

Appendix

The model for determination of oxygen ionic conductivity in BCZY622.

In Hebb-Wagner experiments with an electron blocking electrode configuration, the electronic current should be blocked by the YSZ layer. The requirement for the method to work properly was expressed by Eq.(2) in the main manuscript. Virkar et al. [11] estimated the oxygen ionic resistance at temperature 800 °C of Y-doped barium cerate as ~ 29 Ω, while the electronic resistance of the YSZ blocking electrode was 2.1 x 10⁶ Ω. Therefore, it can be stated that the YSZ pellet can be used as an electron blocking electrode also in this study as the ionic conductivity of BCZY622 studied in this work should not differ by more than one order of magnitude than in the work of Virkar et al. [11] and the HW requirement in Eq. (2) is fulfilled. At the steady state, the flow of electron holes as well as protons vanishes because the protonic as well as electronic conductivity in YSZ is negligible compared to the oxygen ionic conductivity [49]. In this case, the voltage drop U_{13} between Pt(1) and Pt(3) electrodes can be written as:

$$U_{13} = IR_{wire(1)} + IR_{i_{BCZY622}} + IR_{Pt(2)} + IR_{i_{YSZ}} + IR_{wire(3)} \quad (A1)$$

where I is a constant current, $R_{wire(1)}$ denotes the resistance of a wire on the Pt(1) electrode side, $R_{i_{BCZY622}}$ is the ionic resistance of the BCZY622 sample, $R_{Pt(2)}$ is the electronic resistance of the internal Pt(2) electrode, $R_{i_{YSZ}}$ means the total ionic resistance of YSZ blocking electrode sample and $R_{wire(3)}$ denotes the resistance of the platinum wire on the Pt(3) electrode side. Total ionic resistance of the BCZY622 sample, as well as the YSZ blocking electrode, depend on ionic resistance of materials and electrochemical resistances of reversible Pt electrode/material interfaces. Thus, $IR_{i_{BCZY622}}$ and $IR_{i_{YSZ}}$ can be described by Eq. (A2) and (A3):

$$IR_{i_{BCZY622}} = IR_{i_{BCZY622}}^{\frac{Pt(1)}{BCZY622}} + IR_{i_{BCZY622}}^{BCZY622} + IR_{i_{BCZY622}}^{\frac{BCZY622}{Pt(2)}} \quad (A2)$$

$$IR_{i_{YSZ}} = IR_{i_{YSZ}}^{\frac{Pt(2)}{YSZ}} + IR_{i_{YSZ}}^{YSZ} + IR_{i_{YSZ}}^{\frac{YSZ}{Pt(3)}} \quad (A3)$$

where $R_{i_{YSZ}}^{\frac{Pt(x)}{YSZ}}$ and $R_{i_{BCZY622}}^{\frac{Pt(x)}{BCZY622}}$ are electrochemical resistances of the respective interfaces between Pt and YSZ and BCZY622 samples. Inserting equations (A2) and (A3) into (A1) the equation for the U_{13} voltage drop across the whole galvanic cell (A4) is:

$$U_{13} = IR_{wire(1)} + IR_{i_{BCZY622}}^{\frac{Pt(1)}{BCZY622}} + IR_{i_{BCZY622}}^{BCZY622} + IR_{i_{BCZY622}}^{\frac{BCZY622}{Pt(2)}} + IR_{Pt(2)} + IR_{i_{YSZ}}^{\frac{Pt(2)}{YSZ}} + IR_{i_{YSZ}}^{YSZ} + IR_{i_{YSZ}}^{\frac{YSZ}{Pt(3)}} + IR_{wire(3)} \quad (A4)$$

The term concerning the voltage drop on BCZY622 due to the flow of the pure diffusion-driven oxygen ionic current $IR_{i_{BCZY622}}^{BCZY622}$ is related to the presence of difference of electrochemical potential of oxygen ions. This difference will be a driving force for steady-state oxygen ions flow through the cell. Assuming that the steady state is reached, and the flow of electrons and protons is blocked by YSZ, the Galvani potential difference on BCZY622 will vanish like proposed by He et al. in [21]:

$$\Delta\varphi = \varphi_{Pt(1)} - \varphi_{Pt(2)} = 0 \quad (A5)$$

where $\varphi_{Pt(1)}$ and $\varphi_{Pt(2)}$ denote the electrostatic Galvani potentials near the Pt(1) and Pt(2) electrodes, respectively. From this moment, we would assume that the electrochemical potential difference of oxygen ions is equal to the chemical potential difference, because $\Delta\varphi = 0$:

$$\Delta\widetilde{\mu}_{O^{2-}} = \Delta\mu_{O^{2-}} \quad (A6)$$

where $\mu_{O^{2-}}$ is the chemical potential of oxygen ions, $\widetilde{\mu}_{O^{2-}}$ means the electrochemical potential of oxygen ions. The chemical potential difference of neutral oxygen $\Delta\mu_O$ consist both the chemical potential difference of oxygen ions as well as a chemical potential of electrons:

$$\Delta\mu_O = \Delta\mu_{O^{2-}} - 2\Delta\mu_e \quad (A7)$$

These quantities can now be written in terms of the measured voltage drop on the BCZY622 sample corresponding to the oxygen ions charge carriers:

$$IR_{i_{BCZY622}}^{BCZY622} = -\frac{1}{2F}\Delta\mu_O(BCZY622) = -\frac{1}{2F}\left(\mu_{O(Pt(2))} - \mu_{O(Pt(1))}\right) \quad (A8)$$

where $\mu_{O(Pt(x))}$ is the chemical potential of neutral oxygen atoms in the close vicinity to the Pt(1) or Pt(2) electrode and F denotes the Faraday constant. Analogically to (A8), the measured voltage drop on the blocking YSZ electrode can be shown as:

$$IR_{i_{YSZ}}^{YSZ} = -\frac{1}{2F}\Delta\mu_O(YSZ) = -\frac{1}{2F}\left(\mu_{O(Pt(2))} - \mu_{O(Pt(3))}\right) \quad (A9)$$

Let us now define the voltage drop across the blocking electrode, U_{23} . This voltage is related to the interface resistances, ionic resistance of YSZ, and the chemical potential difference which occurs across the YSZ. Therefore, U_{23} can be given as:

$$U_{23} = IR_{i_{YSZ}}^{\frac{Pt(2)}{YSZ}} + IR_{i_{YSZ}}^{YSZ} + IR_{i_{YSZ}}^{\frac{YSZ}{Pt(3)}} + \frac{1}{2F}\left(\mu_{O(Pt(3))} - \mu_{O(Pt(2))}\right) \quad (A10)$$

As can be seen, the U_{23} voltage which is measured between the Pt(2) and Pt(3) electrode, will not give us the information about the oxygen ions flow through the system. It is necessary to stress, that polarization resistances on electrodes and metal/mixed conducting ceramics interfaces have a large contribution to the total resistance. Moreover, since U_{12} diminishes in steady-state conditions, it cannot be used to calculate the partial oxygen ionic conductivity of BCZY622, either. That is why, we introduced an additional, not connected to the current source, Pt(ref) reference electrode in the analyzed system. The usage of this additional reference electrode allows measuring the Nernst thermodynamic voltage across the blocking electrode and allows for direct measurement of BCZY622 oxygen ionic conductivity. As shown in Figure 1a, the voltage measured between the reference Pt(ref) and the internal Pt(2) electrode is marked as U_{2V} . Therefore, U_{2V} can be written as:

$$U_{2V} = IR_{i_{YSZ}^{Pt(2)}} + IR_{i_{YSZ}^{Pt(ref)}} + \frac{1}{2F} \left(\mu_{O(Pt(ref))} - \mu_{O(Pt(2))} \right) \quad (A11)$$

Assuming the negligibility of $IR_{i_{YSZ}^{Pt(ref)}}$ and $IR_{i_{YSZ}^{Pt(2)}}$ in comparison to the third term of (A11), the U_{2V} voltage measured between the Pt(ref) and Pt(2) electrodes includes only the difference of the chemical potentials of oxygen:

$$U_{2V} = \frac{1}{2F} \left(\mu_{O(Pt(ref))} - \mu_{O(Pt(2))} \right) \quad (A12)$$

Noting the symmetry of the system (see the scheme in Figure 1): $\mu_{O(Pt(1))} = \mu_{O(Pt(ref))}$, the chemical potential of the Pt(ref) electrode can be replaced with the value of this related to Pt(1). Then:

$$U_{2V} \approx \frac{1}{2F} \left(\mu_{O(Pt(1))} - \mu_{O(Pt(2))} \right) = IR_{i_{BCZY}} \quad (A13)$$

Summing up, it can be seen that the measurement of the voltage U_{2V} between the Pt(2) and Pt(ref) reference electrode allows determining the partial oxygen ionic resistance of BCZY622 and the transport of oxide ions through sample under steady-state condition is concentration driven. Finally, the conductivity of BCZY622 can be calculated using $R_{i_{BCZY}}$ and the Ohm's law:

$$R_{i_{BCZY622}} = \frac{U_{2V}}{I} = \frac{I \cdot L}{\sigma_{O_{BCZY622}} \cdot S} \quad (A14)$$

$$\sigma_{O_{BCZY622}} = \frac{I \cdot L}{U_{2V} \cdot S} \quad (A15)$$

where L is the length of BCZY622 sample, S denotes the surface area of the Pt(1) platinum reversible electrodes.

[49] Y. Nigara, K. Yashiro, T. Kawada and J. Mizusaki, Hydrogen permeability in $(\text{CeO}_2)_{0.9}(\text{GdO}_{1.5})_{0.1}$ at high temperatures, *Solid State Ionics*, 2003, **159**, 135–141, DOI: 10.1016/S0167-2738(02)00919-0.