DEVELOPMENT OF MATHEMATICAL TRANSFER FUNCTIONS FOR AST DESIGN

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OUTLINES

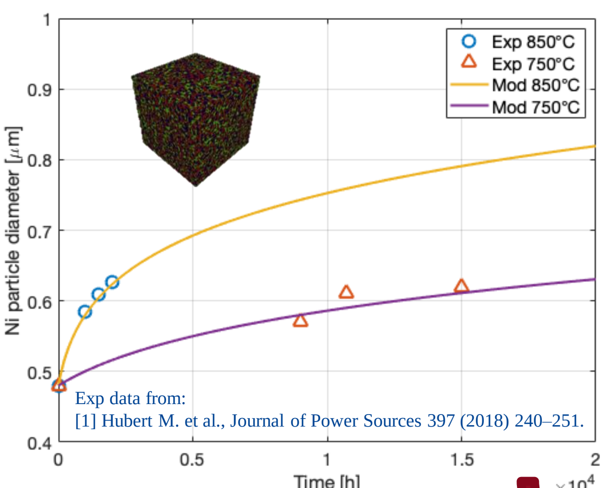
- Context and objectives
- Modelling framework
- Model validation and simulation results
- Transfer function design procedure
- Example of transfer function application
- Conclusions and future works

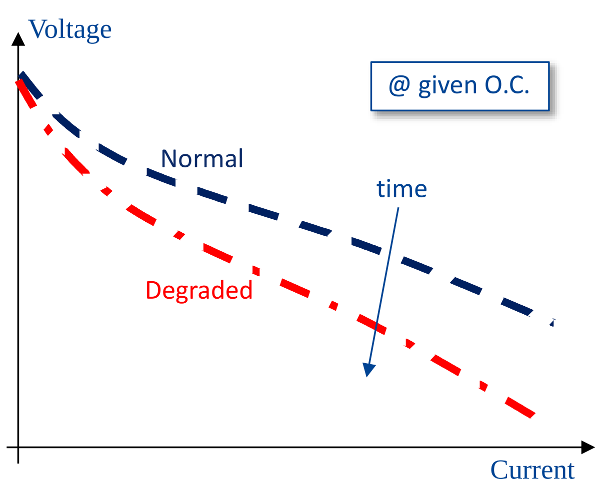
CONTEXT & OBJECTIVES

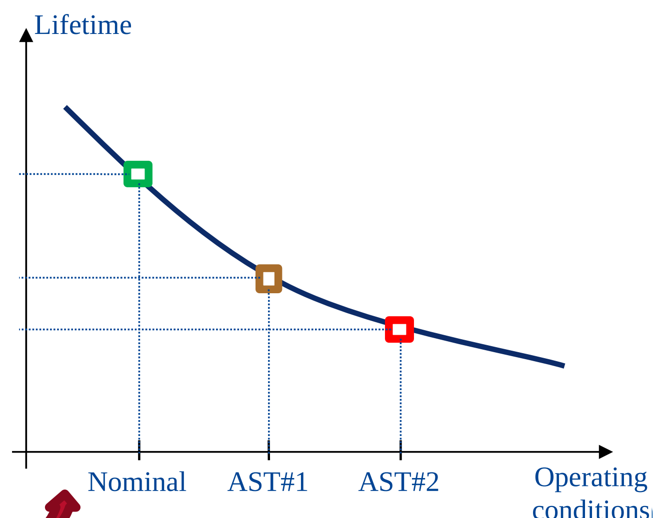
This work settles within the project **AD ASTRA**, which aims at "*the development of **Accelerated Stress Test protocols** that allow quantitative identification and **prediction of critical degradation mechanisms**, correlating them with **overall performance variables** in selected solid oxide fuel cell/electrolyser (SOFC/SOEC, or SOC) stack components (fuel electrode, oxygen electrode and interconnect).*"

OBJECTIVES

1. Identify and model the **most relevant physical parameters** affected by a specific degradation mechanism.
2. Apply a **multi-scale modelling approach** to link the identified parameters to the SOC voltage to **assess voltage degradation** rate at given operating conditions;
3. Build **mathematical transfer functions** through a parametric analysis to link applied operating conditions and degradation rates for AST protocol design.

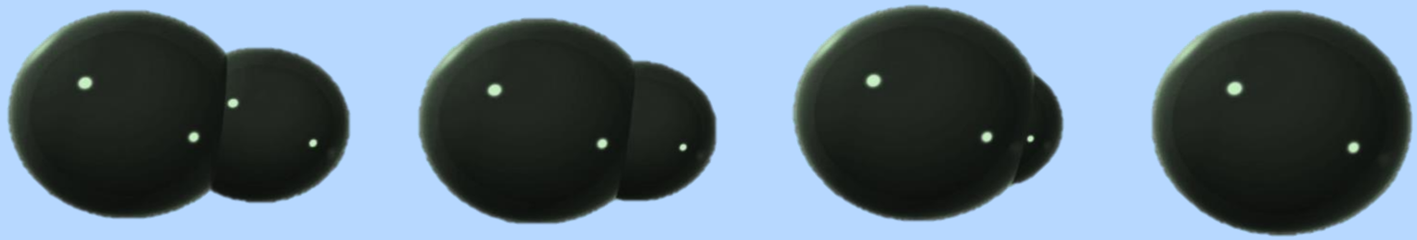






CASE STUDY: NI AGGLOMERATION

Surface diffusion process over time



Microscale level:
microstructural change

Increase in **single particle size** and consequent variation in mean and variance distribution of overall particles sizes

Mesoscale level:
morphological and physical change

Reduction of the **Triple Phase Boundary length**

Reduction of **Anode conductivity**

Macroscale level:
electrical performance change

Increase in **activation losses**

Increase in **ohmic losses**

EFFECTS AT MICRO-SCALE LEVEL

Among many research activities on Ni particle size growth due to Ni agglomeration, the example of modelling here considered is taken from the work of Gao et al. (2014).

Model A

$$r_{Ni}(t)=\left[\frac{5\Gamma}{\lambda}\left(1-e^{-\lambda t}\right)+r_{Ni,0}^{5}\right]^{1/5}$$

$$\lambda=\text{const.}$$

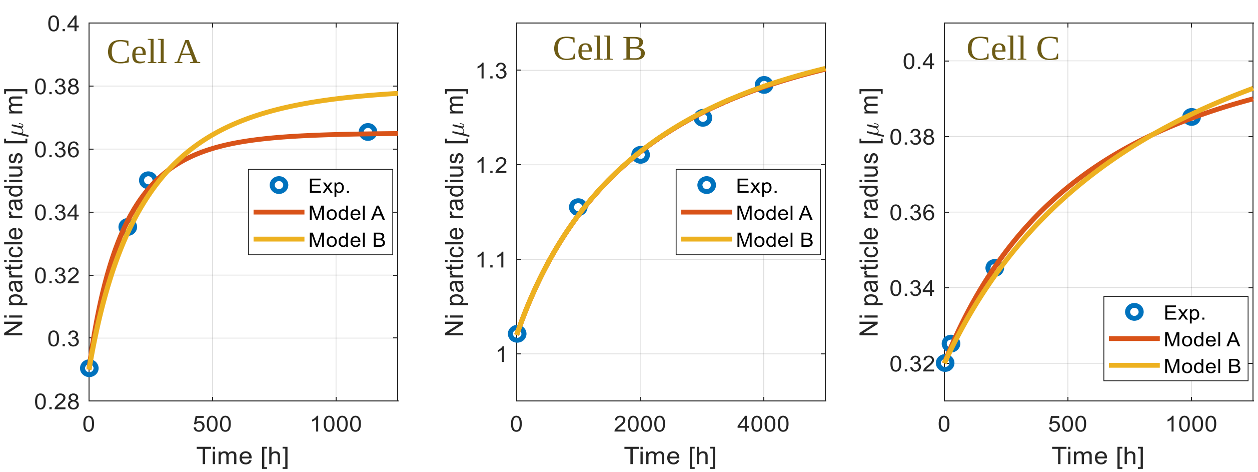
$$\Gamma=f(T)$$

λ: probability of YSZ backbone blocking effect

Model B

$$r_{Ni,\max}=r_{Ni,0}\left[1+\left(1+\left(\frac{1-\beta}{1+\beta}\right)^{3}\right)\frac{\bar{Z}_0}{2}\left(\frac{\psi_{NI}r_{YSZ}}{\psi_{NI}r_{YSZ}+\psi_{YSZ}r_{Ni,0}}\right)\right]^{1/3}$$

$$\lambda=\frac{5\Gamma}{r_{Ni,\max}^{5}-r_{Ni,0}^{5}}$$



	Cell A	Cell B	Cell C
T [K]	850	1000	800
ψ_{Ni} [-]	0.39	0.4	0.39
ψ_{YSZ} [-]	0.61	0.60	0.61
$r_{Ni,0}$ [μm]	0.29	1.02	0.32
$r_{YSZ,0}$ [μm]	0.265	1.0	0.3

Ref: Gao S. et al., Journal of Power Sources 255 (2014) 144-150.

EFFECTS AT MESO-SCALE LEVEL: TPB LENGTH

Ni-YSZ contact perimeter

Coordination number

$$\lambda_{TPB} = \zeta_{Ni,YSZ} n_{Ni} Z_{Ni,YSZ}$$

Ni particles number

Particles contact angle

$$\zeta_{Ni,YSZ} = 2\pi \sin\vartheta \min\left(r_{Ni}, r_{YSZ}\right)$$

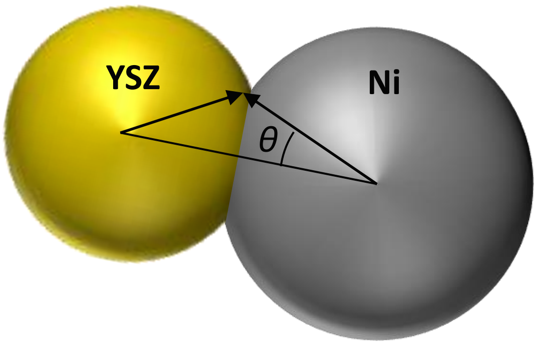
Porosity

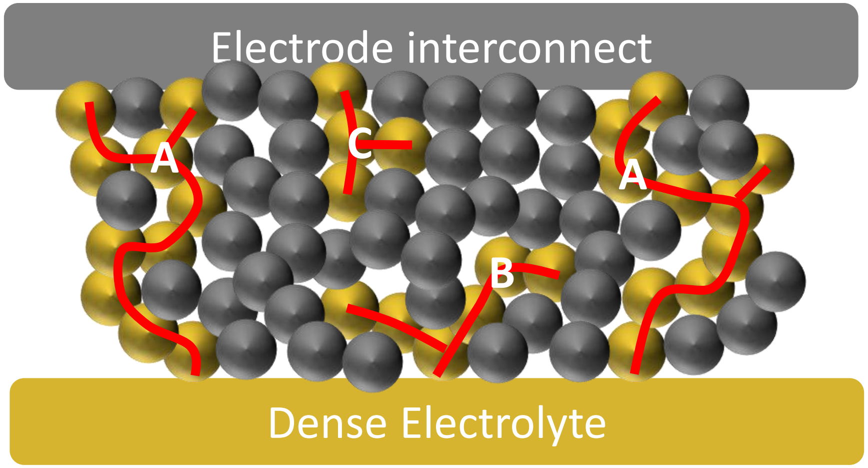
Ni volume fraction

$$n_{Ni} = 3(1-\varphi)\frac{\psi_{Ni}}{4\pi r_{Ni}^3}$$

Average coordination number

$$Z_{Ni,YSZ} = \frac{\bar{Z}}{2}\left(1+\frac{r_{Ni}^2}{r_{YSZ}^2}\right)\left(\frac{\psi_{YSZ} r_{Ni}}{\psi_{YSZ} r_{Ni} + \psi_{Ni} r_{YSZ}}\right)$$





A: full path; B: partial path; C: isolated particles

Percolation theory is accounted

Ref: Chen et al., Journal of Power Sources 195 (2010) 6598-6610.

EFFECTS AT MESO-SCALE LEVEL: ANODE CONDUCTIVITY

Ni conductivity in a dense solid (depends on temperature)

Porosity

Threshold Ni volume fraction

$$\sigma_{Ni} = \sigma_{Ni}^{0}\left[(1-\varphi)\frac{\psi_{Ni}-\psi_{Ni}^{t}}{1-(1-\varphi)\psi_{Ni}^{t}}\right]$$

YSZ conductivity in a dense solid (depends on temperature)

Threshold YSZ volume fraction

$$\sigma_{YSZ} = \sigma_{YSZ}^{0}\left[(1-\varphi)\frac{\psi_{YSZ}-\psi_{YSZ}^{t}}{1-(1-\varphi)\psi_{YSZ}^{t}}\right]$$

$$Z_{Ni,Ni} = \bar{Z}\left(\frac{\psi_{Ni}^{t} r_{YSZ}}{\psi_{Ni}^{t} r_{YSZ} + \psi_{YSZ} r_{Ni}}\right) = 1.764 \qquad Z_{YSZ,YSZ} = \bar{Z}\left(\frac{\psi_{YSZ}^{t} r_{Ni}}{\psi_{YSZ}^{t} r_{Ni} + \psi_{Ni} r_{YSZ}}\right) = 1.764$$

$$\psi_{Ni}^{t} = \frac{1.764\psi_{YSZ}}{(\bar{Z}-1.764)r_{YSZ}} r_{Ni} \qquad \psi_{YSZ}^{t} = \frac{1.764\psi_{Ni}}{(\bar{Z}-1.764)r_{Ni}} r_{YSZ}$$

Ref: Chen et al., Journal of Power Sources 195 (2010) 6598-6610.

EFFECTS AT MACRO-SCALE LEVEL

SOFC performance model (Voltage model)

$$V_{Cell} = V_{Ner} - V_{Act} - V_{Ohm} - V_{Con}$$

Ohmic losses

$$V_{Ohm} = \sum_k \frac{\mu_k}{\sigma_k} J$$

Nernst voltage

$$V_{Ner} = E_0 - \frac{RT}{2F} \ln\left(\frac{p_{H_2O}}{p_{H_2} p_{O_2}^{1/2}} \right)$$

Activation losses

$$V_{act} = \frac{RT}{\alpha F} \left[\sum_{j=an,ca} \ln\left(1 + \frac{J}{J_{ex,j}} \right) \right]$$

$$J_{ex,ca} = k_{ca} l_{TPB,ca}^{eff} \left(\frac{p_{O_2}}{p_{ref}} \right)^{0.25} \exp\left(-\frac{E_{act,ca}}{RT} \right)$$

$$J_{ex,an} = k_{an} l_{TPB,an}^{eff} \left(\frac{p_{H_2}}{p_{ref}} \right) \left(\frac{p_{H_2O}}{p_{ref}} \right) \exp\left(-\frac{E_{act,an}}{RT} \right)$$

Concentration losses

$$V_{Con} = V_{Con,an} + V_{Con,ca}$$

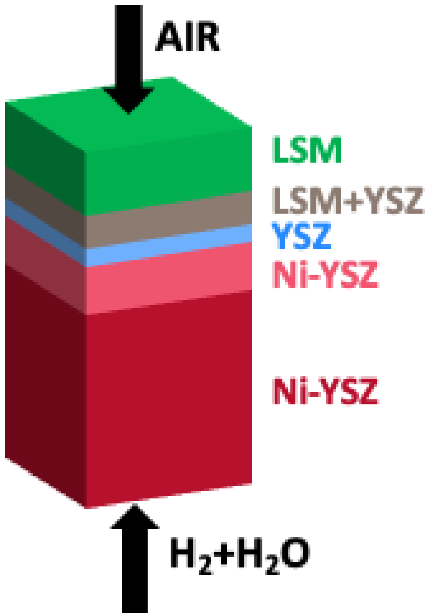
$$V_{Con,an} = \frac{RT}{2F} \ln\left(\frac{1 + J / J_{lim,H_2O}}{1 - J / J_{lim,H_2}} \right)$$

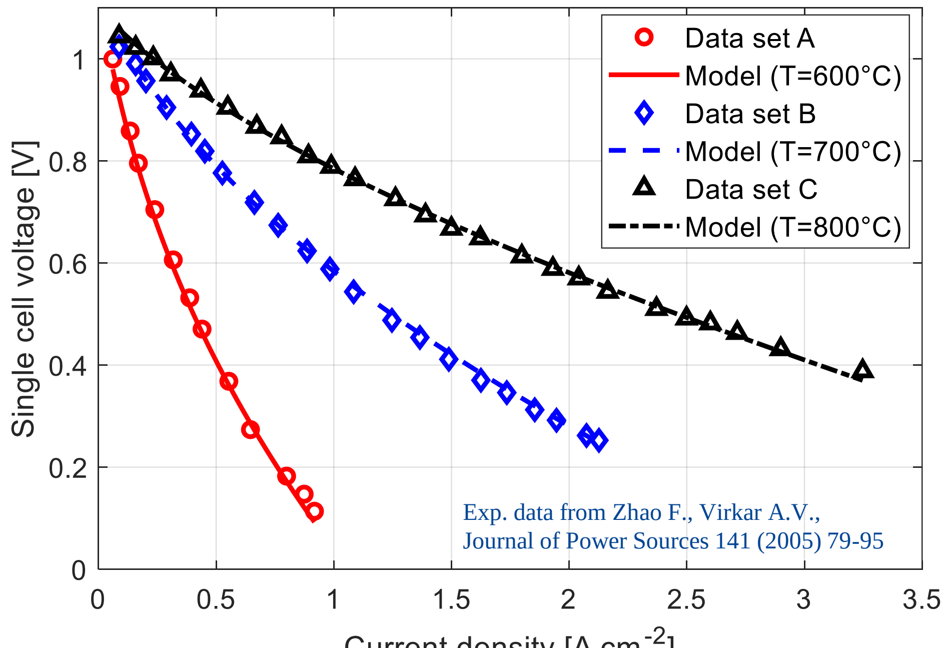
$$V_{Con,ca} = \frac{RT}{4F} \ln\left[\frac{p_{O_2} \delta_{O_2}}{p_{ca} - \left(p_{ca} - p_{O_2} \delta_{O_2} \right) e^{\left[\left(J \delta_{O_2} \right) / J_{lim,O_2} \right]}} \right]$$

MULTISCALE PERFORMANCE MODEL VALIDATION

Parameters	Values		
data set #	data set A	data set B	data set C
T [°C]	600	700	800
J [A/cm2]	~[0 – 1]	~ [0 – 2]	~ [0 – 3]
p_{an} [bar]	1	1	1
p_{ca} [bar]	1	1	1
p_{H2} [bar]	0.97	0.97	0.97
p_{H2O} [bar]	0.03	0.03	0.03
p_{O2} [bar]	0.21	0.21	0.21

Parameter	Anode support	Anode interlayer	Electrolyte	Cathode interlayer	Current collector
composition	Ni+YSZ	Ni+YSZ	dense YSZ	LSM+YSZ	LSM
ϕ	0.48	0.23	-	0.26	0.45
ψ_{Ni}	0.55	0.55	-	-	-
ψ_{YSZ}	0.45	0.45	-	0.525	-
ψ_{LSM}	-	-	-	0.475	1
r_{Ni} [μm]	0.813	0.542	-	-	-
r_{YSZ} [μm]	0.3	0.2	-	0.2	-
r_{LSM} [μm]	-	-	-	0.37	0.6
μ [μm]	1000	20	8	20	50
τ	3	3	3	3	3



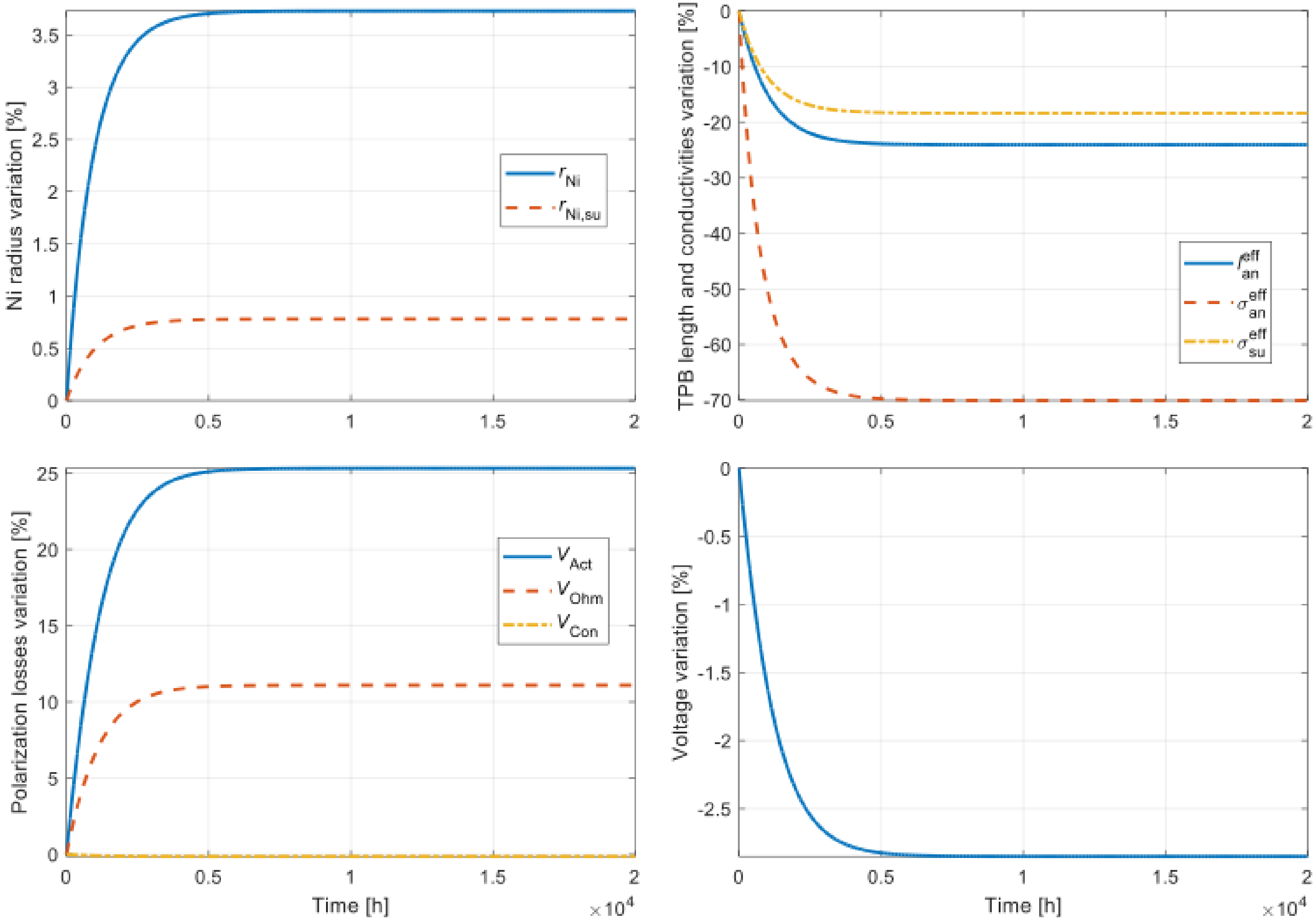


No degradation considered yet

Ref: Polverino et al., Journal of Power Sources 491 (2021)229521.

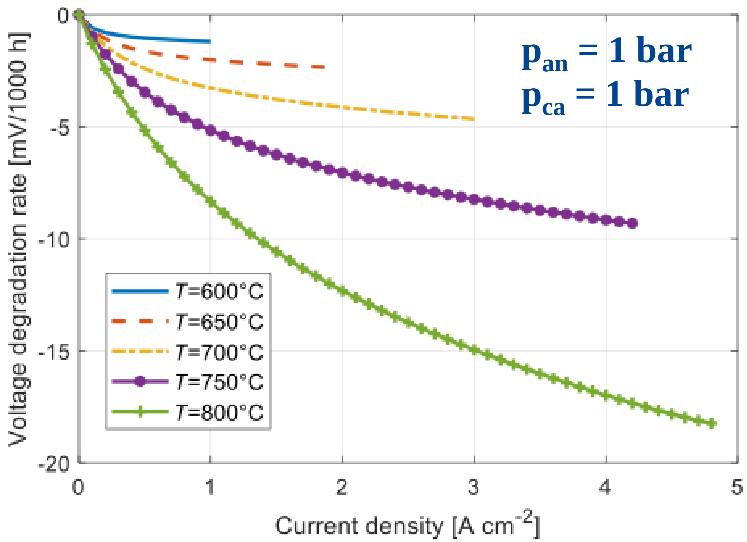
NI AGGLOMERATION SIMULATION AT CONSTANT OPERATION

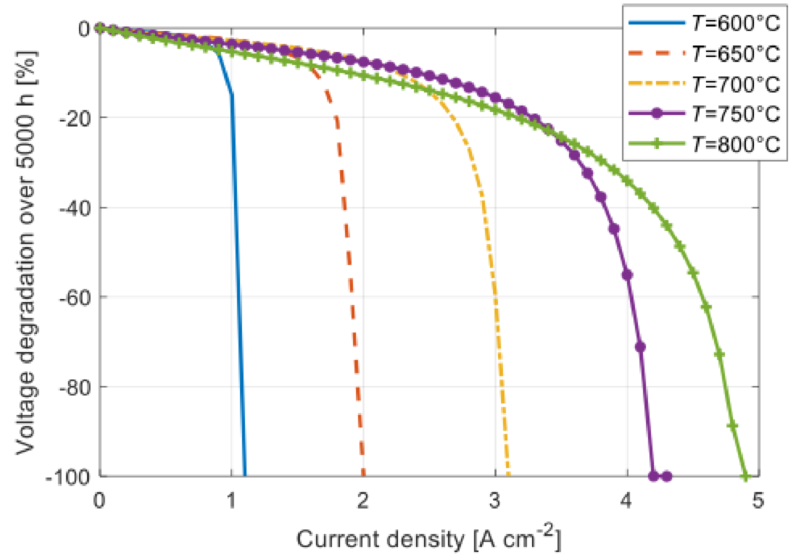
DATA SET C: T = 800°C, i = 0.5 A/cm^2, p_{an} = 1 bar, p_{ca} = 1 bar.

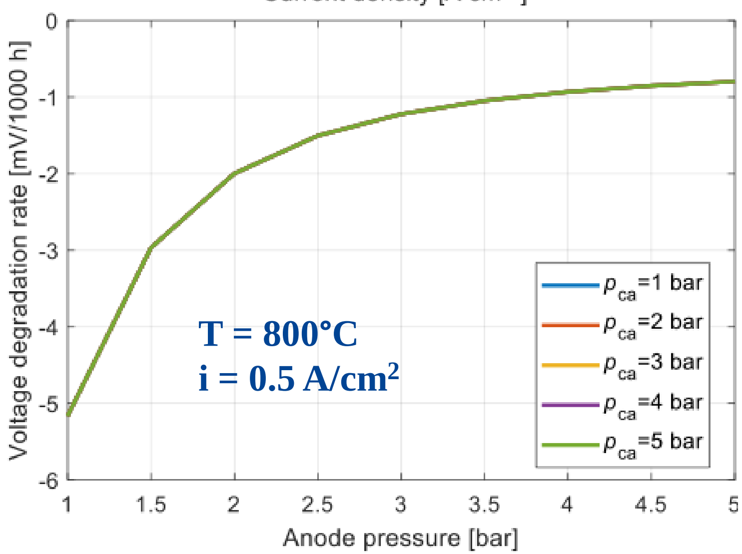


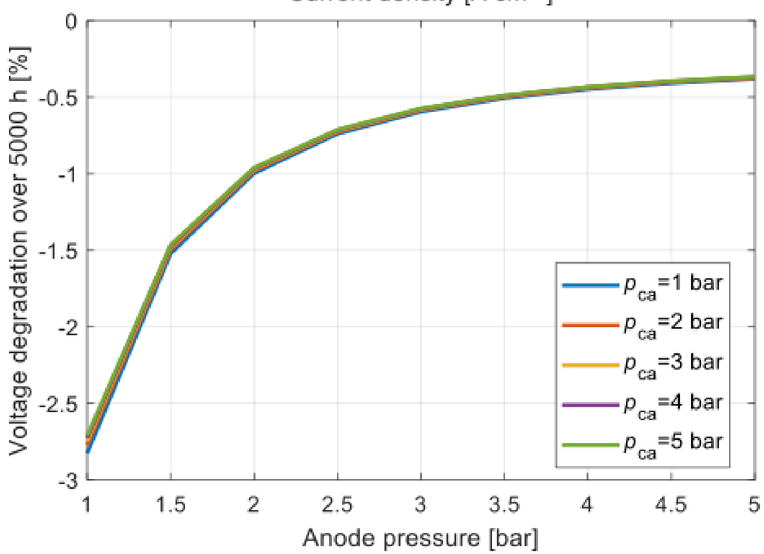
Ref: Polverino et al., Journal of Power Sources 491 (2021)229521.

PARAMETRIC ANALYSIS: ACCELERATING FACTORS IDENTIFICATION









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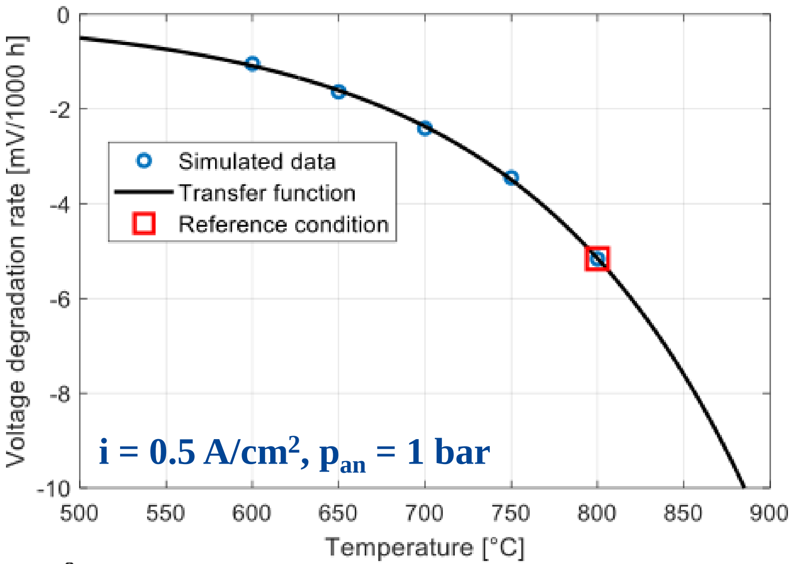
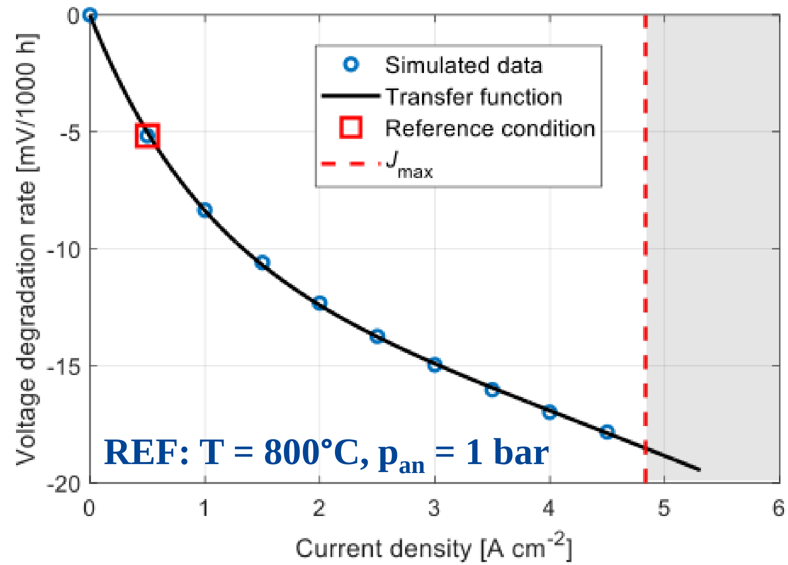
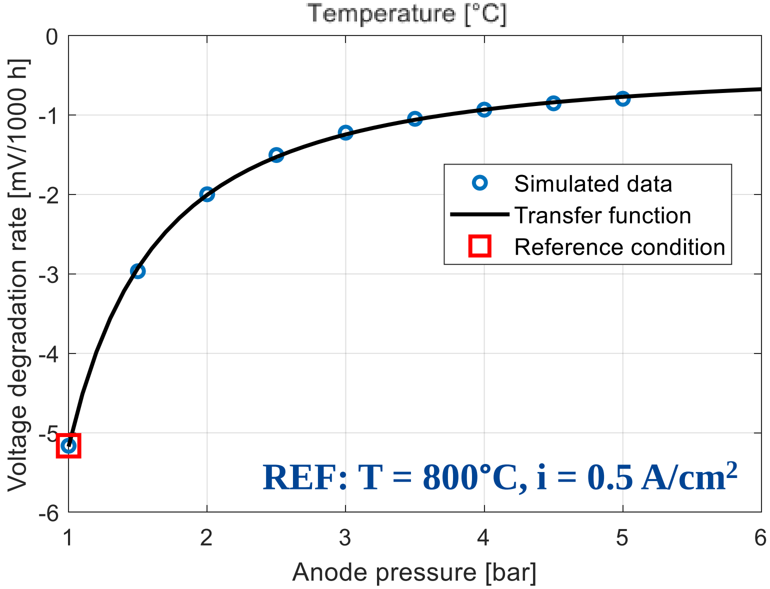
TRANSFER FUNCTION DESIGN 1/2







Ref: Polverino et al., Journal of Power Sources 491 (2021)229521.

Transfer function design:

$$\xi(T)\Big|_{J=0.5\,\mathrm{A/cm^2},\,p_{an}=1\mathrm{bar}} = -1.22\cdot 10^{-3} e^{\left(7.78\cdot 10^{-3}\,T\right)}$$

$$\xi(J)\Big|_{T=800^\circ\mathrm{C},\,p_{an}=1\mathrm{bar}} = 11.54\left(e^{-0.97J} - e^{0.1J}\right)$$

$$\xi(p_{an})\Big|_{T=800^\circ\mathrm{C},\,J=0.5\,\mathrm{A/cm^2}} = -4.79\,p_{an}^{-1.56} - 0.38$$

REF: T = 800°C, i = 0.5 A/cm², p_{an} = 1 bar

TRANSFER FUNCTION DESIGN 2/2

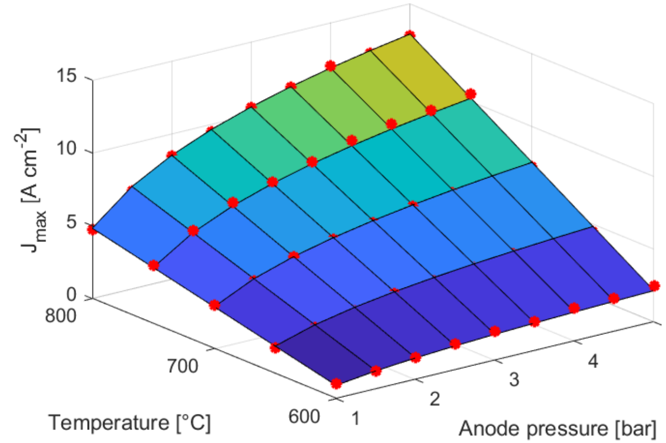
$$\boxed{\xi\left(T, J_N\right) = a_1 e^{a_2 T}\left(e^{a_3 J_N} - e^{a_4 J_N}\right)} \qquad J_N = \frac{J}{J_{\max}}$$

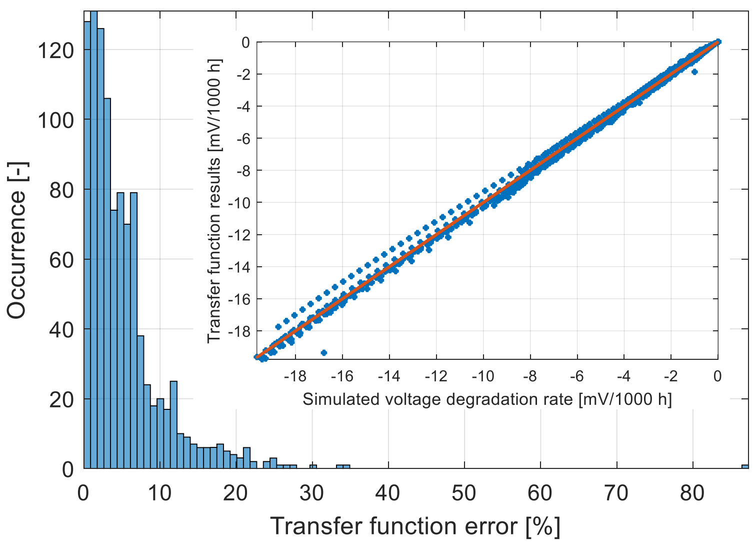
$$J_{max}\left(T, p_{an}\right) = -159.4 + 0.19T + \left(143.2 - 0.17T\right) p_{an}^{-0.14}$$

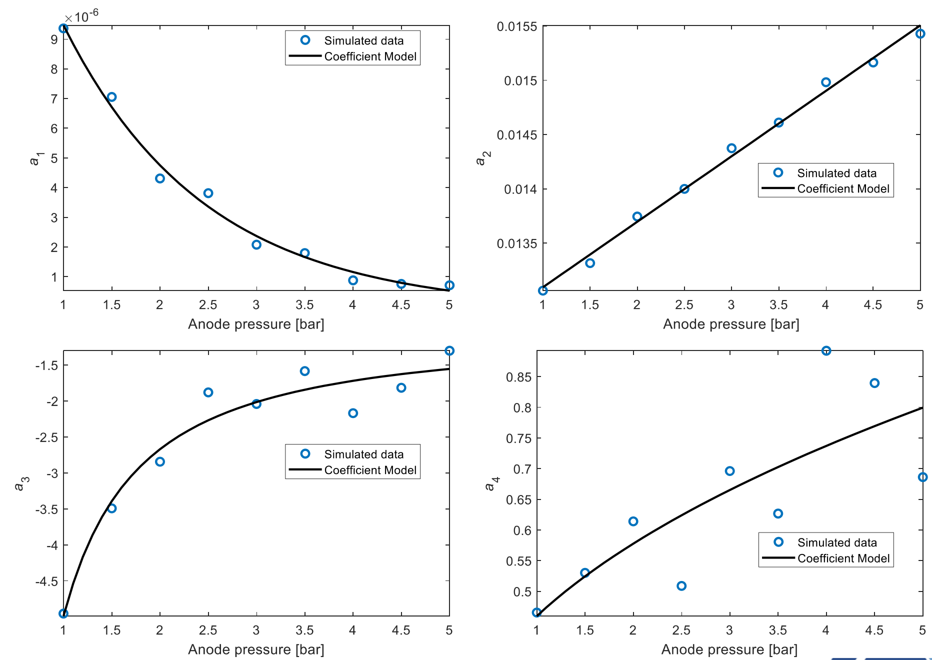
$$a_1\left(p_{an}\right) = -1.20\cdot 10^{-8} e^{0.38\, p_{an}} + 1.88\cdot 10^{-5} e^{-0.69\, p_{an}}$$

$$a_2\left(p_{an}\right) = 6.03\cdot 10^{-4} p_{an} + 1.25\cdot 10^{-2} \qquad a_4\left(p_{an}\right) = 0.34 p_{an}^{0.43} + 0.12$$

$$a_3\left(p_{an}\right) = -3.93 p_{an}^{-1.29} - 1.06$$



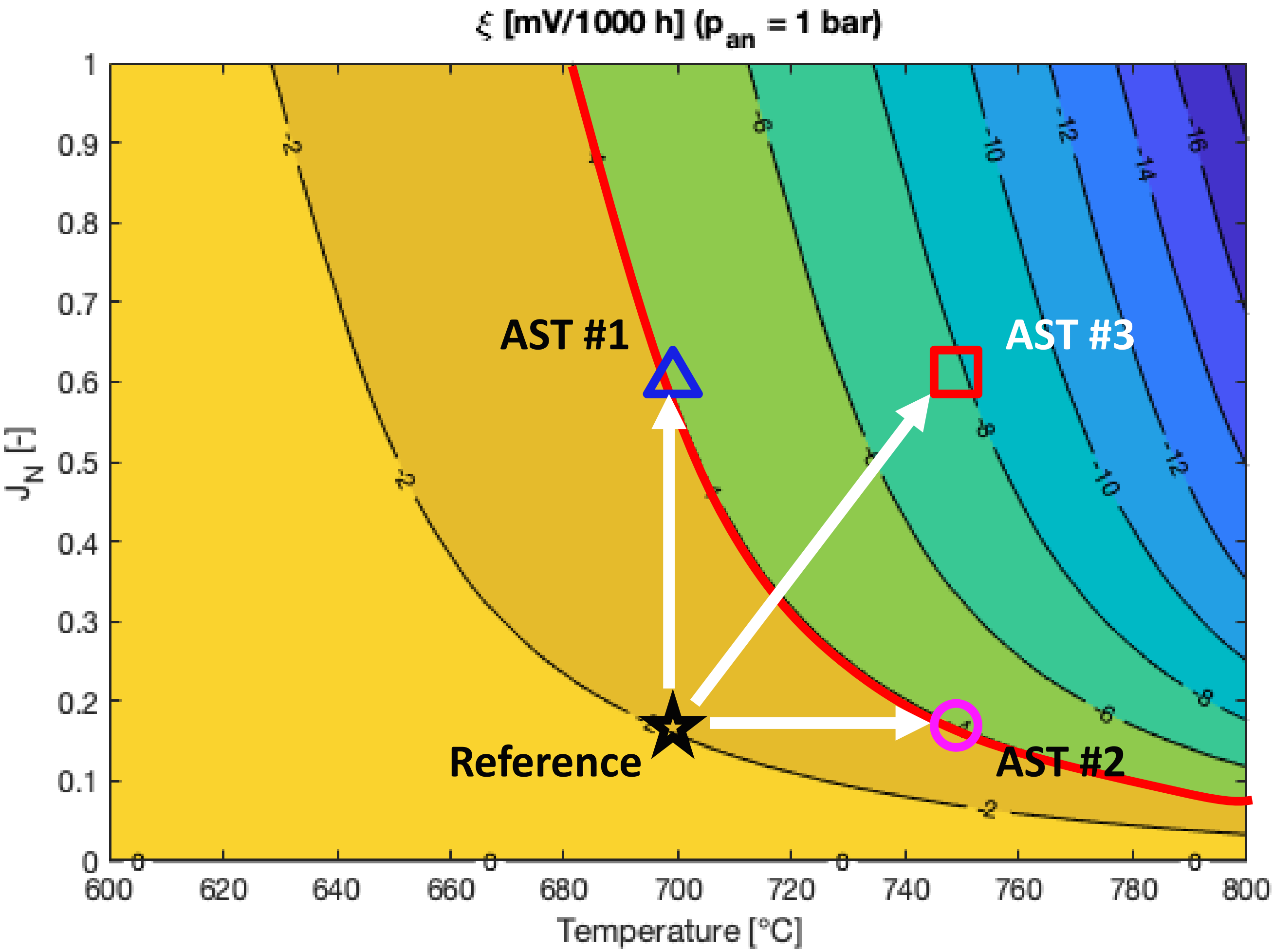




Ref: Polverino et al., Journal of Power Sources 491 (2021)229521.

TRANSFER FUNCTION APPLICATION FOR AST PROTOCOLS

$T \in [600°C \cdots 800°C]$ $\quad J_N \in [0 \cdots 1]$ $\Rightarrow$ $\boxed{\xi(T, J_N) = a_1 e^{a_2 T}\left(e^{a_3 J_N} - e^{a_4 J_N}\right)}$



Parameter	Operating condition
	Reference
T [°C]	700
J [A/cm2]	0.5
p_{an} [bar]	1
J_{max} [A/cm2]	2.87
J_N [-]	0.17
ξ [mV/1000 h]	2.15
Δξ [-]	0

Parameter	Operating condition
	AST #2
T [°C]	750
J [A/cm2]	0.67
p_{an} [bar]	1
J_{max} [A/cm2]	3.85
J_N [-]	0.17
ξ [mV/1000 h]	4.13
Δξ [-]	+92%

Ref: Polverino et al., Journal of Power Sources 491 (2021)229521.

CONCLUSIONS & PERSPECTIVES

The proposed **transfer functions design procedure** can be summarized in 8 steps:

Step 1: Identify degradation process(es), related mechanisms and design/select representative microscale model(s);

Step 2: Identify key parameter(s) influenced by degradation and design/select related mesoscale model(s);

Step 3: Design/select macroscale performance model(s);

Step 4: Combine the different models through a multiscale modelling approach;

Step 5: Perform a parametric analysis to investigate the impact of the operating conditions on degradation rate;

Step 6: Single out the accelerating factor(s), i.e., the operating variable(s) that foster degradation;

Step 7: Design mathematical transfer functions to correlate accelerating factor(s) and degradation rate;

Step 8: Develop guidelines/tools for lifetime estimation and AST protocols design.

As **future work**, more degradation mechanisms can be approached to develop transfer functions that can be used for single or combined phenomena for AST protocols design.

More details can be found in **Polverino et al., Journal of Power Sources 491 (2021) 229521**.

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