Electrostatic spray deposited Ca₃Co₄O₉₋δ and Ca₃Co₄O₉₋δ/Co₀₉Gd₀₁O₁₀₅ cathodes for SOFC: A comparative impedance analysis study

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ABSTRACT

Mixed conducting Ca₃Co₄O₉₋δ (CCO) is an interesting cathode material for application in Solid Oxide Fuel Cells (SOFC). In a previous study it has been shown that addition of Ce₀₉Gd₀₁O₁₀₅ (CGO) significantly enhances the electrode performance, reducing the specific resistance (ASR) to ~0.5 Ω cm² at 700°C for the CGO/CGO 50/50 composition. As the microstructure of a composite electrode has a significant influence on the frequency dispersion, it is of interest to prepare electrodes with quite different microstructures. Electrostatic Spray Deposition (ESD) is a technique that is able to produce a large variety of microstructures by modifying the process parameters. Very different microstructures can help in elucidating the major charge transport and transfer processes in an electrode.

In this study pure CCO and a CCO/CGO composite (50/50%), both prepared with ESD, are compared and analyzed with Electrochemical Impedance Spectroscopy (EIS). The analysis of the ESD-CCO/CGO composition showed remarkable similarities with the screen-printed cathodes from the previous study, although a clear change in the magnitudes of the separate contributions (low-frequency redox, mid-frequency Gerischer and high-frequency diffusion) was observed. The ASR was close to the screen-printed one, but showed two apparent activation energies in the Arrhenius graph. A tentative model indicates that the Gerischer process is related to dissociative oxygen adsorption and (surface) diffusion at the CGO phase. The limiting factor is the density of the triple-phase boundaries (TPBs) between CCO, CGO and the ambient, which is for the ESD-CCO/CGO cathode apparently lower than for the microstructure of the screen-printed cathodes. It was noted that for the ESD-CCO/CGO cathodes the Distribution Function of Relaxation Times (DFRT) presented a more consistent image of the temperature dependence than the standard Complex Nonlinear Least Squares (CNLS) analysis.

The pure ESD-CCO cathode showed a remarkable dispersion, which could be interpreted with a Finite Length Warburg (FLW) model. Although analysis with a simple Equivalent Circuit (EqC) was not feasible, partial CNLS-analysis of the high- and low-frequency regimes resulted in a parameter set that was consistent with the FLW-model. Considering the coral-like microstructure, the oxygen reaction at the electrode could be interpreted as slow oxygen dissociation and fast diffusion towards a more dense CCO layer at the electrolyte interface, followed by a fast oxygen exchange step at the CCO-layer/platelets + ambient interphase. Combining FLW parameters with published chemical diffusion values, an apparent effective layer thickness of 2.2 µm could be estimated.

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1. Introduction

Electrochemical Impedance Spectroscopy (EIS) [1, 2] is a valuable tool for the characterization of solid oxide fuel cell (SOFC) electrodes. Interpretation of the results of the data analysis, generally performed with a complex nonlinear least squares (CNLS)
method in conjunction with an equivalent circuit (EqC) model, is complicated by the complex porous microstructures. Grain-size, grain connectivity, porosity, ..., have all an influence on the impedance. For composite electrodes this is even more so the case, due to volume and size ratios of the constituents, which will have an influence on the overall frequency dispersion as well. This makes it difficult to assign obtained fit-parameters to specific processes. But by adjusting the microstructure (grain size, composition, ...) trends in changes in the equivalent circuits (EqC) can be observed. This will give a good indication which transfer and/or transport processes are rate controlling.

A more recent approach is to use a model-free impedance analysis through the derivation of a distribution (function) of relaxation times (DRT or DFRT) [3–8]. With this method, one can follow the peak positions, related to the major dispersive processes, as function of temperature, or partial pressure of gasses in the ambient. Variations in the microstructure or composition will also be reflected in the shape and positions of the relaxation curves.

Advanced modeling of SOFC-electrodes involves the creation of a true 3-D image of the microstructure, using a focused ion beam (FIB) in combination with scanning electron microscopy (SEM), to create a compilation of cross-sectional images [9–11]. When materials properties (conductivities, redox properties, surface exchange rates, ...) are known a 3-D simulation with finite element modeling (FEM) can provide essential insight into the electrode processes [9,10]. Almar et al. [11] studied the relationship between EIS measurements and microstructure, using FIB-SEM reconstruction. This provides already a significant step in elucidating the electrode processes. The FIB - FEM method, however, is not suitable for general characterization of electrodes, due to the time consuming and costly process.

For screen-printed single-phase porous cathodes, the sintering temperature has a significant influence on grain size and connectivity between grains and with the electrolyte [12,13]. The observed trends already gave significant information on the electrode processes. Adding a dense interlayer of the electrode material between electrolyte and porous electrode not only lowers the polarization resistance, but can also drastically change the appearance of the electrode dispersion. For the porous La$_2$NiO$_4$-δ cathode with a dense La$_2$NiO$_4$-δ interlayer, indications were found for the importance of surface diffusion of, possibly charged, mono-atomic oxygen species [13].

The electrochemical behavior of composite electrodes is controlled further by composition and size distributions of the constituents. A study of the impedance responses of symmetric cells with screen-printed Ca$_{0.5}$Co$_{0.5}$O$_{2-δ}$/Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CCO/CGO) cathodes, as function of composition and layer thickness, showed the lowest ‘area specific resistance’ (ASR) for the 50/50 composition. The low-frequency dispersion could be assigned to adsorbed ions in the mixed conducting CCO compound. The CGO acts as a catalyst for the oxygen dissociation. A small, but consistent Gerischer contribution with a virtually identical characteristic time constant, $\tau_C$, was observed for all compositions [14]. The CCO grains, with sizes between $\pm1$–$5 \mu$m, were covered by CGO grains of $\pm0.2 \mu$m. It can be assumed that this size ratio has a significant influence on the rate-controlling step(s) and hence on the electrode dispersion.

Electrostatic Spray Deposition (ESD) is a unique method that is capable of creating special microstructures [15–18] that are very different from screen-printed ones. In this contribution electrode structures with well-defined platelets were obtained by ESD. Comparing the results of the impedance analysis of both types of electrodes helps in indicating the electrode processes. The aim of this study is not directed to improving the electrode properties (e.g. decreasing the ASR) but to gain insight into the influence of structure and composition on the electrode behavior using EIS.

2. Experimental procedure

2.1. Preparation of electrodes

The electrodes were prepared by Electrostatic Spray Deposition (ESD) on a dense Ca$_{0.5}$Gd$_{0.5}$O$_{1.95}$ pellet. For the pure CCO electrodes a precursor solution of Ca(NO$_3$)$_2$$\cdot$$4$H$_2$O (Acros Organics, 99%) and Co(NO$_3$)$_2$$\cdot$$6$H$_2$O (Fisher Scientific, 98%) in ethanol (Prolabo, 99.9%), adjusted to a $0.02 \text{ M}$ concentration of CCO, was dispensed through a syringe at a rate of $1.5 \text{ ml h}^{-1}$. The substrate temperature was kept at $450^\circ\text{C}$. The distance between the needle and the base plate was $50 \text{ mm}$. A high voltage of $10 \text{ kV}$ was applied between the needle of the syringe and the base plate (see Ref. [15] for details), resulting in the formation of a so-called Taylor cone at the needle tip due to electro-hydrodynamic atomization, Ref. [19]. This caused a fine spray of the precursor solution and subsequent evaporation of the liquid. The physicochemical properties of the precursor solution and the deposition parameters, such as flow rate, substrate temperature, or the distance between the nozzle and the substrate, all play a role in determining the average droplet size in the aerosol. This ultimately determines the morphology of the layer being deposited [15,17].

In a previous publication [16], a ‘platelet’ like growth of a ‘coral’-like 3D microstructure of a Ca$_{0.5}$Co$_{0.5}$O$_{2-δ}$ electrode was obtained by ESD. The electrode surfaces were rough with a layer thickness varying between $350 \text{ nm}$ and $33 \mu$m for deposition times from $30$ to $240 \text{ minutes}$. In this study a deposition time of $240 \text{ min}$ is used, which leads to a rough electrode surface with a layer thickness varying locally between $25$ – $33 \mu$m. The electrodes were sintered for $2 \text{ hours}$ at $880^\circ\text{C}$ with a heating/cooling rate of $3^\circ\text{C min}^{-1}$.

For the formation of the CCO/CGO composite cathodes two syringes connected to a single needle were used. Operating conditions were the same as for the pure CCO cathodes. One syringe dispensed the CCO precursor based on the nitrates, the other syringe dispensed the CGO precursor, also based on the respective nitrates in ethanol, adjusted to a $0.02 \text{ M}$ concentration of CGO. The precursors were each dispensed at $0.75 \text{ mL h}^{-1}$. The impedance measurements were performed on samples obtained with a deposition time of $240 \text{ min}$. The average electrode thickness is $\pm 20 \mu$m.

2.2. Impedance measurements and data analysis

The symmetric cells were placed between gold grid current collectors. Both the pure CCO and the composite CCO/CGO samples were cycled in temperature between $600^\circ\text{C}$ (CCO) or $500^\circ\text{C}$ (CCO/CGO) and $800^\circ\text{C}$ during the EIS measurements. In some figures the measurements taken in a heating sequence are denoted by ‘up’, those in a cooling sequence by ‘down’. The number indicates the half cycle position in the temperature cycling. The impedance data were collected with a Solartron 1260 frequency response analyzer, in the $0.01$–$10^6$ Hz frequency range. As the impedances at high frequencies are distorted by instrumental artifacts (e.g. lead inductances) the frequency range for analysis was generally limited to $-300 \text{ kHz}$. All data sets were validated by a Kramers-Kronig test program [20,21]. Clear outliers were removed from the data set, or replaced by a polynomial interpolation for the derivation of the Distribution Function Of Relaxation Times (DFRT) with the Tikhonov transform program ‘DFRTools’ [22,23]. The impedance data were analyzed with the complex nonlinear least squares (CNLS) fit program, EqWin [24]. In the normalization procedure the high-frequency instrumental inductance and the electrolyte resistance, $R_{\text{sys}}$, have been subtracted from the measured dispersions. Besides the Tikhonov regularization program, also the multi-(RQ)-fit procedure, ‘m(RQ)fit’ from Refs. [6,7], was used.
3. Derivation of a DFRT

A distribution function of relaxation times is a ‘model-free’ representation of the dispersive processes through a presentation of the relaxation times. The DFRT, \(G(\tau)\), is obtained through solving a Fredholm integral of the second kind:

\[
Z(\omega) = R_\infty + R_\text{pol} \cdot \int_0^\infty \frac{G(\tau)}{1 + j\omega \tau} d \ln \tau \tag{1}
\]

\(Z(\omega)\) is the impedance data set, \(R_\infty\) is the high-frequency cut-off resistance and \(R_{\text{pol}}\) is the polarization resistance. In this definition,

\[
\int_0^\infty G(\tau) d \ln \tau = 1
\]

Solving \(G(\tau)\) is known as an ‘ill-posed inverse problem’. Several methods have been derived to find a viable \(G(\tau)\): Fast Fourier Transform (FFT) [3], Fourier Transform with simulated extensions to \(\omega = 0\) and \(\omega = \infty\) [5], Tikhonov Regularization [4,22] and a Maximum Entropy method [25,26]. All these methods require adjusting a shape parameter in order to reduce unwanted oscillations. A way to check the validity of the DFRT is to compare the dispersion reconstructed from the DFRT with the actual measurement, i.e. calculating \(Z(\omega)\) from the obtained \(G(\tau)\) with Eq. (1), see Refs. [6,7].

3.1. Construction of a DFRT from an equivalent circuit

For a number of dispersive elements exact DFRT’s have been derived. A parallel combination of a resistance and a constant phase element, or CPE with \(Y_0(\omega) = Y_0(j\omega)^\alpha\), is represented in the \(\tau\)-domain by:

\[
G_{(RQ)}(\tau) = \frac{1}{2\pi} \sin(\alpha \pi) \cosh(\alpha \ln(t_0/\tau)) + \cos(\alpha \pi) \tag{2}
\]

where the characteristic time constant, \(\tau_0\), is defined by: \(\tau_0 = \sqrt{\frac{\alpha}{\pi}} Y_0\). When \(\alpha = 1\) the CPE becomes a capacitor, i.e. a (RC) circuit. The \(G(\tau)\) function then becomes a \(\delta\)-function. For a proper presentation in the DFRT graph the \(\delta\)-function can be approximated by a narrow Gaussian function, see Refs. [6,7]:

\[
G_\delta(\tau) \approx \frac{1}{\sqrt{\pi \tau}} \cdot e^{-\left(\frac{\tau}{\tau_0}\right)^2} \tag{3}
\]

\(W\) defines the width of the Gaussian peak. A value of \(W = 0.15\) has been shown to provide acceptable results in the \(\tau\)-domain and a small error in the reconstructed impedance. It was previously found that many dispersions could be modelled with a series of (RQ) elements close to the expected noise level in the data [6,7]. With Eq. (2) a DFRT can be constructed, the occurrence of a (RC) circuit is then presented by a narrow Gaussian curve, Eq. (3). This method has been dubbed the \(m(RQ)\)fit, but it should be realized that this fit has only a meaning in the \(\tau\)-domain, yielding a likely distribution of time constants (which directly fulfills the requirements of Eq. (1)). The frequency domain parameters are in principle meaningless.

The typical Gerischer dispersion [27] or ‘Chemical Element’ [28], \(Z_c(\omega) = \frac{\omega_0}{\sqrt{\omega_0^2 + j\omega}}\), has also an exact representation in the \(\tau\)-domain:

\[
G_c(\tau) = \frac{1}{\pi} \sqrt{\frac{\tau}{\tau_0 - \tau}}, \tau \leq \tau_0 \text{ and } G_c(\tau) = 0, \tau > \tau_0 \tag{4}
\]

This dispersion represents a semi-infinite diffusion coupled to a side reaction [27], which causes a finite length effect and leads to a dc-value for \(\omega \to 0\). Similarly, an exact DFRT has been found for the Finite Length Warburg (FLW, Ref. [29]), a finite length diffusion process with one boundary with infinite fast exchange between the ambient and the mobile ion, see Ref. [30]. The FLW is defined as:

\[
Z_{\text{FLW}}(\omega) = \frac{R_0}{\sqrt{\tau_0^2 + \omega^2}} \tanh \sqrt{j\omega \tau_0} = \frac{R_0}{\sqrt{\tau_0^2 + \omega^2}} \tanh \left( \frac{L_\text{0}}{\sqrt{\tau_0}} \right) \tag{5}
\]

where \(R_0\) is the dc-resistance, \(\tau_0 = L^2 \cdot D^{-1}\) with \(L\) the diffusion distance (layer thickness) and \(D\) the chemical diffusion coefficient. Hence, \(R_0 = R_0' \cdot L \cdot D^{-1}\), where \(R_0'\) is defined as [30]:

\[
Z_0 = \frac{RT}{nF^2SC^0} \int \frac{d \ln a}{d \ln C} = \frac{RT}{nF^2SC^0} \cdot \Gamma \tag{6}
\]

with \(n\) the number of electrons per mobile ion, \(S\) the surface area, \(C^0\) the equilibrium concentration of the mobile ion. The term between brackets is the Thermodynamic Factor, \(\Gamma\) [30], which provides a relation between activity, \(a\), and concentration, \(C\), of the mobile ion.

The exact DFRT is a set of \(\delta\)-functions, with \(\tau_0\) the characteristic time constant:

\[
G_{\text{FLW}}(\tau) = \sum_{k=1}^{\infty} 2\tau_k \cdot \delta(\tau_k), \text{ with } \tau_k = \frac{\tau_0}{2\pi^2(k - 0.5)^2} \tag{7}
\]

The mathematical area of the \(\delta\)-functions are given by \(R_0 = 2 \cdot \tau_k \cdot R_0\).

When an Equivalent Circuit (EqC) consisting of a linear combination of any of these elements is obtained, the exact DFRT can be constructed:

\[
R_{\text{pol}} G(\tau) = \sum_i R_i G_i(\tau), \text{ with } i R_{\text{pol}} = \sum_i R_i \tag{8}
\]

This allows the comparison of DFRT’s obtained by the other inversion methods, Refs. [3,4].

4. Results and analysis

4.1. Microstructure

The development of the microstructure of the ESD-CCO electrode, as function of deposition time, has been presented by Djurado et al., Ref. [16]. For the EIS measurements electrodes were deposited for 240 min. Fig. 1A shows the top view of an ESD-CCO electrode, Fig. 1B the cross-section. The well-defined platelets can be seen in the top view, which leads to an open structure with a relatively large surface area. The ESD-CCO/CGO electrodes have a similar, rather heterogeneous structure with dispersed outcrops. Fig 1C shows the top view, with on the left-hand side the top of an outcrop and the right-hand side the area between outcrops. The CCO phase presents large platelets, as in the ESD-CCO samples, with diameters up to ~15 \(\mu\)m. The much finer CGO particles are unevenly dispersed over the electrode area, as can be seen in Fig. 1C. Fig. 1D presents the cross-section of the ESD-CCO/CGO electrode. Further details on the evolution of the microstructure for the ESD-CCO/CGO with spraying time will be published elsewhere.

4.2. Comparison of pure CCO and CCO/CGO

The impedances at about 700°C for the CCO and the CCO/CGO electrodes show already a remarkable difference, see Fig. 2. The high-frequency inductance and electrolyte resistance, \(R_{\text{eltyr}}\), have been subtracted from the measured dispersions. Through the addition of an equal amount of CGO to the ESD precursor the polarization resistance, \(R_{\text{pol}}\), has dropped by almost a factor 7. This is in good agreement with earlier observations with screen-printed CCO/CGO electrodes, where addition of the CGO phase lowered
the polarization resistance significantly, with the lowest resistance for the 50/50% composition \[14\]. Fig. 2B shows that the polarization resistances are almost the same for the ESD-CCO/CGO and the screen-printed CCO/CGO 50/50% electrodes (see arrow at ‘Scr.pr. CCO/CGO’ in Fig. 2B). Besides the large difference in polarization resistance for the pure ESD-CCO and the ESD-CCO/CGO electrodes, there is also a clear difference in the shape of the electrode dispersions. For the CCO electrodes the dispersion has the form of a Finite Length Warburg (FLW, Ref. [30]), as will be demonstrated in the following section. CCO/CGO shows a more complex dispersion, which resembles the results for the screen-printed CCO/CGO samples, Ref. [14]. Fig. 2A presents the DFRT's at ~700°C. The DFRT's were obtained with the m(RQ) fit method \[6,7\]. The ESD-electrodes are dominated by two sharp peaks, but with a significant offset between the two. The addition of the CGO component apparently increases the rate of the electrode reaction(s), indicated by the shift of the peaks to shorter relaxation times. The DFRT for the ESD-CCO/CGO clearly resembles the DFRT for the screen-printed CCO/CGO 50/50% electrode (dashed line). The low-frequency peaks (\(\tau \approx 0.1\) s) almost coincide.

### 4.3. Analysis of the pure \(\text{Ca}_{3}\text{Co}_4\text{O}_{9+\delta}\) cathodes

The temperature-dependent impedances of the ESD-CCO electrodes all showed the same general shape. The high-frequency range is characterized by a straight line with a slope of 45° (\(\pi/4\)), indicating semi-infinite diffusion (Warburg behavior). With decreasing \(\omega\), the dispersion turns over into a (RC) type semicircle at low frequencies. The small upturn above the 45° line for decreasing \(\omega\) indicates a Finite Length Warburg type dispersion, FLW Eq. (5), rather than a Gerischer type. A Gerischer dispersion shows
Fig. 3. Combination of all normalized FLW-type dispersions showing the extensive similarity. The straight line represents the semi-infinite (Warburg) diffusion. Adapted from Ref. [7]. Measurement temperatures are indicated in °C.

Fig. 4. Analysis of the impedance at 702°C. The broken lines present a single FLW fit. The CNLS-fit with three FLW's (code 3FLW) with circuit LR(RQ)\(W_1\), \(W_2\), \(W_3\) is shown in red. Parenthesis indicate elements in parallel. The residuals plot is presented in the inset.

Fig. 5. Arrhenius graph of \(R_{pol}\) of the FLW and the electrolyte resistance. Lines represent least-squares fit to the data.

Fig. 6. Arrhenius graph of the Warburg \(Y_0\) values. The capacitance of the low-frequency R(0C) fit is also presented. The red line shows the average value of \(C_{app}\). The inset shows the fit of the If(R(RQ)). Closed symbols present the fit range.

Considering the rather rough geometry of the ESD-electrode, one may consider a distribution in the length parameter (thickness of the dense layer). In an attempt to simulate this, the data were fitted with three FLW's in parallel (indicated by: \(W_3\)), resulting in an excellent fit as can be seen from the residuals plot in the inset in Fig. 4. Hence, it can be concluded that the major part of the dispersion of the ESD-CCO cathode is of the finite length Warburg (FLW) type. Further analysis of the impedance data is based on this assumption.

Fig. 5 presents an Arrhenius graph of the polarization resistance, \(R_{pol}\), and the electrolyte resistance, \(R_{eltype}\). The activation energy for \(R_{pol}\), \(E_{act} = 134 \pm 2\) kJ mol\(^{-1}\), is in the range that has been observed earlier for screen-printed pure CCO electrodes (121 - 147 kJ mol\(^{-1}\), Ref. [32]). The electrolyte resistance shows an activation energy of \(38 \pm 1\) kJ mol\(^{-1}\), which is rather low for a CGO electrolyte, but in a previous study with screen printed electrodes, Ref. [14], values between 34 and 52 kJ mol\(^{-1}\) were observed. The high frequency straight line was modeled with a Warburg (semi-infinite diffusion), with \(Z_W(\omega) = (Y_0\sqrt{j\omega})^{-1}\) in a partial CNLS fit. The frequency range was limited to the straight section, resulting a pseudo \(X^2\)CNLS Value less than \(10^{-6}\). \(Y_0\) also shows Arrhenius behavior, see Fig. 6. The observed activation energy of \(E_{act} = 68 \pm 1.5\) kJ mol\(^{-1}\) is, within the error margin, half the value of \(E_{act}\) for \(R_{pol}\).

a smooth transition from a 45° line at high frequencies to a (RC) type semicircle, see Fig. 5 in Ref. [5].

Fig. 3 (adapted from Ref. [7]) shows a compilation of all normalized data. In the normalization procedure the instrumental inductance and electrolyte resistance, \(R_{eltype}\), have been subtracted from the measurement data. These \(L\) and \(R_{eltype}\) values were obtained through CNLS-fitting. The resulting dispersions are finally divided by their respective polarization resistances, \(R_{pol}\). Fig. 3 clearly shows that, except for the lowest temperatures, all dispersions coincide. The reproducibility of the impedance spectra upon temperature cycling is also very good.

An attempt to fit the data with a single FLW dispersion did not give a good result. Fig. 4 shows two approximations (labeled 'small' and 'large') of a FLW to the data set at 702°C. Another modelling option is the 'Fractal FLW', see Refs. [30,31]. The impedance representation has the form:

\[
Z_{fractal} = \frac{R_0}{\alpha \sqrt{j\omega \tau_0}} \tanh \alpha \sqrt{j\omega \tau_0} \tag{9}
\]

The slope of the high-frequency line, \(\sqrt{\alpha / \pi}\), will be smaller than 45°, which is not in agreement with the 45° line in Fig. 3. Hence, the \(f\)-FLW is not applicable in our case.
For \( \omega \tau_0 \ll 1 \), the hyperbolic and goniometric functions in Eq. (5) can be replaced by the first few terms of their series expansions. The FLW impedance function then reduces to:

\[
\lim_{\omega \to 0} Z_{\text{FLW}}(\omega) = R_0 - j \frac{R_0 \tau_0 \omega}{3} = R_0 - j \tilde{C}_p \omega = \frac{Z_0 L}{D} - j \frac{Z_0 L^2 \omega}{3D^2} \quad (10)
\]

Considering the small temperature dependence of \( Z_0 \), \( R_0 \) will be inversely proportional to \( D \). In the high-frequency limit the tanh() function will become unity, resulting in the semi-infinite diffusion or Warburg term:

\[
Y_W(\omega) = (1 + j \sqrt{\omega D}) \frac{\sqrt{\omega D}}{Z_0} \quad (11)
\]

Thus the activation energy for the high frequency Warburg should be half the value for \( R_0 \), which is clearly observed. The low-frequency semi-circle was fitted with a \( R_0(R_pC_p) \) circuit, with \( R_0 \) a resistance in series with a parallel \( R_p \) and \( C_p \) combination. The partial CNLS fit was performed over a limited frequency range, such that the pseudo \( \chi^2_{\text{CNLS}} \) values were around, or less than, 10\(^{-6}\). The fit range is indicated by the red diamonds in the inset of Fig. 6. This analysis yields for the imaginary part in the low frequency limit:

\[
\lim_{\omega \to 0} Z_{\text{im}}(\omega) = -R_p^2 \omega C_p = -\frac{Z_0 L^2 \omega}{3D^2} \quad (12)
\]

Hence the parallel capacitance observed in the \( R_0(R_pC_p) \) fit can be equated to:

\[
C_p = \frac{Z_0 L^3}{3R_p^2 D^2} \quad (13)
\]

According to Eq. (34) in Ref. [30], \( R_p \) will be equal to \(-0.8 \times R_0\). Consequently, as \( R_0 \) is inversely proportional to \( D \), \( C_p \) will become virtually temperature independent, as is also observed in Fig. 7. Using Eq. (6) it can be shown that \( C_p \) is inversely proportional to the thermodynamic factor, \( \Gamma \):

\[
C_p \propto \frac{C_0}{T} \frac{d \ln a}{d \ln C} \quad (14)
\]

\( C_0 \), the equilibrium oxygen ion concentration, will have a rather small temperature dependence. This implies that, with \( C_p \) virtually temperature independent, the thermodynamic factor has a small temperature dependence. This is an important result, as there are very few literature reports [33] on this quite important materials parameter.

It is obvious that for the pure ESD-CCO electrode the CNLS-analysis gives consistent results, although separate high- and low-frequency range fits are made instead of a full analysis with one EqC. Conversion to a DFRT will give less information, which is due to the rather complex exact DFRT for the finite length Warburg, see Eq. (7) and Ref. [30].

4.4. Analysis of the CCO/CGO composite electrode

The addition of Gd-doped cerium oxide significantly decreases the polarization resistance by a factor of 6–7, as has been shown in Fig. 2. Fig. 7 shows a compilation of the normalized impedance spectra for the ESD-CCO/CGO electrode. At the highest temperature two major dispersions become visible. This temperature behavior is quite similar to what earlier has been observed for the series of screen-printed CCO/CGO electrodes [14].

Fig. 8 shows a compilation as function of temperature of the normalized DFRT’s, obtained with the \( m(RQ) \) fit method [6,7]. The distribution functions show two major time constants. The largest time constant (lowest frequency) shows the same behavior as previously observed for the screen-printed series, i.e. a temperature-independent peak position at temperatures above \(-650^\circ \text{C}\), see Fig. 8. The position of the second peak shows Arrhenius behavior. There are two more, small relaxation processes. These will be discussed further on.

For the screen-printed samples one equivalent circuit (EqC) could be used to fit all data for all compositions. This EqC consisted of a low-frequency (RC), a Gerischer contribution at intermediate frequencies and two, strongly overlapping, high-frequency (RQ)’s with frequency exponents close to 0.5, i.e. diffusion related. For the ESD-CCO/CGO electrodes similarly one EqC was found that could fit all data, but with a single high-frequency (RQ), see the EqC inset in Fig. 7. The corresponding CNLS-fits are also presented as continuous curves in the frequency dispersions of Fig. 7. Again a low frequency (RC) is observed. At mid-frequencies a Gerischer is present, while the high-frequency part can be modelled with a single (RQ) with \( \alpha \) close to 0.5, indicating a diffusion process.

Fig. 9 presents the Arrhenius graph of the electrolyte resistance, \( R_{\text{eltype}} \), and the polarization resistance, \( R_{\text{pol}} \). This graph shows that the repeatability upon temperature cycling is very good. \( R_{\text{pol}} \) shows a clear bend, most likely indicating a change in the rate-determining step with increasing temperature. This was also observed for the screen-printed electrodes with only a 30/70 com-
position, (Fig. 13 in Ref. [14]). All other electrodes with a lower CGO content showed clear Arrhenius behavior with an activation energy, $E_{act} = 116-128$ kJ mol$^{-1}$. The grey curve in Fig. 9 is the sum of two activated processes that have been fitted to the $R_{pol}$ data. Activation energies are $E_{act} = 158$ kJ mol$^{-1}$ (low $T$) and 37 kJ mol$^{-1}$ (high $T$). This curve presents an excellent fit to the data.

Fig. 10 presents the Arrhenius graph for the low-frequency resistance, $R_{low}$, and the time constant related to the $(RC)_{low}$ sub-circuit. The activation energy for $R_{low}$ is with $158 \pm 2$ kJ mol$^{-1}$, virtually the same as found previously for the screen-printed cathodes: $E_{act} = 152-157$ kJ mol$^{-1}$ (Fig. 15 in Ref. [14]). The time constant becomes almost constant at temperatures above ~700°C, with $\tau_{low} = 0.08 - 0.09$ s, which again is very close to the value of ~0.12 s for the screen-printed cathodes, Ref. [14]. The changeover to a constant value occurs at a lower temperature for the ESD-CCO/CGO electrode than for the screen-printed ones.

The Gerischer parameters show a quite different behavior than observed for the screen-printed cathodes. The Arrhenius graph in Fig. 11 clearly shows a changeover of both $K_{s}$ and $Y_{0}$ at 600–625°C. The high-temperature $K_{s}$ coincides quite closely with the same values observed for the screen-printed cathodes, presented as a heavy grey line in Fig. 11. This parameter is considered to be a materials property.

The high-frequency $(RQ)_{high}$ component is presented in Figs. 12–14. Fig. 12 shows the Arrhenius graph for $R_{high}$. The activation energy, $E_{act} = 99 \pm 2$ kJ mol$^{-1}$, is somewhat smaller than observed for the screen-printed electrodes, $E_{act} = 110 - 117$ kJ mol$^{-1}$. The frequency power, $\alpha$, varies with temperature between 0.5 and 0.65, as shown in Fig. 13. The graph of the CPE parameter, $Y_{0}$, ver-
sus inverse temperature does not provide a clear Arrhenius dependence, see inset in Fig. 14. Using a similar approach as for deriving the apparent capacitance for a (RQ)-circuit, Eq. (4), the apparent Warburg-Y₀ can be derived with:

\[
Y₀_{\text{app}} = \left( \frac{R \cdot Y₀}{R} \right)^{0.5/α}
\]  

(15)

This results in quite acceptable Arrhenius behavior with an activation energy, \( E_{\text{act}} = 73 \pm 2 \text{ kJ mol}^{-1} \), as shown in Fig. 14. Whereas the high frequency dispersion for screen-printed electrodes presented a significant contribution to \( R_{\text{pol}} (~40-60\%) \), for the ESD-CCO/CGO electrode the contribution is limited to ~5%.

The CNLS-analysis does not provide a clear picture for the Gerischer contribution. Interpretation of the decrease in \( K₀ \) and \( Y₀ \) with increasing temperature is not clear. It could be an effect of the complex microstructure, leading to a distribution of parameter values that changes with temperature. In this case it can be very valuable to use the ‘model- free’ presentation of the DFRT’s. For one temperature set also the DFRT’s were calculated using the free ‘DRTTools’ program [23], which is based on Tikhonov regularization. Fig. 15 shows a compilation of the results obtained with this program. The Tikhonov DFRT’s show wider peaks than the \( m(RQ)\) fits. For several wide peaks it is possible to separate these into two Gauss curves, thus improving the details in the peak positions. An example of a Gauss-curve deconvolution is presented in the inset in Fig. 15.

An Arrhenius graph with a compilation of the relaxation times obtained from the \( m(RQ)\) fits and the de-convoluted Tikhonov regularizations is presented in Fig. 16. The relaxation times, derived from the CNLS-analysis with the EqC from Fig. 7, are also presented for comparison.

Both the \( m(RQ)\) fit method and Tikhonov regularization agree on the position of the relaxation times connected to the low frequency (RC), \( τ_{\text{low}} \). The \( τ_{\text{low}} \) obtained from the CNLS-analysis (open red squares, Fig. 16) coincides at high temperatures, but deviates for \( T < 650°C \). The average \( τ_{\text{low}} \) value for the screen-printed electrodes is presented by the heavy grey line. The peak position for the Gerischer related relaxation times are also quite close for both inversion techniques (\( τ_2 \), filled circles Fig. 16). Again, the CNLS-analysis derived \( τ_C \) closely matches the \( τ_2 \) at high temperatures. While the CNLS-derived \( τ_C \) shows a shift in the Arrhenius curve (open circles connected with dashed lines, Fig. 16), both \( τ_2 \)-values show proper Arrhenius behavior with an average activation energy of \( 111 \pm 3 \text{ kJ mol}^{-1} \).

The origin of time constants \( τ_2 \), green diamonds, is not clear. The time constants related to the high-frequency (RQ) are between \( 5\cdot10^{-6} \) and \( 5\cdot10^{-5} \text{ s} \) (not shown). The related DFRT peaks are quite wide (because of the small \( α \) value) with a very low peak height, hence they hardly show up in the DFRT graphs. On the other hand, it has been shown that the Gerischer dispersion is not properly transferred to the exact DFRT, Eq. (4), either with the Tikhonov regularization, the \( m(RQ)\) fit method, or even the Fourier transform, see Refs. [5,6]. Besides the major peak, secondary (and with the \( m(RQ)\) fit even more) peaks show up in the DFRT. Hence it is quite likely that the peaks marked with \( τ_3 \) are also related to the Gerischer contribution. Fig. 16 shows virtually identical slopes for the \( τ_2 \) and \( τ_3 \) graphs, which can be taken as a strong indication that the \( τ_3 \) are related to the \( τ_2 \) process. Both DFRT methods show a clear single activated behavior for \( τ_2 \), in contrast with the CNLS-fit results for \( τ_C \).

5. Discussion

5.1. Comparison of the ESD electrodes

The two DFRT’s for both ESD electrodes in Fig. 2A are quite similar in shape, showing two major relaxation peaks. The CNLS-analysis shows, however, totally different frequency dispersion be-
Fig. 17. $\hat{D}(D_{\text{hem}})$ values for CCO from literature. Open circles, Ref. [31], recalculated from $D^*$ and $\Gamma$. Drawn line represents $\hat{D}$ for $L = 2.2 \ \mu$m, Eq. (17).

5.2. Interpretation of the CCO results

A remarkable result for the ESD-CCO electrode is the modelling with a finite length Warburg. Application of this dispersive element requires that at the electrode/ambient interface the transfer of oxygen (the mobile ion) is very fast, i.e. the oxygen activity at this interface is virtually constant. The general dispersion relation for diffusion through a thin layer with a reaction rate, $k_{\text{exch}}$, for the oxygen exchange is given by the generalized finite length Warburg, see Ref. [34]:

$$Z_{\text{FLW}}(\alpha) = Z_0 \left[ \coth L \sqrt{\frac{k_{\text{exch}}}{jD}} + \frac{k_{\text{exch}}}{jD} \coth L \sqrt{\frac{1}{D} + 1} \right]$$

(16)

When $k_{\text{exch}} \gg D$ (eq. 16) reduces to the FLW form, Eq. (5). Combination of the FLW Eqs. (6),(13), with $R_p \approx 0.8 \times R_0$ (see Ref. [30]), leads to a simple expression for $\hat{D}$ without $\Gamma$:

$$\hat{D} = \frac{L^2}{(2R_0 - C_p)} \left[ \text{cm}^2 \cdot \text{s}^{-1} \right]$$

(17)

Comparing Eq. (17) with literature data will give an effective thickness for the FLW layer. Hu et al. [35] have presented $\hat{D}$ values for CCO obtained with electrical conductivity relaxation measurements (ECR), see the open squares in Fig. 17. The observed $E_{\text{act}} = 117 \pm 9$ kJ mol$^{-1}$, which is somewhat lower than $134 \pm 2$ kJ mol$^{-1}$ for $R_0$, and hence $\hat{D}$, found here. The open circles in Fig. 17 are obtained from Ref. [33], by combining the tracer diffusion coefficients, $D^*$, and the thermodynamic factors, $\Gamma$, obtained at approximately 0.2 Bar oxygen with $\hat{D} = \Gamma \cdot D^*$. By adjusting the effective thickness to $-2.2 \ \mu$m for the ESD-CCO electrodes, a very good match is obtained with the published $\hat{D}$ values (Fig. 17).

A simulation of Eq. (16) with $T = 700^\circ \text{C}$, $\hat{D} = 2.7 \times 10^{-10} \ \text{cm}^2 \cdot \text{s}^{-1}$, $k_{\text{exch}} = 1.7 \times 10^{-4} \ \text{cm} \cdot \text{s}^{-1}$ and $L = 2.2 \times 10^{-4} \ \text{cm}$, shows that the overall surface exchange rate, $k_{\text{exch}}$, is too small to result in a pure FLW dispersion. This discrepancy can be solved by assuming a combination of a (slow) dissociative adsorption and subsequent (fast) incorporation steps in the overall exchange reaction [36]. This results in a model as depicted with the cartoons of Fig. 18, in analogy with an earlier publication on La$_2$NiO$_4$-δ electrodes with a dense LNO interlayer, Ref. [13]. The protruding platelets, Fig. 1A, provide a large area for the dissociation reaction. As CCO is a two-dimensional ionic conductor, it can be assumed that fast surface diffusion of, possibly charged, mono-atomic oxygen provides a sufficient oxygen flux at the ambient boundary of the dense CCO-layer, see Fig. 18B. This implies that the incorporation rate is significantly faster than the dissociation rate.

It should be noted that in Fig. 18 it is tentatively assumed that oxygen will dissociate to $O_{\text{ad}}^-$ species which will show fast surface diffusion on the CCO platelets. But further investigations are needed to clarify which species, $O_{\text{ad}}^-$ or $O_{\text{ad}}^+$, is actually involved.

5.3. Interpretation ESD-CCO/CGO results

It is remarkable that the Eqc used in the analysis of the ESD-CCO/CGO impedance spectra, Fig. 7 - top, is almost identical to the Eqc for the screen-printed CGO/CCO electrodes (Fig. 7a in Ref. [14]). The main difference is that for the ESD electrode a single high-frequency (RQ) is found, for the screen-printed two, closely related, (RQ)'s are observed. But in both cases the frequency power, $\alpha$, is close to 0.5, indicating a diffusion process. Both electrode systems show an almost identical low-frequency (RC), which is assigned to the CCO redox process. The chemical capacitance depends on the thermodynamic factor, $\Gamma$:

$$C_{\text{low}} = V_{\text{eff}} \frac{8F^2C^0}{RF \cdot \Gamma}$$

(18)

with $V_{\text{eff}}$, the effective active electrode volume.

The specific CCO redox capacitance at 700°C, based on the thermodynamic factor published by Thoréton et al. (Ref. [33]) is 1840 F cm$^{-3}$. With known electrode area (0.885 cm$^2$), 60% porosity and a 50/50% composition, this results for the ESD-CCO/CGO electrodes in an electrochemically active layer of $13 \ \mu$m, quite close to an average layer thickness of $17 \ \mu$m. This indicates that the entire electrodes layer is electrochemically active, as was also observed for the screen-printed electrodes [14].

The oxygen adsorption-dissociation process at the CGO particles becomes important at the intermediate frequencies. Here the charge transfer of mono-atomic oxygen at the triple-phase boundary (TPB line delineating the external CCO/CGO boundary) becomes the rate-limiting step. A possible sequence of steps is indicated in the cartoon of Fig. 18C with fast oxygen dissociation on the catalytically active CGO, a first charge transfer at the CGO/CCO TPB to $O_{\text{ad}}^-$ and final charge transfer and incorporation in the bulk at the CCO/CGO cathode/electrolyte interface: $O_{\text{ad}}^+ + e^+ + V_o^0 \rightarrow O_{\text{ad}}^0$.

The combination of surface exchange and diffusion of dissociated oxygen on the CGO surface results in a Gerischer type dispersion. The derivation of a Gerischer contribution for such a situation has been presented in Ref. [13]. For the screen-printed CGO/CCO 50/50% cathode the Gerischer contribution was relatively small, $-25\%$. For the ESD-CCO/CGO cathode the Gerischer contribution to $R_{\text{pol}}$ is $-50\%$. This most likely indicates a lower TPB density than for the screen-printed composition, which is due to the larger CGO particles in the ESD electrode.

In the high-frequency range the Gerischer process can no longer follow the voltage (oxygen activity) swings. The dispersion in this region is controlled by diffusion of adsorbed oxygen species and is possibly also limited by the electronic conduction of the CCO structure, resulting in a (RQ) circuit where the frequency exponent, $\alpha$, of the CPE is close to 0.5, i.e. Warburg behavior.
6. Conclusions

A significant change in the microstructure of a SOFC electrode can yield extra information on the electrode processes and the rate-determining steps. For the pure CCO-electrode, prepared with electrostatic spray deposition, a quite different frequency dispersion, as compared to the CCO/CGO impedances, was observed, which clearly points to finite length diffusion behavior. It can be interpreted as dissociative adsorption of oxygen on the large open surface on the CCO-platelets, followed by rapid surface diffusion towards a more dense CCO-layer on top of the electrolyte. The rate-controlling step is then the oxygen ion diffusion through this layer, as the oxygen exchange rate at the layer/ambient interface is apparently very fast.

Furthermore, the analysis shows that partial CNLS-analysis, i.e. separately in the high- and the low-frequency regions, gives adequate and consistent results, making a full range CNLS-fit with a complex EqC unnecessary. A transformation to the $\tau$-domain cannot provide the same information as obtained in the frequency domain, due to the complex exact DRFT of a FLW.

The addition of CGO to the ESD-CCO cathode provides a significant decrease in the electrode polarization. This effect has been observed earlier for a series of screen-printed CCO/CGO cathodes [14]. For the ESD-CCO/CGO cathode the Arhenius presentation of the polarization resistance, ASR of Fig. 9, shows a clear bend indicating a change in the rate-controlling process. Whereas the screen-printed composite electrodes consisted of CCO grains (1-5 μm) with well-dispersed CGO particles of ~0.2 μm, the ESD-CCO/CGO consists of platelets/particles of 0.5-3 μm. A tentative explanation is that oxygen dissociation and surface adsorption is much faster on CGO than on CCO, thus enhancing the electrode properties.

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