

Supplementary information to

Excellent kinetics of single-phase Gd-doped ceria fuel electrodes in solid oxide cells

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Indication of gas diffusion in the impedance spectra

The treatment of gas diffusion in impedance spectroscopy is extremely complex, because the spatial variation of gas composition can only be treated with a three-rail transmission line equivalent circuit.¹ Often, gas diffusion is treated as a Warburg impedance in series to the electrochemical polarization. However, this is an approximation which is only valid when gas diffusion and electrode polarization features differ strongly in their peak frequencies and when the main contribution to the gas diffusion resistance lies outside of the electrochemically active interface, in a stagnant gas layer.

For our GDC-based electrodes, neither of these conditions is fulfilled: The characteristic frequencies differ by less than one order of magnitude, and Knudsen diffusion within the active layer is likely to significantly contribute to the total gas diffusion resistance. Still, some impedance spectra show a weakly separated low frequency feature that is most likely caused by gas diffusion. Due to the larger gas diffusion resistance of the 14 μm thick GDC electrode, impedance spectra and distribution of relaxation times (DRT) plots of the same are shown in Fig. S1. DRT was computed with the open-source MATLAB code "DRTtools"².

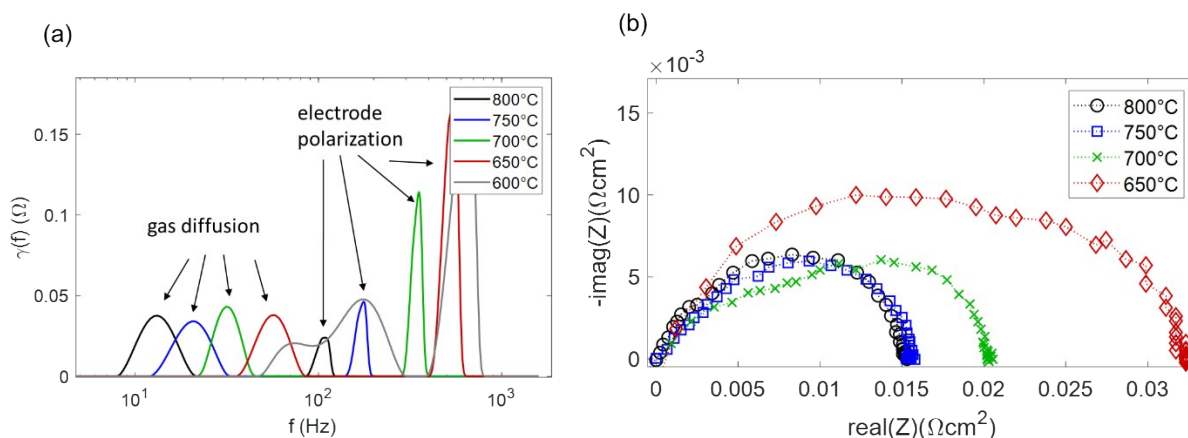


Fig. S1 (a) distribution of relaxation times (DRT) and (b) impedance plots of a 14 μm thick GDC|Pt electrode in $\text{H}_2+\text{H}_2\text{O}$ atmosphere.

The impedance spectra contain a temperature dependent high frequency arc, and a relatively temperature independent low frequency arc. The latter is also visible as a low-frequency peak in the DRT plot in Fig. S1a. Also in the DRT plot, the area (corresponding to resistive magnitude) of the low-frequency feature is relatively independent of temperature. The area of this peak is $0.011 \pm 0.0015 \Omega\text{cm}^2$, and therefore in excellent agreement with the fit from the Arrhenius plot in the main manuscript ($0.012 \Omega\text{cm}^2$), Table 2.

The same effect is also visible for the measurements in $\text{CO}+\text{CO}_2$ gas mixtures shown in Fig. S2. Also there, a temperature independent low-frequency feature is clearly observed in the Nyquist plots and DRT representation, where it is labelled. The processes at higher frequencies grow with lower temperature, so they are assigned to electrode polarization processes. Due to the slower gas diffusion coefficients in $\text{CO}+\text{CO}_2$ mixtures, the total area of the gas diffusion feature equals $0.1 \pm 0.01 \Omega\text{cm}^2$. Again, the same value was also determined from the Arrhenius fit in the main text.

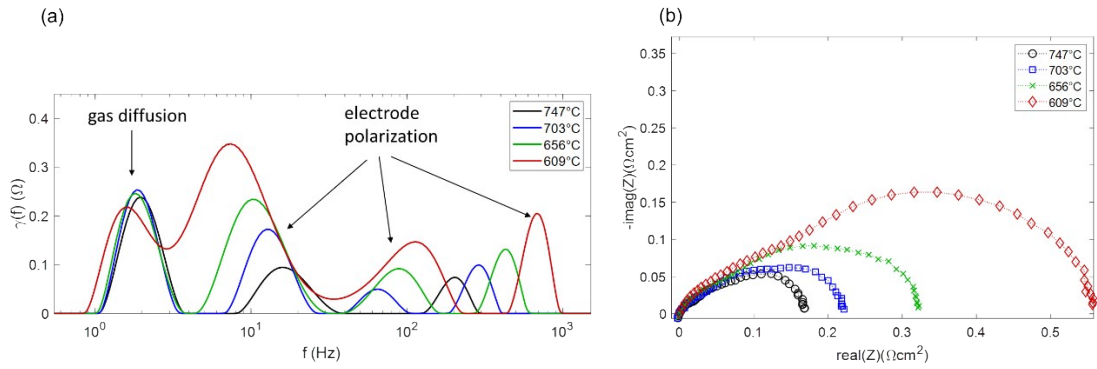


Fig. S2 (a) distribution of relaxation times (DRT) and (b) impedance plots of a 14 μm thick GDC|Pt electrode in $\text{CO}+\text{CO}_2$ atmosphere.

Also variation of the gas phase composition changes the gas diffusion resistance. The gas diffusion resistance reaches a minimum when the $\text{H}_2:\text{H}_2\text{O}$ mixing ratio is close to unity, and increases in atmospheres with very low (< 10 mbar) and high (> 200 mbar) H_2 partial pressures, or in presence of an inert gas³. Therefore, impedance spectra recorded close to a 1:1 $\text{H}_2:\text{H}_2\text{O}$ mixing ratio exhibit one arc, whereas spectra with high and low $p(\text{H}_2)$ exhibit two arcs. This was already shown in the main paper, Fig. 6. For electrodes with thicker GDC functional layer, this effect is even more pronounced, see Fig. S3b. These spectra were fitted with an equivalent circuit containing an ohmic offset and two R|CPE elements. Also, the ohmic offset resistance of the 14 μm thick electrode changes more with $p(\text{H}_2)$ than the spectra of the electrode with 3 μm GDC layer, which is shown in the main manuscript, figure 6.

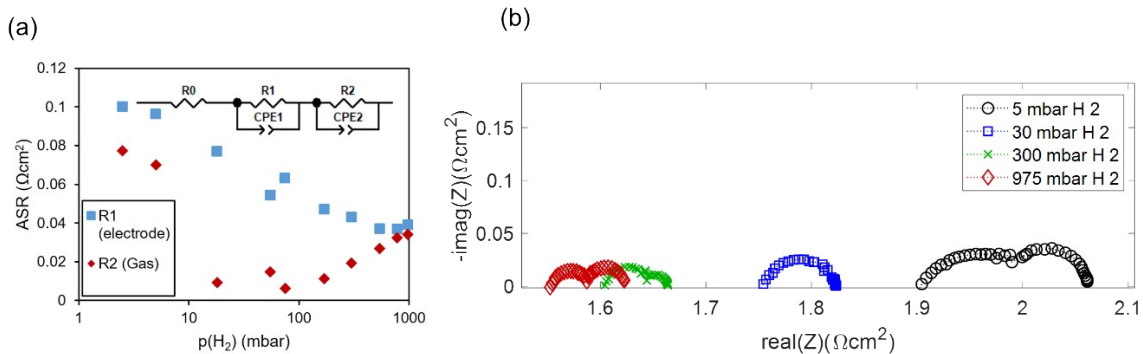


Fig. S3 (a) resistance of HF and LF features in the EIS spectra and (b) impedance plots of a 14 μm thick GDC|Pt electrode at 600°C, in a gas phase of 25 mbar H_2O with varying $p(\text{H}_2)$.

Possible catalytic effect of the Pt current collector

The catalytic activity of the Pt current collector may have a strong impact on the total polarization resistance. In order to rule out this effect, a cell with PtGDC|Pt current collector directly prepared on the YSZ electrolyte was also prepared and measured. Clearly visible in Figure S4, the polarization resistance of the electrodes without GDC functional layer is much larger. Therefore, a catalytic effect of the Pt in the current collecting layer can be excluded.

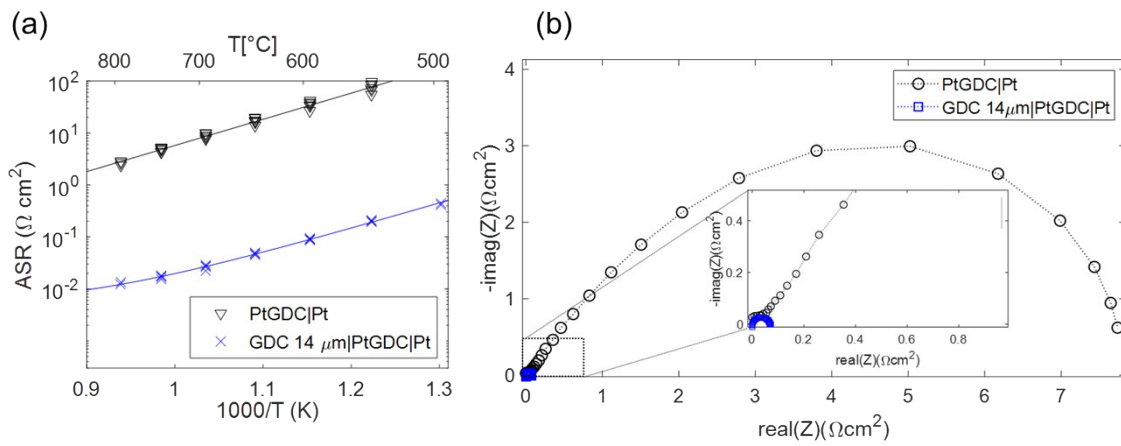


Fig. S4 (a) Area specific resistance (electrode arc diameter) of GDC|PtGDC|Pt and PtGDC|Pt electrodes as function of temperature (b) Nyquist plots of both electrodes at 600°C, in a gas phase of 25 mbar H_2O + 35 mbar H_2 . Inset: magnification to show the much smaller arc of the electrode with GDC functional layer.

References

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- 2 T. H. Wan, M. Saccoccio, C. Chen and F. Ciucci, *Electrochimica Acta*, 2015, **184**, 483–499.
- 3 A. Nanning, C. Bischof, J. Fleig, M. Bram and A. K. Opitz, *Energies*, 2020, **13**, 987.