UNIVERSITÀ
DEGLI STUDI
DI TRIESTE

Dipartimento di
Ingegneria
e Architettura

WATER ELECTROLYSIS AND ELECTROLYSER TECHNOLOGIES

- PART 3 -

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A.A. 2023-2024

OUTLINE

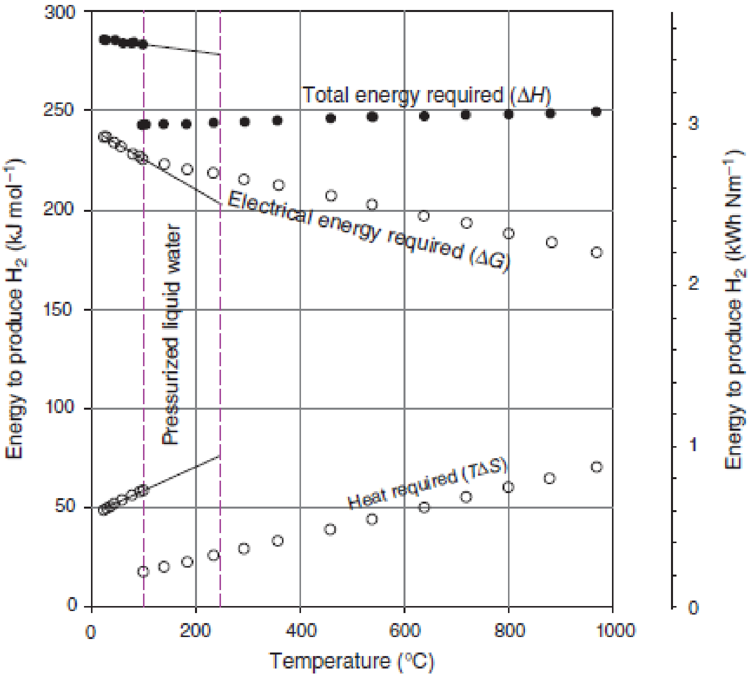
1. Solid-state Electrochemistry
2. Solid Oxide Water Electrolysers

OUTLINE

Reference	Paragraph/Pages
Hydrogen production by electrolysis, Agata Godula-Jopek, 2015 Wiley	Ch. 6

1. SOLID-STATE ELECTROCHEMISTRY

SOLID-STATE ELECTROCHEMISTRY FOR HIGH TEMPERATURE WATER ELECTROLYSIS



This technology started to be studied form the 1980s, about a decade afterward solid oxide fuel cells were developed (1970s).

When water electrolysis is carried out at higher temperatures, heat is contributing to increase the efficiency of the process and the dissociation of steam requires less energy compared to liquid water.

In HT electrolysis:

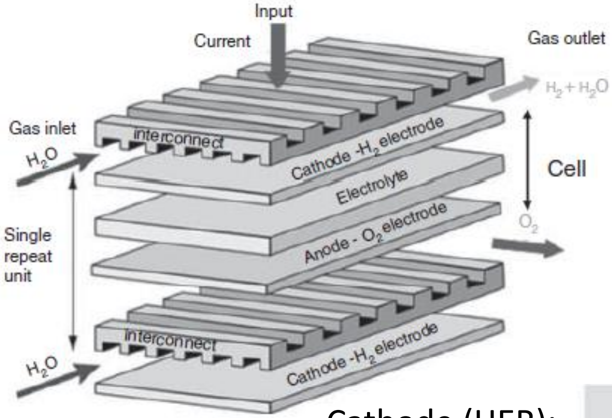
$$2H_2O_{(g)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

Nonetheless, material limitations impose a upper limit set in between 700 ÷ 1000 °C at which such a process can be performed.

SOLID-STATE ELECTROCHEMISTRY AND SOLID OXIDE WATER ELECTROLYSERS

In order to sustain the high operating temperatures, the electrochemical cell is here composed by ceramic materials.

Deriving from the architecture used in high temperature solid oxide fuel cells, the EC cell is divided in three functional layers only: a dense electrolyte and two porous electrodes (cathode and anode, where hydrogen and oxygen are respectively produced) placed on both sides of the electrolyte, and surrounded by the bipolar plates.



Cathode (HER):

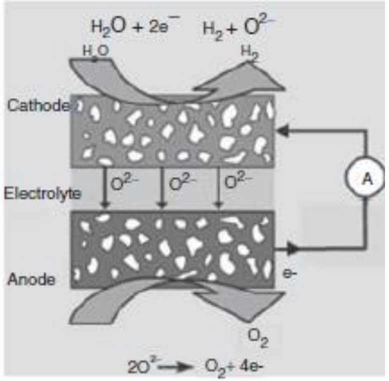
$$2H_2O + 4e^- \rightarrow 2H_2 + 2O^{2-}$$

Anode (OER)

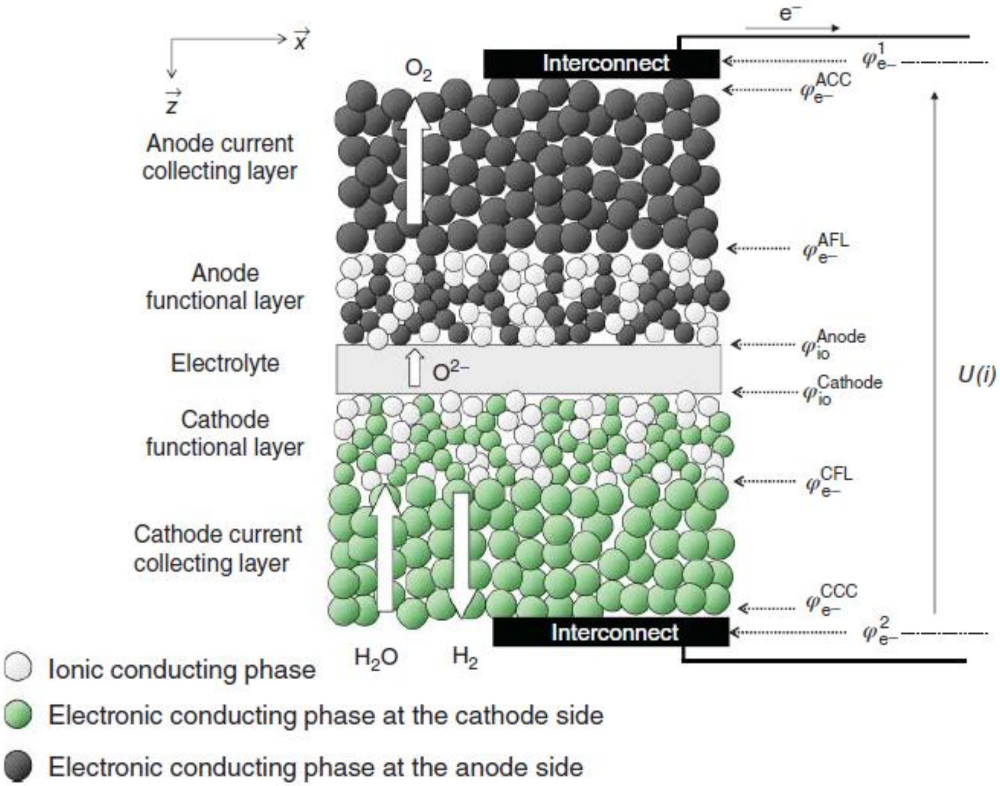
$$2O^{2-} \rightarrow O_2 + 4e^-$$

Total:

$$2H_2O \rightarrow 2H_2 + O_2$$



CHARGE TRANSPORT



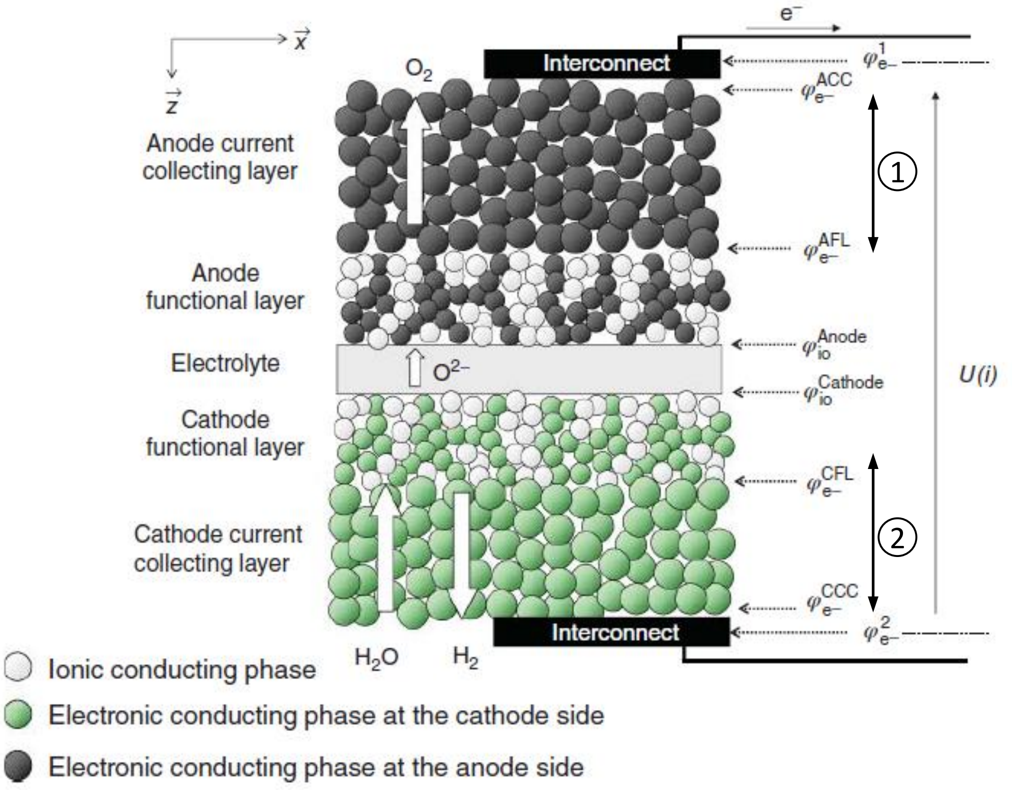
As for other electrolysis technologies, a difference of potential is needed to start the water splitting reaction.

At the sides of the electrochemical cell, the difference of potential

$$V = \varphi^1_{e^-} - \varphi^2_{e^-}$$

Can be recorded. Such a difference of potential can be here divided along the cell cross-section to evaluate all of the phenomena contributing to the evolution of its polarization curve.

CHARGE TRANSPORT



The electrical current flowing across the WE needs to reach the functional layers to sustain the redox reactions. In this extent, the current collecting layers need to be crossed. Such layers are characterized by an effective electrical resistance ($R_{e,xC}$) which can be easily expressed in terms of the Ohm's Law:

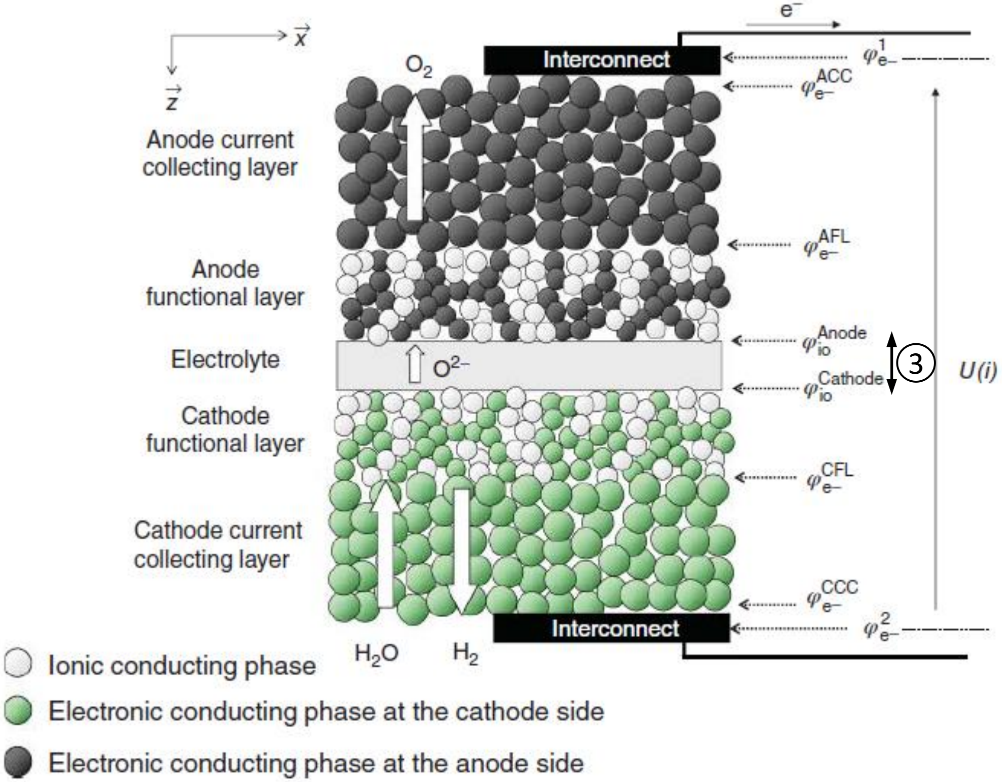
① $$\varphi_{AC(e^-)} - \varphi_{AF(e^-)} = |i| \cdot R_{e,AC}$$

② $$\varphi_{CC(e^-)} - \varphi_{CF(e^-)} = |i| \cdot R_{e,CC}$$

Where: $$R_{e,xC} = \frac{t_x}{\sigma_{e,xC(e^-)}}$$

is related to the ratio among layer thickness (t_x) over its effective conductivity.

CHARGE TRANSPORT



An analogous resistance can be thus used to account for the oxygen transport across the electrolyte:

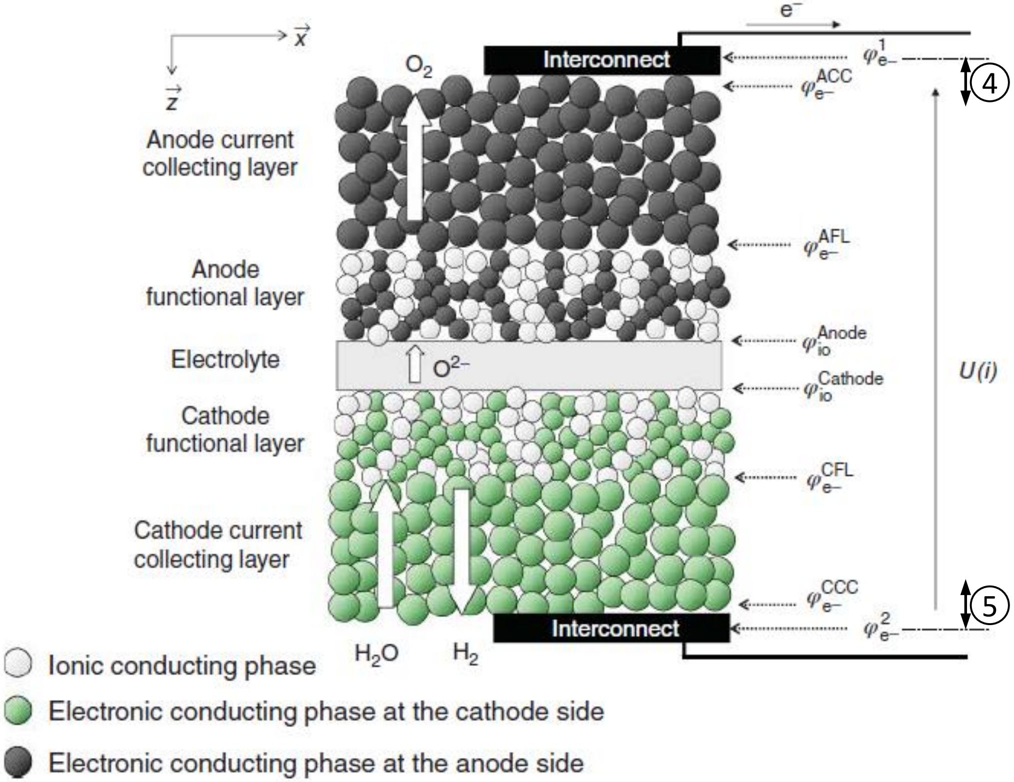
$$③ \qquad \varphi_{A,(O^{2-})} - \varphi_{C,(O^{2-})} = |i| \cdot R_{el}$$

Where the effective electrolyte resistance:

$$R_{el} = \frac{t_{el}}{\sigma_{(O^{2-})}}$$

is given by the ratio among electrolyte thickness and its bulk ionic conductivity.

CHARGE TRANSPORT



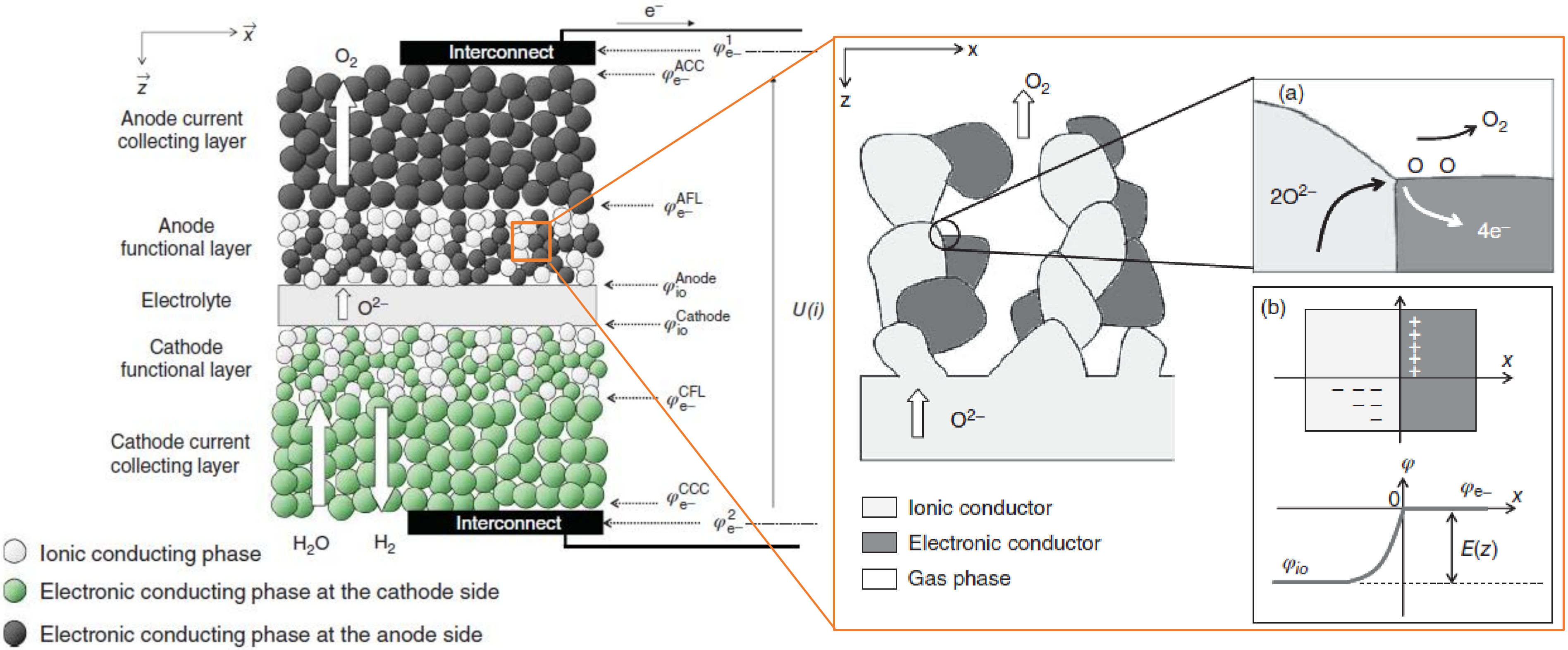
In addition to charge transport resistances, also the effects of contact resistances can be considered via the Ohm’s Law:

④ $$\varphi_{1(e^-)} - \varphi_{AC(e^-)} = |i| \cdot R_{C,A}$$

⑤ $$\varphi_{CC(e^-)} - \varphi_{2(e^-)} = |i| \cdot R_{C,C}$$

Where the contact resistances ($R_{C,x}$) are caused by the non-perfect electrical contact at the electrode-interconnection interface.

CHARGE TRANSFER

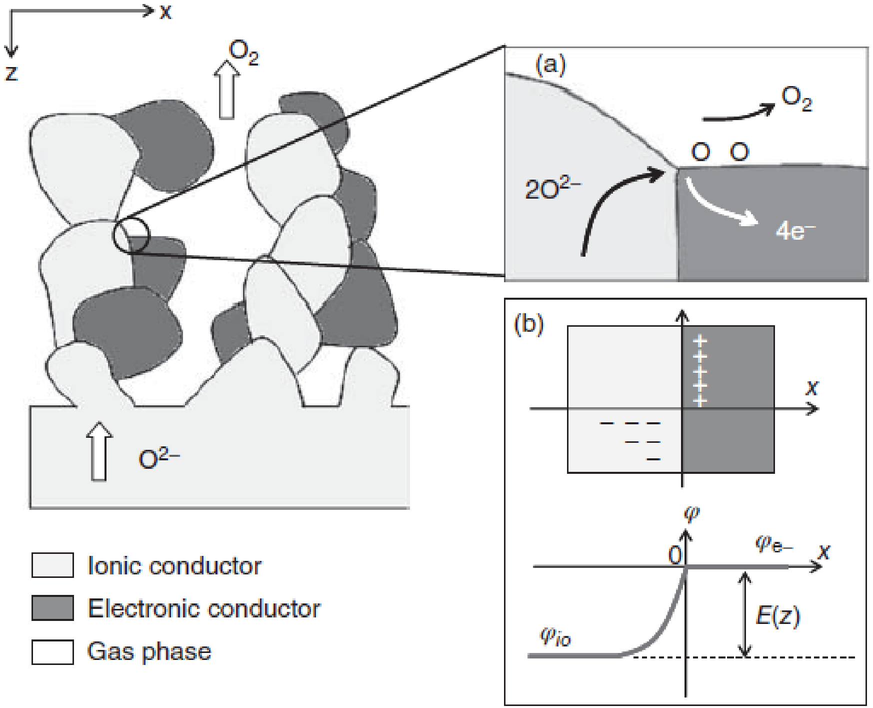


CHARGE TRANSFER

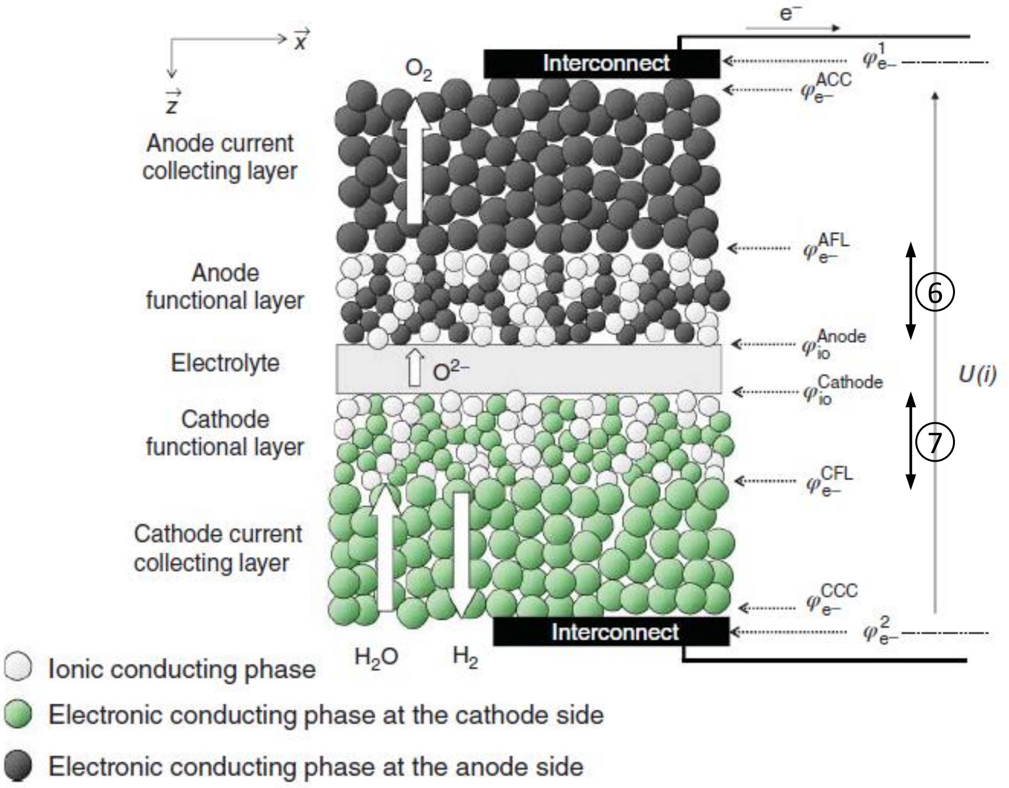
More in depth, the excess of charge on each side of the metal-electrolyte interface gives rise to an electrical potential forming between the electronic and the ionic conductors

This difference in potential corresponds in solid-state electrochemistry to the well-known (Helmholtz) double layer, which allows to define the local electrode potential E as:

$$E(x,z) = \varphi_{e^-}(x,z) - \varphi_{O^{2-}}(x,z)$$



CHARGE TRANSFER



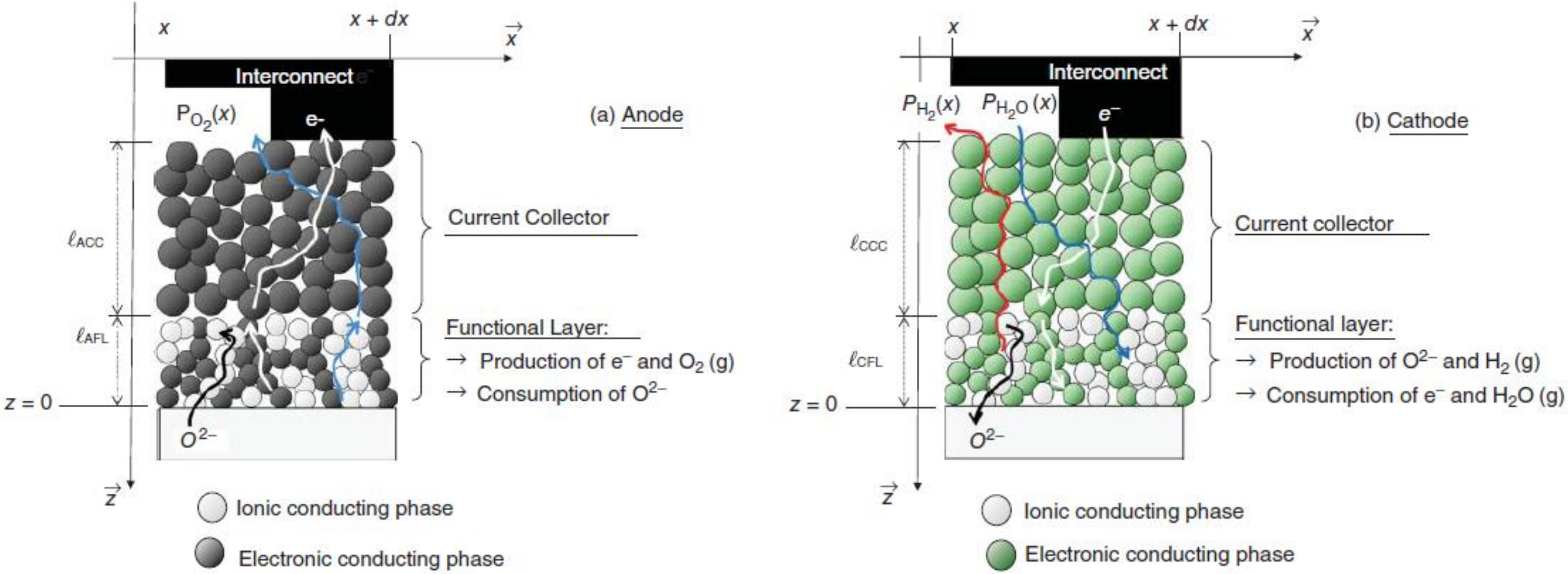
The electrochemical reactions locally absorb or generate charges and gas species that modify the electronic, ionic and gas fluxes. This phenomenon leads to a steep evolution of the local electrode potential all along the thickness of the active layer. Thus, the resulting potential for the cell electrodes can be defined as the difference of electronic and ionic potentials taken at the triple boundary length, which can be expressed as the difference of potential across the functional layers:

6 $$\varphi_{AF(e^-)} - \varphi_{A,(O^{2-})} = E_A^0$$

7 $$\varphi_{C,(O^{2-})} - \varphi_{CF(e^-)} = E_C^0$$

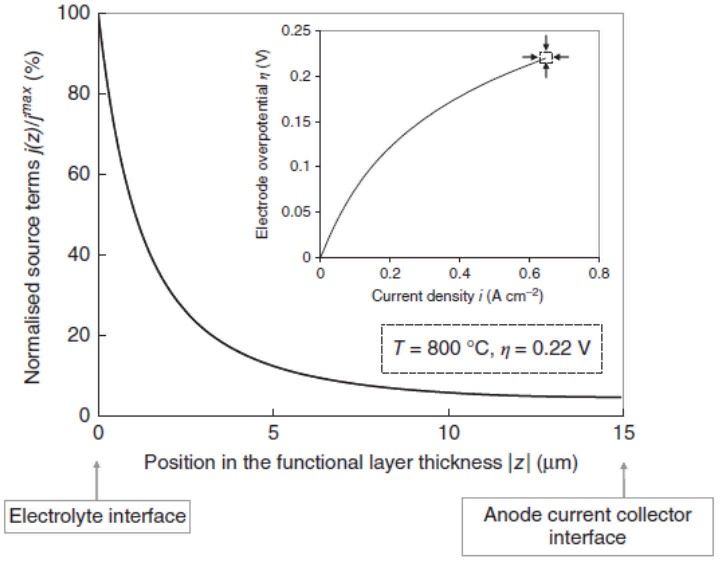
CHARGE TRANSFER

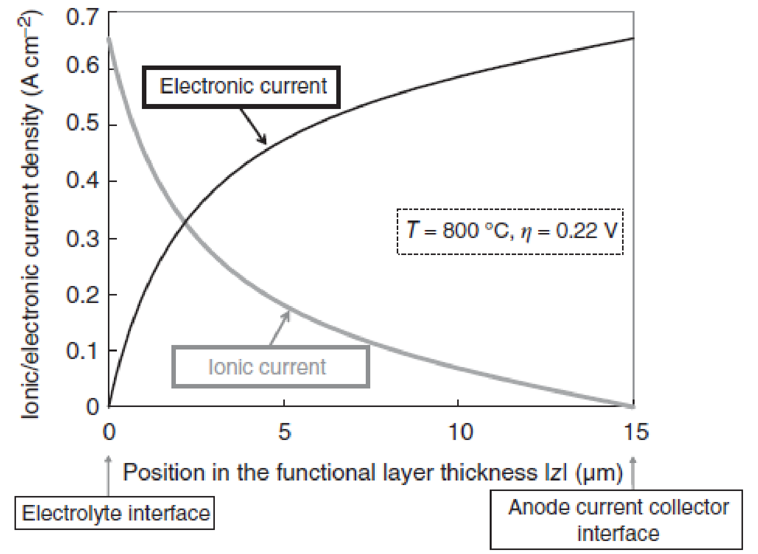
The importance of optimizing charge transport is due to the need of maximizing production and consumption rates at the anode and cathode, respectively.



CHARGE TRANSFER

Also in this case, the low mobility of oxygen anions limits the efficiency of the whole process limiting the occurrence of the reaction within the range of 5 to 40 μm of distance from the interface among the electrolyte and the functional layer. The extension of the active zone, depends on material conductivities, electrode microstructure properties, and temperatures.





STANDARD POTENTIAL OF FORMATION AND GIBBS FREE ENERGY VARIATION

Summarizing, by referring to an ideal gas behaviour and atmospheric pressure conditions (where reaction activities can be approximated by partial pressure values), the reversible potentials of the electrodes can be expressed as:

$$E_A = E_A^0(T) + \frac{RT}{4F}\ln p_{O_2} \qquad E_C = E_C^0(T) + \frac{RT}{2F}\ln \frac{p_{H_2}}{p_{H_2O}}$$

And the so-called cell reversible voltage can be expressed as the sum among the OCV and a cell polarization due to gas conversion:

$$V_{rev} = V_{OCV} + \Delta V_{rev}$$

$$V_{rev} = E_A^0(T) - E_C^0(T) + \frac{RT}{4F}\ln\frac{p_{O_2}}{p_{O_{2OCV}}} - \frac{RT}{2F}\ln\frac{p_{H_{2OCV}}\cdot p_{H_2O}}{p_{H_2}\cdot p_{H_2O_{OCV}}}$$

$$V_{rev} = \frac{-\Delta G^0(T)}{nF} + \Delta V$$

Where p_x is the gas partial pressure in the channel at the interconnection with the current collector layers.

REVERSIBLE POTENTIAL AND LIMITATION BY GAS CONVERSION

The term related to the variation of the open circuit voltage in function of the specimen partial pressure can be defined as variation of the cell voltage ΔV. With the occurrence of redox reactions, gases partial pressures vary according to the reaction rates. In particular:

$$\Delta V_A = \frac{RT}{4F}\ln\frac{p_{O_2}}{p_{O_{2}\_OCV}} \qquad \Delta V_C = \frac{RT}{4F}\ln\frac{p_{H_{2}\_OCV}\cdot p_{H_2O}}{p_{H_2}\cdot p_{H_2O\_OCV}}$$

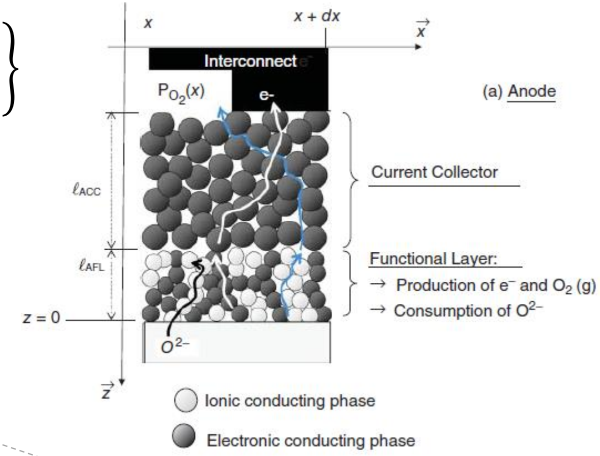
Where p_x is the effective partial pressure at the channel and p_{x_OCV} the partial pressure at open circuit voltage (that is with no current flowing in the WE).

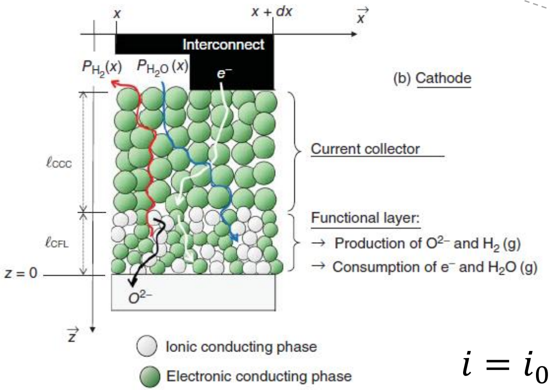
At very high steam conversion rate, water partial pressure becomes negligible, and the variation of voltage result bounded at an asymptotic limit, in correspondence than the current density limiting current.

PARTIAL PRESSURE EFFECTS

Gases partial pressure at the reaction sites (p*) modulate the efficiency of the device as perfectos in the Butler-Volmer equations expressed in their generalized form ($\eta_A > 0, \eta_C < 0, i < 0$):

$$i = i_{0,A}\left\{\left(\frac{p^*_{O_2}}{p_{O_2}}\right)^{1/2} e^{\frac{-(1-\alpha_A)\,2F\,\eta_A}{RT}} - e^{\frac{\alpha_A 2F\,\eta_A}{RT}}\right\}$$





$$i = i_{0,C}\left\{\left(\frac{p^*_{H_2}}{p_{H_2}}\right)^{1/2} e^{\frac{(1-\alpha_C)\,2F\eta_C}{RT}} - \left(\frac{p^*_{H_2O}}{p_{H_2O}}\right) e^{\frac{\alpha_C 2F\eta_C}{RT}}\right\}$$

ELECTRODE OVERPOTENTIALS

As previously discussed, also here electrode overpotential is given by as a sum of activation and concentration overpotentials:

$$\eta_x = \eta_{act,x} + \eta_{conc,x}$$

Activation overpotentials

Occurring within the functional layer, they are due to the kinetic rates of reaction. Being the redox reactions here evolving in several steps, each of them characterized by its own reaction rate. Activation overpotentials can be quantified by means of the Butler-Volmer equations with symmetrical factors equal to 0.5:

$$i = i'_{0,A}\left\{e^{\frac{-F}{RT}\eta_{act,A}} - e^{\frac{F}{RT}\eta_{act,A}}\right\} \qquad i = i'_{0,C}\left\{e^{\frac{F}{RT}\eta_{act,C}} - e^{\frac{-F}{RT}\eta_{act,C}}\right\}$$

Here the apparent exchange current densities ($i'_{0,x}$) are tuned in order to take into account for the electrode microstructure, and operating conditions.

ELECTRODE OVERPOTENTIALS: CONCENTRATION OVERPOTENTIAL

Concentration overpotentials

- Related to electrode morphology, which can oppose resistance to the gas diffusion,
- as gas transport across the electrode is being limited, partial pressure gradients from across the electrodes (strongly dependent on the microstructural properties of porous electrodes)
- and polarization losses due to an insufficient supplying of gases at the electrodes are induced.

They can be evaluated with a simplified version of the Butler-Volmer equations, considering that, for $i \gg 0, \eta \rightarrow \eta_{conc}$. Moreover, at high temperatures, the evolution of redox reactions can be considered fast (that is: $i \ll i_0$). Then the Butler-Volmer equations can be simplified to express the concentration overpotentials as:

$$\eta_{conc,A} = \frac{RT}{4F} \ln \frac{p^*_{O_2}}{p_{O_2}} \qquad \eta_{conc,C} = \frac{RT}{4F} \ln \frac{p_{H_2} \cdot p^*_{H_2O}}{p^*_{H_2} \cdot p_{H_2}}$$

POLARIZATION CURVE

Summarizing, the potential forming across a solid oxide water electrolysing cell can be expressed as:

$$V = V_{rev} + \eta_{ohmic} + \eta_{act,A} + \eta_{conc,A} - \eta_{act,C} - \eta_{conc,C}$$

Where the reversible voltage can be decomposed in the sum of OCV and the variation of the reversible potential due to gas conversion losses:

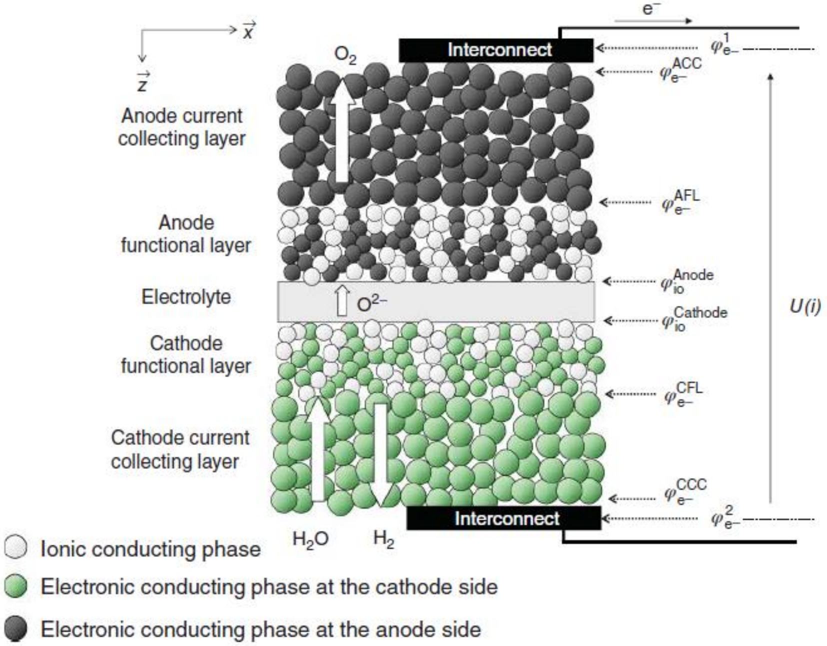
$$V_{rev} = V_{OCV} + \Delta V_{rev}^{A} + \Delta V_{rev}^{C}$$

Where

$$\eta_{ohmic} = i\left(R_{el} + R_{e,AC} + R_{e,CC} + R_{CA} + R_{CC}\right)$$

When moving from single cell to stacks the contact resistance of the electrode/interconnect junction depends on many parameters, and might be needed to be included.

ELECTRODE IRREVERSIBLE OVERPOTENTIALS



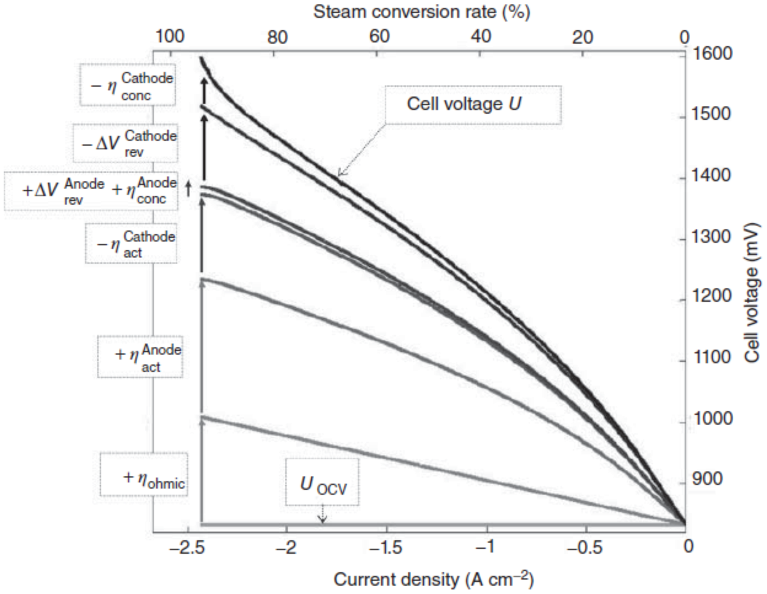


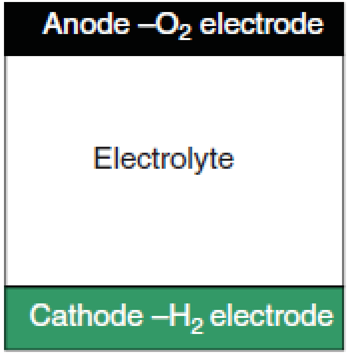
Figure 6.6 Decomposition of a typical polarization curve for cathode-supported cell (Ni–8YSZ//8YSZ//LSM–8YSZ, $T = 800\,°C$, $R_c = 5 \times 10^{-2}\ \Omega\ cm^2$, air feeding at the anode side, composition of the inlet cathodic gas: 90% $H_2O + 10\%\ H_2$, electrode microstructural properties are given in Ref [9], $\ell^{support}_{cathode} = 1\ mm$, $\ell_{electrolyte} = 10\ \mu m$, $\ell_{anode} = 40\ \mu m$). Numerical decomposition calculated by using the model presented in Ref [17].

2. SOLID OXIDE WATER ELECTROLYSERS

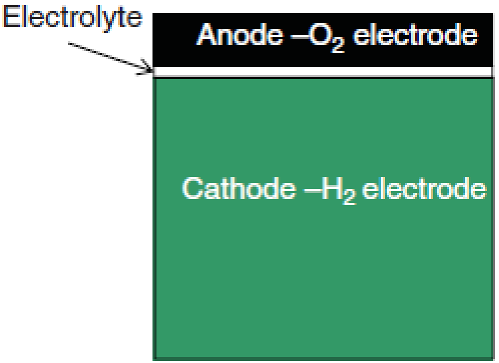
SOLID OXIDE TECHNOLOGY: ARCHITECTURES

Architecture of solid oxide electrochemical evolved over time. Historically three different architectures were developed:

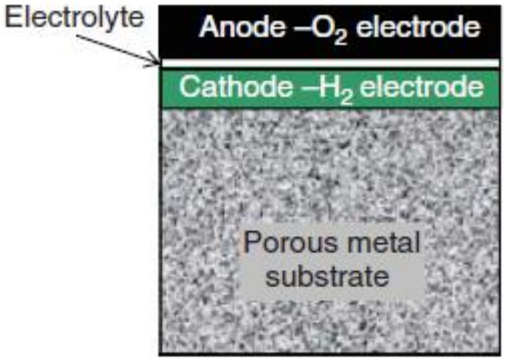
Electrolyte-supported cell



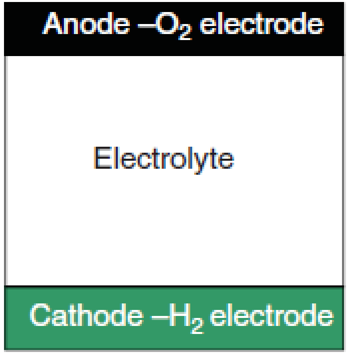
Electrode-supported cell



Metal-supported cell



SOLID OXIDE TECHNOLOGY: ARCHITECTURES



Electrolyte-supported cell

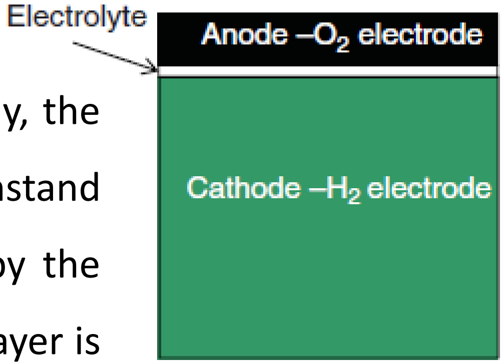
A thick electrolyte layer (100 ÷ 200 µm) is mechanically supporting the catalyst layers (≈50 µm), which are deposited at the electrolyte sides.

In this architecture Zirconia (ZrO_2) is used as electrolytic material.

Operating temperatures must range between 850 ÷ 1000°C in order to guarantee enough ionic conductivity to the cell. Materials used need to be thermally stable.

Expensive materials and/or materials which are difficult to manufacture need to be used as electrodes (in example: $LaCrO_3$, Ni- or Cr-based alloys, such as Ducralloy®, special ferritic stainless steels), as well there are needed to interconnects single cells within a stack.

SOLID OXIDE TECHNOLOGY: ARCHITECTURES

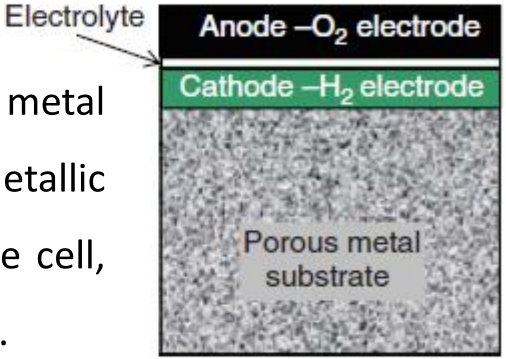


Electrode-supported cell

Developed to reduce the thickness of the electrolyte layer, and consequently, the electrolyte resistivity. Here the electrolyte is 5 ÷ 20 µm thick, but it can withstand temperatures in the range 700 ÷ 800°C. Mechanical support is provided by the cathode electrode, which is designed to be 0.2 ÷ 1.5 mm thick (but catalyst layer is only few tens of µm thick).

By lowering electrolyte thickness, its ohmic resistance decreases, higher current densities could be obtained, the operating temperature range can be lowered and cheaper stainless steels could be used to produce and interconnect cells and stacks. Reduction of operating temperature aiming at further lifetime improvement and a decrease in cost.

SOLID OXIDE TECHNOLOGY: ARCHITECTURES



Metal-supported cell

Most recently, a third architecture has been introduced, the so-called metal supported cell was introduced. Here, an electrochemically inactive metallic support (about 1 mm thick) is used to host the ceramic components of the cell, which are deposited onto it, as thin layers (thickness: up to some tens of µm).

Potentially they can overcome most of the limitations characterizing the previous architectures, allowing to use cheap materials in lower amounts, they can operate at medium-to-low temperatures (around 650 °C), and having a significant lower degradation rate (compared to state-of-the-art Ni-YSZ electrode-supported cells). Nonetheless, long-term operation and effects due to different thermal expansion of metallic and ceramic materials still need to be investigated.

SOWE – THE ELECTROLYTE

Usually made by yttria-stabilized zirconia oxide, YSZ (ZrO_2 with 8 mol% of Y_2O_3), which is satisfying the requirements of a optimal electrolyte for HT electrolysis:

- Good ionic conductivity between 700 and 900 °C (10^{-2} S cm^{-1} at operating temperature)
- Adequate gas-tightness (with a density >95%, it has zero open porosity)
- A thermal expansion coefficient close to the expansion coefficient of the electrodes (to limit mechanical stresses)
- Chemically inert with respect to the electrode materials and stable in both oxidizing and reducing environments

Properties of the ceramic electrolyte can be slightly tuned by changing the dopant specimen type and concentration, and according to the temperature of operation. In example, due to the lower operating temperature a standard for metal supported architecture is represented by the Gallium-doped-Ceria oxide, which cannot be used above 600°C to avoid electrolyte corrosion.

SOWE – THE ELECTRODES

They should be characterized by:

- High electronic conductivity at high temperature
- A slight degree of ionic conductivity would be preferred, in order to limit ohmic losses and delocalize the electrochemical reaction across the bulk of the electrode.
- High porosity to allow steam diffusion, but equally allow hydrogen removal at the cathode and oxygen removal at the anode
- Porosity should be tuned in order to avoid local overpressures, which would tend to delaminate the constituent layers of the electrodes
- Intermediate layers should be added to adjust the lattice mismatch with the electrolyte when needed.

SOWE – THE ELECTRODES

Cathode

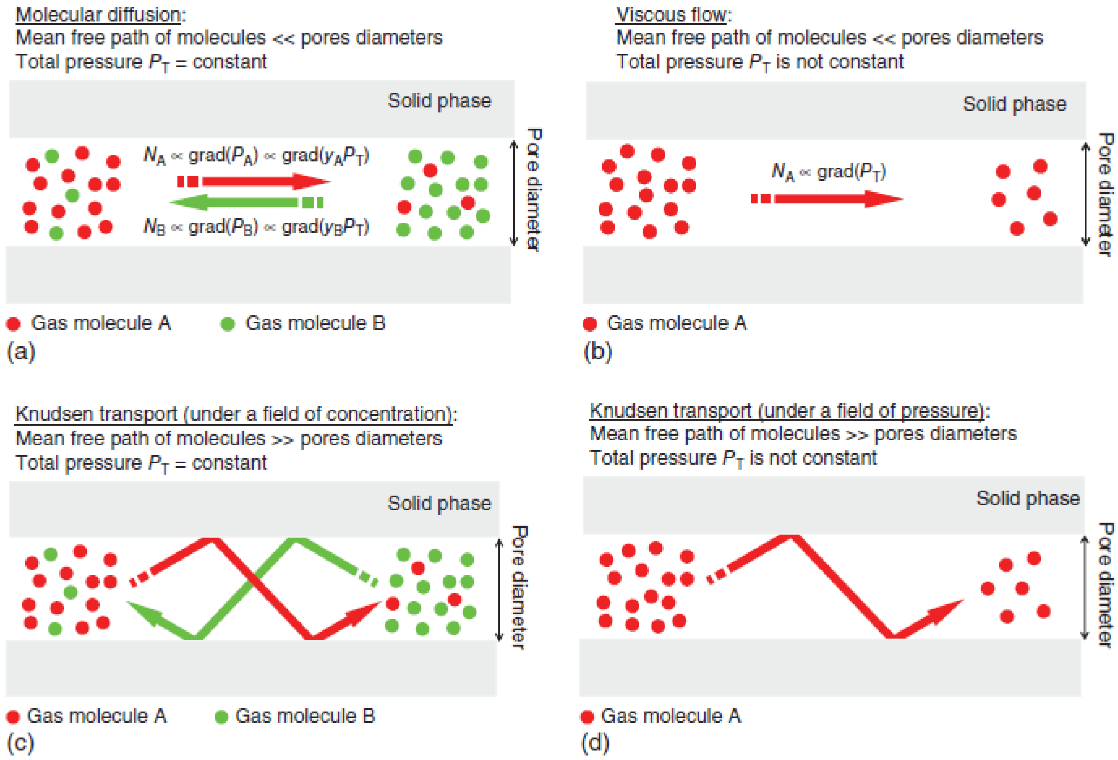
It should be additionally stable in a reducing environment, and catalyze the water splitting. It is usually composed by the composite Ni/YSZ a cermet (a composite material made by a ceramic and a metal), being Ni an effective electrocatalyst for the HER. Other solutions (such as Ni/gadolinia-doped ceria, or Ni/samaria-doped ceria in example) are currently studied in order to reduce the operating temperature.

Anode

It should be additionally stable in oxidative environment and catalyze the oxidation of oxygen anions. Here, ceramic compounds based on an ABO_3 structure are used. Such compounds can be in some cases mixed with YSZ to increase their charge transport properties, as contact resistances for this electrode is bigger than for cathode.

SOWE – GAS TRANSPORT IN THE ELECTRODES

In porous electrodes, reactant and product mass transport takes place according to three possible phenomena, according to the operating conditions and electrode morphology



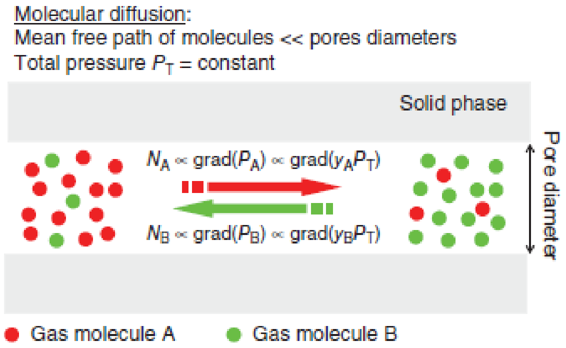
SOWE – GAS TRANSPORT IN THE ELECTRODES

Diffusion

It develops in presence of a gradient of concentration, it is related to thermal motion of gas (it is thus controlled by the collision frequency between the molecules), and is proportional to the gas diffusivity in molecular form (for a system of two molecules):

$$N_A = -\frac{D_{A,B}}{RT}\nabla(P_A) = \frac{D_{A,B}}{RT}\nabla(P_B) = -N_B$$

It is predominant for microstructures presenting large pores, and makes negligible the evaluation of the interaction of gas species with the pore walls is negligible.



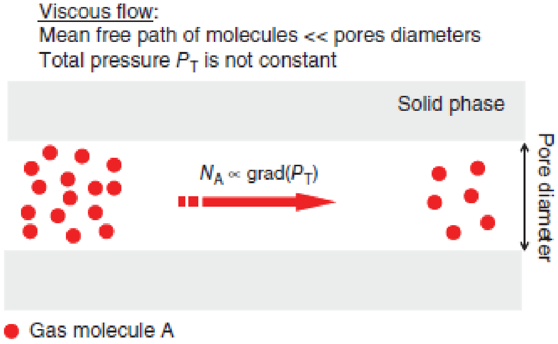
SOWE – GAS TRANSPORT IN THE ELECTRODES

Convection

It develops in presence of a gradient of total pressure arising across the electrode. Modelled by means of the Darcy's law:

$$N_A = -\frac{B_0 P_T}{\mu RT} \nabla(P_T)$$

And is related to the gas dynamic viscosity μ (in Pa s) and a permeability coefficient B_0, which depend on electrode microstructure. Usually negligible with respect diffusion



SOWE – GAS TRANSPORT IN THE ELECTRODES

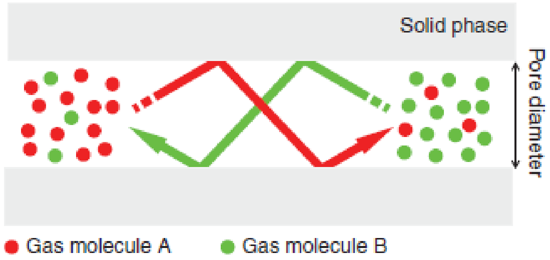
Knudsen regime

It develops when the mean pore diameter D_P is smaller than the mean free path of molecules λ. Molecules do not interact anymore among themselves and gas flux is exclusively governed by the collision of gas species with the wall of the porous medium. There is no fundamental distinction between viscous flow and diffusion, and the molar flux can be driven either by a gradient of concentration or pressure. In both cases, fluxes are described through a single effective 'Knudsen' coefficient

$$N_A = -\frac{D_{k,A}}{RT}\nabla(P_A) \qquad\qquad N_A = -\frac{D_{k,A}}{RT}\nabla(P_T)$$

The balance among 'regular' diffusion and the establishment of the Knudsen regime depends on electrode microstructure.

Knudsen transport (under a field of concentration):
Mean free path of molecules >> pores diameters
Total pressure P_T = constant



Knudsen transport (under a field of pressure):
Mean free path of molecules >> pores diameters
Total pressure P_T is not constant

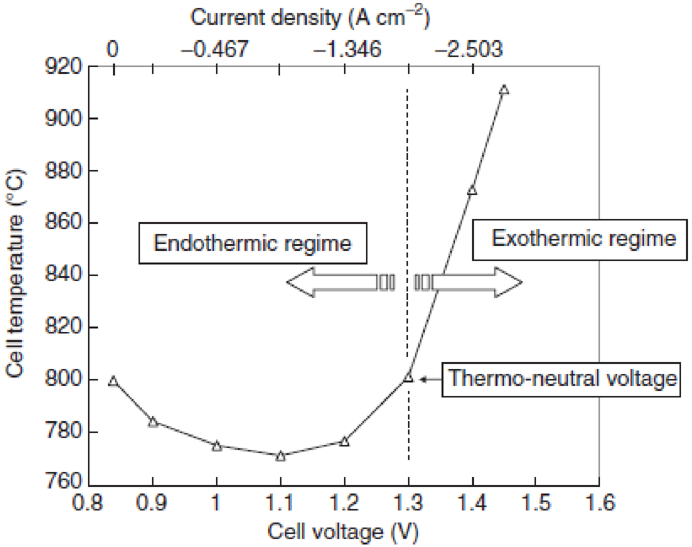
SOWE – STACKING

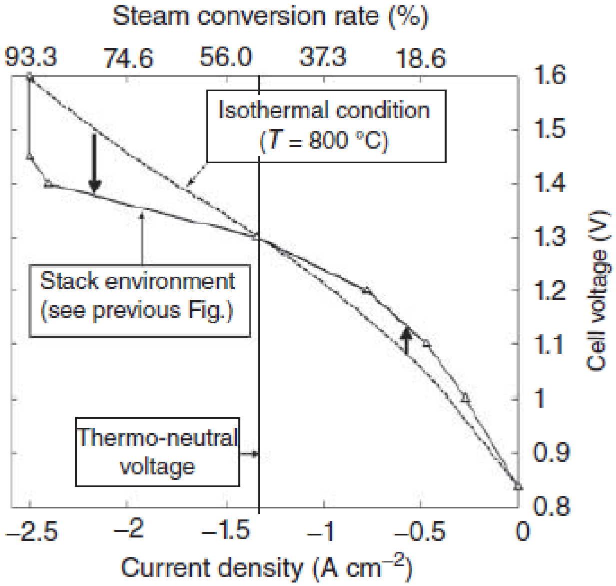
Stacking is not as straightforward as for in the other technologies.

- In mechanical terms, the challenge is to preclude any rupture of the ceramic cells, selecting material exhibiting comparable thermal expansion characteristics not releasing emitting compounds detrimental to electrodes. Research is still operating in this point, evaluating different formulation of metal alloys and exploring the possibility to develop coatings.
- Gas tightness must be guaranteed: glass and glass–ceramic sealants are the most used solutions. They exhibit strong bonding to the interface; their adherence to the cell provides hermetic sealing, they can show self-healing features and their fabrication is easy to control.

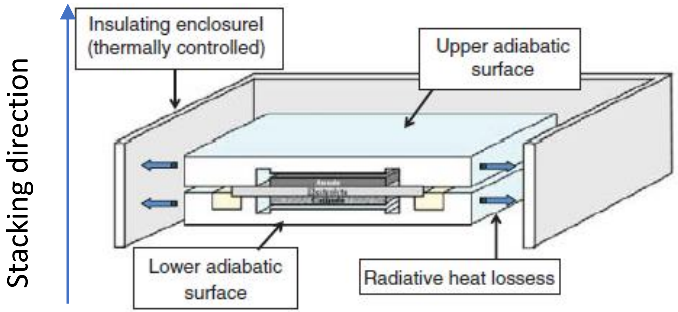
SOWE – STACKING AND THERMAL MANAGEMENT

SOWE systems operate among two thermal regimes: endothermic, below the thermo-neutral voltage, and exothermic, above it (in example: 1.23 V at 800°C).





SOWE – STACKING AND THERMAL MANAGEMENT



In a stack, the heat flux can be considered negligible in the staking direction and adiabatic conditions can be assumed on the surfaces connecting two adjacent elementary units.

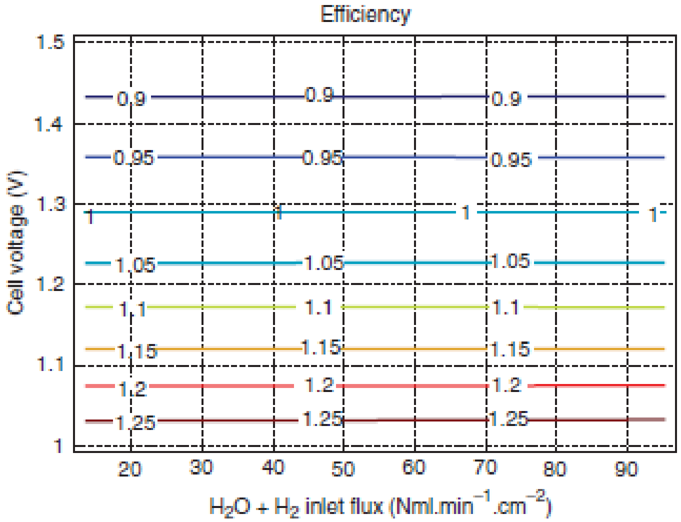
Thermal boundary conditions are given by the temperature of gases introduced in the electrolyser and by the temperature considered for the stack-insulating enclosure. Thus:

- heat can be exhausted (or brought) by the anodic and cathodic gas flow. This corresponds to the convective heat transfers that take place all along the gas channel distribution
- heat can also be transferred by the radiative heat exchanges between the edge of the electrolyser (i.e. free surface defined by the outline of the stack) and the wall of the stack-insulating enclosure (preferred due to high temperature reached)

SOWE – OPERATION

From the analysis of the temperature profile in the central cell of a SOWE stack it can be noticed as operating in proximity of the thermo-neutral voltage is convenient at most. Here in fact:

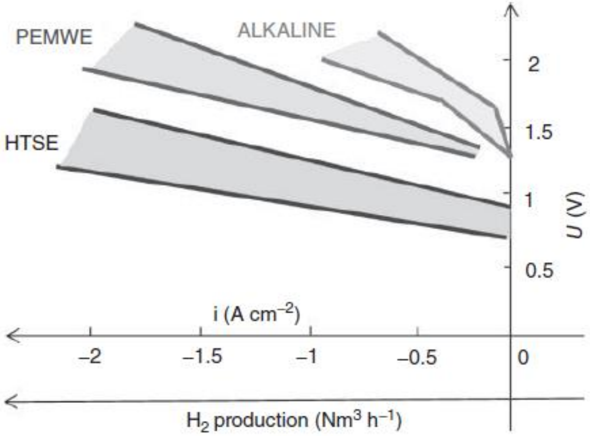
- Satisfying efficiency is reached (about 96%, which decreases to 89% if the system components are included)
- High temperature formation is avoided
- Thermal management is easier
- Degradation is minimized

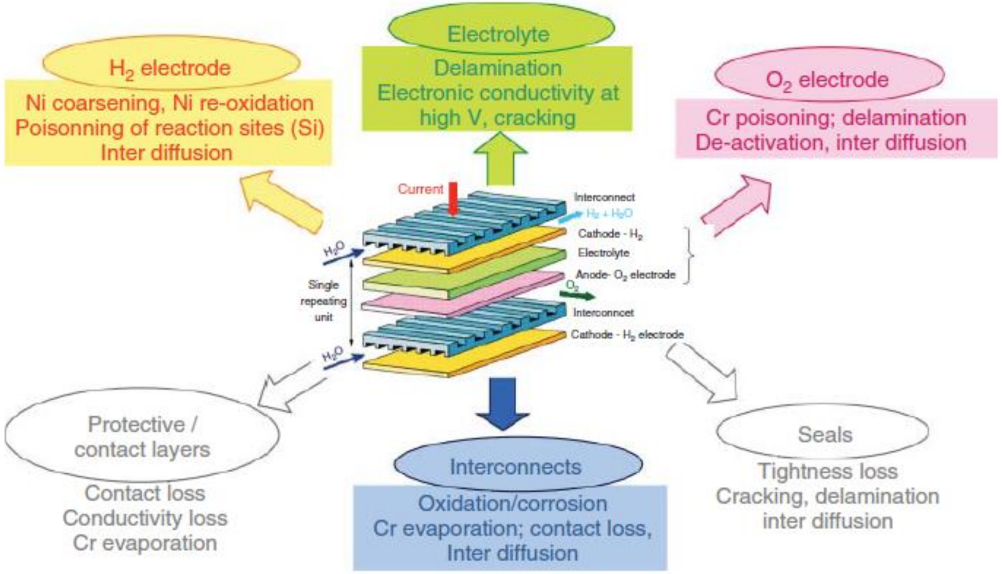


SOWE – PERFORMANCES, DURABILITY, AND DEGRADATION

While HT water electrolysis show the best performances in terms of efficiency, durability is still limited to few thousand hours.

Durability is limited by chemical, physical-chemical or electrochemical phenomena that are thermally activated.





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