GAS CONVERSION IMPEDANCE:
SOFC ANODES IN H₂/H₂O ATMOSPHERES

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ABSTRACT

Impedance spectra are obtained in H₂/H₂O on Ni/YSZ cermet anodes. These impedance spectra are fitted to the equivalent circuit $LR(RQ)_i(RQ)_2(RC)_3$. The subcircuit $(RC)_3$ is found to have a capacitance in the order of 0.1-1.1F only when the current-bearing electrodes are in separate atmospheres. This impedance is derived analytically and shown to represent the change in composition of a gas volume above the anode. This impedance has no direct relations to anode composition or electrochemical performance, but will inevitably contribute to the measured polarisation resistance.

INTRODUCTION

Impedance spectroscopy is often used to characterize SOFC anodes. The dependency of fitted resistive parameters upon gas composition and temperature is frequently discussed, whereas little results appear in literature discussing the capacitive parameters. Also the designation of parameters to specific chemical or physical processes is scarce. In a previous paper (1) impedance spectra obtained on Ni/YSZ cermet anodes are characterized using the circuit $LR(RQ)_1(RQ)_2(RC)_3$ where $Q=Y_0(jω)^n$. The present paper is focused on identifying the nature of the low frequency arc $(RC)_3$ as a gas conversion impedance caused by the applied AC-signal.

EXPERIMENTAL

A Ni/YSZ cermet anode (40 vol% Ni after reduction) is prepared by spraying a slurry containing green NiO and TZ8Y (Tosoh, ZrO₂ with 8 mol% Y₂O₃) and firing at 1300°C according to the description in (2). The sintered thickness is in the range of 40-60 μm, where 20 μm is known to be the limit for sufficient inplane conductivity (1). Two different electrolyte bodies are used: A Risø 3-electrode pellet and a 180 μm thin YSZ tape with anodes on both sides (i.e. a two-electrode setup with symmetrical...
anodes). Smaller samples are broken from a 20 cm² tape for electrochemical characterisation.

A second type of Ni-based anode has been applied to a 3-electrode pellet. Here Ni(NO₃)₂ is decomposed in moist 9% H₂ at 1420°C on the electrolyte (3), and afterwards a 90/10 vol% Ni/YSZ paint is deposited without sintering. A reasonable contact and stability is obtained. This anode is intended to have active sites only on the interface towards the electrolyte, as opposed to the cermet anodes having active sites in the bulk of the cermet structure.

In all electrochemical characterizations the rig of Fig. 1 is applied in a 4-leads mode with three or two electrodes (pellets or symmetrical anodes, respectively). Pellets are measured with a central current collector (short length of 0.3 mm Pt wire pressed to the anode), Fig. 2a. Symmetric tapes are mounted with a folded 0.3 mm Pt wire as current collector on both electrode surfaces, Fig. 2b. The symmetric tape is placed in the rig of Fig. 1 between a clean 3-electrode pellet and a perforated and baffled Al₂O₃ disk to distribute the springload. The essential differences between these two measurements are a) shape and bulk of the electrolyte, and b) whether the two current-bearing electrodes are in a common or in separate atmospheres during testing.

Electrochemical characterization is performed using the following Solartron equipment: Frequency response analyzers 1260A and 1250 in combination with potentiostats 1287A and 1286, respectively. Impedance spectroscopy is conducted at OCV with an applied amplitude of 20-30 mV. This amplitude is verified to be well inside the linear range, and a maximum of 3/4 of the applied amplitude is perturbing the electrode due to the series resistance of the electrolyte. The used frequency range is 1 MHz to 0.1 Hz. The atmosphere composition is varied by saturating H₂/N₂ mixtures with water on an oilbath. The water content is verified by OCV against Pt in air according to (4). The anode areas are 0.4 cm² for pellets and 0.2-0.3 cm² on each side for tapes, the gas flowrate is 100 Nml/min. A standard measurement condition is defined as OCV at 1000°C in H₂ + 2-3% H₂O.

RESULTS

Comparing impedance data

Obtained impedance spectra are fitted with EQUIVCRT (5) to equivalent circuits of the type LR(Q₁)(RQ₂)(RC)₃ where Q=Yo(jω)ⁿ. The subcircuits are ordered by decreasing summit frequency, and the n-values are fixed at (n₁,n₂)=(0.8,0.75) according to (1,6).
Impedance plots at standard conditions are given for nominally identical cermet anodes with current electrodes in a common and separate atmospheres, Fig. 3. These impedance spectra are corrected for effective electrode area and series resistance. The spectra are basically of the same shape, and the symmetrical anodes on a tape can be fitted well with the n-values established for anodes on a pellet. Fit parameters before area-correction are given in Table I. The most important observation from Fig. 3 is the dramatic change of time constant for the low frequency arc.

Table I  Uncorrected fit parameters according to the equivalent circuit LR1(RQ)1(RQ)2(RC)2. The electrode area is 0.204 cm² on each side for the symmetric anodes and 0.44 cm² for the pellet.

|       | Rs, Ω | Y0.1, Ss0.80 | R2, Ω | Y0.2, Ss0.75 | R3, Ω | C3, mF |
|-------|-------|--------------|-------|--------------|-------|-------|
| tape  | 0.26  | 0.4          | 0.36  | 2            | 0.41  | 0.8   |
| pellet| 0.15  | 3            | 0.07  | 70           | 0.31  | 450   |

In Fig. 4 impedance spectra for the Ni-rich anode and the Ni/YSZ cermet anode are plotted after aligning the spectra to the same resistance at DC-conditions. Both anodes are deposited on 3-electrode pellets and measured with current electrodes in separate atmospheres. Despite the differences in anode structure and polarisation resistance (Rp), the low frequency arcs are identical. The same effect is observable in another paper dealing with four different Ce0.6Gd0.4O1.8 based anodes (7), also on 3-electrode pellets with current electrodes in separate atmospheres. These observations are taken as evidence of the low frequency arc being related to the test rig geometry rather than the actual anode.

Gas phase impedance

The high capacitance $C_3$ present in measurements on pellets (1.1 F at $pH_2O = 25\%$) is not observed for anodes on tapes. Capacitances of this magnitude can only be attributed to changes in chemical composition of a bulk phase, as capacitances related to double layers and surface adsorption are orders of magnitude smaller. A change of composition in the bulk of the electrolyte pellet could be speculated. Vacancy depletion zones in the electrolyte (8) and capacitances at grain interfaces are associated with much lower time constants in-between that of the bulk electrolyte and the electrode response, and can therefore be disregarded. The solubility of e.g. water in YSZ is also too small (1) to account for the observed magnitude of $C_3$.

In the following the impedance of the fuel gas over the anode is considered. When an AC-potential is applied to the anode, an AC-current follows. In general the current causes a hydrogen/water conversion, leading to a change in $pH_2/pH_2O$ and the anode potential according to the Nernst equation. Ideally a sufficiently high gas flowrate...

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should render this effect insignificant. However, for high performance (low $R_p$) anodes it has proven difficult to obtain a near constant atmosphere composition in a test configuration where the current electrodes are in separate atmospheres. If the electrodes are placed in the same atmosphere, only a minor local net conversion of the test atmosphere is expected for small samples and at high temperatures with high gas diffusion rates.

The impedance related to the change of atmosphere composition over the anode has been considered before (9), and is derived analytically as follows: Consider a volume $V$ over the anode in a separate atmosphere, Fig. 5. Gas fluxes are denoted $J$ with subscripts i=incoming, o=outgoing and a=anode reaction. Perfect mixing of gasses is assumed at 800-1000°C due to the high diffusion rates, and partial pressures in the outlet gas is identical to partial pressures in the entire volume. The current is defined as positive in the anodic direction. The AC-potential $\eta$ over the anode causes an AC current $I$ [1] and a gas conversion according to [2].

$$I = I^0 \exp(j\omega t)$$  \[1\]

$$H_2(g) + O^{2-} \leftrightarrow H_2O(g) + 2e^-$$  \[2\]

Considering the variation in water partial pressure with time $dp_{H_2O}/dt$ one obtains [3], where $N$ is a flowrate in mole/sec and $RT$ has the usual meaning.

$$\frac{V}{RT} \frac{dp_{H_2O}}{dt} = J_{in,H_2O} + J_{a,H_2O} - J_{o,H_2O} = N_i p_{i,H_2O} + J_{a,H_2O} - N_o p_{a,H_2O}$$  \[3\]

As the anodic reaction [2] involves no changes in the number of gas molecules, it is possible to define a volumetric flowrate $N=\dot{N}=N_o$. Further the variation in partial pressure is defined as $\Delta p=p_o-p_i$, and the flux of water from the anode follows the current [4]. Inserting in [3] and rewriting gives the differential equation [5] with the general solution [6]. Using the boundary condition of $\Delta p=0$ for $t=0$, one obtains $c=0$ and the specific solution [7].

$$J_{a,H_2O} = \frac{I}{2F} = \frac{I^0}{2F} \exp(j\omega t)$$  \[4\]

$$\frac{d\Delta p_{H_2O}}{dt} = -\frac{RTN}{V} \Delta p_{H_2O} + \frac{RT}{2FV} \frac{I^0}{2F} \exp(j\omega t)$$  \[5\]
\[
\Delta p_{H_2O} = \frac{RT_0}{2F(N+j\omega V)} \exp(j\omega t) + c \exp\left(-\frac{N}{V} t\right) \tag{6}
\]

\[
\Delta p_{H_2} = \frac{RT I}{2F(N+j\omega V)} \tag{7}
\]

The variation in hydrogen partial pressure \(\Delta p_{H_2}\) is given as [8].

\[
\Delta p_{H_2} = \frac{-RT I}{2F(N+j\omega V)} \tag{8}
\]

The overpotential \(\eta_s\) of the anode relating to the change in gas composition is defined as [9] according to the Nernst equation. Introducing the variation in partial pressure \(\Delta p\) and the criterion \(\Delta p \approx p_i\) this equation is linearized by the first part of the Taylor series \(\ln(1+x)=x\) for \(x \ll 1\) resulting in eq. [10].

\[
\eta_s = \frac{RT}{2F} \ln\left(\frac{p_{i,H_2O} \cdot p_{i,H_2}}{p_0,H_2O \cdot p_{i,H_2}}\right) \tag{9}
\]

\[
\eta_s = \frac{RT}{2F} \left(\frac{\Delta p_{H_2O}}{p_{i,H_2O}} - \frac{\Delta p_{H_2}}{p_{i,H_2}}\right) \tag{10}
\]

Calculating now the impedance \(Z\) associated with this variation in partial pressures using [10], [7] and [8] one obtains [11].

\[
Z = \frac{\eta_s}{I} = \left(\frac{RT}{2F}\right)^2 \left(\frac{1}{p_{i,H_2O}} + \frac{1}{p_{i,H_2}}\right) \frac{1 - j(\omega V/N)}{N\left(1 + (\omega V/N)^2\right)} \tag{11}
\]

The last term in [11] describes a semicircle in a plot of \((Z_{Re. vs. } - Z_{imag.})\) for \(\omega\) going from 0 to \(\infty\). This indicates the impedance is describable by an equivalent circuit containing only a resistor \(R_g\) and a capacitor \(C_g\) in parallel. Such circuits are conveniently described by the admittance \(Y\) [12]. Rewriting [11] to the admittance \(Y=1/Z\) yields the expression [13].

\[
Y = \frac{1}{R_g} + j\omega C_g \tag{12}
\]
By combining [12] and [13], R is found as the real part and C as the imaginary, still with the restriction of Δp=π from the linearization.

\[ Y = \left( \frac{2F}{RT} \right)^2 \frac{1}{N + jωV} \]  \hspace{1cm} \text{[13]}

Calculating \( R_g \) from [14] with the applied flowrate of 100 Nml/min and standard conditions (1000°C, 3% \( \text{H}_2 \), 97% \( \text{H}_2 \text{O} \)), one obtains an \( R_g \) of 0.6 Ω, a factor of 2 higher than measured, Table I. This may indicate how the assumption of perfect mixing of gases in the volume is not quite fulfilled. The absolute value of \( C_g \) using [15] should match the 450 mF measured under standard conditions, Table I. This indicates a volume \( V \) of 0.5 cm\(^3\), a reasonable value in a cylindrical design with a cross-section of 0.5 cm\(^2\).

From [14] \( R_g \) is seen to go through a minimum for \( \text{pH}_2 = \text{pH}_2 \text{O} \). The dependency \( R_g \propto \text{pH}_2 \text{O}^{-1} \) is expected for e.g. \( \text{pH}_2 = 0.5 \text{ atm} \) and \( \text{pH}_2 \text{O} < 0.25 \text{ atm} \) as also found for \( R_3 \) in (1) under the same conditions. If \( \text{pH}_2 \text{O} \) is low, e.g. 0.03 atm, no dependency on \( \text{pH}_2 \) is expected from [14]. Nevertheless, the approximate relation \( R_3 \propto \text{pH}_2^{-1} \) was found in (1) under the same conditions. In Fig. 6 the dependency of \( C_3 \) on \( \text{pH}_2 \text{O} \) up to 0.25 atm is given with \( \text{pH}_2 \) fixed at 0.5 atm for current electrodes in a common and in separate atmospheres. Others have found a more pronounced dependency of the low frequency part of \( R_p \) on \( \text{pH}_2 \text{O} \) for symmetrical Ni/YSZ cermet anodes (10). This is assumed to be caused by the higher gas transport restrictions for samples used in (10) (6.8 cm\(^2\) as opposed to the 0.2 cm\(^2\) used here).

The parameters \( R_g \) and \( C_g \) are verified to be independent on applied amplitude as predicted by [14] and [15] over one order of magnitude from 7 mV to 70 mV. It follows from [16], that the summit frequency \( f_s \) is constant with temperature and partial pressures as also observed in (1).

\[ f_s = \frac{1}{2\pi R_g C_g} = \frac{N}{2\pi V} \]  \hspace{1cm} \text{[16]}

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For our work on 3-electrode pellets the high time constant of the gas conversion impedance has been fortunate, keeping this arc well separated from the electrode processes prevailing at higher frequencies.

The identification of the gas conversion impedance helps to explain discrepancies in the actual shape of impedance spectra presented in literature. As both volume and flowrate influences on \((RC)_g\), different results can be expected with the different design of test-rigs used and the order of magnitude of the total \(R_P\) relative to \(R_g\). The effect of changing the gas flow in the rig of Fig. 1 is illustrated for current electrodes in separate atmospheres in Fig 7.

Although \(R_g\) is not related to the anode composition and electrochemical performance, it is inevitably a part of the measured polarization resistance in AC experiments. \((RC)_g\) is easily recognized and compensated for in the AC measurements with current electrodes in separate atmospheres where \(C_g\) reaches the order of Farads. \(R_g\) may be minimized by keeping the flowrate as high as feasible. For DC experiments the atmosphere composition changes with the current, and the applied potential must be corrected for this change in \(pO_2\) at a given current density and gas flowrate as pointed out in (11).

CONCLUSION

The low frequency arc found in impedance spectra obtained on SOFC anodes when tested with current electrodes in separate atmospheres is shown to be a gas conversion impedance. This impedance is described as an \((RC)_g\) parallel subcircuit, caused by the AC-current changing the composition of the atmosphere above the anode.

Expressions for \(R_g\) and \(C_g\) are derived analytically, and corroborated by experiments. Both \(R_g\) and \(C_g\) depends on the partial pressure of hydrogen and water. \(C_g\) is proportional to the volume of gas above the anode, whereas \(R_g\) is proportional to the inverse gas flowrate.

The gas conversion impedance has no relation to the anode composition or electrochemical performance as such, but will inevitably be included in measured AC- and DC-response.

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Fig. 1 The rig used for electrochemical testing of anodes.

Fig. 2 Test geometries with current electrodes in a) separate and b) common atmosphere. A: anode, B: top of YSZ pellet, C: Pt wire for current collection, D: pushrod, E: perforated Al₂O₃ disk and F: YSZ tape with symmetrical anodes.

Fig. 3 Impedance spectra obtained on nominally identical Ni/YSZ cermet anodes in different geometries. Note the shift in frequency on going from one atmosphere to two separate ones for the current-bearing electrodes. 1 Hz, 100 Hz and 10 kHz are marked.
Fig. 4 Impedance spectra obtained on two types of anodes on 3-electrode pellets with current electrodes in separate atmospheres.

Fig. 5 Model for considering the impedance of gas conversion in a limited volume V over an SOFC anode. The other current electrode is in a separate atmosphere.

Fig. 6 Experimental gas phase capacitance $C_3$ by pH$_2$O, current electrodes in common and separate atmospheres. pH$_2$=0.5 atm at 1000°C.

Fig. 7 Experimental parameters of the (RC) subcircuit by gas flowrate N. The gas flow is normally kept at 100 Nml/min equal to 250 Nml/cm$^2$min.