, and by optimizing the materials and their properties.

Fleig *et al.* [26] performed numerical calculations to analyze the influence of the electrolyte thickness on the resulting ohmic resistance. They concluded that electrolyte films with a thickness below the particle-to-particle distance of the electrode (300 nm) do not lead to a reduction in the ohmic resistance due to current constrictions at the triple phase boundaries. Hence, thin film electrolyte for  $\mu$ -SOFC should not be as thin as possible, but ought to be thicker than ~300 nm.

Huang *et al.* [22] from Stanford University fabricated ultra thin  $\mu$ -SOFCs on a silicon substrate by microfabrication technology. The total thickness of the positive electrode – electrolyte – negative electrode system does not exceed 300 nm. One 4-inch silicon wafer contains 832 active membranes with dimensions ranging from 50 × 50  $\mu$ m<sup>2</sup> to 240 × 240  $\mu$ m<sup>2</sup>. These fuel cells can operate at very low temperatures from 473 to 673 K.

A recent publication by Su et al. [27] describes the fabrication of  $\mu$ -SOFCs with a corrugated thin film membrane. This is achieved by patterning the silicon wafer with standard lithography and creating 10  $\mu$ m to 40  $\mu$ m deep trenches by reactive-ion etching. The thin film electrolyte is then deposited onto the silicon template. Etching with KOH and sputtering the electrodes leads to free-standing corrugated membranes with a total thickness of ~300 nm and a side dimension of up to 2 mm. These  $\mu$ -SOFCs were operated successfully from 673 to 723 K. The advantage of a corrugated membrane structure compared to a flat membrane design is that the electrochemically active area is larger than the projected area.

The main difference in the designs is the membrane size which varies from several hundred micrometers to a few millimeters. This wide range of sizes is due to two factors. Firstly, thin films can easily suffer from pinholes. In the case of large membranes, a single pinhole can detrimentally affect the performance of the entire membrane. The probability of failure of this type FC is much lower for smaller areas and favors small membranes for  $\mu$ -SOFC application. Secondly, however, the overall performance is directly related to the membrane area. Hence, many small membranes are required in order to obtain the same power output as for a large membrane. Small membranes have to be coupled and interconnected – and in this respect, larger membranes are favorable. This discussion shows that, in principle, large membranes would be best; however, membrane quality might limit the size. So far, no rules relating to ideal membrane size can be drawn up, since size limitations are strongly conditioned by the fabrication methods. Thus, further and more detailed studies are required.

#### 4.3. Impedance spectroscopy

Impedance describes a measure of opposition to a sinusoidal alternating current (AC). Electrical impedance extends the concept of complex resistance to AC circuits, describing not only the relative amplitudes of the voltage and current, but also the relative phases. Impedance is a complex parameter  $\check{Z}$  and the term complex impedance may be used interchangeably; the polar form conveniently captures both magnitude and phase characteristics,

$$\check{Z} = Z e^{i\theta}$$
[4.3.1]

where the magnitude Z represents the ratio of the voltage difference amplitude to the current amplitude, while the argument  $\theta$  gives the phase difference between voltage and current and *i* is the imaginary unit. In Cartesian form,

$$\check{Z} = Z' + iZ''$$
[4.3.2]

$$\delta = \arctan\left(Z'/Z''\right)$$
 [4.3.3]

where the real part of impedance Z' is the resistance *R*, the imaginary part Z'' is the reactance, and  $\delta$  is the phase angle [28, 29].

Any parameter entering the model can in principle be used as a free fit parameter; care must be taken, however, to stay within the limits of physical sense [29]. Typical free parameters are the geometrical factor  $f_{geo}$  representing structural properties of the electrode; the exchange current density  $j_o$  or chargetransfer resistance of the charge-transfer reaction; chemical reaction rate coefficients; and diffusion coefficients. In complex nonlinear least-squares fitting method (CNLS [30]), |Z| vs.  $\omega -$ ,  $\delta$  vs.  $\omega$  – and Z'' vs. Z' data sets are used. However, current density (j) versus overpotential ( $\eta$ ) plots calculated from polarization curves, or (if available) species concentrations or surface coverage versus j or  $\eta$  also represent meaningful fit targets.

In this work, experimental impedance data were mainly analyzed using the equivalent circuits illustrated in Fig. 1, where  $R_{ex}$  is the total very high frequency series resistance of the system  $[R_{ex} \equiv Z_1(\omega \rightarrow \infty)] CPE_1$ ,  $R_1$ ,  $CPE_2$  and  $R_2$  are the so-called high-frequency and low- frequency constant phase element and charge transfer resistance values, respectively;  $Z_W$  is Warburg-like semi-infinitive diffusion impedance.

Usually constant phase element CPE is used in a model replacing an ideal capacitor to compensate the energetic and crystallographic non-homogeneity of the experimental system and corresponding impedance can be expressed as

$$Z_{CPE} = \frac{1}{A(j\omega)^{\alpha}}$$
 [4.3.4]

where *A* is a CPE coefficient and  $\alpha$  is a CPE fractional exponent. If  $\alpha = 1$ , then *A* is equal to the electrical double layer capacitance, if  $\alpha = 0.5$ , then  $Z_{\text{CPE}} = Z_{\text{W}}$  and if  $\alpha = 0$ , then  $Z_{\text{CPE}}$  is equal to the resistance *R* [28, 31–34].

Taking into account the mass transfer limited steps in complicated thin layer cathode matrix in equivalent circuit b in Fig. 1, the low-frequency constant phase element  $CPE_2$  have been exchanged to the generalized finite-length Warburg element (EC b) (GFW) for a short circuit terminus model, expressed as

$$Z_{\rm GFW} = \frac{R_{\rm D} \tanh\left[\left(i\omega L^2 / D\right)^{\alpha_{\rm W}}\right]}{\left(i\omega L^2 / D\right)^{\alpha_{\rm W}}}$$
[4.3.5]

where  $R_D$  is the limiting diffusion resistance, *L* is the effective diffusion layer thickness, *D* is the effective diffusion coefficient of a particle and  $\alpha_w$  is fractional exponent for Warburg-like diffusion impedance [28, 35–41].

There are two accurate ways to obtain an indication of quality of a modeling function, the chi-square function  $(\chi^2)$  and the weighted sum of the squares  $(\Delta^2)$  giving a main general indication about the preciseness of a fit and observing the parameter values and their relative error estimates (in %) [42].











**Figure 1.** Equivalent circuits used for fitting the complex impedance plane plots.  $R_{ex}$  is the high-frequency series resistance ( $R_{ex} \rightarrow Z'$  if  $\omega \rightarrow \infty$ );  $C_{gb}$  and  $R_{gb}$  are the grain boundary capacitance and resistance;  $CPE_1$  and  $R_1$  are the high-frequency constant phase element and resistance;  $CPE_2$ ,  $R_2$  and  $C_2$  are the low-frequency constant phase element, resistance and capacitance, respectively;  $Z_W$  is a Warburg-like diffusion impedance. "An", "cath" and "dif" describe anode-, cathode- and diffusion processes for single cells, respectively.

## 4.4. Oxygen reduction mechanisms

An investigation of the potential loss mechanisms by in situ impedance spectroscopy as well as the use of reference electrodes revealed that the cathode governs the main part of the polarization losses inside semi-cells [43]. In the case of pure electronic conducting electrode material like metals or some perovskite type oxides (LSMO), the electrochemical reactions are almost restricted to the triple phase boundaries (TPB). The transport of oxide ions within the electrode material is advantageous concerning the number of possible reaction pathways. Therefore, electrodes should be either a composite consisting of an electronic and an ionic conducting phases or a mixed conducting metal oxides to enlarge the active area into the electrode volume.



Figure 2. Oxygen reduction at a pure electronic, porous composite and mixed conducting cathode.

An oxygen molecule, which has diffused through the gas phase to the cathode, must first be adsorbed before it can participate in the reduction reaction. This adsorption can occur very close to the TPB or further away, depending on the diffusivity of the adsorbed species. It has been proposed in fact, that oxygen reduction in an electronic conductor can be co-limited by both adsorption and surface diffusion step rates. Both adsorption and surface diffusion depend on the specific surface area, i.e. on the pore surface area; therefore, pore surface area is one of the key microstructural parameters for our investigation. The overall cathode reaction can be expressed as:

$$O_{2,g} + 2V_{O,electrolyte}^{\bullet \bullet} + 4e_{cathode}^{-} \Leftrightarrow 2O_{O,electrolyte}^{x}$$
 [4.4.1]

The gaseous molecular oxygen is reduced in several steps and finally incorporated into the electrolyte via vacancies  $V_0^{\bullet\bullet}_{,electrolyte}$  and transported to the anode side of the fuel cell ( $O_{O,electrolyte}^x$  is oxygen atom in the regular site).

Thus, based on the data in Figure 2, there are actually three macroscopic pathways available for  $O_2$  electroreduction process to occur on porous cathode solid electrolyte interface, and kinetics of this reaction is influenced by several factors [6, 43, 44]: (a) the reaction of molecular oxygen with electrolyte (CGO) surface (what can be neglected at low temperature as the surface exchange coefficient is very low) [6]; (b) dissociative adsorption of oxygen molecules followed by the surface diffusion step toward the three-phase boundary (TPB); and (c) surface reduction reaction followed by dissolution (adsorption/ absorption) of charged oxygen species inside the cathode and mass transfer of oxygen ions toward the cathode | electrolyte boundary. It should be noted that all of these stages can be the rate-determining steps depending on T, oxygen partial pressure  $p_{02}$  and cathode polarization. However, the concentration polarization of the cathode reaction, caused by the diffusion and exchange of oxygen species to the electrode | electrolyte interface, can be the rate determining process at lower T[6]. The solid state mass transfer of oxygen ions includes normal bulk lattice diffusion together with contribution from the grain boundary and dislocation core pathways, depending on the level of bulk diffusivity [6, 10, 43, 44].

It should also be noted that although there is an agreement about the possible pathways, there remain uncertainty and disagreement about the rate-controlling steps, explained by the difficulties in separating the relative effects of micro-structure and electrocatalytic activity of a material [45, 46]. The actual role of micro-, meso- and macropores in a porous electrode can be rather complicated as if there is rapid transport of electronic and ionic species along the pore surfaces due to surface diffusion, then an additional phase should be assigned to represent the surface or interfacial layer in the composite cathode [6]. According to IUPAC classification, micropores are pores with diameter lower than 2 nm, mesopores have diameter from 2 to 50 nm and macropores are wider than 50 nm.

The experimental results presented in Refs. [5–10] show that the activation energy of the electroreduction reaction is strongly influenced by the preparation method for the synthesis of cathode material used, i.e. by the microscopic/macroscopic parameters of the electrode. However, for the future development of SOFC, the time-stability tests during thousand of working hours and under the conditions of thermocycling and cathodic polarisation are inevitable.

If we, to a first approximation, assume that the relationship between the current density *j* and the overpotential  $\eta$  across the interface ( $\eta = E - E_{OCV}$ , where *E* is the working electrode potential and  $E_{OCV}$  is the open-circuit potential), can be described by the usual Butler – Volmer equation [43]

$$j = j_0 \left[ \exp(\alpha_a nF\eta / RT) - \exp(-\alpha_c nF\eta / RT) \right]$$
 [4.4.2]

where  $j_0$  is the exchange current density, *F* is the Faraday's constant, *R* is the universal gas constant, *n* is the number of electrons transferred in the elementary step, and *T* is the absolute temperature,  $\alpha_a$  and  $\alpha_c$  are the transfer coefficients for the oxidation (anode) and reduction (cathode) reactions, respectively. Thus, the total polarization resistance  $R_p$  can be approximated as

$$R_{\rm p} = \left(\frac{\partial \eta}{\partial j}\right) = \frac{RT}{nF} \left(\frac{1}{\alpha_{\rm a} + \alpha_{\rm c}}\right) \frac{1}{j_0}$$
[4.4.3]

and the exchange current density at these conditions is given as

$$j_0 = \frac{RT}{nF} \left(\frac{1}{\alpha_a + \alpha_c}\right) \frac{1}{R_p}$$
 [4.4.4]

At very high cathodic overpotentials ( $|\eta_c| >> 0$ ; i.e. in the case of totally irreversible reduction of oxygen) then Eq. 4.4.2 simplifies to

$$j = j_0 - \exp\left(-\frac{\alpha_c nF\eta}{RT}\right)$$
 [4.4.5]

and

$$\alpha_{\rm c} = -\frac{RT}{\eta_{\rm c} nF} \ln \left| -\frac{j}{j_0} \right|$$
 [4.4.6]

It should be noted that the Butler-Volmer equation can be used for the analysis of the electroreduction of oxygen under certain conditions, but this analysis gives no information about the microscopic details of the reaction. For that reason, various models have been developed [4, 7, 44, 47–50]. According to these models the electroreduction of O<sub>2</sub> at porous cathode (and porous Pt as well) can take place only at the three-phase boundary (if  $\eta \sim 0$ ) while both the TPB and the open surface of La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3-\delta</sub> can be active at the high

overpotential values [48–50]. There are still considerable discrepancies in understanding about the reaction mechanism and rate determining steps for the  $O_2$  reduction at various cathodes (LSMO, LSCFO etc.) [48–51], and therefore more information is needed for the detailed analysis of  $O_2$  electroreduction at micro-, meso- and macroporous LSCO, PSCO and GSCO cathodes under study in this work.

# **4.5.** The influence of the cathode microstructure on the cathode performance

Among many microstructural parameters for SOFC commonly studied, four are considered to be the most critical to electrochemical efficiency of FC. These include pore surface area, triple phase boundary length  $L_{TPB}$ , total porosity, and tortuosity. The electrochemical behavior is described by the polarization resistance  $R_p$  as well as the area specific resistance ASR. There have been worked out some effective models [52, 53] by using ionic and electronic conductivities and microstructure parameters.

Total porosity is the ratio of the void space in the microstructure to total volume. Before the cathodic reaction can occur in an electronic conducting cathode such as LSMO, oxygen molecules must first diffuse through the open pores to the vicinity of the TPB, i.e. to the area, where the cathode, electrolyte, and oxidant (gas phase) meet. An ideal microstructure has ample void space for molecular gas diffusion, while a partially dense microstructure impedes the flow of molecules to the TPB, thus inhibiting the cathodic reaction. Particle sizes and the contact area between particles generally increase with increasing the firing temperature. At 1573 K, there is extensive sintering with substantial reduction in porosity. Relatively poor sintering at 1273 K is evidenced by poor mechanical strength and weak bonding to the electrolyte. At temperatures of 1373 K and above, the two phases are better sintered as indicated not only by the micrographs, but by better mechanical strength of system and good adhesion to the electrolyte [54]. With porous electrodes, it has been observed that, at low oxygen pressure, the charge transfer reaction with a preceding dissociative adsorption is the rate determining step [55–57].

Key microstructural parameters including the TPB density, phase connectivity, and phase tortuosity are measured and used in electrochemical models to understand better the relationship between cathode structure and performance. The focused ion beam-scanning electron microscopy (FIB-SEM) serial sectioning method and 3D data analysis techniques developed [58, 59] can be used for 3D characterization of complex multiphase materials, especially electrodes in electrochemical devices.

Tortuosity is a property that quantifies the complexity of the path through which a diffusing particle must travel in order to reach a desired destination. In terms of SOFCs, tortuosity is a unitless parameter defined as the distance traveled by a molecule exiting an impinging gas flow as it travels through the porous cathode to reach the solid electrolyte, divided by the straight-line distance. A large tortuosity corresponds to a convoluted path for a given gas molecule to traverse from the gas stream to the TPB [60]. Because the data in three dimensions are necessary for a true tortuosity analysis, little work is published for actual systems. The cathode microstructures with a large tortuosity will show an increase in gas diffusion polarization resistance and related electrochemical properties. This is fairly consistent with the tortuosity from 2.5–3 found by Williford et al. [61] for modern SOFC materials, and is also within the range of 1–3 that seems most physically reasonable [62].

One of the first authors to utilize knowledge of a relationship between polarization resistance and  $L_{TPB}$  was Ostergard, who decreased polarization resistance by forming composite cathodes, increasing  $L_{TPB}$  [63]. It has been reported that the dependence of polarization resistance on composite cathode thickness depends on the measurement temperature, and as the composite cathode thickness increases, the polarization resistance decreases until gas diffusion effects become important [64, 65].

One of the first models for the mixed conducting cathode materials was developed by Adler et al. [52, 53]. The quality of this model has been proved by fitting of theoretical impedance spectra to experimental data for cathodes in symmetrical cells with microstructure in physical parameters. The oxygen surface exchange process as well as solid-state bulk diffusion is responsible for the kinetic limitation.

The adhesion to the electrolyte is an important requirement for a suitable cathode in order to ensure an appropriate transfer of oxygen ions either via the triple phase boundary or from the bulk of the cathode into the electrolyte material [66]. Good contact between cathode and electrolyte is the first precondition for a good electrochemical performance of the cathode | electrolyte interface.

The polarization resistance of an electronically or mixed ionic-electronic conductor (MIEC) material can often be reduced by the development of composite cathode, i.e. by adding a second phase with a high oxygen ion conductivity into the good electronic conductor cathode phase [67]. The second phase, doped ceria or LSGMO in the composite cathodes dismisses [53, 68] triple-phase boundaries in the case of an electronically-conducting cathode material, or simply provides short-circuit paths for ion transport for mixed conducting materials [67].

On the other hand, several groups have reported results that indicate the importance of the contribution of three-phase boundaries (TPB) within the electrode to the overall cathodic electrochemical reactions [69, 70]. In particular, Tsai and Barnett [71] pointed out the detailed microstructural effects of the cathode, such as powder composition, particle size distribution, volume fraction, and phase distribution on the cathode performance. Moreover, Barbucci et al. [69] proposed a method to optimize the structure and composition of

composite cathodes of SOFCs via experimental and modelling studies. In particular, they analyzed the influence of gas-phase diffusion in the micropores of the electrode structure and showed that the diffusion limitations became significant, if the electrode was composed of the random packing of very small particles (particle diameter  $d < 0.2 \mu$ m) [69, 70].

# 5. EXPERIMENTAL

## 5.1. Cells preparation and experimental setup

 $Ln_0 \delta Sr_0 \Delta CoO_{3-\delta}$  (Ln = La, Pr or Gd) cathode powders were synthesized from  $La(NO_3)_3 * 6H_2O$ ,  $Pr(NO_3)_3 * 6H_2O$ ,  $Gd(NO_3)_3 * 6H_2O$ ,  $Sr(NO_3)_2$  (Aldrich, 99.9%) and  $Co(NO_3)_2 * 6H_2O$  (98%, Riedel-de Haën), using the nitrate solution thermal decomposition method (NSTDM) [72-75]. The solution, prepared from corresponding salts, glycine as a reducing agent and Millipore water, was heated to form viscous solution and added drop-wise to a preheated Pt beaker (from 575 to 675 K). The solvent was quickly evaporated, the formed viscous liquid reacted autothermally to form the cathode powder with the specific surface area  $S_{BET}$  up to 210 m<sup>2</sup>/g [73–75] due to evolution of gases during highly exothermic reaction. At last the powder was sintered at T = 1273 K during 2 hours to achieve perovskite-like structure stable in time. The La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3- $\delta$ </sub> (LSCO) powder was fortified with controlled amounts (0%, 0.21%, 0.81%, 1,36%, 2,67%, 5,25%, 9,93%) of pore forming agent (PFA) (carbon acetylene black powder with medium diameter from 100 nm to 10  $\mu$ m). Subsequently, ethyl cellulose, xylene, ethylene glycol methyl ether and  $\alpha$ -terpineol were added to form the screen-printing ink. Thereafter the cathode pastes were screen printed onto the electrolyte pellets to form cathodes with surface area S = 0.5 cm<sup>2</sup>. The sintering procedure up to T = 1423 K decreases the cathodes specific area as low as  $\tilde{S}_{BET} < 20 \text{ m}^2/\text{g}$  (however, depending strongly on the sintering temperature and durability of the cathode).

The supporting electrolyte pellets were prepared by dry-pressing commercial  $Ce_{0.9}Gd_{0.1}O_{2-\delta}$  powder (99.9%, NexTech,  $S_{BET} = 19.9 \text{ m}^2/\text{g}$ ) at 90 MPa, followed by a 15 h sintering cycle at T = 1773 K in a high-temperature furnace (Carbolite HTF-1700). The resulting pellets were  $720 \pm 11 \mu \text{m}$  in thickness,  $19.86 \pm 0.02 \text{ mm}$  in diameter and  $1.49 \pm 0.02 \text{ g}$  in weight, corresponding to 99.9% of the theoretical density.

The anode was built up in two layers. The anode functional layer was prepared from a mixture of commercial NiO and CGO with  $S_{BET} = 70.8 \text{ m}^2/\text{g}$ . More porous anode diffusion layer was prepared from commercial NiO/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub> ( $S_{BET} = 6.5 \text{ m}^2/\text{g}$ ) with addition of 1 wt% of carbonaceous pore former. The anode layers were deposited onto the electrolyte by applying the ink through a screen printing textile. The sintered (T = 1623 K) anode had a flat gross section surface area of 1.65 cm<sup>2</sup> and a thickness of 30 µm. In some experiments the cathode was prepared so as to have a surface area identical to that of the anode. Thus, in these experiments the so called symmetric cell design has been used (in order to allow truthful electrochemical measurements to be conducted) (Fig. 3a) [76]. The cathode thickness was found to be approximately 20 µm. Platinum paste was used to make electrical contacts.

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**Figure 3.** Experimental setup used for two electrode single cell (a) and semicell (three electrode system) (b) studies.

The single cell prepared was fixed between two alumina tubes. A gold ring (NexTech Materials) was used to seal the anode compartment from the cathode side. Fibre-free high temperature sealing welt (Microtherm) was used on the cathode side for softer contact between the  $Al_2O_3$  tube and the single cell and for additional sealing. Electrical contact with the cell was achieved via 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 half-cell measurements were carried out using three electrode setup for more detailed analysis of cathode reaction mechanism. The electrodes were located symmetrically, on opposite sides of an electrolyte pellet (Fig. 3b). The reference electrode was placed near the working electrode inside a drilled hole on the other side of pellet. Platinum paste (MaTeck) was applied to generate the reference and counter electrodes (Pt / porous Pt / O<sub>2</sub>) in order to ensure electrical contact without contributing to the electrochemical processes. The areas of the Pt counter and Luggin-like reference electrodes were  $S \sim 3$  cm<sup>2</sup> and S = 0.04 cm<sup>2</sup>, respectively. The cathode (the surface area S = 0.5 cm<sup>2</sup>) was prepared on the other side of counter electrode.

Experimental details for single cell measurements were as follows: anode gas flow  $v(H_2) = 10 \text{ ml/min}$ , v(Ar) = 90 ml/min,  $v(H_2O) = 3 \text{ ml/min}$ ; cathode gas flow v(air) = 100 ml/min. All measurements were conducted under open circuit conditions, at T = 873 K [77].

All electrochemical measurements were carried out using a Solartron 1260 frequency response analyzer in conjunction with a Solartron 1287A potentiostat/galvanostat electrochemical interface. The ac voltage amplitude was 5 mV. The impedance spectra were recorded at 10 points per decade. For fitting of the impedance data (including Z', Z'-plots), the Zview 2.2 software was used [42].

## 5.2. Physical characterisation of electrode materials

The structural data were obtained at room temperature by a refinement of the X-ray diffraction patterns (Difractometer DRON-1) for cathodes (Fig.4). When the as-prepared LSCO powders were heated up to T = 1423 K there were no additional phases, but otherwise (T < 1350 K) there was reported the second orthorhombic phase belonging to SrCO<sub>3</sub> [78]. The XRD patterns for LSCO cathode can be fitted using a trigonal unit cell with space group R-3c. The lattice parameters for hexagonal cell are:  $a \equiv b = 5.442(3)$  Å, c = 13.227(3) Å. The XRD patterns for PSCO cathode can be fitted with a ortorombic unit cell with space group Pnma. The XRD patterns for GSCO cathode can be simulated with a cubic and hexagonal unit cell with space group Pm3m and R3c, respectively. It should be noted that solubility of  $Sr^{2+}$  in GdCoO<sub>3- $\delta$ </sub> is lower than in LaCoO<sub>3- $\delta$ </sub> and the doping levels used in this work lead to segregation of second perovskite-like phase and thus,  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  is not a single phase cathode [74, 75, 79]. No impurity peaks were observed for the LSCO and PSCO cathode materials synthesized. The powders were sintered at different temperatures to analyse influence of sintering temperature on the cathode crystal structure and electrochemical activity of cathodes. As the temperature increases. the crystallinity also increases, as we can see, from the XRD data (Figure 5). The particle diameter also increases with sintering temperature, but the total porosity decreases [78, 79]. Therefore the optimum sintering temperature for active LSCO, PSCO and GSCO cathodes is found to be at T = 1423 K.



**Figure. 4.** X-ray diffraction data for raw cathode powders (noted in figure) sintered at temperature T = 1423 K during 5 hours.



Figure 5. X-ray diffraction data for GSCO cathode powders, heated at different temperatures, noted in figure.

The data obtained by Brunauer – Emmet – Teller gas adsorption (BET) and SEM methods show that the cathodes synthesized have the macro-, micro- and mesoporous systems, but the electrolytes are practically homogeneous. Using the N<sub>2</sub> gas adsorption measurement method at T = 77 K, the specific surface area, pore size distribution, micropore volume and gas phase characteristics have been obtained by Gemini 2375 system (Micrometrics Inc.). The specific surface area, obtained by the BET method, demonstrates comparatively high values for initial cathode powders (before sintering procedure): 217 m<sup>2</sup>/g for PSCO, 147 m<sup>2</sup>/g for LSCO and 105 m<sup>2</sup>/g for GSCO. The micropores with a medium pore diameter (15...18 Å) prevail inside of the cathode materials.

The surfaces of the cathode, electrolyte and anode have been investigated by SEM. The presented SEM micrographs (Fig. 6) show, that very nice meso-, macroporous cathodes and anodes have been prepared on to the practically compact electrolyte. The data for cathode / electrolyte and electrolyte / anode interface show, that there is a very good contact between these phases, respectively shown in Fig. 6a and 6b, both half cells did not involve any severe internal cracks between cathodes and electrolyte. Moreover, based on the analysis of SEM-EDX images, there was no evidence from the interfacial reaction products, originating from a reaction between Co-containing cathode and CGO. The electrolyte layer appears to be almost fully dense expect for some isolated pores, but no crosslayer pinholes or cracks were observed.

The cathode and anode porosities also depend strongly on the pore forming agent amount in the raw material (Fig. 6e, 6f). The SEM data show, that very mesoporous LSCO cathode electrodes have been prepared and the mesoporosity depends strongly on the amount of PFA in the raw cathode material [80, 81]. The platinum counter electrode, as well as reference electrode, is quite porous, as we can see in Figure 6d.



**Figure 6.** SEM images of the anode and electrolyte interface (a), cathode and electrolyte interface (b), electrolyte surface (c), Pt-paste counter electrode (d), LSCO cathode without PFA (e), LSCO cathode with 5,25 wt % PFA (f).

# 6. RESULTS AND DISCUSSION

### **6.1.** Impedance complex plane plots

The impedance complex plane plots ( $Z^{\prime\prime}, Z^{\prime}$ - i.e. so called Nyquist plots, Fig. 7) as well as Bode plots (impedance Z and phase angle  $\delta$  vs. log plots (where f is ac frequency), Fig. 8) were measured using potentiostat/galvanostat and frequency response analyser [74, 75, 79, 82]. The frequency was varied from  $1 \times 10^7$  to  $1 \times 10^{-1}$  Hz. The ohmic series resistance  $R_{\rm ex}$  of system (bulk electrolyte + contact + Pt wire resistances) has been determined from the impedance data at very high frequency ( $R_{ex} = Z(\omega \rightarrow \infty)$ ;  $\omega = 2\pi f$ ) at cell potential  $\Delta E = 0$  vs Pt / porous Pt / O<sub>2</sub> reference electrode. The influence of temperature and composition of the cathode material on the electrochemical characteristics and reaction mechanism, prevailing for O<sub>2</sub> reduction, is very well visible in the phase angle  $\delta$  vs. log plots. These data show mixed kinetics behaviour of systems under study at  $T \le 773$  K because  $20^{\circ} < |\delta| < 40^{\circ}$ , (i.e. for diffusion limited step  $\delta = -45^{\circ}$  (the slow mass transfer step) and for charge transfer limited step  $\delta = 0^{\circ}$  [28, 33, 34]. At higher negative potentials and higher temperature the systems tend toward purely charge transfer limited mechanism  $(|\delta| \le 5^{\circ})$  [74, 75, 79, 80]. However, the shape of  $\delta$  vs. log plots shows that there seems to be only one (or two, but not clearly separable) mainly diffusionlimited charge transfer process for analysed systems at  $f \le 20$  kHz and  $T \leq 773$  K. Still the noticeable dependence of  $\delta$  on the electrode potential  $\Delta E$ applied indicates the very complicated mass transfer process (semi-infinite diffusion, migration, surface diffusion as well as Knudsen-like diffusion) [7, 28, 52, 53] of the charged oxygen particles inside the porous cathode for all systems studied (Fig. 9) [73-75, 80-82].

Surprisingly, there is no significant dependence of characteristic relaxation time constant  $\tau_{\text{max}}$  (equal to  $(2\pi f_{\text{max}})^{-1}$ , where  $f_{\text{max}}$  is the frequency of the maximum in the Nyquist plot) on the electrode potential applied (Figure 7). On the contrary, this dependence is quite impressive in temperature scale (Figure 8). It is seen in Figure 8, that for LSCO half-cell the limiting processes are quicker compared with PSCO half-cell.

The limiting cathode processes nature changes in temperature scale, as we can see on the phase angle vs. log*f* plots. Smaller phase angle absolute values  $(|\delta| < 5^{\circ})$  indicate nearly pure charge transfer limitation, which is characteristic of PSCO and LSCO at T > 873 K. For GSCO half-cell the absolute values of phase angle are higher, which refer to diffusion limitation in less porous cathode structure (Figure 9). Thus, at high temperature (T > 873 K), the biggest potential losses are caused by oxygen electro-reduction process rate, i.e. reaction mechanism at the catalytically active cathode surface. At lower temperature (T < 873 K) mixed kinetic processes are dominating [73–75, 80–82].



**Figure 7**. Nyquist plots for half cell with  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$  cathode at *T* and  $\Delta E$ , given in figure.



**Figure 8**. Bode plots for half cells with  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$  and  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$  cathodes at *T* and  $\Delta E$ , given in figure.



**Figure 9**. Bode plots for half cell with  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  cathode at *T* and  $\Delta E$ , given in figure.

Comparison of Z'', Z' plots for systems investigated in Figure 10 indicates that the shape of impedance spectra depends noticeably on chemical composition of the cathode studied. The lowest very high frequency series resistance has been obtained for LSCO | CGO and PSCO | CGO half cells. The low frequency polarisation resistance  $(R_p)$  values increase in the order of half-cells LSCO  $CSO \leq PSCO \mid CGO < GSCO \mid CGO$ . Thus, the higher values of  $R_p$  have been obtained for the GSCO cathodes, based on Gd<sup>3+</sup> where the noticeable dependence of  $R_p$  on  $\Delta E$  has been established as well (Fig. 11). This activity order of cathodes can be explained by the effective relaxation frequency  $f_{\rm eff}$  of the atoms in the A position of the perovskite-like structure. Therefore, the processes at the GSCO cathode are much more diffusion limited than at LSCO or PSCO. However at higher cathodic potentials, similarly to LSCO and PSCO the diffusion limitation decreases. For that reason the characteristic frequency increases, because the charge transfer process is quicker compared with the mass transfer process. As the temperature is increased, the relaxation frequency of process moves towards higher frequencies [73–75, 80–82]. The processes are quicker for LSCO cathode than for other cathodes studied (Fig. 8, 9).

For all systems studied, the total polarisation resistance  $R_p$  decreases with increasing *T* and  $|\Delta E|$ . The characteristic relation time  $\tau_{max}$ , obtained from the low frequency part of the *Z*'', *Z*'-plots, depends noticeably on the chemical composition of cathode. Thus,  $\tau_{max}$  decreases with increasing temperature ( $\tau_{max} = 0.025$  s at T = 973 K), but  $\tau_{max}$  is independent of electrode potential  $\Delta E$  applied [74, 75, 81, 82].



**Figure 10**. Nyquist plots for  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$ ,  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  and  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$  cathodes at *T* and  $\Delta E$ , given in figure.



**Figure 11**. Nyquist plots for  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  at *T* and  $\Delta E$ , given in figure.

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# 6.2. Influence of pore forming agent in raw cathode paste on the electrochemical activity of sintered cathodes

The shape of Nyquist (Fig. 12) and Bode plots depends noticeably on PFA wt% in raw cathode paste [80, 82]. The lowest total polarization resistance  $R_p$ (Fig. 13) has been obtained at 1.36 wt% of PFA addition ( $S_{BET} = 7.8 \text{ m}^2/\text{g}$ ;  $V_{tot} \approx 31\%$ ). The Nyquist plots have been normalized for the better kinetic analysis. In Nyquist plots at T > 873 K (PFA content  $\ge 2.67 \text{ wt}\%$ ) there is only one very well visible semicircle determining the characteristic relaxation time constant  $\tau_{max}$ , varing from 0.12 s to 0.20 s, different from cathode without PFA ( $0.18 < \tau_{max} < 0.20 \text{ s}$ ). It was found that there is no linear dependence of  $R_p$  on the total porosity of cathode studied. The lowest high frequency polarization resistance values correspond for systems prepared from raw cathode paste with 5.24 wt% PFA [80, 82]. It is very interesting to mention that at optimal PFA wt% in raw cathode paste,  $R_p$  only very weakly depends on the potential applied.



**Figure 12**. Nyquist plots for La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3- $\delta$ </sub> prepared using different amount of pore forming agent in raw cathode paste.



**Figure 13**. Dependence of total polarization resistance  $R_p$  on the weight % of PFA in raw cathode paste at *T* and  $\Delta E$ , given in figure.

# 6.3. Equivalent circuit modeling of Nyquist plots and analysis of parameters obtained

To a first approximation, the calculated impedance curves can be fitted to experimental data by the equivalent circuits (EC) presented in Figure 1a, with the chi-square function  $\chi^2 \le 6 \times 10^{-4}$  and weighted sum of squares  $\Delta^2 < 0.1$ . In figure 1a,  $R_{ex}$  is the total very high frequency series resistance of a system;  $R_{\text{ex}} \equiv Z_1 \ (\omega \rightarrow \infty)$  (practically independent of  $\Delta E$ ). To a first approximation,  $R_1$ characterizes the charge transfer resistance and therefore  $R_2$  describes mass transfer resistances inside cathode material [39–41, 80–83].  $C_1$  and  $CPE_2$ describe the capacitative behaviour of the cathodes (adsorption of partially reduced oxygen) under study. (Constant phase element impedance  $Z_{CPE}$  =  $A^{-1}(j\omega)^{-\alpha}$ , where A is a CPE coefficient and  $\alpha$  is a CPE fractional exponent). It is an empirical model, but its behaviour is very similar to the Randles model (Fig. 1b), which has been modified by adding the generalised finite length Warburg element (GFW) into the classical EC (Fig. 14a, first EC) and can be applied at  $T \ge 873$  K. The very small chi-square function values  $\chi^2 < 2 \times 10^{-4}$  and weighted sum of squares  $\Delta^2 < 0.03$  have been established. At higher temperatures (T > 873 K), the charge transfer resistances show the same values for both circuits (Fig. 14). The fractional exponent values of  $\alpha_{\rm W} \leq 0.5$  for generalised

Warburg element  $Z_{\text{GFW}} = R_{\text{D}} \tanh\left[\left(i\omega L^2 / D\right)^{\alpha_{\text{W}}}\right] / \left(i\omega L^2 / D\right)^{\alpha_{\text{W}}}$  indicate

that there are deviations from the classical semi-infinite diffusion model toward the generalized finite length Warburg diffusion model [39–41, 73–75, 80–82]. The relative residuals obtained at T < 873 K for the second circuit are very low and have a random distribution in the whole frequency region studied. Therefore it seems that, taking into account the very high  $C_2$  values obtained, the low-frequency arc at  $T \le 873$  K characterizes the kinetically mixed, both charge transfer and mass transfer (migration and diffusion-like) limited adsorption processes ( $|\delta| > 15^{\circ}$ ). GSCO cathode based half cell is modelled by using equivalent circuit c (Fig. 1c), which consist of three fitting (elements) blocks. However, the semisircles for GSCO are not very well separable and the fitting parameters have to be taken with some reservations.



Figure 14. Dependence of charge transfer resistances for both equivalent cirquits.

The Nyquist and Bode plots for micro-, meso- and macroporous LSCO at  $T \le 813$  K, prepared using various PFA wt% in raw cathode paste [80, 82], can be fitted by the equivalent circuit a in Figure 1, where the low-frequency process (electroreduction of O<sub>2</sub> inside mesopores) is characterized with constant phase element impedance  $Z_{CPE2}$  and charge transfer resistance  $R_2$ ; and high-frequency electroreduction of O<sub>2</sub> at more open surface areas is simulated with capacitance  $C_1$  and resistance  $R_1$ . Very high electrical double layer capacitance the accumulation of partially reduced oxygen species inside the highly porous cathode structure. Additionally, very low values of charge transfer resistances  $R_1$  (not shown) and  $R_2$  (Fig. 16) have been obtained.  $R_1$  depends only weakly on

PFA wt%, however,  $R_2$  depends on PFA wt%, being minimal at 1.36 wt% and indicating that the optimal porosity of the cathode is very important. The effect of the high frequency process is negligible at PFA > 0.21 wt% and at T > 873 K, the equivalent circuit simplifies, and only  $R_{el}$ ,  $R_2$  and  $C_{PE2}$  are important.



**Figure 15**. Dependence of low-frequency  $CPE_2$  coefficient on  $\Delta E$  at various additions of PFA (wt%).



**Figure 16**. Dependence of charge transfer resistance  $R_2$  on  $\Delta E$  at various additions of PFA (wt%).



**Figure 17**. Dependence of mass transfer resistance  $R_D$  on  $\Delta E$  at various additions of PFA (wt%) and temperatures.

However, a better fit of calculated with experimental impedance data given in Fig. 14 and 15 can be obtained if  $CPE_2$  and  $R_2$  elements have been exchanged to the finite-length Warburg diffusion impedance  $Z_W$  element (Fig.14a). Modified EC includes also additional charge transfer resistance  $R_1$  and  $C_1$  elements, depending on PFA wt%. Diffusion resistance  $R_D$  (Fig. 17) depends on  $\Delta E$  applied, indicating that  $R_D$  is not a simple diffusion process resistance and, in addition to diffusion, the migration of  $O^{2-}$  anions, surface diffusion etc. are important at electrode potentials contrary to open circuit polarization conditions  $\Delta E \neq 0$  [39–41, 80–82]. Based on fitting data, it was established that  $R_1$  depends only weakly on PFA wt%. However,  $R_2$  depends on PFA wt%, being minimal at 1.36 wt% and indicating that the optimal meso-, macroporosity of the cathode is very important.

## 6.4. Analysis of single cells

The electrochemical impedance spectra of three single cells prepared, each from a different cathode material but with identical anode microstructure, have been prepared and tested [77, 81]. Humidified mixture of 10% H<sub>2</sub> in argon was fed to the anode, and ambient air was pumped to the cathode at 100 ml/min. These spectra were taken as the basis for subsequent equivalent circuit modelling. The methodology of differential derivative impedance  $\Delta \partial Z$  plots, developed by

Barfod *et al.* [84], was applied in order to deconvolute the cell response into anodic and cathodic contributions. A fuel variation experiment was conducted, in which  $p_{\text{H2}}$  in the anode compartment was changed from 0.1 atm to 1.0 atm. The quantity

$$\Delta \partial Z_{\text{fuel}} = \frac{\partial \left| Z_{\text{H}_2 + \text{Ar}} \right|}{\partial \log f} - \frac{\partial \left| Z_{\text{H}_2} \right|}{\partial \log f}$$
[6.4.1]

was then calculated and plotted against frequency in order to extract the frequency dependence of the anodic process. Similarly, based on the results of oxygen partial pressure variation experiments, the quantity

$$\Delta \partial Z_{\text{oxidant}} = \frac{\partial |Z_{\text{air}}|}{\partial \log f} - \frac{\partial |Z_{\text{oxygen}}|}{\partial \log f}$$
[6.4.2]

was calculated and thus, the frequency dependence of the cathodic process was obtained and analysed. Based on these results (Fig. 18), the overall cell response was found to consist of contributions from both the anode and cathode of the cells. Equivalent circuit shown in Figure 1d was found as most suitable for fitting experimental data for either LSCO or PSCO cathodes. As can be seen from Figure 19, the values of the characteristic relaxation frequency obtained from the model circuit analysis are in an excellent agreement with the  $\Delta \partial Z'$  vs. f experimental data. Very low values of the chi-squared function were obtained  $(\chi^2 < 8.10^{-4})$ , indicating that a good fit was achieved. The equivalent circuit unit shown in brackets was used to model the very low frequency gas diffusion impedance data that were present in the spectra of some cells at low  $p_{H2}$ pressure [85]. Due to the higher relaxation frequencies (25 Hz  $< f_{max} < 30$  Hz) of the cathodic process, the 45° angle characteristic of Warburg diffusion-like process was not visible in the Nyquist plots for GSCO cells and thus, the Randles equivalent subcircuit had to be changed with a simple RO-unit. Thus equivalent circuit shown in Fig. 1e was used for the fitting of all cells with GSCO cathodes in this study [81].

The very low frequency semicircle (Fig.20) observed in some experiments, 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). It should be noted that 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 (variation in porosity, pore size distribution, specific surface area, ratio of micro-, meso-, macropores) are inevitable. The occurrence of such disturbances further elucidates the importance for an experimental approach to the issue of the possible effects of cell geometry and microstructure of the electrodes on the properties of electrochemical systems.



**Figure 18.**  $\Delta \partial Z'$  vs. log *f* plots for Ni/CGO|CGO|LSCO upon gas composition variation: closed symbols –  $\Delta \partial Z'_{\text{fuel}}$  for a shift from 10% H<sub>2</sub> + 87% Ar + 3% H<sub>2</sub>O to 97% H<sub>2</sub> + 3% H<sub>2</sub>O on the anode side at a constant air flow of 100 ml/min, open symbols –  $\Delta \partial Z'_{\text{oxidant}}$  for a shift from air to pure oxygen on the cathode side at constant 97% H<sub>2</sub> + 3% H<sub>2</sub>O flow of 100 ml/min. All measurements were conducted in open circuit conditions at 873 K.



**Figure 19.** Nyquist plots for LSC|CGO|Ni/CGO (a), PSC|CGO|Ni/CGO (b) and GPSC|CGO|Ni/CGO (c) single cells. The corresponding fits are shown as black lines, experimental data are shown as dots.



**Figure 20.** Nyquist plot for Ni/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub>|Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub>|La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3- $\delta$ </sub> single-cell at 873 K. Filled symbols denote experimental data, black lines are the complex non-linear least squares fit. Fuel: 10% H<sub>2</sub> + 87% Ar + 3% H<sub>2</sub>O at 100 ml/min. Oxidant: air at 100 ml/min.

It should be noted that the values of characteristic relaxation frequencies,  $f_{\text{max}}$ , did not coincide with the values obtained from fuel and oxidant concentration variation experiments for LSCO and PSCO cells, when the data were fitted with simple R-CPE-elements in series. Furthermore, the very low *CPE* exponent values ( $\alpha_{\text{CPE}} \leq 0.75$ ), especially for LSCO cells, imply that slow diffusion process probably contributes to the overall impedance.  $R_s$  is a so called high-frequency (i.e. contact and electrolyte) resistance,  $C_{\text{an}}$ ,  $R_{\text{an,ct}}$  and  $Z_W$  are the capacitance, charge transfer resistance and resistance of the anode process ( $O_2$  electroreduction), and  $C_{\text{diff}}$  and  $R_{\text{diff}}$  are the capacitance and resistance of the low-frequency [81].

The influence of electrode potential on the electrocatalytic activity is very well visible in Figure 21, where  $\Delta \partial Z'$ , log plots at constant O<sub>2</sub> partial pressure but at different  $\Delta E$  are given. Based on the experimental data, the frequency range for which the magnitude of |Z|, Z' or 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 (Fig. 18). 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' impedance of the single cell [77, 81, 86, 87]. The  $\Delta \partial Z'$  vs. log f plots for Ni/CGO|CGO|LSCO suggest that, based on the oxygen or air variation experiments for semi cells (Fig. 22) and our previous data [77, 81, 88], the process of highest characteristic frequency corresponds to an anodic (i.e. fuel oxidation) process (Fig. 21), whereas the lower-frequency process can be assigned to the electroreduction of O<sub>2</sub>[39–41, 81, 88].

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**Figure 21.**  $\Delta \partial Z'$  vs. log *f* plots for Pt|CGO|LSCO half-cell upon oxidant variation conditions (from pure oxygen to air) at different electrode potentials, noted in figure.



**Figure 22.**  $\Delta \partial Z'$  vs. log *f* plots for Ni/CGO|CGO|LSCO at different fixed cell potentials at constant fuel (10 % H<sub>2</sub> + 87 % Ar + 3 % H<sub>2</sub>O; flow 100 ml min<sup>-1</sup>) and oxidant (air, 100 ml min<sup>-1</sup>) compositions.

### 6.5. Activation energy and current relaxation plots

The capacitive parts of the impedance spectra at  $f \le 20$  kHz were used to determine the total polarisation resistance ( $R_p$ ) from the difference between the intercepts of the very low and high frequency parts of the spectra with the Z-axis of Nyquist plots. The increase in concentration of the "charged oxygen" particles with increasing the negative cathode potential will improve the catalytic activity of the cathode and the decrease in the values of  $E_{act}$  (Fig. 23) in a good agreement with experimental results was found [73–75, 80–82].



Figure 23. Activation energies as a function of the applied electric potential for studied half-cells, noted in figure.

Chronoamperometry curves obtained indicate that the shape of the  $j_c$ , *t*-curves depends on  $S_{\text{BET}}$ , T,  $\Delta E$ , as well as on the cathode compositions investigated (Fig. 24). The stable  $|j_c|$  values have been established at  $T \le 773$  K in the case of t > 5.0 s, but at  $T \ge 973$  K even at very short charging times t < 1 s. The decrease in the cathodic current density with time t < 1 s can be explained by extending the active reaction zone from the open surface area to the porous surface of mixed conducting cathode [39–41].

The cyclic voltametry curves (Fig. 25) show that very high current density (catalytic activity) was obtained for the micro-mesoporous LSCO cathode electrode, where addition of the carbon acetylene black powder (PFA) in to the raw cathode material varied from 2,56 to 1,36 wt %. The activation energy has minimal values for cathode with amount of PFA from 0,5 to 2,5 wt % (Fig.26). The values of  $E_{act}$  decrease with increasing the cathode potential.



Figure 24. Chronoamperometry dependences for systems studied.



Figure 25. The cyclic voltametry curves for micro-mesoporous LSCO half cells with different PFA additions in to raw paste, noted in figure.



**Figure 26.** Activation energy as a function of the applied electric potential for LSCO half cell with different PFA additions in to raw cathode paste, noted in figure.

Comparison of the data shows that the total polarisation resistance has minimum at optimal porosity, i.e. at optimal  $S_{\text{BET}}$ , which is caused by the low mass transfer resistance  $R_D$  inside the optimal porous cathode. The value of  $E_{\text{act}}$ , obtained from Z', Z'-plots, is in a reasonable agreement with the value of  $E_W$ , obtained from the diffusion resistance  $R_D$  vs. temperature plots. Thus, the slow mass transfer process at lower T and  $|\Delta E|$  characterises mainly the total electroreduction process, i.e. the generalized diffusion-like limited process of the electrochemically active oxygen particles into the reaction centre is the lowest rate determining step. The very low values of  $E_{\text{act}}$  were obtained for porous cathodes at higher negative potentials. However, there is no linear dependence of  $E_{act}$  on  $S_{BET}$ , indicating that  $R_p$  depends crucially on the active surface area, macroporosity and electronic / ionic conductivity of the cathode synthesized.

Temperature and oxygen partial pressure variation experiments allowed the Arrhenius activation energy values for the cathodic process to be determined as 1.36 eV (Fig. 27a). The values calculated are in a very good agreement with results for three electrode systems, as well as with the results of Horita [89], who observed a value of 1.32 eV for charge transfer limitation in the  $La_{0.6}Sr_{0.4}CoO_{3-\delta}|La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{2.8}$  (cathode|electrolyte) system under comparable experimental conditions. Moreover, the experimentally observed apparent reaction order of 0.22 of oxygen partial pressure (theoretical value: 0.25) suggests that the low-frequency process can be assigned to a slow charge transfer step at the TPBs of the cathode in a good agreement with the data for the three electrode system.

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**Figure 27**. Arrhenius-like activation energy plots (a) and resistive components ( $R_2$ ;  $R_W$ ,  $R_3$ ) (b) vs. cell potential plots for two identically prepared Ni/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub>|Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub>|La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3- $\delta$ </sub> single-cells. Circular symbols stand for  $R_3$ , triangular symbols for  $R_W$ , rectangular symbols for  $R_2$ . Regression lines have been added to (a) along with the corresponding Arrhenius activation energy values.

Experimentally observed activation energy values of 0.93 and 1.22 eV for the anodic charge transfer resistance,  $R_3$ , and the Warburg-like 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 fact that  $R_W$  was found to be practically independent of applied cell potential (Fig. 27b) provides further support for the involvement of non-charged intermediate species in the anodic electro-oxidation process of hydrogen fuel in Ni/Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub>|Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>2- $\delta$ </sub>|La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3- $\delta$ </sub> single-cells. However, it should be noted that 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  $R_W$  on  $\Delta E$  applied indicates that this process is not significant at porous Ni + porous CGO cermet anode [80–82].

## 7. SUMMARY

Electrochemical characteristics of the half-cells  $Ce_{0.8}Gd_{0.2}O_{1.9} | La_{0.6}Sr_{0.4}CoO_{3-\delta}$  $Ce_{0.8}Gd_{0.2}O_{1.9} | Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$  and  $Ce_{0.8}Gd_{0.2}O_{1.9} | Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  and single cells  $La_{0.6}Sr_{0.4}CoO_{3-\delta} | Ce_{0.8}Gd_{0.2}O_{1.9} | NiO + Ce_{0.9}Gd_{0.1}O_{2-\delta}$ ,  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta} | Ce_{0.8}Gd_{0.2}O_{1.9} | NiO + Ce_{0.9}Gd_{0.1}O_{2-\delta}$ ,  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta} | Ce_{0.8}Gd_{0.2}O_{1.9} | NiO + Ce_{0.9}Gd_{0.1}O_{2-\delta} | Ce_{0.8}Gd_{0.2}O_{1.9} | Ce_{0.8}Gd_{0.2}O_{1.9} | NiO + Ce_{0.9}Gd_{0.1}O_{2-\delta} | Ce_{0.8}Gd_{0.2}O_{1.9} | Ce_{0.8}Gd_{0.2}O_{1.9} | Ce_{0.8}Gd_{0.2}O_{1.9}$ 

Systematic analysis of electrochemical results demonstrates that kinetics of oxygen electroreduction depends noticeably on porosity and chemical composition of the cathodes used.

Detailed analysis of the impedance complex plane ( $Z^{,*}, Z^{,*}$ ) plots shows that the total polarization resistance increases with the rise of atomic mass of the cation in the A-site position of perovskite-like structure. The phase angle versus ac frequency plots indicate that at  $T \leq 773$  K the mixed kinetics behavior prevails for most half-cells studied (i.e. slow mass transfer and charge transfer limiting steps have been established). At higher negative potentials and temperatures the processes tend toward purely charge transfer limited oxygen electroreduction mechanism (phase angle  $\delta \geq -5^{\circ}$ ). However, the noticeable dependence of  $\delta$  on  $\Delta E$  indicates the very complicated mass transfer process of the charged oxygen species inside porous cathode.

The addition of pore forming agent (PFA) into the raw cathode material increases mainly macroporosity and, thus, the specific surface area  $S_{BET}$  of the cathodes. The mesopore volume and micropore size distribution only slightly change in comparison with a diameter of the powder particles used. Very low total polarization resistance for oxygen electroreduction ( $R_p = 0.03 \ \Omega \ cm^2$  at 873 K) has been obtained for 1.36 wt% of PFA in raw La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3- $\delta$ </sub> (LSCO) cathode paste.

The total activation energy  $E_{act}$  for oxygen electroreduction depends on the meso- and macroporosity of the cathodes, and the lowest  $E_{act}$  ( $E_{act} > 0.5$  eV at open circuit potential) has been obtained for LSCO with total porosity of 31% and  $S_{BET} = 7.8 \text{ m}^2 \text{ g}^{-1}$  (i.e. with 1.36 wt% PFA). However, there is no linear dependence of  $E_{act}$  on  $S_{BET}$ , indicating that total polarization resistance  $R_p$  depends crucially on the active surface area, macroporosity and electronic / ionic conductivity of the cathode synthesized.

Systematic analysis of electrochemical data indicates that the three electrode half-cell setup provides 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 (LSCO cathode), and therefore, such cell geometry can be considered as suitable for fundamental research of the electrochemical properties of SOFC cathode materials at different cathode potentials. However, it was found that in order to obtain an estimate of how these cathode materials behave in real operating conditions, the two electrode single-cell experimental setup should be considered as well. Using the differential derivative Nyquist plot method, i.e. analysis of the  $\Delta \partial Z'$  vs. logf plots, in combination with fuel and oxidant composition variation experiments, the impedance spectra of symmetric single-cell can be deconvoluted even when the simple two-electrode configuration is used for measurements. Thus, these two experimental setups can be considered as complementary to one another, and should be used jointly in order to gain a thorough insight into the electrochemical properties of SOFC cathodes.

The values of total activation energy, calculated for various cathodes, decrease with increasing the cathode negative polarisation. In addition to the electron transfer process (reduction of oxygen), the mass transfer process of electrochemically active pieces inside micro-, mesoporous solid cathode material can probably be the rate-determining step in agreement with the fitting results of the Nyquist plots.

## 8. REFERENCES

- [1] S. C. Singhal, Solid State Ionics 135, 305 (2000).
- [2] Weber, E. Ivers-Tiffée, J. Power Sources 127, (2004) 273.
- [3] S. P. Jiang, Solid State Ionics 146 (2002) 1.
- [4] B. C. H. Steele, Solid State Ionics 129 (2000) 95.
- [5] S. P. S. Badwal, Solid State Ionics 143, 39 (2001).
- [6] G.O. Yamamoto, *Electrochimica Acta* 45, 2423 (2000).
- [7] M. Morgesen, N. M. Sammes, G. A. Tompsett, Solid State Ionics 129, 63 (2000).
- [8] V. Ramani et al., Interface 13 (2004) 17.
- [9] O. Yamamoto, Y. Takeda, R. Kanno, M. Noda, Solid State Ionics 22 (1987) 241.
- [10] Ringuede, J. Fouletier, Solid State Ionics 139 (2001) 167.
- [11] V. Dusastre, A. Kilner, Solid State Ionics 126 (1999) 163.
- [12] G. Ch. Kostogloudis, Ch. Ftikos, Solid State Ionics 126 (1999) 143.
- [13] Y. Teraoka, T. Nobunaga, K. Okamoto, M. Miura, N. Yamazoe, Solid State Ionics 48 (1991) 207.
- [14] R.A. De Souza, J.A. Kilner, Solid State Ionics 106 (1998) 175.
- [15] E. Siebert, A. Hammouche, M. Kleitz, Electrochim. Acta 40 (1995) 1741.
- [16] T. Kawada, K. Masuda, J. Suzuki, A. Kaimai, K. Kawamura, Y. Nigara, J. Mizuaki, H. Yugami, H. Arashi, N. Sakai, H. Yokokawa, *Solid State Ionics* 121 (1999) 271.
- [17] W. Zhou, Z. Shao, R. Ran, H. Gu, W. Jin and N. Xu, Journal of the American Ceramic Society 91 (2008) (4), p. 1155.
- [18] Per Hjalmarsson, Martin Søgaard, Anke Hagen, Mogens Mogensen, Solid State Ionics 179 (2008)
- [19] E. Tsipis and V. Kharton, Journal of Solid State Electrochemistry 12 (2008) (9), p. 1039.
- [20] U.P. Muecke, D. Beckel, A. Bernard, A. Bieberle-Hütter, S. Graf, A. Infortuna, P. Müller, J.L.M. Rupp, J. Schneider, L.J. Gauckler, *Adv. Funct. Mater.* 18 (2008) 1.
- [21] S. Rey-Mermet, P. Muralt, Solid State Ionics 179 (2008) 1497.
- [22] H. Huang, M. Nakamura, P.C. Su, R. Fasching, Y. Saito, F.B. Prinz, J. Electrochem. Soc. 154 (2007) B20.
- [23] C.D. Baertsch, K.F. Jensen, J.L. Hertz, H.L. Tuller, S.T. Vengallatore, S.M. Spearing, M.A. Schmidt, J. Mater. Res. 19 (2004) 2604.39
- [24] T.R. Dietrich, W. Ehrfeld, M. Lacher, M. Kramer, B. Speit, *Microelectron. Eng.* 30 (1996) 497.
- [25] Y. Yamazaki, *Electrochim. Acta* 50 (2004) 663.
- [26] J. Fleig, H.L. Tuller, J. Maier, Solid State Ionics 174 (2004) 261.
- [27] P.C. Su, C.C. Chao, J.H. Shim, R. Fasching, F.B. Prinz, Nano Lett. 8 (2008) 2289.
- [28] J. R. MacDonald, Editor, Impedance Spectroscopy: Emphasisizing Solid Materials and Systems, Wiley, New York, (1987).
- [29] Lloyd R. Fortney. Principles of Electronics, NY, 1987
- [30] W.G. Bessler / Solid State Ionics 176 (2005) 997-1011
- [31] B.A. Boukamp, *Solid State Ionics* 20 (1986) 31.
- [32] B.A. Boukamp, Solid State Ionics, 169 (2004) 65-73.
- [33] M. Sluyters-Rehbach, J. Sluyters, in A. Bard (ed.) *Electroanalytical Chemistry*, Vol. 4, Macel Dekker, New York, 1970, p. 76.

- [34] Lasia, in B.E. Conway, J. O'M. Bockris, R.E. White (Eds.), *Modern Aspects of Electrochemistry*, Vol 32, Kluwer Academic / Plenum Publishers, New York, 1999, p 143.
- [35] E. Lust, G. Nurk, P. Moller, I. Kivi, S. Kallip, A. Jänes, V. Sammelselg, H. Mändar, Proc. of the Internat. Symp. on Solid Oxide Fuel Cells, Paris, 2003, 1176.
- [36] G. Nurk, S. Kallip, I. Kivi, P. Möller, E. Lust, Proc. of 6th European Fuel Cell Forum, Lutzern, 2004, p. 887.
- [37] E. Lust, G. Nurk, S. Kallip, I. Kivi, P. Möller, P. Nigu, K. Lust, Proc. of 6th European Fuel Cell Forum, Lutzern, 2004, p. 1271.
- [38] E. Lust, G. Nurk, P. Möller, I. Kivi, S. Kallip. 26th Risø International Symposium on Materials Science, Risø, 2005, p. 279.
- [39] E. Lust, G. Nurk, S. Kallip, I. Kivi, P. Möller. Journal of Solid State Electrochemistry, 9 (2005) 674.
- [40] E. Lust, P. Möller, I. Kivi, G. Nurk, S. Kallip. Journal of Solid State Electrochemistry, 9 (2005) 882.
- [41] E. Lust, P. Möller, I. Kivi, G. Nurk, S. Kallip, P. Nigu, K. Lust. Journal of the Electrochemical Society, 152 (2005) A2306.
- [42] ZPLOT for Windows (Version 2.2) fitting program, Scribner Inc., Southern Pines, North Carolina.
- [43] A. Weber, E. Ivers-Tiff'ee, Journal of Power Sources 127 (2004) 273-283
- [44] S. B. Adler, J. A. Lane, B. C. H. Steele, J. Electrochem. Soc. 143 (1996) 3354.
- [45] H. Ullmann, N. Trofimenko, F. Tietz, D. Stöver, A. Ahmad-Khanlou, Solid State Ionics 138 (2000) 79.
- [46] S.H. Chan, X.J. Chen, K.A. Khor, J. Electrochem. Soc. 151 (2004) A154.
- [47] M. Mogensen, N. M. Sammes, G. A. Tompsett, Solid State Ionics 129, (2000) 63.
- [48] S. Wang, X. Lu, M. Liu, J. Solid State Electrochem. 6 (2002) 384.
- [49] D. Y. Wang, A. S. Nowick, J. Electrochem. Soc. 126, (1979) 1155.
- [50] Y. Jiang, S. Wang, Y. Zang, J. Yan, W. Li, Solid State Ionics 110, (1998) 111.
- [51] G.O. Yamamoto, *Electrochimica Acta* 45, (2000) 2423.
- [52] w.B. Adler, J.A. Lane and B.C.H. Steele, *Journal of The Electrochemical Society* 143 (1996) (11), p. 3554.
- [53] S.B. Adler, Chemical Reviews 104 (2004) (10).
- [54] Y. Lin, S.A. Barnett, Solid State Ionics 179 (2008) 420-427
- [55] Y. Takeda, R. Kanno, M. Noda, Y. Tomida, O. Yamamoto, J. Electrochem. Soc. 134 Ž1987. 2656.
- [56] M. Go¨dickemeier, K. Sasaki, L.J. Gauckler, I. Riess, Solid State Ionics 86–88 Ž1996. 691.
- [57] T. Inoue, N. Seki, K. Eguchi, H. Arai, J. Electrochem. Soc. 137 Z1990. 2523.
- [58] J. R. Wilson, W. Kobsiriphat, R. Mendoza, H.-Y. Chen, J. M. Hiller, D. J. Miller, K. Thornton, P. W. Voorhees, S. B. Adler and S. A. Barnett, *Nat. Mater.* 5 (2006) 541–544.
- [59] J.R. Wilson, A.T. Duong, M. Gameiro, H-Y. Chen, K. Thornton, D.R. Mumm, S.A. Barnett, *Electrochemistry Communications*, 11, (2009), 1052–1056.
- [60] Y. Jiang, A.V. Virkar, J. Electrochem. Soc. 150 (2003) A942–A951.
- [61] R.E. Williford, L.A. Chick, G.D. Maupin, S.P. Simmer, J.W. Stevenson, J. Electrochem. Soc. 150 (2003) A1067–A1072.
- [62] Anchasa Pramuanjaroenkij, Sadik Kakac, Xiang Yang Zhou, International Journal of Hydrogen Energy 33 (2008) 2547 – 2565.

- [63] M. Ostergard, C. Clausen, C. Bagger, M. Mogensen, *Electrochim. Acta* 40 (1995) 1971.
- [64] M. Juhl, S. Primdahl, C. Manon, M. Mogensen, J. Power Sources 61 (1996) 173.
- [65] T. Kenjo, M. Nishiya, Solid State Ionics 57 (1992) 295.
- [66] Yongjun Leng, Siew Hwa Chan, Qinglin Liu, International Journal of Hydrogen Energy 33 (2008) 3808 – 3817.
- [67] E.P. Murray, M.J. Sever, S.A. Barnett, Solid State Ionics 148 (2002) 27.
- [68] H. Fukunaga, M. Ihara, K. Sakaki, K. Yamada, Solid State Ionics 86–88 (1996) 1179.
- [69] A. Barbucci, R. Bozo, G. Cerisola, P. Costamagna, *Electrochim. Acta*, 47 (2002) 2183.
- [70] P. Holtappels, C. Bagger, J. Eur. Ceram. Soc. 22 (2002) 41.
- [71] L. Tsai, S.A. Barnett, Solid State Ionics 93 (1997) 207.
- [72] N.P. Bansal, Z. Zhong, J. Power Sources 158 (2006) 148.
- [73] G. Nurk, R. Küngas, I. Kivi, H. Kurig, V. Grozovski, S. Kallip, E. Lust, ECS Trans. 7 (2007) 1609.
- [74] E. Lust, G. Nurk, P. Möller, I. Kivi, S. Kallip, P. Nigu, ESC Trans. 5 (2007) 423.
- [75] E. Lust, I. Kivi, G. Nurk, P. Möller, S. Kallip, V. Grozovki, H. Kurig, ECS Trans. 7 (2007) 1071.
- [76] B.W. Chung, A.Q. Pham, J.J. Haslam, R.S. Glass, J. Electrochem. Soc. 149(3) (2002) A325.
- [77] R. Küngas, I. Kivi, K. Lust, G. Nurk, E. Lust, Journal of Electroanalytical Chemistry, Volume 629, 1–2, (2009), 94–101.
- [78] Narottam P. Bansal and Zhimin Zhong, *Journal of Power Sources*, 15 November 2005.
- [79] Enn Lust, Priit Möller, Gunnar Nurk, Indrek Kivi, Silvar Kallip, Honolulu ECS transaction (2008).
- [80] I. Kivi, P. Möller, H. Kurig, S. Kallip, G. Nurk, E. Lust, *Electrochemistry Communications*, 10 (2008) 1455–1458.
- [81] R. Küngas, I. Kivi, E. Lust, Journal of the Electrochemical Society, 156(3), (2009), B345–B352.
- [82] E. Lust, G. Nurk, P. Möller, I. Kivi, S. Kallip, A. Jänes, H. Kurig, Patent WO 2008/145145 A1.
- [83] M. Sase et al. / Journal of Physics and Chemistry of Solids 66 (2005) 343-348
- [84] R. Barfod, M. Mogensen, T. Klemensø, A. Hagen, Y.-L. Liu, P. V. Hendriksen, J. Electrochem. Soc. 154(4) B371 (2007).
- [85] Lloyd R. Fortney. Principles of Electronics, NY, 1987
- [86] R. Barfod, M. Mogensen, T. Klemensø, A. Hagen, Y.-L. Liu, P. V. Hendriksen, J. Electrochem. Soc. 154(4) B371 (2007).
- [87] 33. S. H. Jensen, A. Hauch, P.V. Hendriksen, M. Mogensen, N. Bonanos, T. Jacobsen, J. Electrochem. Soc. 154 B1325 (2007).
- [88] E. Lust, G. Nurk, I. Kivi, R. Küngas, P. Möller, H. Kurig, S. Kallip, ECS Transactions 12 293 (2008).
- [89] T. Horita, K. Yamaji, N. Sakai, H. Yokokawa, A. Weber, E. Ivers-Tiffée, *Electrochimica Acta* 46 1837 (2001).

## 9. SUMMARY IN ESTONIAN

# Tahkeoksiidkütuselemendi poorse katoodimaterjali süntees ja analüüs

Käesolevas töös uuriti süstemaatiliselt poolelementide  $Ce_{0.8}Gd_{0.2}O_{1.9}$  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$  $Ce_{0.8}Gd_{0.2}O_{1.9}$  $Ce_{0.8}Gd_{0.2}O_{1.9}$ ia  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  ja ühikrakkude  $La_{0.6}Sr_{0.4}CoO_{3-\delta} | Ce_{0.8}Gd_{0.2}O_{1.9} | NiO +$  $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ ,  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$  |  $Ce_{0.8}Gd_{0.2}O_{1.9}$  | NiO +  $Ce_{0.9}Gd_{0.1}O_{2-\delta}$  ja  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta} | Ce_{0.8}Gd_{0.2}O_{1.9} | NiO + Ce_{0.9}Gd_{0.1}O_{2-\delta}$  omadusi elektrokeemiliste meetoditega (impedantsspektroskoopia, kronokulonomeetria, tsükliline voltamperomeetria). Samuti analüüsiti sünteesitud materialide füüsikalisi karakteristikuid, kasutades skanneerivat elektronmikroskoopiat, dilatomeetriat, aatomjõumikroskoopiat, röntgendifraktsioonanalüüsi jt. meetodeid. Eripinna määramiseks kasutati Brunauer-Emmett-Telleri lämmastiku adsorbtsiooni meetodit

Elektrokeemilised uuringud näitasid, et materjalide elektrokatalüütiline aktiivsus sõltub väga oluliselt nende poorsusest ja keemilisest koostisest.

Impedantsspektroskoopia andmete analüüsimisel saadud tulemustest selgub, et perovskiidi A-positsioonis oleva elemendi aatommassi kasvades polarisatsiooniline takistus kasvab. Faasinurga sagedusest sõltuvustest selgub, et madalamatel temperatuuridel ( $T \le 773$  K) on valdavalt tegemist segakineetiliste protsessidega (limiteerivaks on nii laenguülekande- kui ka massiülekandeprotsessid), kuid kõrgematel temperatuuridel ja elektroodi polarisatsioonidel viitavad faasinurga suhteliselt väikesed negatiivsed väärtused ( $\delta \ge -5^{\circ}$ ) põhiliselt laenguülekande poolt limiteeritud protsessile. Faasinurga väärtuste oluline sõltuvus elektroodi polarisatsioonist madalamatel temperatuuridel viitab komplitseeritud laetud hapnikuosakeste massiülekandeprotsessile poorses katoodis.

Poorimoodustaja kasutamine katoodi valmistamisel, suurendab peamiselt elektroodi makropoorsust, samas suureneb ka eripinna väärtus. Mikro- ja mesopooride poorijaotus ja pooride diameeter ei sõltu oluliselt poorimoodustaja kontsentratsioonist lähtesegus. Madalaim molekulaarse hapniku redutseerumisprotsessi polarisatsiooniline takistus ( $R_p = 0.03 \ \Omega \ cm^2$  temperatuuril  $T = 873 \ K$ ) on saavutatud 1,36 massi % suuruse poorimoodustaja lisandi korral. Summaarne katoodprotsessi aktivatsioonienergia sõltub oluliselt elektroodi poorijaotusest. Madalaim väärtus ( $E_{act} > 0.5 \ eV$  avatud ahela potentsiaalil) saavutati LSCO katoodiga poolelemendi jaoks (31 % üldpoorsusega,  $S_{BET} = 7.8 \ m^2 \ g^{-1}$  ja 1,36 massi % poorimoodustaja lisandiga).

Leiti, et katoodprotsessi kui limiteeriva staadiumi uuringuks sobib paremini kolmeelektroodiline poolelemendi konfiguratsioon, mis võimaldab detailsemalt kirjeldada hapniku redutseerumisprotsessi sõltuvust uuritava elektroodi potentsiaalist. Reaalseid TOKE töötingimusi kirjeldab paremini kahe elektroodne ühikrakuga süsteem. Kasutades impedantsspektroskoopia andmetest leitud nn. diferentsiaalseid  $\Delta \partial Z'$  vs. log f sõltuvusi ja varieerides gaaside osarõhke elektroodiruumides, saame edukalt eraldada anood- ja katoodprotsessid.

Leiti, et katoodse polarisatsiooni suurenedes aktivatsioonienergia väärtused vähenevad. Lisaks aeglase laenguülekandeprotsessile (hapniku redutseerumine katoodi pinnal või kolme faasi piirpinnal) on elektrokeemilise polarisatsioonilise takistuse allikaks veel difusioonilised raskused (vakantside difusioon,  $O_{ads}^{-}$  pind-difusioon,  $O_2$  molekulaarne difusioon, nn. Knudseni difusioon (mis on  $O_2$  difusioon nanopoorides, kui poori diameeter on väiksem kui  $O_2$  molekuli vaba tee pikkus gaasifaasis antud temperatuuril) või  $O_{ads}^{-}$  migratsioon kolmikpunkti tahkes katoodimaterjalis).

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# **II. PUBLICATIONS**

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1999–2003	University of Tartu, B. Sc. in material science, 2003

#### Professional employment

2006 –	University of Tartu, Institute of Physical Chemistry, researcher
2005–2006	University of Tartu, Institute of Physical Chemistry, contrac-
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2002–2005	University of Tartu, Institute of Physical Chemistry, chemist

#### List of publications

- 1. Küngas, R.; Kivi, I.; Lust, E. (2009). Effect of Cell Geometry on the Electrochemical Parameters of Solid Oxide Fuel Cell Cathodes. Journal of the Electrochemical Society, 156(3), B345–B352.
- Lust, E.; Nurk, G.; Kivi, I.; Küngas, R.; Möller, P.; Kurig, H.; Kallpi, S. (2008). Influence of Cathode Porosity on the Characteristics of Medium-Temperature SOFC Single Cells. Williams, M.; Krist, K.; Satyapal, S.; Garland, N. (Toim.). Fuel Cell Seminar 2007 (293–302). The Electrochemical Society Inc.
- 3. Kivi, I.; Möller, P.; Kurig, H.; Kallip, S.; Nurk, G.; Lust, E. (2008). Development of porous cathode powders for SOFC and influence of cathode structure on the oxygen electroreduction kinetics. Electrochemistry Communications, 10, 1455–1458.

- Lust, E.; Nurk, G.; Kivi, I.; Küngas, R.; Möller, P.; Kurig, H.; Kallpi, S. (2008). Influence of Cathode Porosity on the Characteristics of Medium-Temperature SOFC Single Cells. Williams, M.; Krist, K.; Satyapal, S.; Garland, N. (Toim.). Fuel Cell Seminar 2007 (293–302). The Electrochemical Society Inc.
- 5. Lust, E.; Möller, P.; Nurk, G.; Kivi, I.; Kallip, S. (2007). Influence of Electrode Porosity and Potential of the Oxygen Reduction Kinetics on the Intermediate Temperature SOFCs Cathodes . ECS Transactions (423).ECS
- Lust, E.; Kivi, I.; Nurk, G.; Möller, P.; Kallip, S.; Grozovski, V; Kurig, H. (2007). Influence of Cathode Porosity and Potential on Oxygen Reduction Kinetics at Intermediate Temperature SOFCs Cathodes. ECS Transactions (1071–1080).ECS Transactions
- Nurk, G.; Küngas, R.; Kivi, I.; Kurig, H.; Grozovski, V.; Kallip, S.; Lust, E. (2007). Influence of mesoporosity of the anode on the characteristics of mediumtemperature SOFC single cells. ECS Transactions (1609–1616).ECS Transactions
- Nurk, G.; Möller, P.; Kivi, I.; Nigu, P.; Lust, E. (2006). Influence of the Cathode Composition on the Intermediate Temperature SOFC Cathode Characteristics. *In: MA2006-01, Meeting Abstracts, E1 – Electrode Materials and Processes for Energy Conversion and Storage : Meeting of Electrochemical Society; Denver; May 7– May 12, 2006.* ECS, 2006, 216.
- Nurk, G.; Kivi, I.; Möller, P.; Lust, E. (2006). Electrochemical analysis of La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> and Pr<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> cathodes with different porosities supported on Ce<sub>0.2</sub>Gd<sub>0.8</sub>O<sub>1.9</sub> electrolyte. In: Book of Abstracts. Innovative Electrochemistry, Enterprising Science: 57th Annual Meeting of the International society of Electrochemistry; Edinburgh, UK; 27 August 1 September 2006., 2006, S10-P-52.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, E.; Kallip, S. (2005). Influence of electrode potential on the oxygen reduction kinetics on the intermediate temperature SOFC cathodes. SSI-15, International Conference on Solid State Ionics; Baden-Baden, Germany; July 17–22, 2005. , 2005, 525.
- 11. Lust, E.; Nurk, G.; Kallip, S.; Kivi, I.; Möller, P. (2005). Electrochemical characteristics of  $Ce_{0.8}Gd_{0.2}O_{1.9}|La_{0.6}Sr_{0.4}CoO_{3-\delta} + Ce_{0.8}Gd_{0.2}O_{1.9}$  half-cell. Journal of Solid State Electrochemistry, 9(10), 674–683.
- Lust, E.; Möller, P.; Kivi, I.; Nurk, G.; Kallip, S.; Nigu, P.; Lust, K. (2005). Optimisation of the cathode composition for the intermediate temperature SOFC. Singhal, S.C.; Mizusaki, J. (Toim.). Solid Oxide Fuel Cells IX (SOFC-IX), Vol. 2: Materials (1607–1616). USA: The Electrochemical Society Inc.
- 13. Lust, E.; Moller, P.; Kivi, I.; Nurk, G.; Kallip, S. (2005). Electrochemical characteristics of  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ ,  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$  and  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  on  $Ce_{0.85}Sm_{0.15}O_{1.925}$  electrolyte. Journal of Solid State Electrochemistry, 9(12), 882–889.
- Lust, E.; Moller, P.; Kivi, I.; Nurk, G.; Kallip, S.; Nigu, P.; Lust, K. (2005). Optimization of the cathode composition for the intermediate-temperature SOFC. Journal of the Electrochemical Society, 152(12), A2306–A2308.
- 15. Kivi, I.; Möller, P.; Kallip, S.; Lust, E.; Nurk, G. (2004). Electrochemical characterization of some electrolyte | cathode semicells for SOFC. 55th Annual Meeting of the International Society of Electrochemistry; Thessaloniki, Greece; September 19–24, 2004. Thessaloniki:, 2004, 1231.

- Lust, E.; Nurk, G.; Kallip, S.; Kivi, I.; Möller, P.; Nigu, P.; Lust, K. (2004). Systematic analysis of some medium temperature half-cells for SOFC. 6th European Solid Oxide Fuel Cell Forum; Lucerne, Switzerland; June 28 – July 2, 2004. (Toim.) Mogensen, M.: Lucerne:, 2004, 1271–1280.
- 17. Nurk, G.; Kallip, S.; Kivi, I.; Möller, P.; Lust, E. (2004). Electrochemical characteristics of  $Ce_{1-x}Gd_xO_{2-\delta} | La_{1-x}Sr_xCoO_{3-\delta} + Ce_{1-x}Gd_xO_{2-\delta}$  half-cell. 6th European Solid Oxide Fuel Cell Forum; Lucerne, Switzerland; June 28 July 2, 2004. (Toim.) Mogensen, M.. Lucerne:, 2004, 887–896.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, I.; Kallip, S. (2004). Comparative analysis of cathode materials for half cells of the intermediate temperature SOFCs. Fuel Cell Seminar; San Antonio, Texas, USA; November 1–5, 2004. San Antonio:, 2004, CD 4 pp..
- 19. Nurk, G.; Möller, P.; Kivi, I.; Kallip, S.; Jänes, A.; Lust, E. (2003). Medium temperature half-cells for SOFC-s. *In: Abstracts of 2003 Fuel Cell Seminar: Miami Beach, US; November 3–7, 2003.* Miami, Florida, USA:, 2003, 427–430.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, I.; Kallip, S.; Jänes, A.; Mändar, H. (2003). Electrochemical Impedance Characteristics of Some Medium Temperature Semicells for SOFC. *In: Proceedings of the International Symposium on Solid Oxide Fuel Cells: 8th International Symposium on Solid Oxide Fuel Cells; Paris, France; 27. April – 2. May 2003.* Paris:, 2003, 1176–1185.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, I.; Kallip, S.; Jänes, A. (2003). The stability of the electrochemical impedance characteristics of some medium temperature semicells for SOFC. *In: Ext. Abstacts: 54th Annual Meeting of ISE; Sao Pedro, Brasil; 31 August – 5 September, 2003.*, 2003, 86.

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- 1. Küngas, R.; Kivi, I.; Lust, E. (2009). Effect of Cell Geometry on the Electrochemical Parameters of Solid Oxide Fuel Cell Cathodes. Journal of the Electrochemical Society, 156(3), B345–B352.
- Lust, E.; Nurk, G.; Kivi, I.; Küngas, R.; Möller, P.; Kurig, H.; Kallpi, S. (2008). Influence of Cathode Porosity on the Characteristics of Medium-Temperature SOFC Single Cells. Williams, M.; Krist, K.; Satyapal, S.; Garland, N. (Toim.). Fuel Cell Seminar 2007 (293–302). The Electrochemical Society Inc.
- Kivi, I.; Möller, P.; Kurig, H.; Kallip, S.; Nurk, G.; Lust, E. (2008). Development of porous cathode powders for SOFC and influence of cathode structure on the oxygen electroreduction kinetics. Electrochemistry Communications, 10, 1455– 1458.
- Lust, E.; Nurk, G.; Kivi, I.; Küngas, R.; Möller, P.; Kurig, H.; Kallpi, S. (2008). Influence of Cathode Porosity on the Characteristics of Medium-Temperature SOFC Single Cells. Williams, M.; Krist, K.; Satyapal, S.; Garland, N. (Toim.). Fuel Cell Seminar 2007 (293–302). The Electrochemical Society Inc.

- 5. Lust, E.; Möller, P.; Nurk, G.; Kivi, I.; Kallip, S. (2007). Influence of Electrode Porosity and Potential of the Oxygen Reduction Kinetics on the Intermediate Temperature SOFCs Cathodes . ECS Transactions (423).ECS
- Lust, E.; Kivi, I.; Nurk, G.; Möller, P.; Kallip, S.; Grozovski, V; Kurig, H. (2007). Influence of Cathode Porosity and Potential on Oxygen Reduction Kinetics at Intermediate Temperature SOFCs Cathodes. ECS Transactions (1071–1080).ECS Transactions
- Nurk, G.; Küngas, R.; Kivi, I.; Kurig, H.; Grozovski, V.; Kallip, S.; Lust, E. (2007). Influence of mesoporosity of the anode on the characteristics of mediumtemperature SOFC single cells. ECS Transactions (1609–1616).ECS Transactions
- Nurk, G.; Möller, P.; Kivi, I.; Nigu, P.; Lust, E. (2006). Influence of the Cathode Composition on the Intermediate Temperature SOFC Cathode Characteristics. *In: MA2006-01, Meeting Abstracts, E1 – Electrode Materials and Processes for Energy Conversion and Storage : Meeting of Electrochemical Society; Denver; May 7– May 12, 2006.* ECS, 2006, 216.
- Nurk, G.; Kivi, I.; Möller, P.; Lust, E. (2006). Electrochemical analysis of La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> and Pr<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> cathodes with different porosities supported on Ce<sub>0.2</sub>Gd<sub>0.8</sub>O<sub>1.9</sub> electrolyte. In: Book of Abstracts. Innovative Electrochemistry, Enterprising Science: 57th Annual Meeting of the International society of Electrochemistry; Edinburgh, UK; 27 August – 1 September 2006., 2006, S10-P-52.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, E.; Kallip, S. (2005). Influence of electrode potential on the oxygen reduction kinetics on the intermediate temperature SOFC cathodes. SSI-15, International Conference on Solid State Ionics; Baden-Baden, Germany; July 17–22, 2005. , 2005, 525.
- Lust, E.; Nurk, G.; Kallip, S.; Kivi, I.; Möller, P. (2005). Electrochemical characteristics of Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub>|La<sub>0.6</sub>Sr<sub>0.4</sub>CoO<sub>3-δ</sub> + Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>1.9</sub> half-cell. Journal of Solid State Electrochemistry, 9(10), 674–683.
- Lust, E.; Möller, P.; Kivi, I.; Nurk, G.; Kallip, S.; Nigu, P.; Lust, K. (2005). Optimisation of the cathode composition for the intermediate temperature SOFC. Singhal, S.C.; Mizusaki, J. (Toim.). Solid Oxide Fuel Cells IX (SOFC-IX), Vol. 2: Materials (1607–1616). USA: The Electrochemical Society Inc.
- 13. Lust, E.; Moller, P.; Kivi, I.; Nurk, G.; Kallip, S. (2005). Electrochemical characteristics of  $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ ,  $Pr_{0.6}Sr_{0.4}CoO_{3-\delta}$  and  $Gd_{0.6}Sr_{0.4}CoO_{3-\delta}$  on  $Ce_{0.85}Sm_{0.15}O_{1.925}$  electrolyte. Journal of Solid State Electrochemistry, 9(12), 882–889.
- Lust, E.; Moller, P.; Kivi, I.; Nurk, G.; Kallip, S.; Nigu, P.; Lust, K. (2005). Optimization of the cathode composition for the intermediate-temperature SOFC. Journal of the Electrochemical Society, 152(12), A2306–A2308.
- Kivi, I.; Möller, P.; Kallip, S.; Lust, E.; Nurk, G. (2004). Electrochemical characterization of some electrolyte | cathode semicells for SOFC. 55th Annual Meeting of the International Society of Electrochemistry; Thessaloniki, Greece; September 19–24, 2004. Thessaloniki:, 2004, 1231.
- Lust, E.; Nurk, G.; Kallip, S.; Kivi, I.; Möller, P.; Nigu, P.; Lust, K. (2004). Systematic analysis of some medium temperature half-cells for SOFC. 6th European Solid Oxide Fuel Cell Forum; Lucerne, Switzerland; June 28 – July 2, 2004. (Toim.) Mogensen, M.: Lucerne:, 2004, 1271–1280.

- 17. Nurk, G.; Kallip, S.; Kivi, I.; Möller, P.; Lust, E. (2004). Electrochemical characteristics of  $Ce_{1-x}Gd_xO_{2-\delta} | La_{1-x}Sr_xCoO_{3-\delta} + Ce_{1-x}Gd_xO_{2-\delta}$  half-cell. 6th European Solid Oxide Fuel Cell Forum; Lucerne, Switzerland; June 28 July 2, 2004. (Toim.) Mogensen, M.. Lucerne:, 2004, 887–896.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, I.; Kallip, S. (2004). Comparative analysis of cathode materials for half cells of the intermediate temperature SOFCs. Fuel Cell Seminar; San Antonio, Texas, USA; November 1–5, 2004. San Antonio:, 2004, CD 4 pp..
- Nurk, G.; Möller, P.; Kivi, I.; Kallip, S.; Jänes, A.; Lust, E. (2003). Medium temperature half-cells for SOFC-s. *In: Abstracts of 2003 Fuel Cell Seminar: Miami Beach, US; November 3–7, 2003.* Miami, Florida, USA:, 2003, 427–430.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, I.; Kallip, S.; Jänes, A.; Mändar, H. (2003). Electrochemical Impedance Characteristics of Some Medium Temperature Semicells for SOFC. *In: Proceedings of the International Symposium on Solid Oxide Fuel Cells: 8th International Symposium on Solid Oxide Fuel Cells; Paris, France; 27. April – 2. May 2003.* Paris:, 2003, 1176–1185.
- Lust, E.; Nurk, G.; Möller, P.; Kivi, I.; Kallip, S.; Jänes, A. (2003). The stability of the electrochemical impedance characteristics of some medium temperature semicells for SOFC. *In: Ext. Abstacts: 54th Annual Meeting of ISE; Sao Pedro, Brasil; 31 August – 5 September, 2003.*, 2003, 86.

# DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS

- 1. **Toomas Tamm.** Quantum-chemical simulation of solvent effects. Tartu, 1993, 110 p.
- 2. **Peeter Burk.** Theoretical study of gas-phase acid-base equilibria. Tartu, 1994, 96 p.
- 3. Victor Lobanov. Quantitative structure-property relationships in large descriptor spaces. Tartu, 1995, 135 p.
- 4. **Vahur Mäemets.** The <sup>17</sup>O and <sup>1</sup>H nuclear magnetic resonance study of H<sub>2</sub>O in individual solvents and its charged clusters in aqueous solutions of electrolytes. Tartu, 1997, 140 p.
- 5. Andrus Metsala. Microcanonical rate constant in nonequilibrium distribution of vibrational energy and in restricted intramolecular vibrational energy redistribution on the basis of slater's theory of unimolecular reactions. Tartu, 1997, 150 p.
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