State-Space Modeling of Electrochemical Processes

„Who uses up my battery power ?“

Michel Prestat

ETH-Zürich
Institute for Nonmetallic Materials
Head: Prof. L.J. Gauckler

Electrochemistry

Electrochemical Impedance Spectroscopy and State-Space Modeling

Oxygen reduction at solid oxide fuel cell cathodes

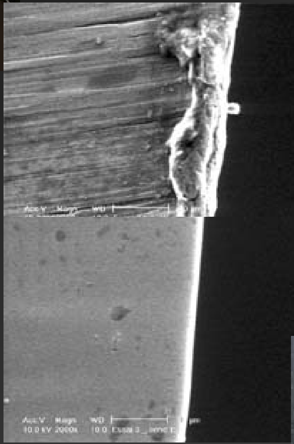
Comparison modeling – experiments

Summary

Electrochemistry

corrosion

electropolishing



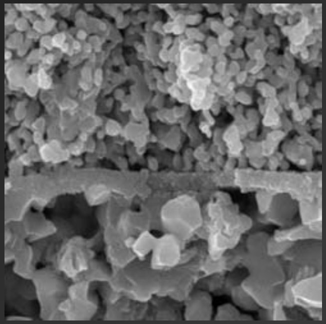
coloration of titanium

batteries, fuel cells

Solid Oxide Fuel Cell (SOFC)

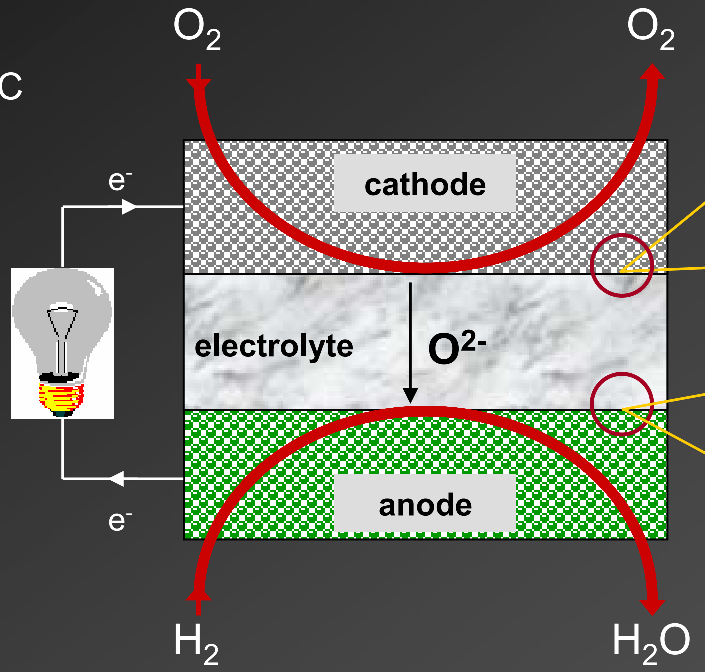
Sulzer Hexis SOFC

single cell



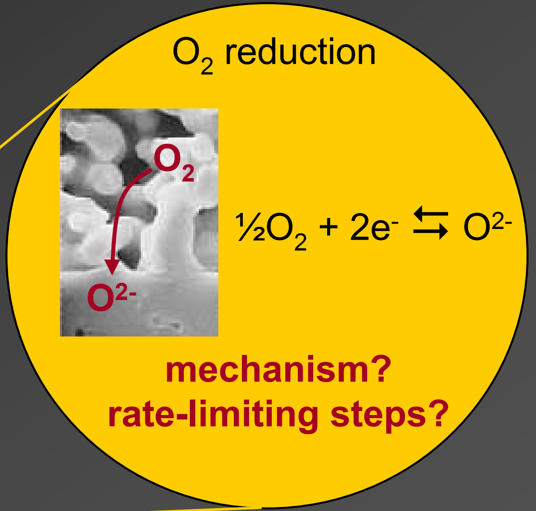
microstructure

800-1000°C



$\frac{1}{2}O_2 + 2e^- \leftrightarrows O^{2-}$

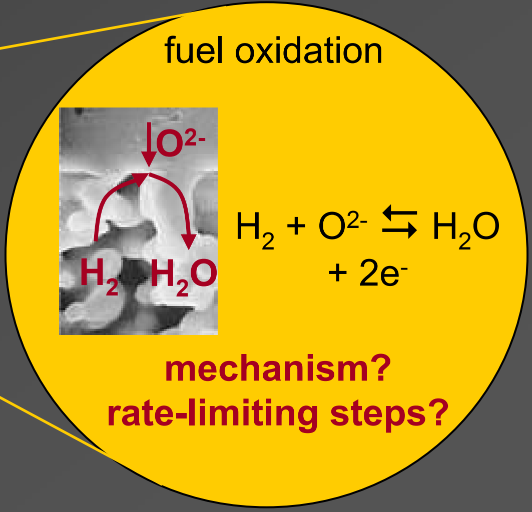
$H_2 + O^{2-} \leftrightarrows H_2O + 2e^-$



O_2 reduction

$\frac{1}{2}O_2 + 2e^- \leftrightarrows O^{2-}$

mechanism?
rate-limiting steps?

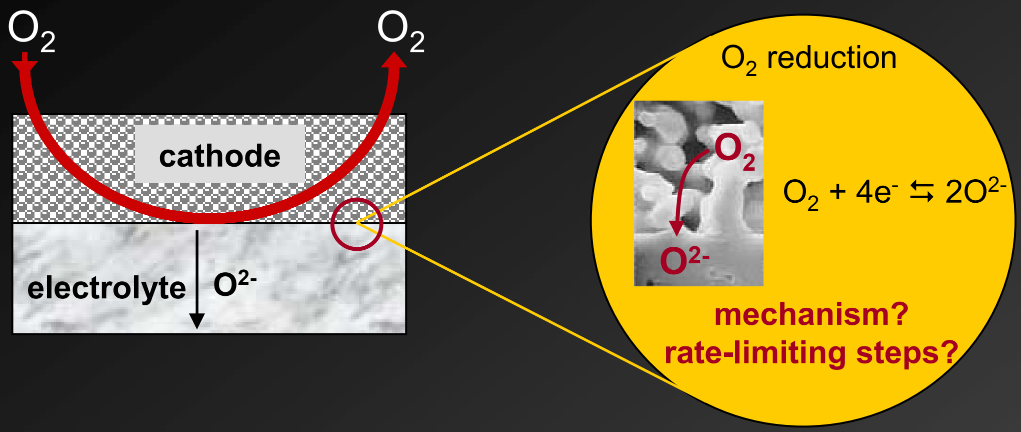


fuel oxidation

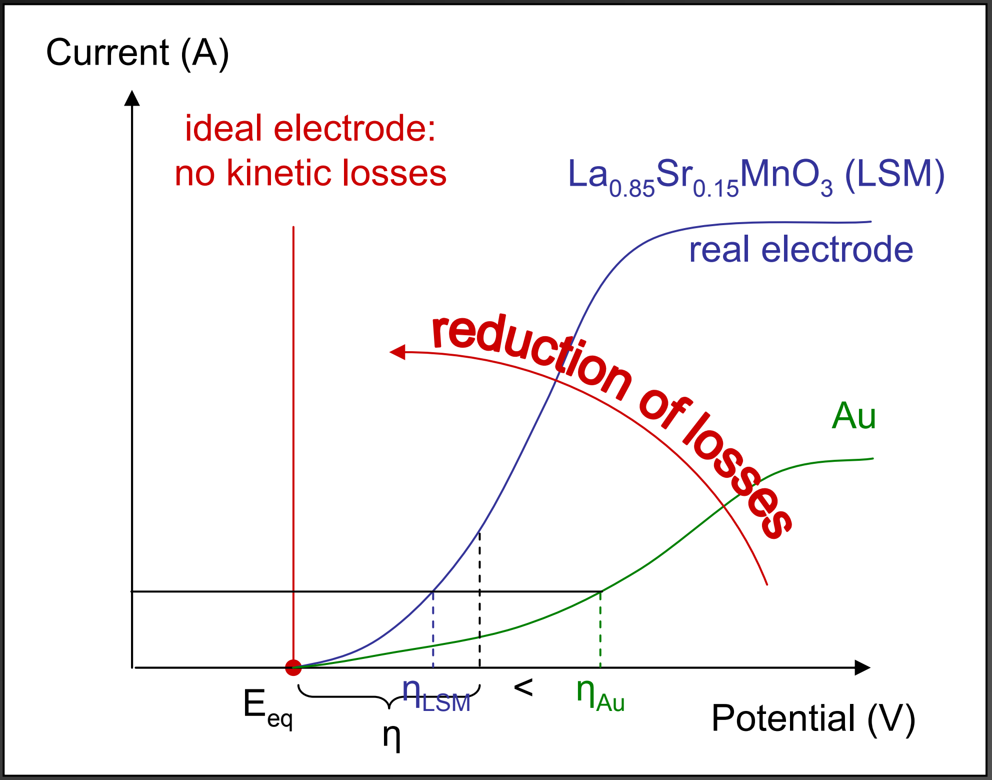
$H_2 + O^{2-} \leftrightarrows H_2O + 2e^-$

mechanism?
rate-limiting steps?

overall: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$



mechanism?
rate-limiting steps?



Overpotential $\eta = E - E_{eq}$

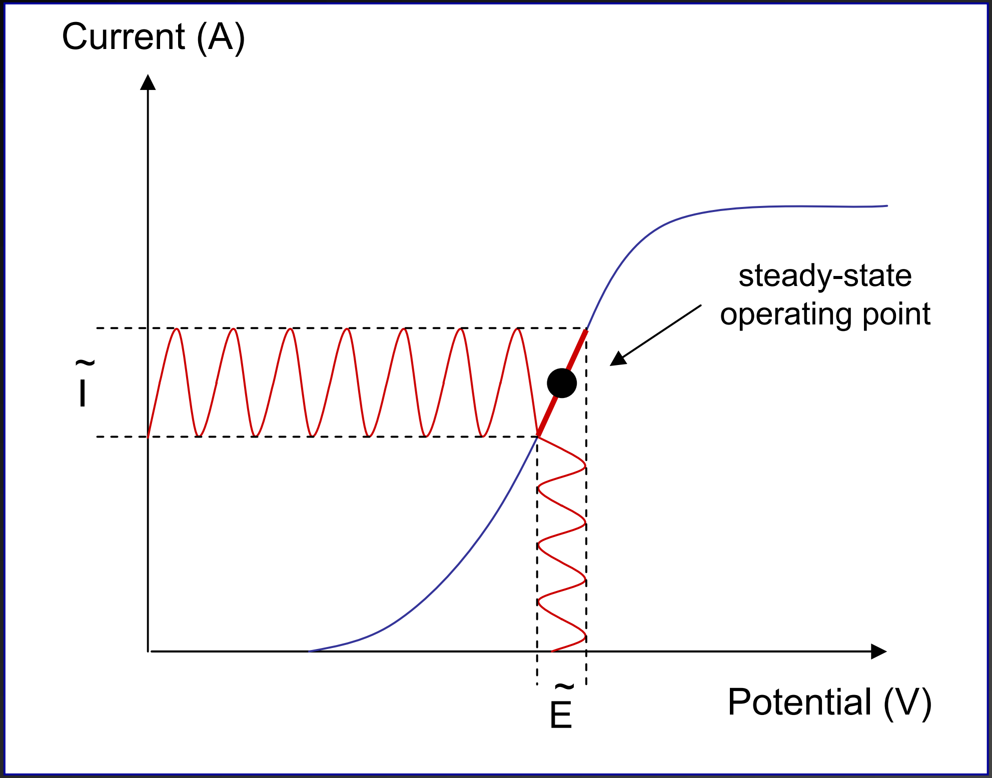
~ electrokinetic losses

η strongly dependant on the material

Aim:
find the appropriate material to get high current and low overpotential (reduction of electrokinetic losses)

What limits the performance of my system ?

Electrochemical Impedance Spectroscopy (EIS)



Small amplitude (5-10 mV) input signal

→ Linearization

$$\tilde{I} = \boxed{\frac{1}{Z(j\omega)}}\,\tilde{E}$$

↓

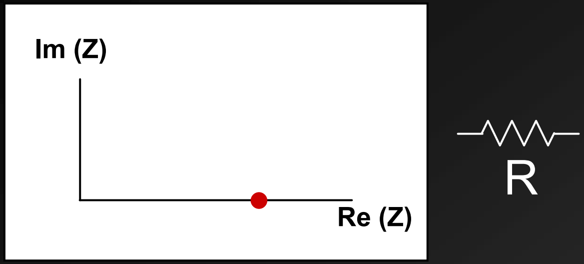
Admittance Transfer Function

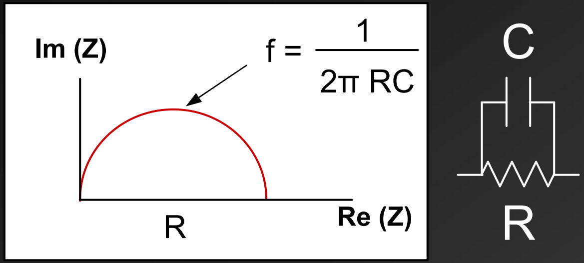
Z = impedance

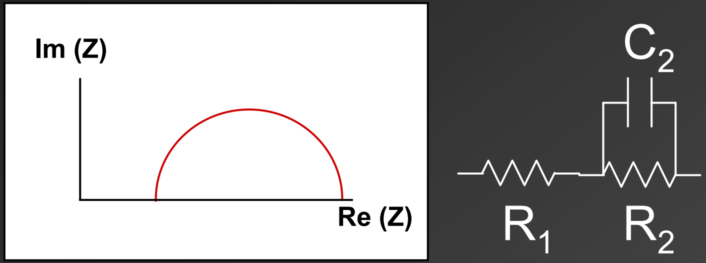
complex ($j^2 = -1$)

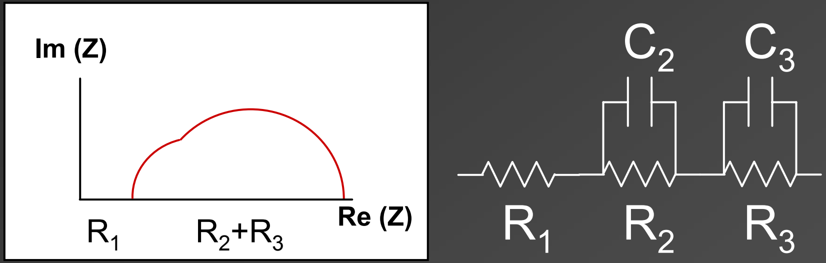
frequency dependant ($\omega = 2\pi f$)

EIS spectra and equivalent circuits

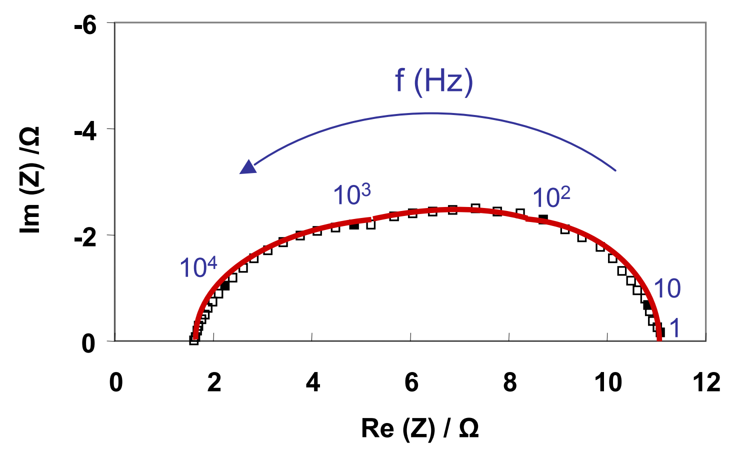


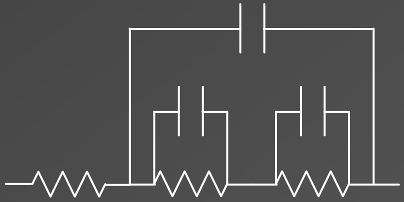






experimental EIS spectra





How to interpret
the experimental equivalent circuit ??

Alternative approch: modeling the impedance

new model

reaction model

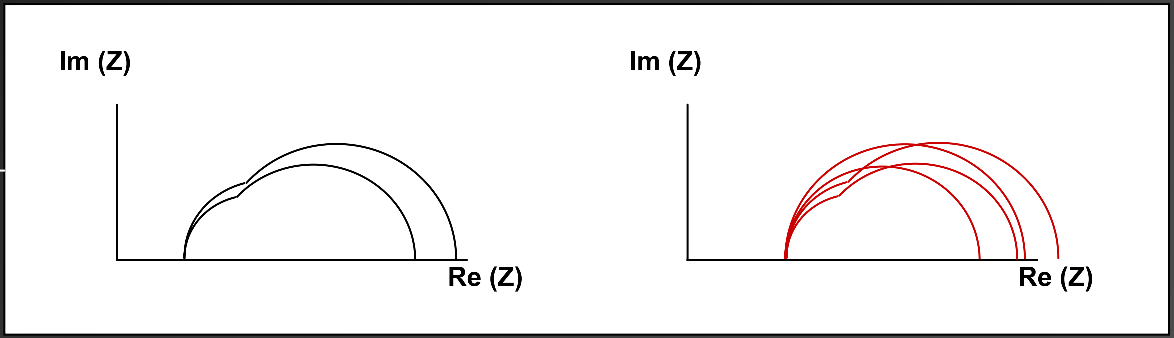
$O_2 \rightleftarrows O_{ads} \rightleftarrows O^{2-}$

$O_2 \rightleftarrows O_{2,ads} \rightleftarrows O^{2-}$

state-space modeling

experimental impedance

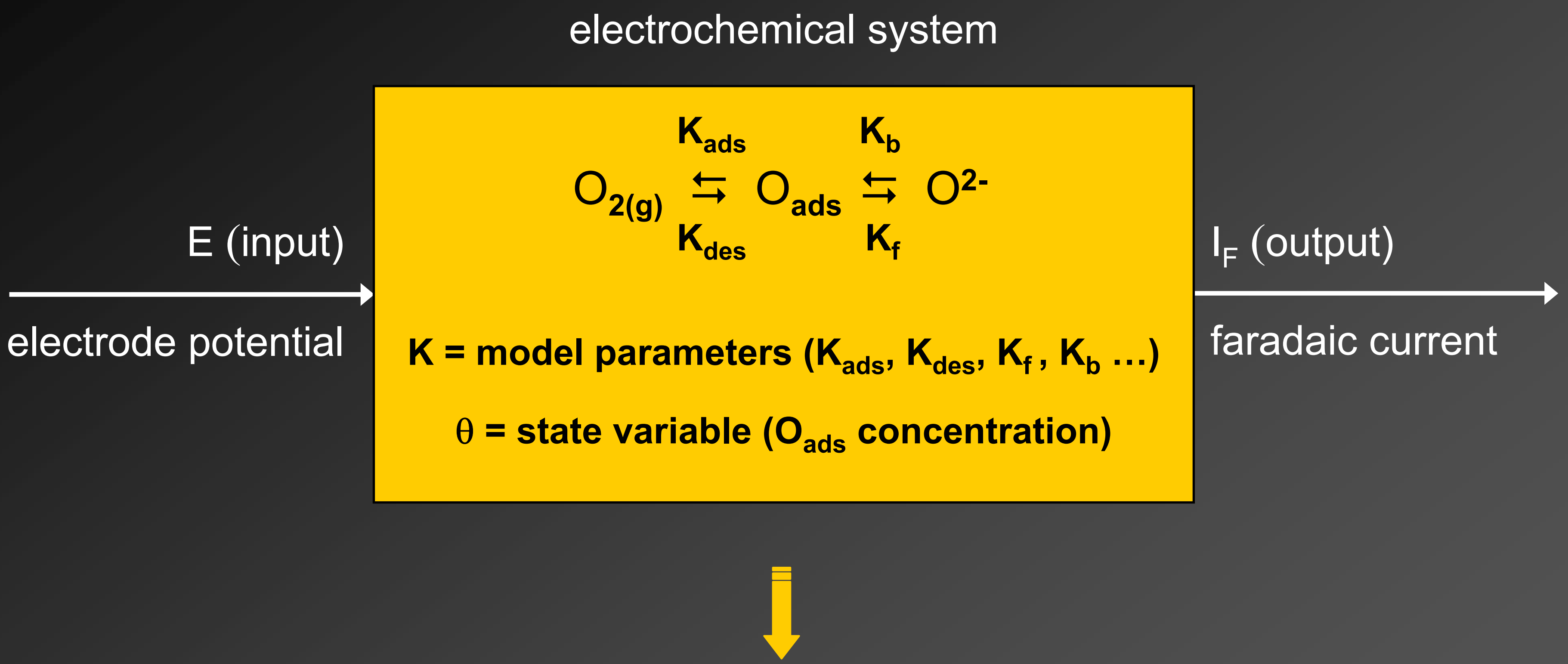
faradaic impedance



validation of the model
assessment of kinetics

State-Space Modeling (SSM)

State-Space Model



electrochemical system

$$O_{2(g)} \underset{K_{des}}{\overset{K_{ads}}{\leftrightarrows}} O_{ads} \underset{K_{f}}{\overset{K_{b}}{\leftrightarrows}} O^{2-}$$

E (input)

electrode potential

I_F (output)

faradaic current

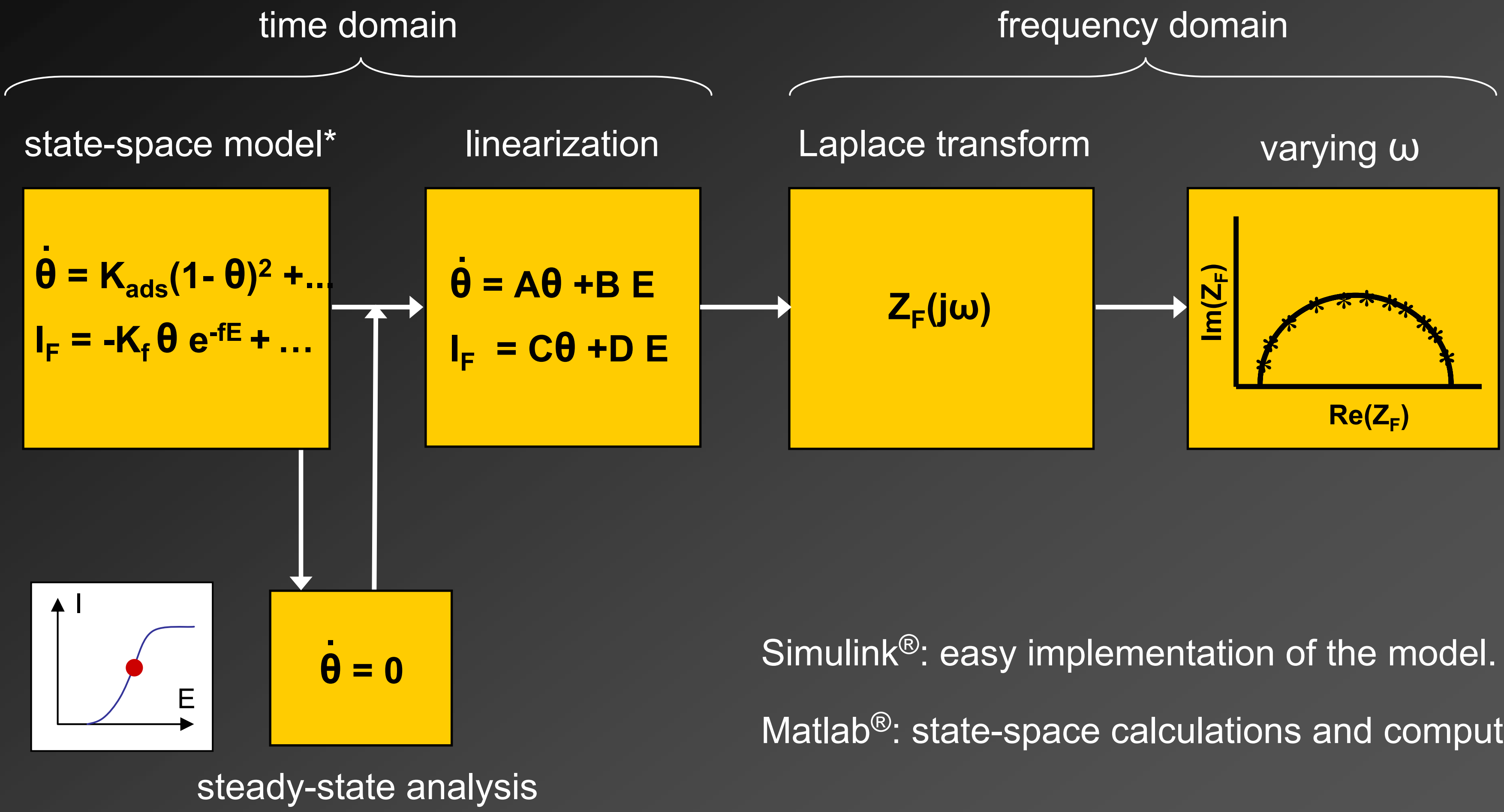
K = model parameters (K_{ads}, K_{des}, K_f , K_b …)

θ = state variable (O_{ads} concentration)

State-Space Model

$$\begin{cases} \dfrac{d\theta}{dt} = f(\theta, E, K) & \rightarrow \text{state equation} \\ I_F = g(\theta, E, K) & \rightarrow \text{output equation} \end{cases}$$

State-Space Modeling



time domain

frequency domain

state-space model*

$$\dot{\theta} = K_{ads}(1-\theta)^2 + \ldots$$

$$I_F = -K_f\,\theta\, e^{-fE} + \ldots$$

linearization

$$\dot{\theta} = A\theta + B\,E$$

$$I_F = C\theta + D\,E$$

Laplace transform

$$Z_F(j\omega)$$

varying ω

$$\dot{\theta} = 0$$

steady-state analysis

Simulink®: easy implementation of the model.

Matlab®: state-space calculations and computing

Oxygen Reduction

at

Solid Oxide Fuel Cell Cathodes

Reaction Models

Dissociative adsorption: $O_{2(g)} + 2s \leftrightarrows 2O_{ads}$

Surface diffusion: $O_{ads} \rightarrow O_{ads}$ (*tpb*)

Charge transfer at the *tpb*: $O_{ads} + 2e^{-} \leftrightarrows O^{2-}$

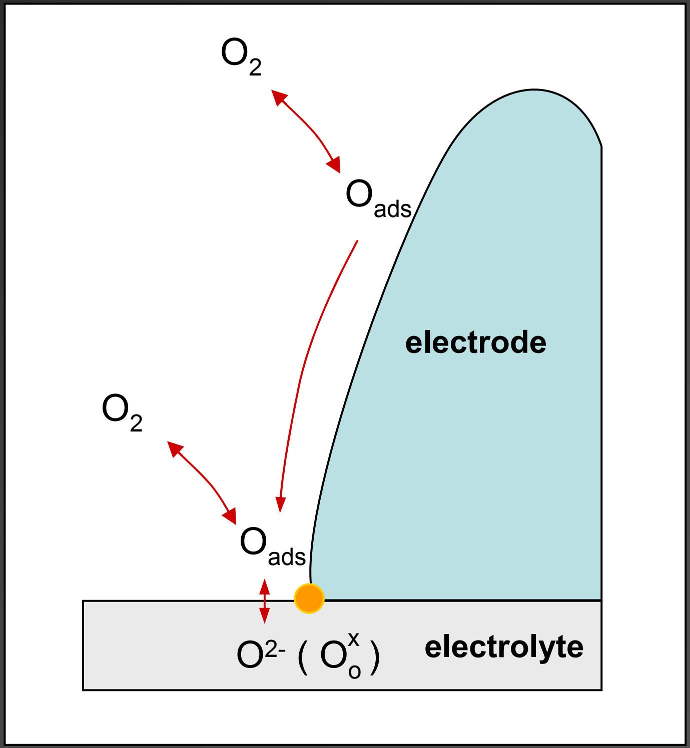
s = adsorption site

Electrolyte = O^{2-} conductor ($V_o^{\cdot\cdot}$ and O_o^x)
Typically YSZ (Y_2O_3 - ZrO_2)

p_{O2} , $[O_o^x]$ and $[V_o^{\cdot\cdot}]$ are constant

Model 1: surface diffusion negligible

Model 2: with surface diffusion



● triple phase boundary (*tpb*)

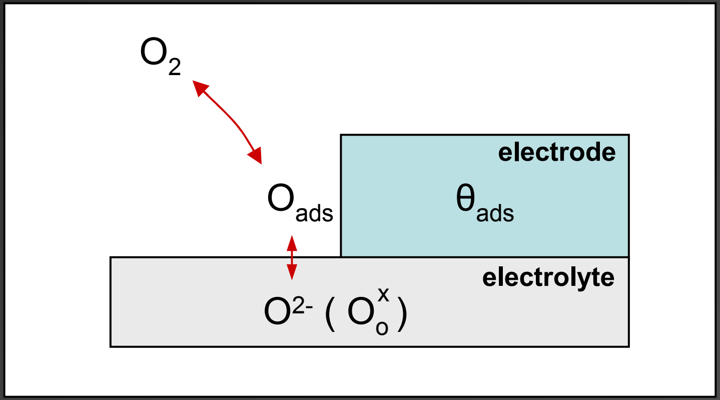
Model 1 (without surf. diffusion)

Dissociative adsorption:

$$O_{2(g)} + 2s \underset{K_{des}}{\overset{K_{ads}}{\leftrightarrows}} 2O_{ads}$$

Charge transfer:

$$O_{ads} + 2e^{-} \underset{K_b(E)}{\overset{K_f(E)}{\leftrightarrows}} O^{2-}$$



→ consecutive reaction steps

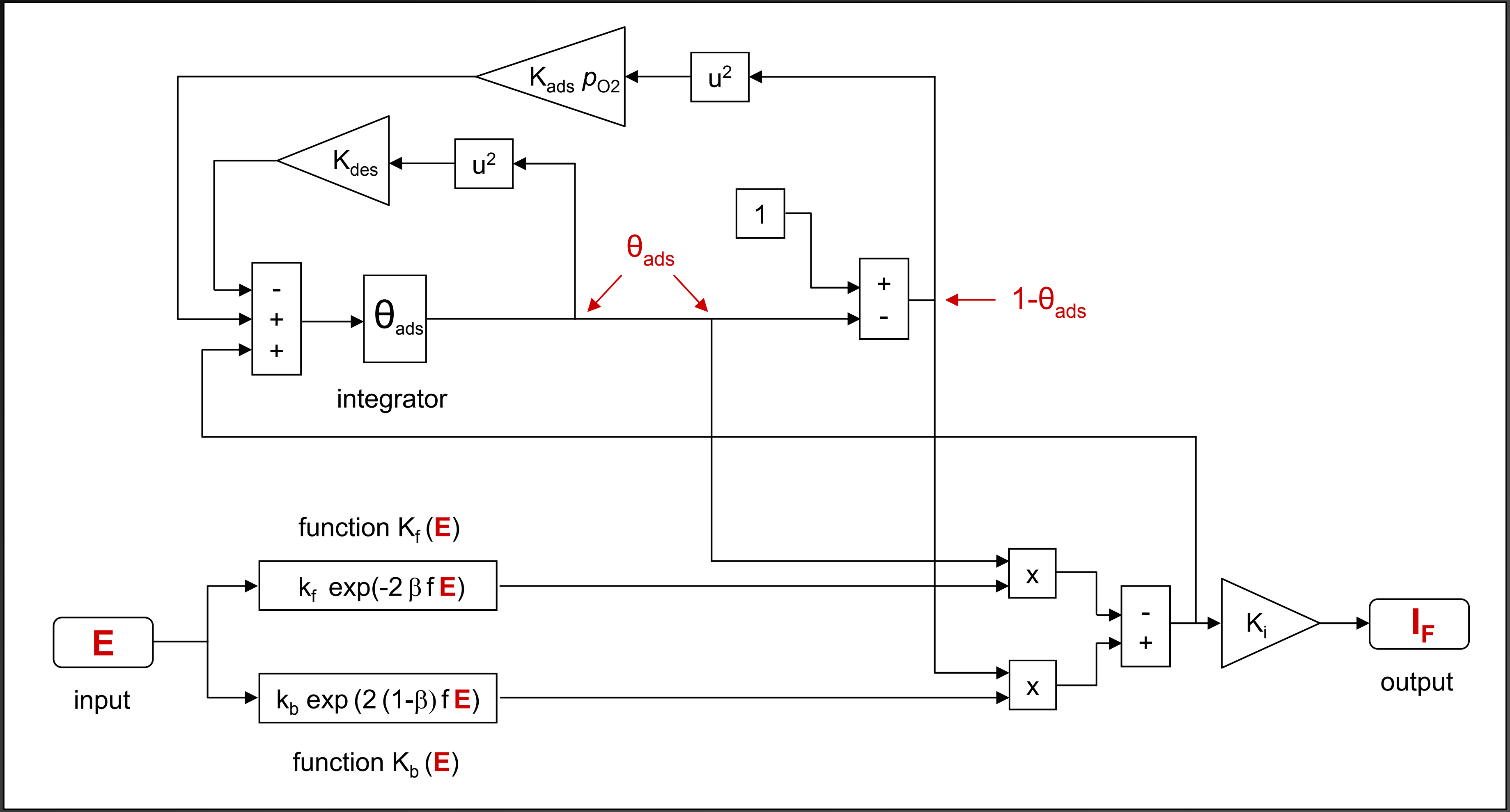
→ state variable θ_{ads} = scalar

→ state-space model

$$\left\{ \begin{array}{l} \dfrac{d\theta_{ads}}{dt} = K_{ads}\, p_{O2}(1-\theta_{ads})^{2} - K_{des}\theta_{ads}^{2} - K_f(E)\,\theta_{ads} + K_b(E)\,(1-\theta_{ads}) \\[2ex] I_F = K_i\,[- K_f(E)\,\theta_{ads} + K_b(E)\,(1-\theta_{ads})] \end{array} \right.$$

Model Implementation in Simulink®

$$\left\{ \begin{array}{l} \boxed{\frac{d\theta_{ads}}{dt} =} \boxed{K_{ads}\, p_{O2}(1-\theta_{ads})^{2}} \boxed{- K_{des}\theta_{ads}^{2}} \boxed{- K_f(E)\,\theta_{ads} + K_b(E)\,(1-\theta_{ads})} \\ \boxed{I_F = K_i} \boxed{[- K_f(E)\,\theta_{ads} + K_b(E)\,(1-\theta_{ads})]} \end{array} \right.$$



Model 2 (with surf. diffusion)

$$O_{2(g)} + 2s \underset{K_{des}}{\overset{K_{ads}}{\leftrightarrows}} 2O_{ads}$$

$$O_{ads} \xrightarrow{K_{dif}} O_{ads}$$

$$O_{ads} + 2e^- \underset{K_b(E)}{\overset{K_f(E)}{\leftrightarrows}} O^{2-}$$

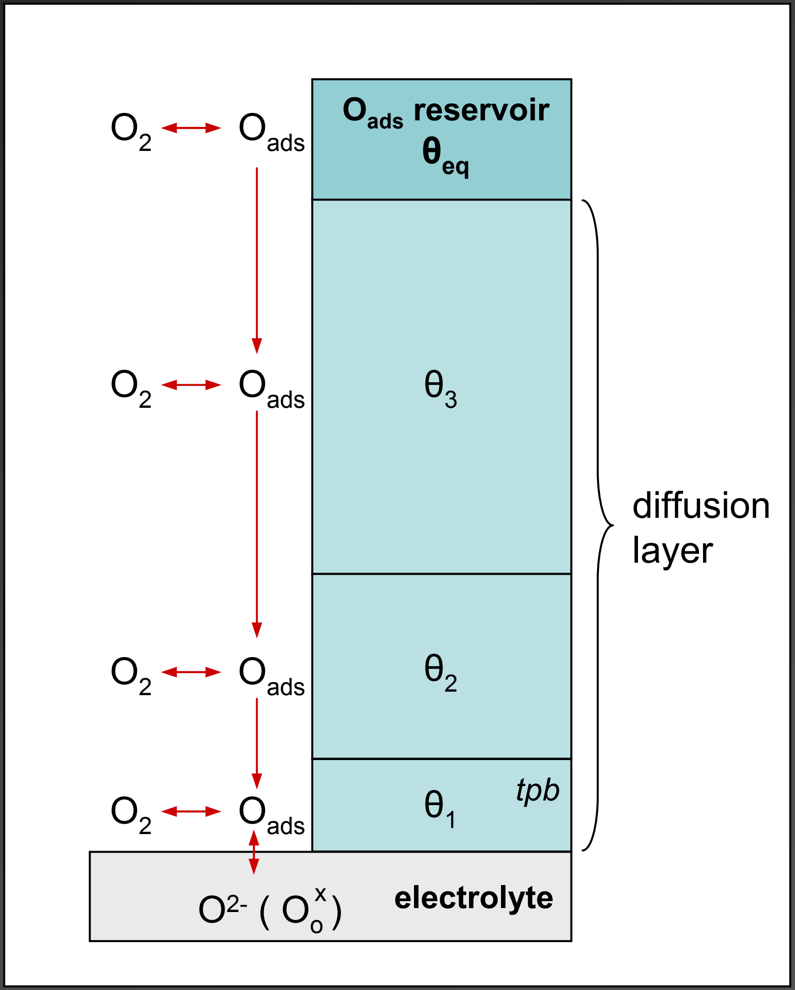
Diffusion processes
2nd Fick‘s law:

$$\frac{\partial \theta}{\partial t} = \frac{\partial^2 \theta}{\partial z^2}$$

→ Finite difference approach to estimate time and space derivatives

→ state variable θ $(\theta_1, \theta_2, \theta_3)$ = vector
$\theta_1 \leq \theta_2 \leq \theta_3$

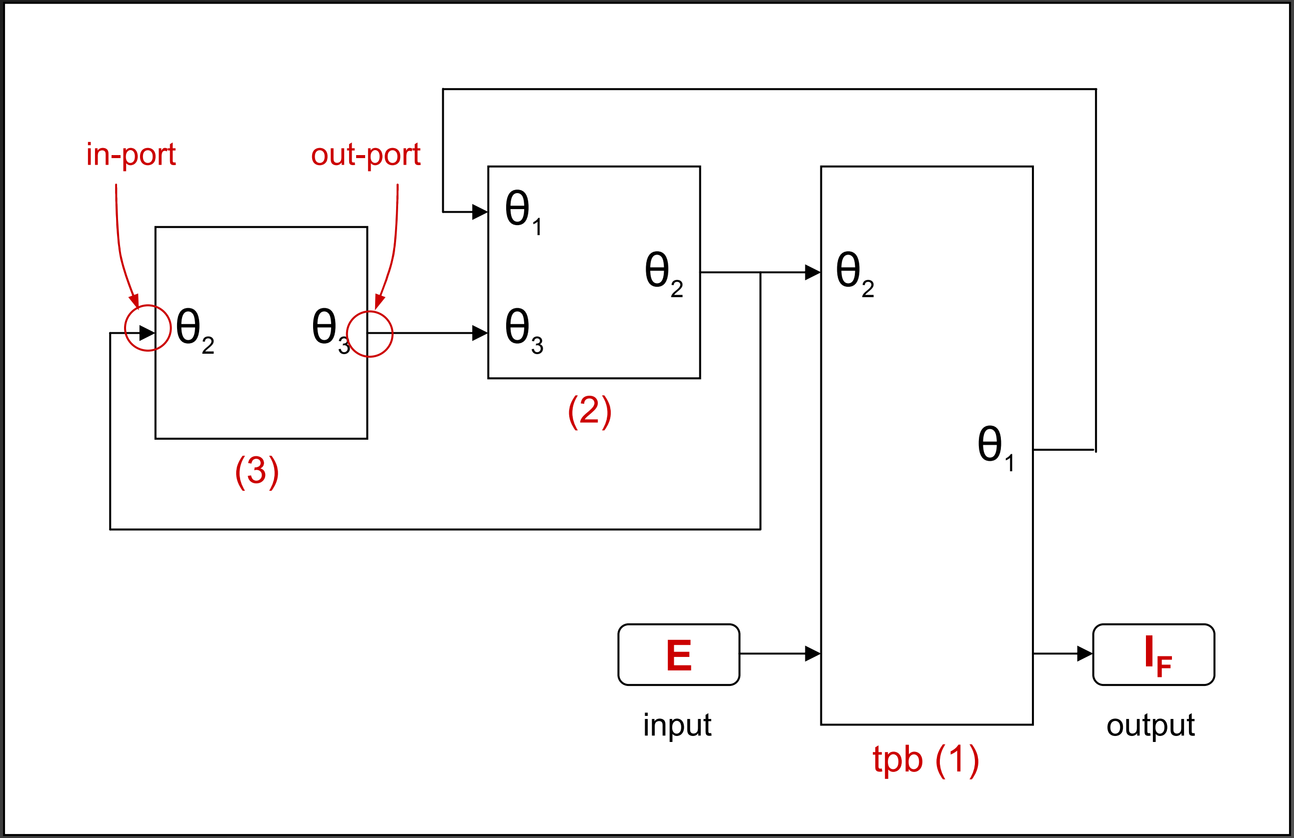
→ Parallel reaction pathways



Model Implementation in Simulink®

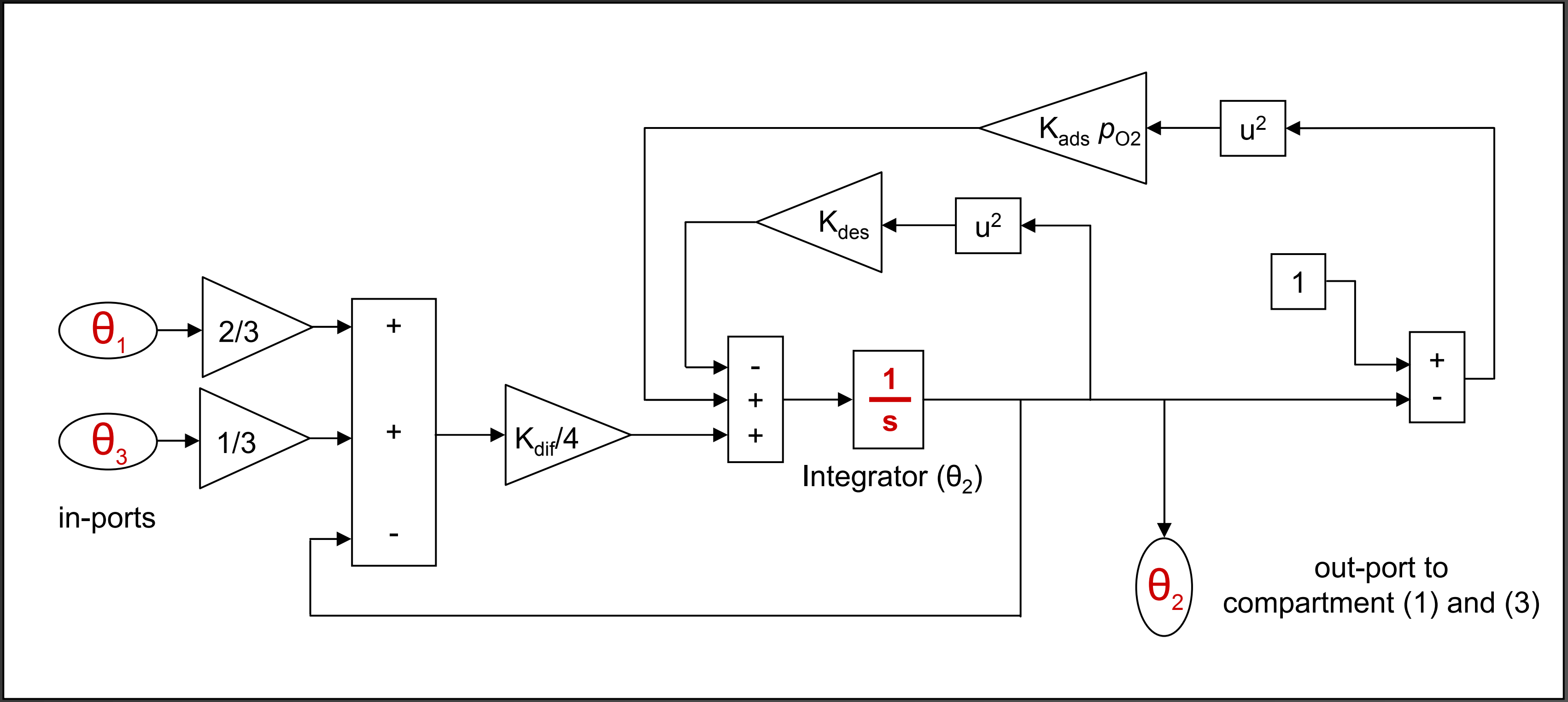
Subsystems: as many as compartments

$$\frac{\partial\theta_i}{\partial t} = K_{ads}\,p_{O_2}\,(1-\theta_i)^2 - K_{des}\theta_i^{\,2} + \frac{K_{dif}}{2^{2i-2}}\left(\frac{2\theta_{i-1}}{3} - \theta_i + \frac{\theta_{i+1}}{3}\right)\ (+\ \text{chg transfer kinetics})$$

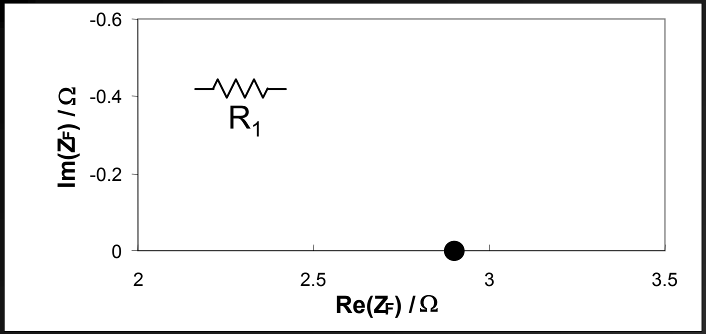


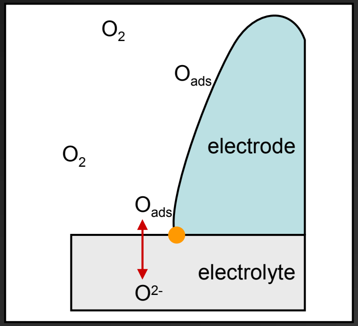
Compartment n°2

$$\frac{\partial \theta_2}{\partial t} = \boxed{K_{ads} p_{O_2} (1-\theta_2)^2 - K_{des} \theta_2^{\,2}} + \boxed{\frac{K_{dif}}{4}\left(\frac{2\theta_1}{3} - \theta_2 + \frac{\theta_3}{3}\right)}$$

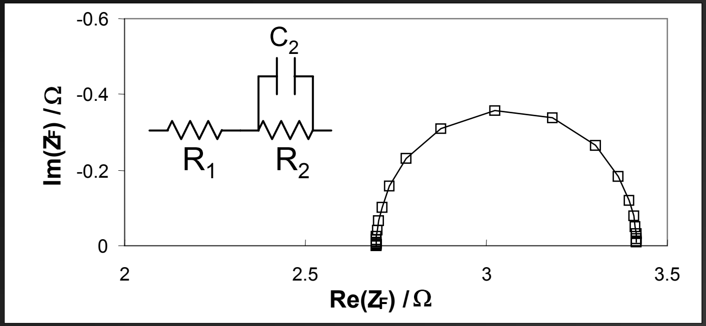


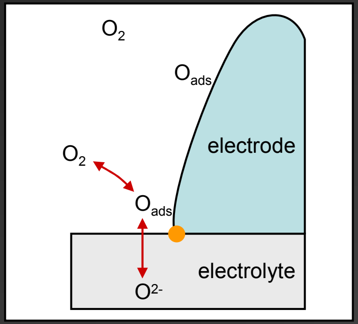
Modeling results



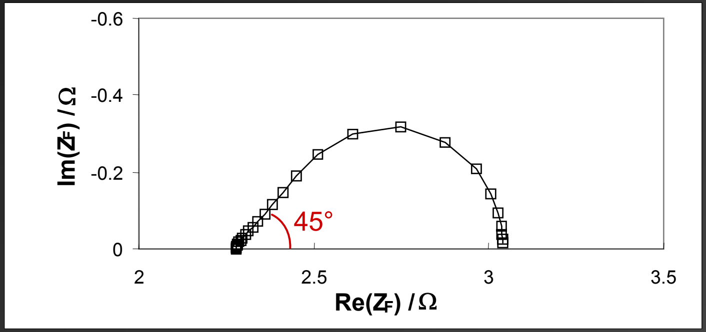


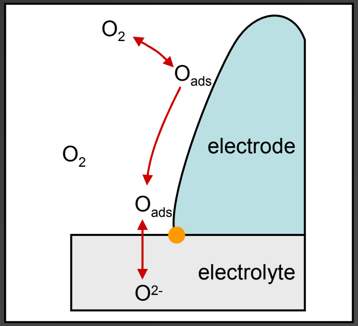
charge transfer
(model 1 = diffusion slow)



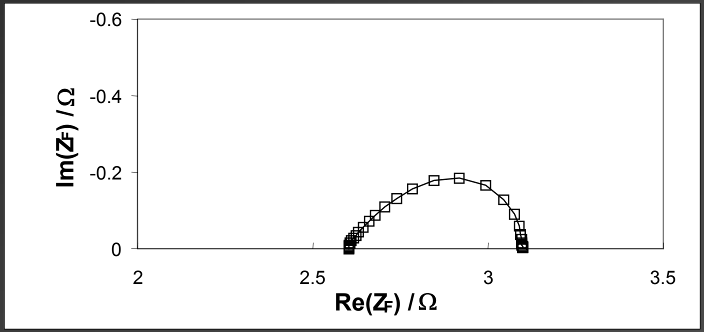


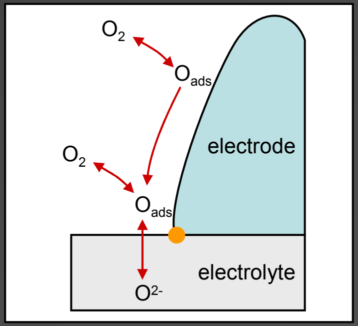
adsorption - charge transfer
(model 1 = diffusion slow)





diffusion - charge transfer
(model 2)



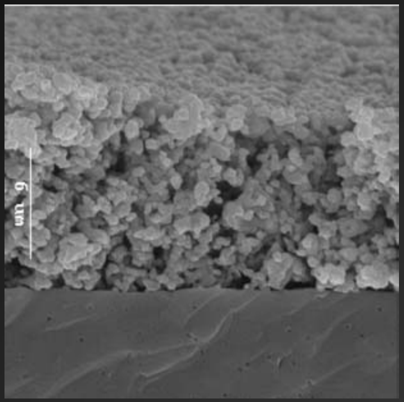


ads. – diff. - charge transfer
(model 2)

Comparison Modeling - Experiments

Electrode / electrolyte interfaces

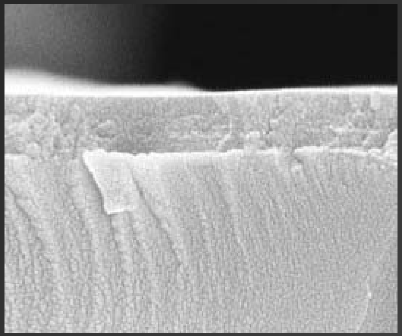
porous



~10-30 µm

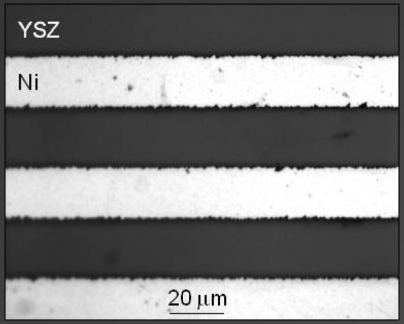
industrial application

dense



~100 nm -1 µm

microstructured

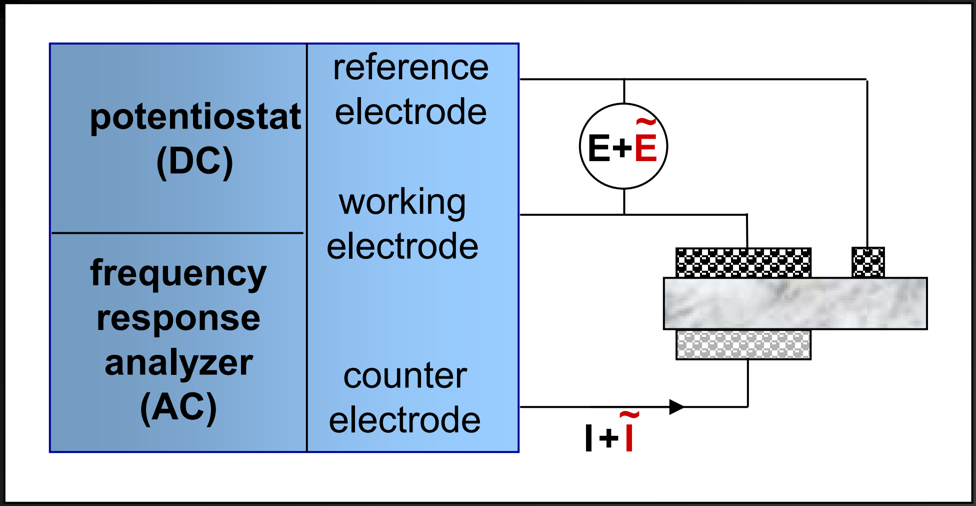


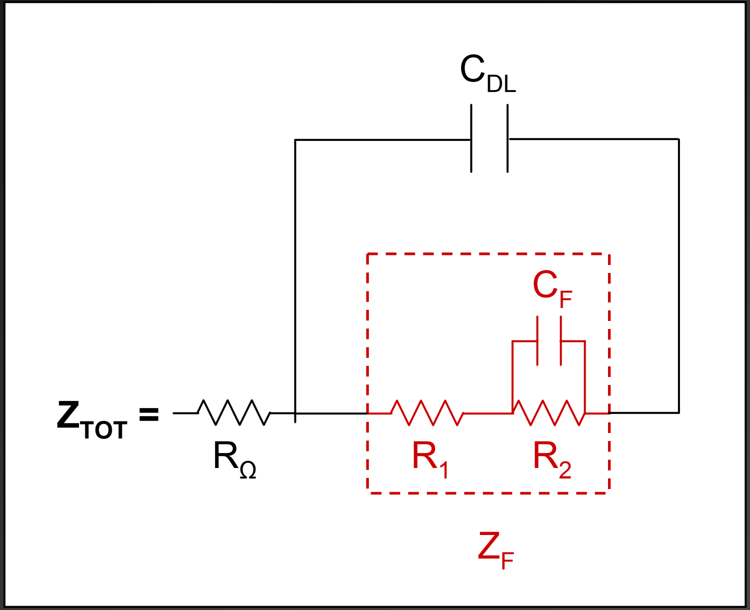
~20 µm -100 µm

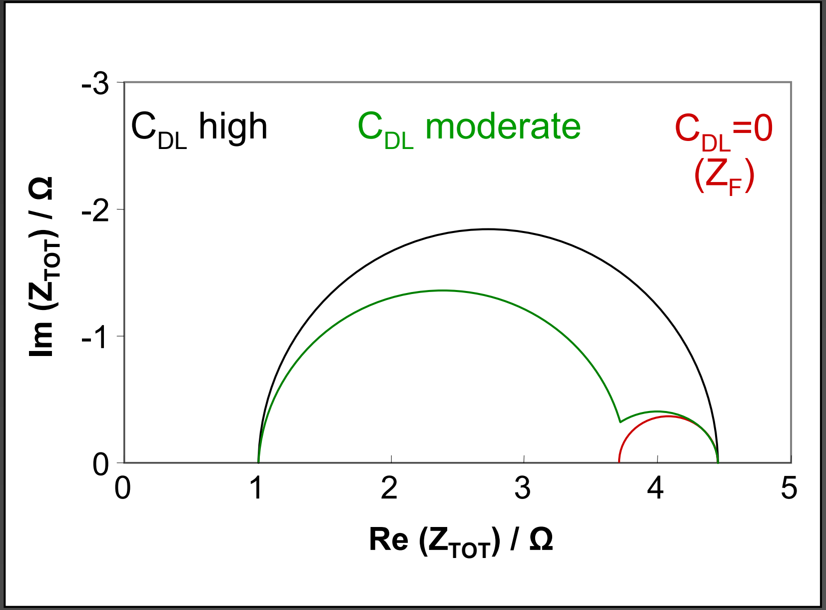
top view

control of the electrode dimensions

Experimental

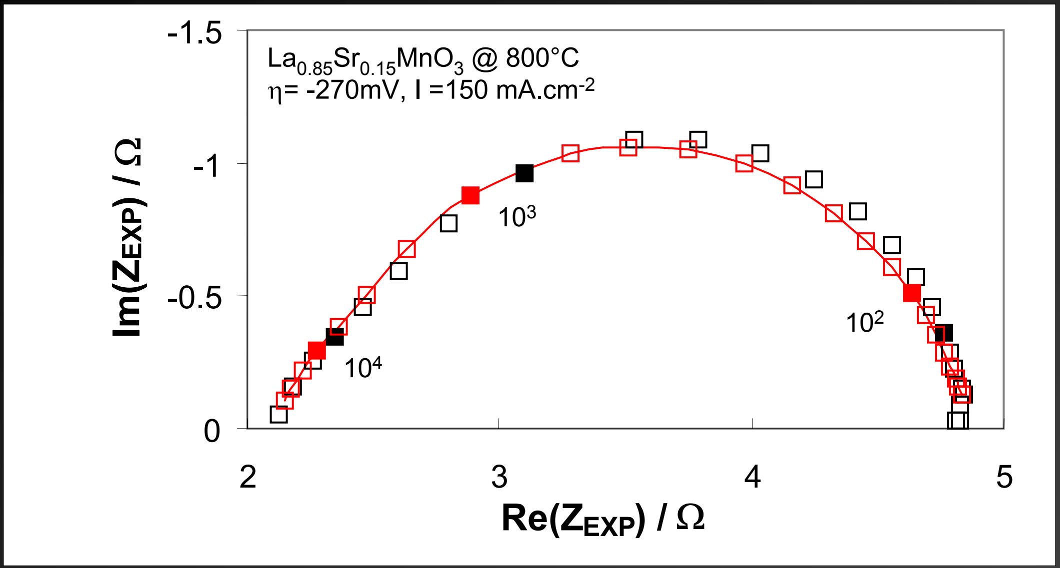




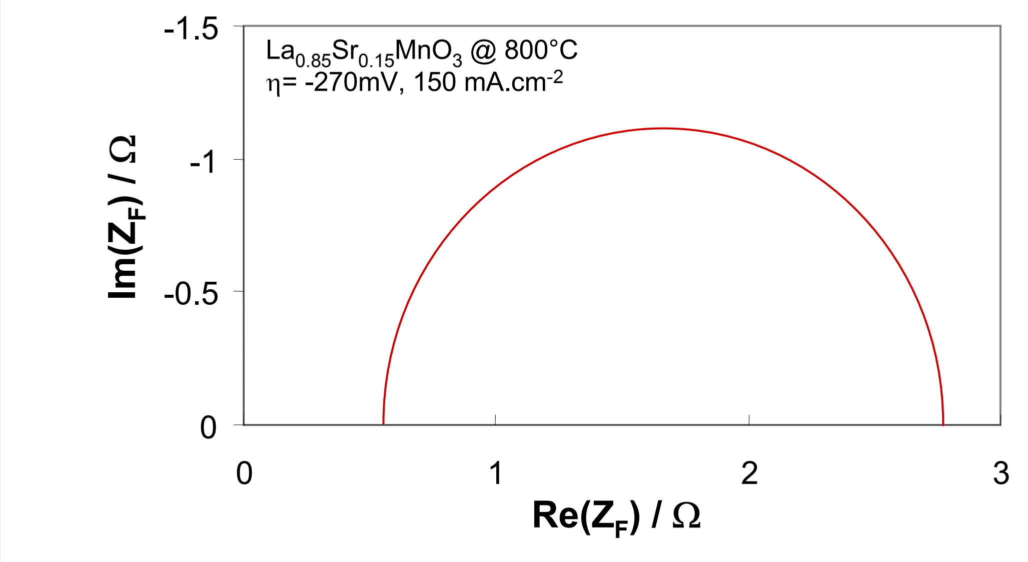


C_{DL} may mask Z_F → Berthier's method in *Corrosion* 51 (1995) 105

Comparison modeling - experiments

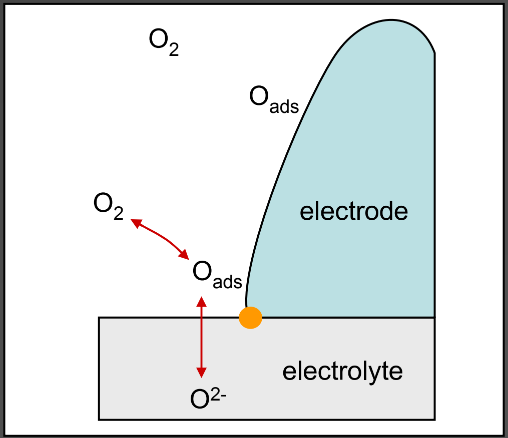


$$- (R_{\Omega}, C_{DL})$$



$$K_{dif} << K_{ads}, K_f$$

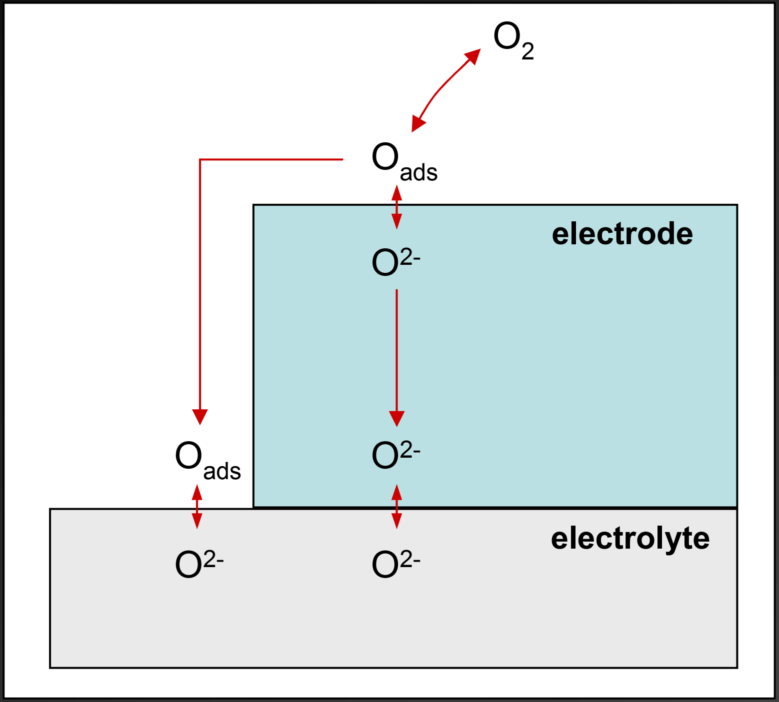
slow surface diffusion = Model 1



mixed control
adsorption - charge transfer

Ongoing SOFC projects

Mixed ionic-electronic electrodes

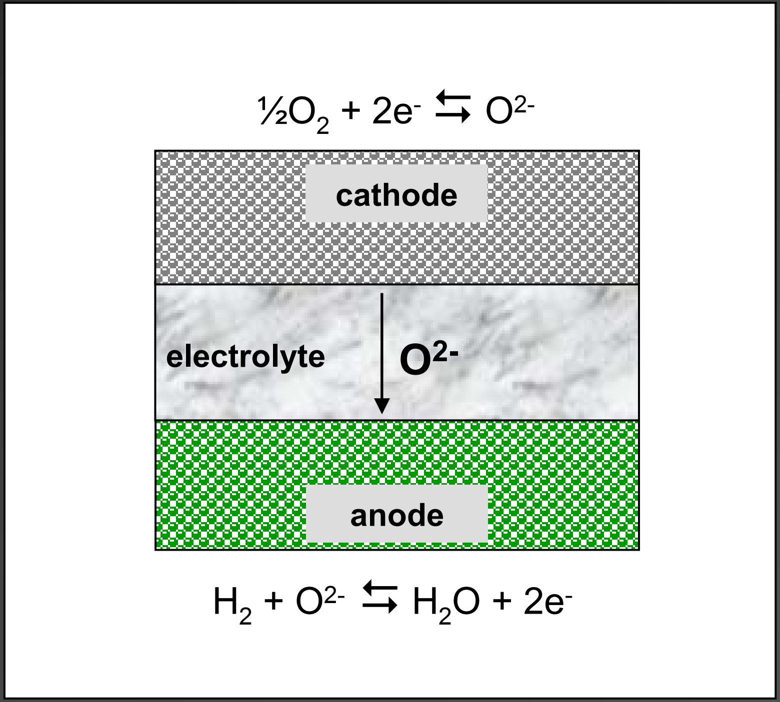


Additional reaction pathway through the electrode bulk.

Intermediate T° SOFC (600-800°C).

Typical material: $La_xSr_{1-x}Co_yFe_{1-y}O_3$ (LSCF).

Modeling the whole SOFC



Oxygen reduction, fuel oxidation, transport in the electrolyte.

Summary

- electrochemical reactions yield sophisticated impedance behavior
$\Rightarrow$ necessity of a modeling approach (analytical or numerical).

- SSM (with modern computation tools) enables to simulate the faradaic impedance of such reactions.
$\Rightarrow$ “fingerprint” of reaction models.

- SSM approach applicable to any other field of electrochemistry.

Many thanks to ...

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

SOFC group

Prof. L.J. Gauckler

References

M. Prestat and L.J. Gauckler, Solid State Ionics, submitted (2003)
Faradaic impedance of oxygen reduction at solid oxide fuel cell cathodes
Part I: adsorption and charge transfer limited reactions

M. Prestat and L.J. Gauckler, Solid State Ionics, submitted (2003)
Faradaic impedance of oxygen reduction at solid oxide fuel cell cathodes
Part Ii: surface diffusion limited reactions

A. Bieberle and L.J. Gauckler, Solid State Ionics, **146** (2002) 23
State-Space Modeling of the anodic SOFC system Ni, H_2-H_2O|YSZ

A. Mitterdorfer and L.J. Gauckler, Solid State Ionics, **117** (1999) 187
Identification of the reaction mechanism of the Pt, O_2 (g)|Yttria-Stabilized Zirconia system,
Part I: general framework, modelling and structural investigation

A. Mitterdorfer and L.J. Gauckler, Solid State Ionics, **117** (1999) 203
Identification of the reaction mechanism of the Pt, O_2 (g)|Yttria-Stabilized Zirconia system,
Part II: model implementation, parameter estimation and model validation