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An Agglomerate Model for the Rationalisation of MCFC Cathode Degradation

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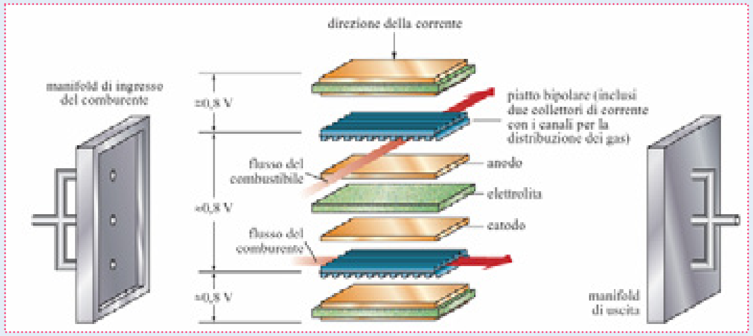
MOLTEN CARBONATE FUEL CELLS (MCFC)

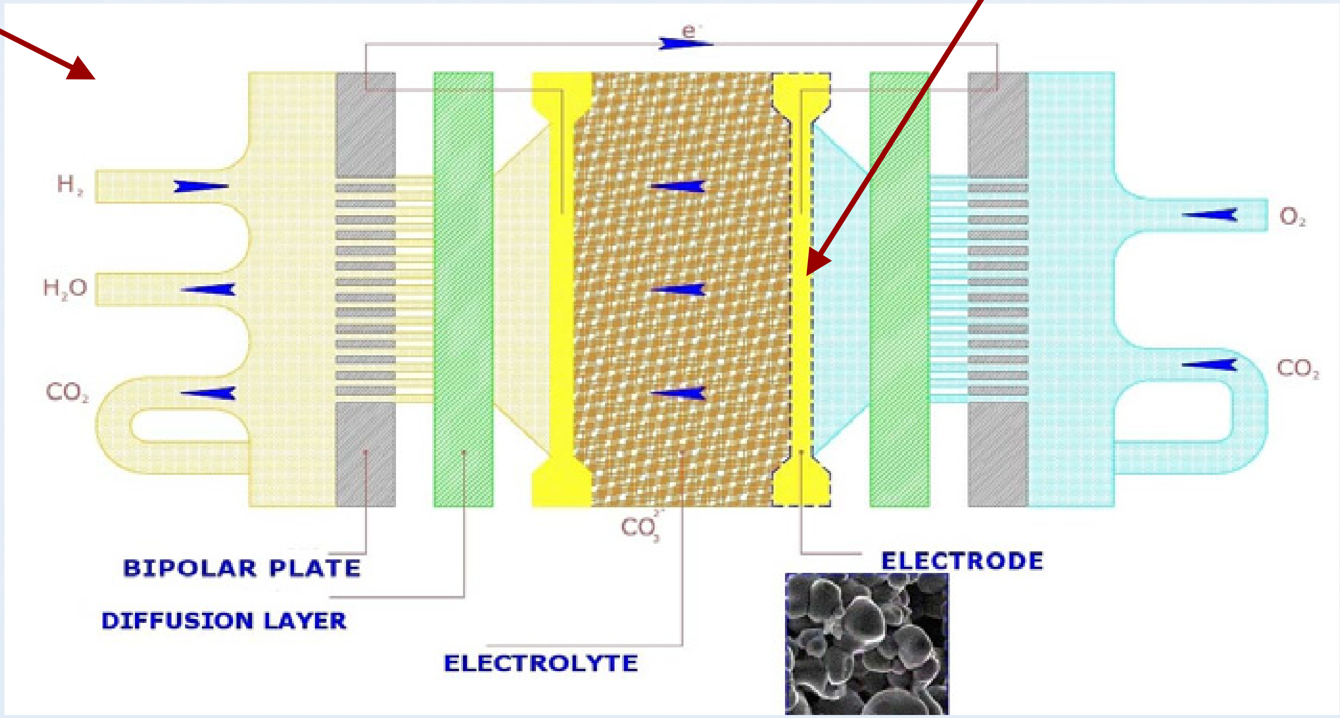
STACK



Schematic view of charge and mass transport in an MCFC

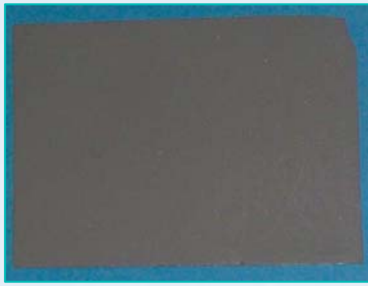
REGION OF INTEREST FOR THE ***MATHEMATICAL MODELING***

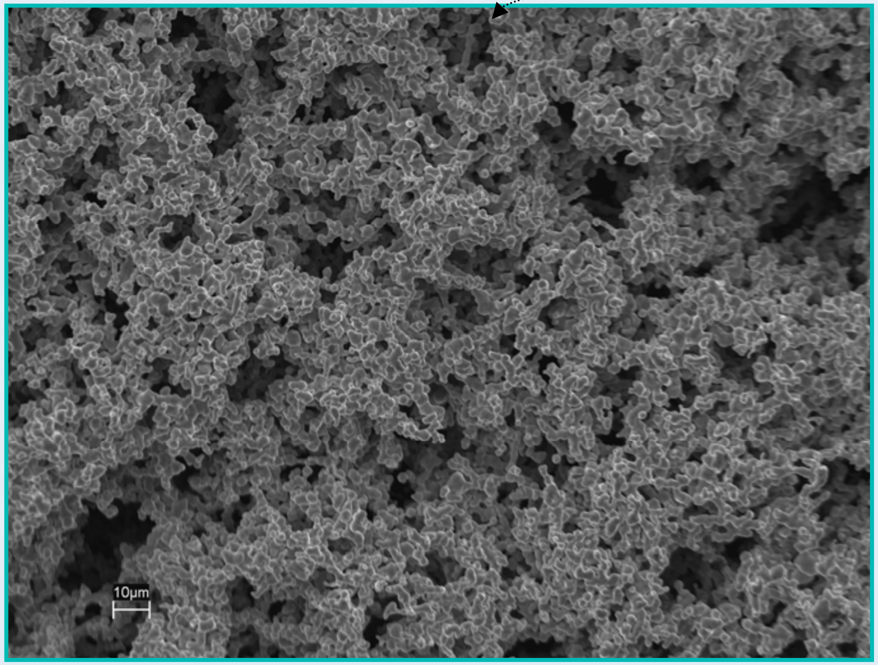
UNIT



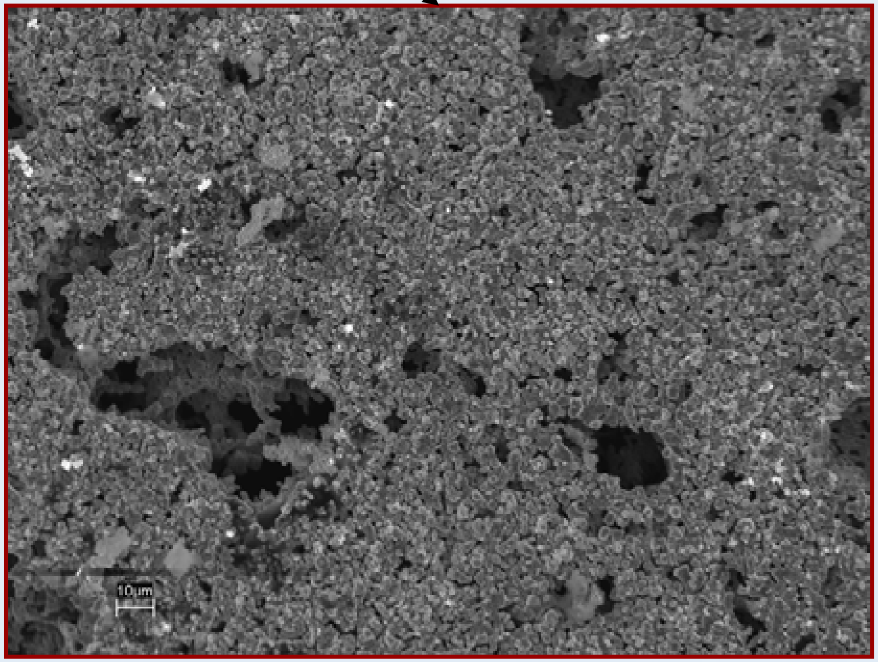
CATHODE REACTION $\frac{1}{2}O_2 + CO_2 + 2e^- \rightarrow CO_3^{=}$

SINGLE MOST CRITICAL SYSTEM DURABILITY ISSUE: CATHODE DEGRADATION



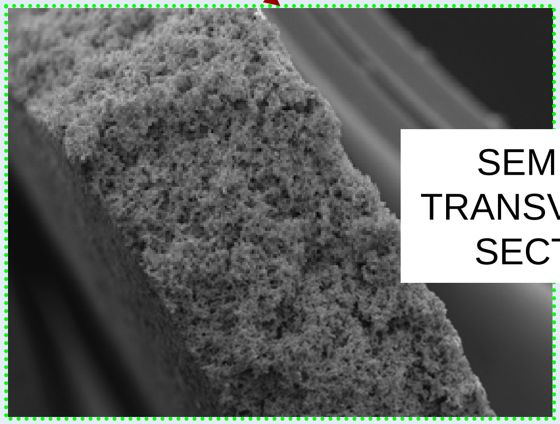


Pristine NiO cathode



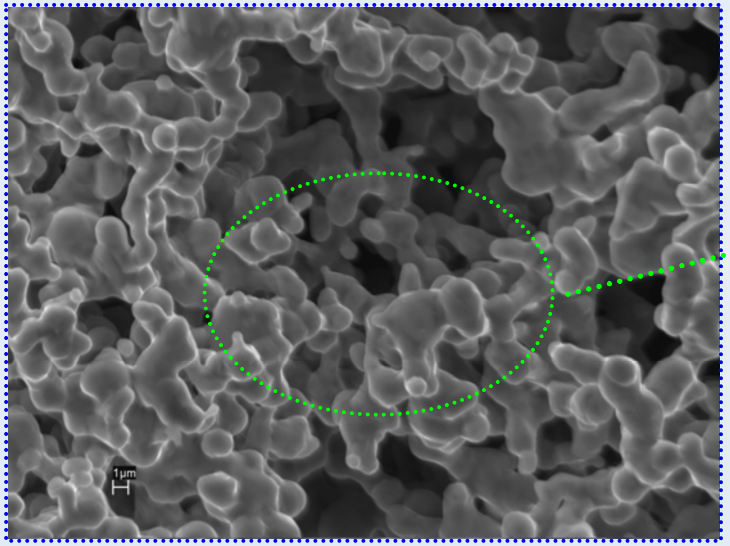
Same, after
1000 h of operation in MCFC

AGGLOMERATE STRUCTURE OF A POROUS ELECTRODE

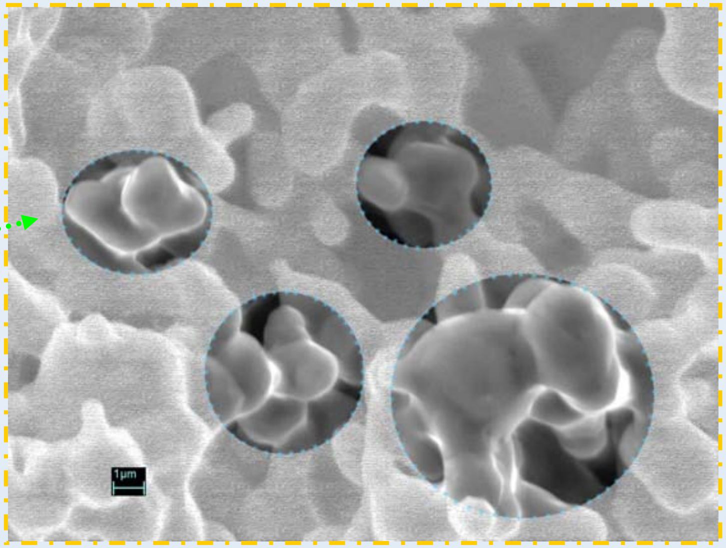


SEM 100x
TRANSVERSAL
SECTION

Microstructure of pristine NiO cathodes



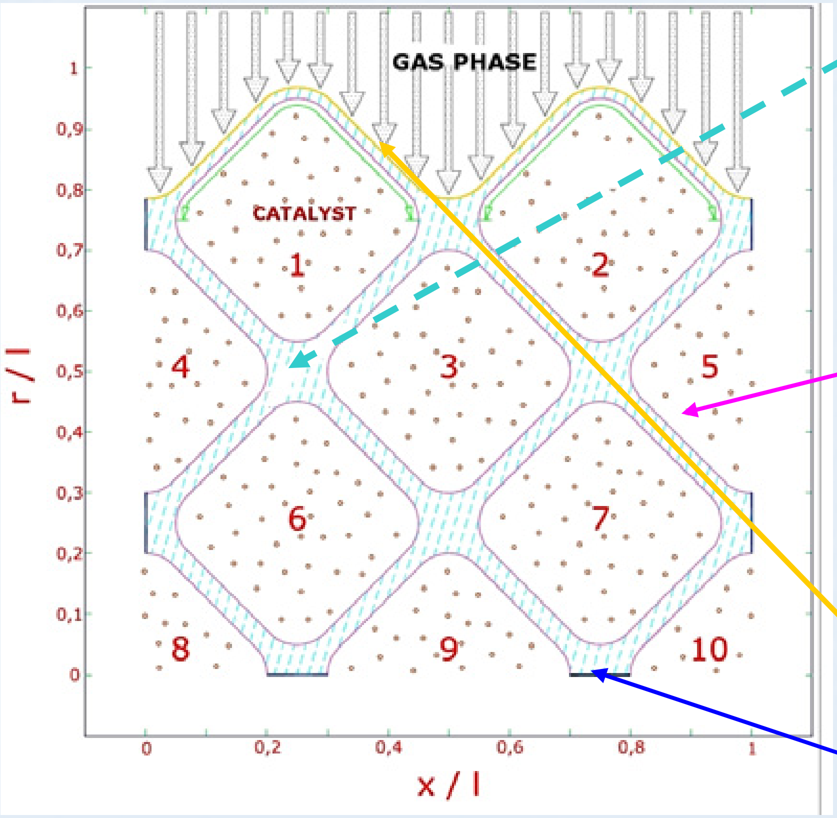
2500x SEM Micrograph



ZOOM 5000x : typical agglomerate structure

MCFC Electrochemistry in the 2D Agglomerate Model: PDEs, geometry, BCs

System of coupled reaction-diffusion PDEs, corresponding to the the steady state mass-balance equations for the concentrations of peroxide $c^{ox}(x)$ of carbon oxide $c^{cd}(x)$ and for the potential $\eta(x)$.



$$x \in \boldsymbol{\Omega} \qquad electrolyte-domain$$

$$\nabla^2 c^{ox} = 0 \quad \nabla^2 c^{cd} = 0 \quad \nabla^2 \phi = 0$$

Electrochemical kinetics has been accounted for by non-linear boundary conditions (b.c.)

$\{x,r\} \in \partial\boldsymbol{\Omega}_1$ *electrode – electrolyte*

$$\begin{cases} \nabla_N c^j = k_j \cdot g(c^{ox}, c^{cd}, \phi) \quad j = ox, cd \\ \nabla_N \phi = \kappa \cdot g(c^{ox}, c^{cd}, \phi) \end{cases}$$

$$g(c^{ox}, c^{cd}, \phi) = i_0 \cdot \{(c^{cd})^{-2} \cdot \exp[\alpha_a \cdot (\phi - \phi_{0,ox})] - c^{ox} \cdot \exp[-\alpha_c \cdot (\phi - \phi_{0,ox})]\}$$

Butler-Volmer eq. for the O_2 reduction reaction (s-o m)

$\{x,r\} \in \partial\boldsymbol{\Omega}_2^g$ *gas – electrolyte*

$$\begin{cases} c^{ox} = c^{ox}_{sat}, c^{cd} = c^{cd}_{sat} \\ \nabla_N \phi = 0 \end{cases}$$

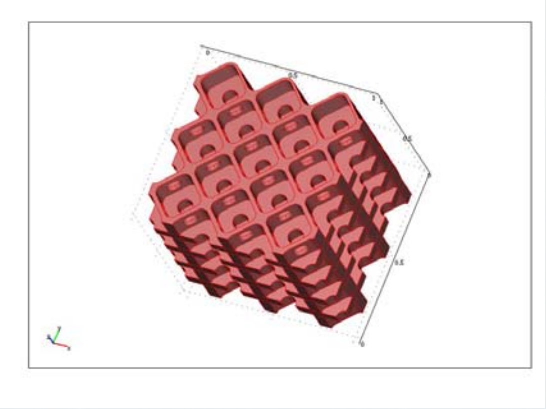
$\{x,r\} \in \partial\boldsymbol{\Omega}_2^e$ *porous matrix – electrolyte*

$$\begin{cases} \nabla_N c^{ox} = 0, \quad \nabla_N c^{cd} = 0 \\ \phi \equiv \phi_0 \end{cases}$$

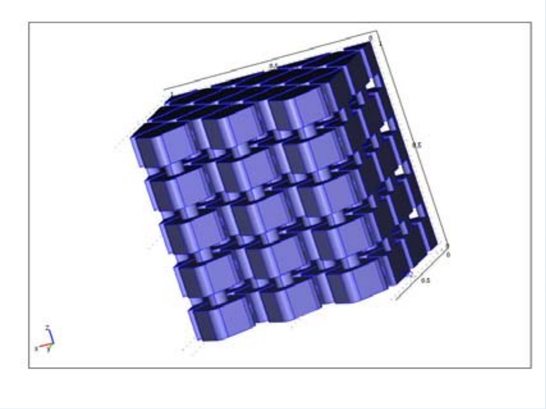
E. Fontes et al. -*Electrochim. Acta*, 1993,1995
J. Appl. Electrochem 1997

3D Agglomerate Model

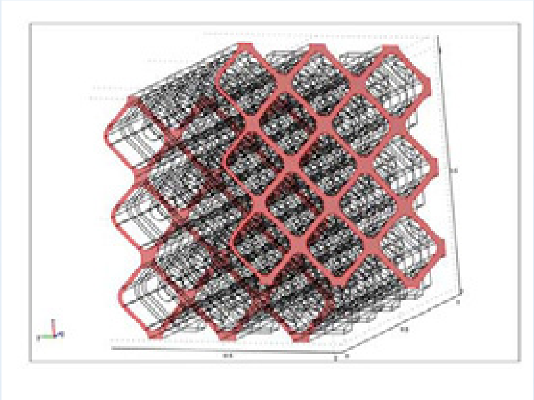
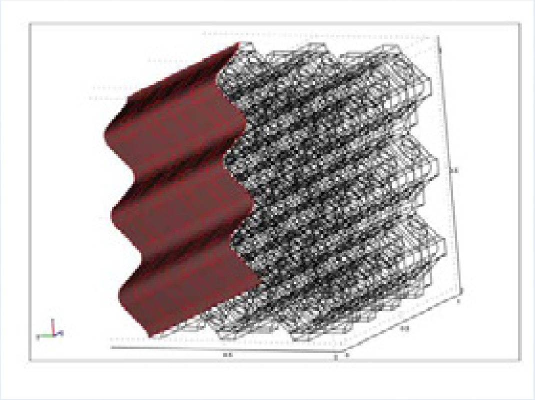
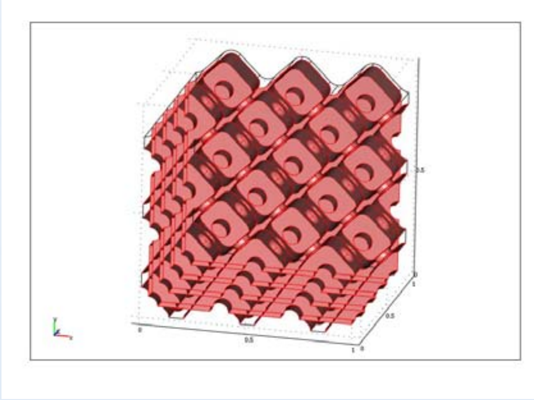
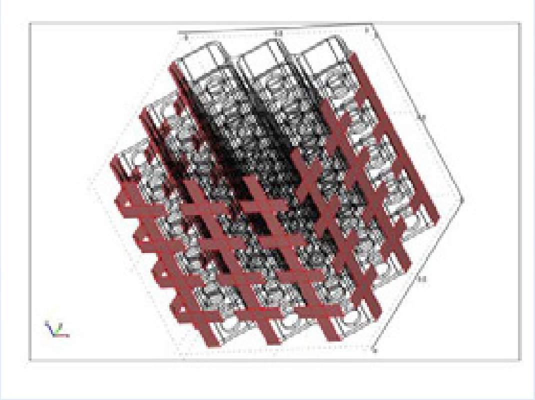
3D DOMAIN Ω
(= ELECTROLYTE)



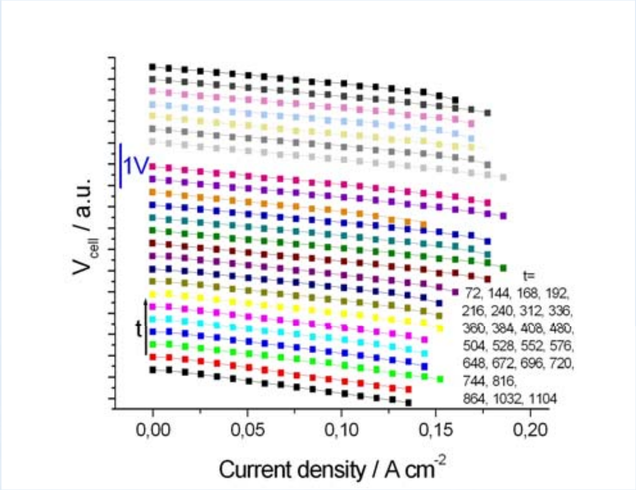
COMPLEMENTARY DOMAIN
(= CATALYST PARTICLES)

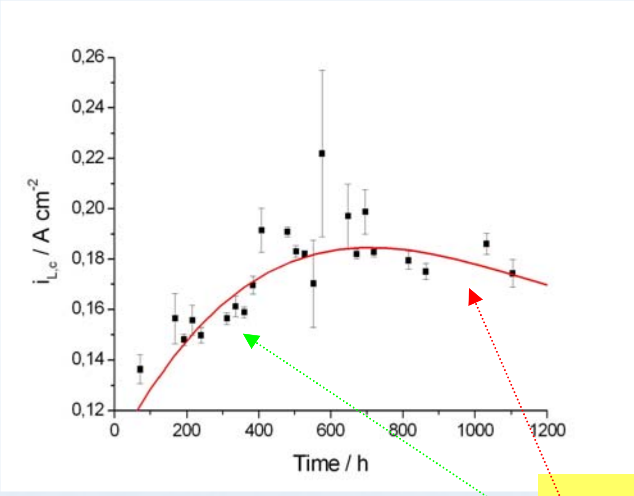


BOUNDARIES $\partial\Omega$

$\partial\mathbf{\Omega}_2^e$	$\partial\mathbf{\Omega}_2^g$
	
$\partial\mathbf{\Omega}_1$	$\partial\mathbf{\Omega}_2^e$
	

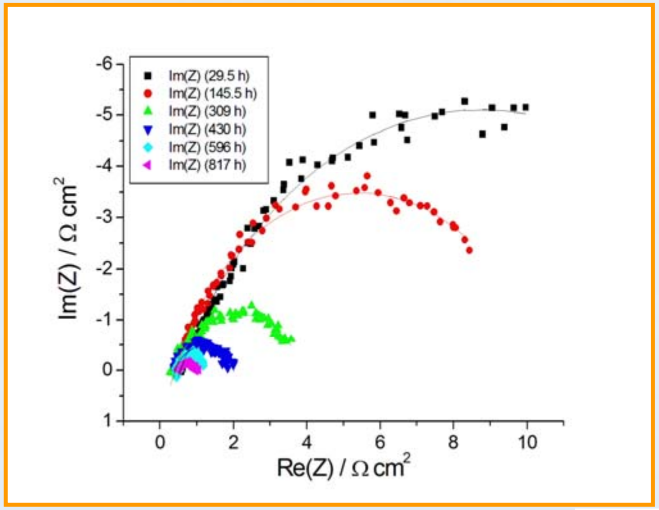
Time-dependent Electrochemical Efficiency of MCFC

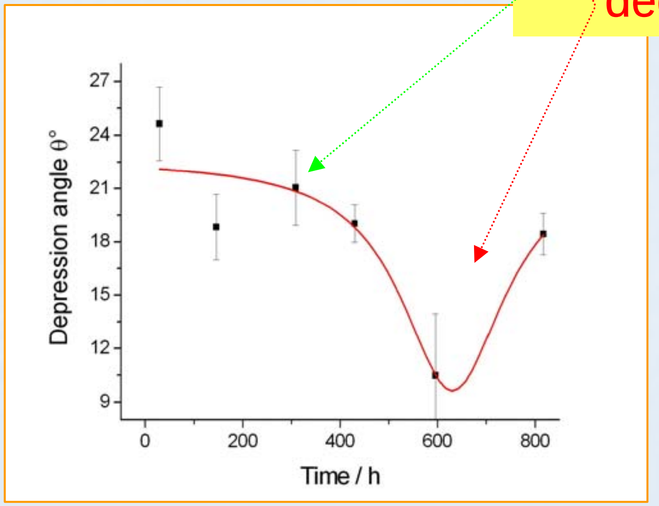


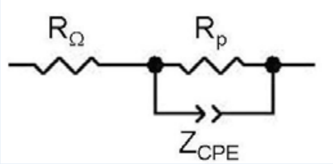


$$V_{cella}(I) = V_{cella}^{eq} - \frac{RT}{\alpha_c F}\cdot\ln\frac{i}{i_{oc}} + \frac{RT}{n_c F}\cdot\ln\left(1-\frac{i}{i_{L,c}}\right) - \frac{RT}{\alpha_a F}\cdot\ln\frac{i}{i_{oa}} + R_\Omega\cdot i$$

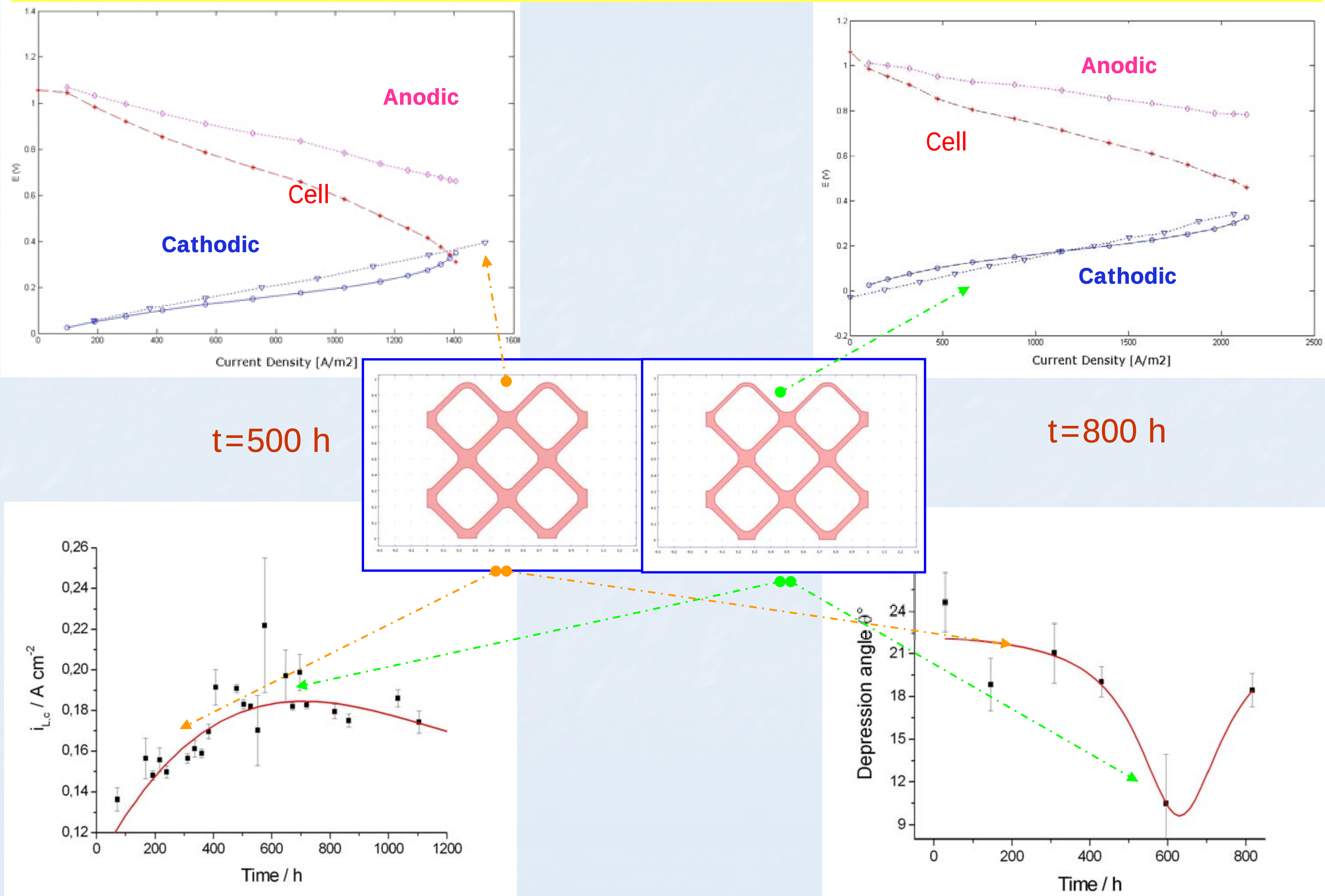
Electrocatalysis: improves, degrades







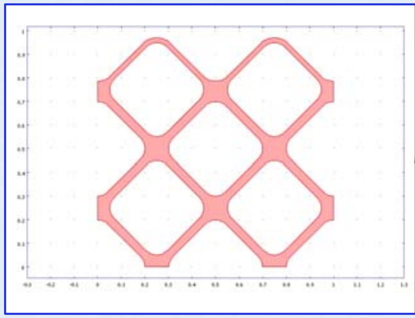
Transient Improvement of Cathode Performance by Lithiation (particle growth, constant volume, no morphology changes)



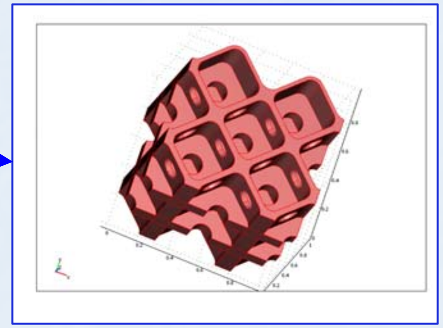
Simulation of Cathode Degradation by Particle Agglomeration

N= number of catalyst particles

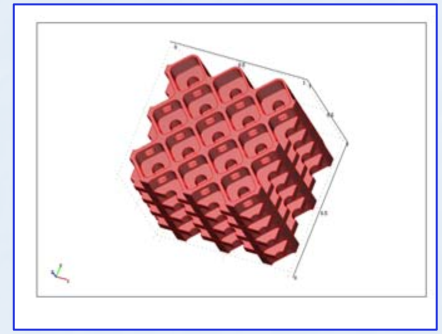
2D BASIC (N_0=7)

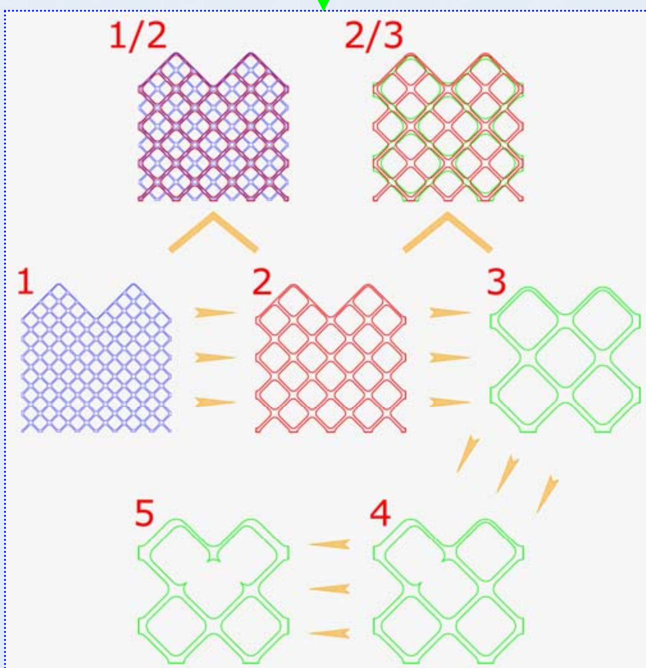


3D BASIC (N_0=21)

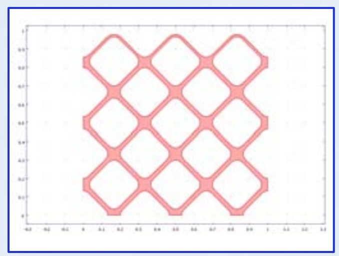


N_1=82.5

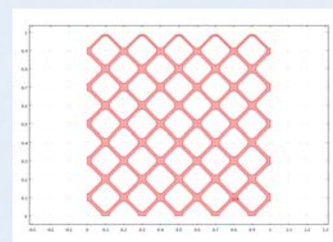




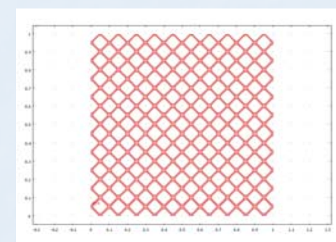
N_1=16.5



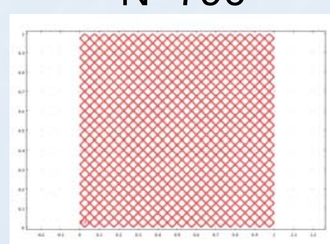
N=47.5



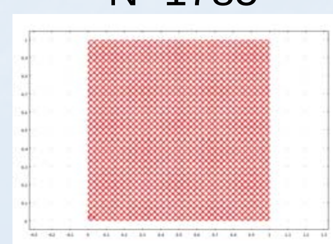
N=195



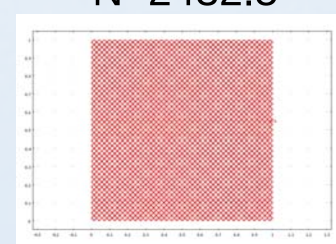
N=790



N=1785



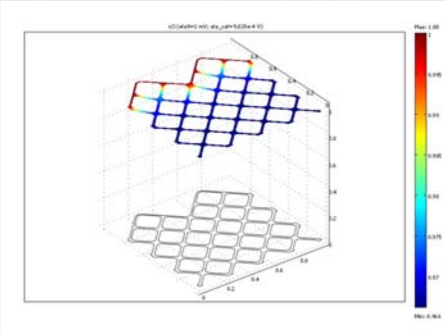
N=2432.5



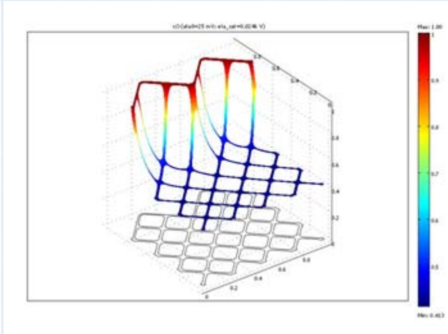
Simulation of Local Electrokinetic Quantities in 2D and 3D Geometries

c_{ox}

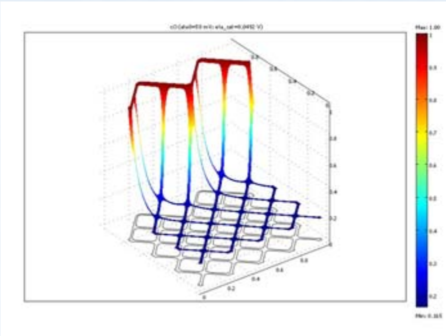
2D DOMAIN



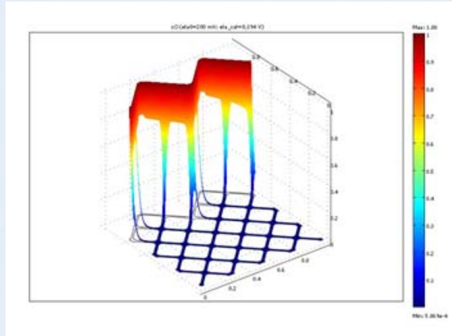
$\eta = -\langle\phi\rangle + \phi_o = 1$ mV



η=25 mV

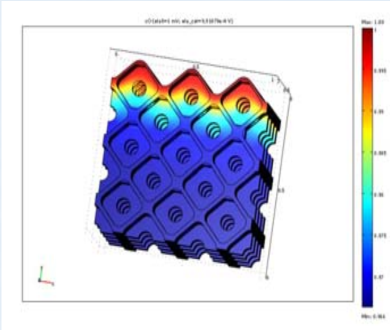


η=50 mV

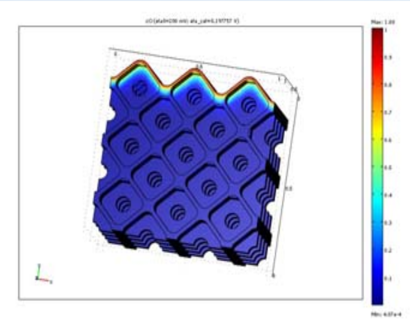


h=200 mV

3D DOMAIN

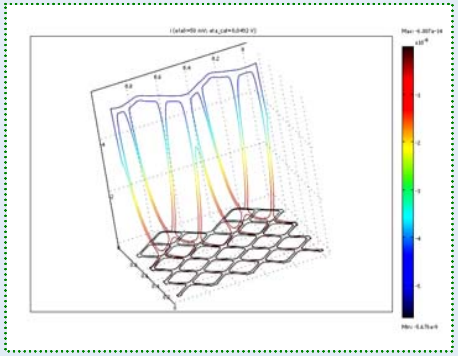


η=1 mV

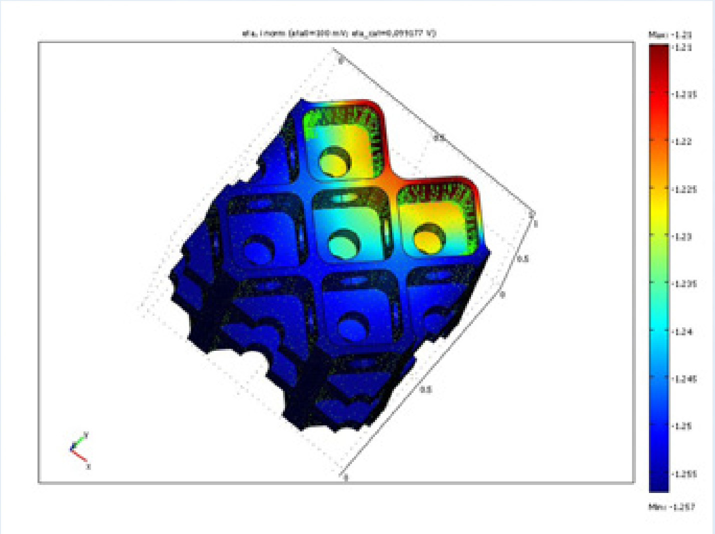


η=200 mV

ϕ and i

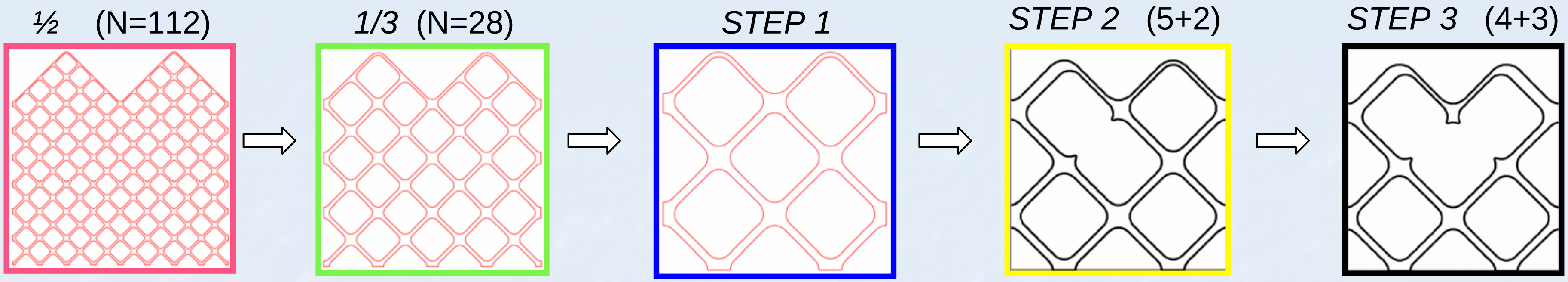


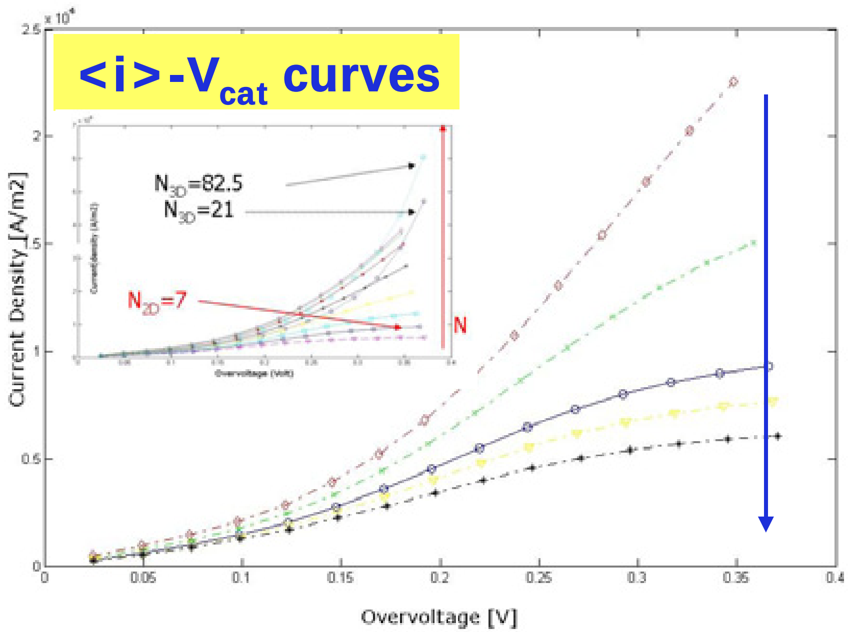
η=50 mV

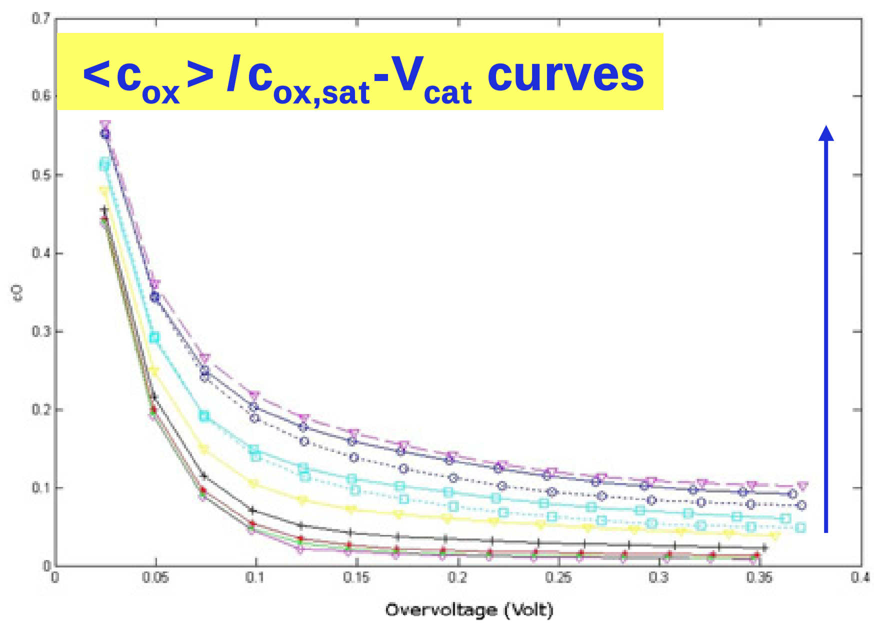


η=100 mV

Simulation of Global Electrokinetic Quantities for Successive 2D Agglomeration Steps



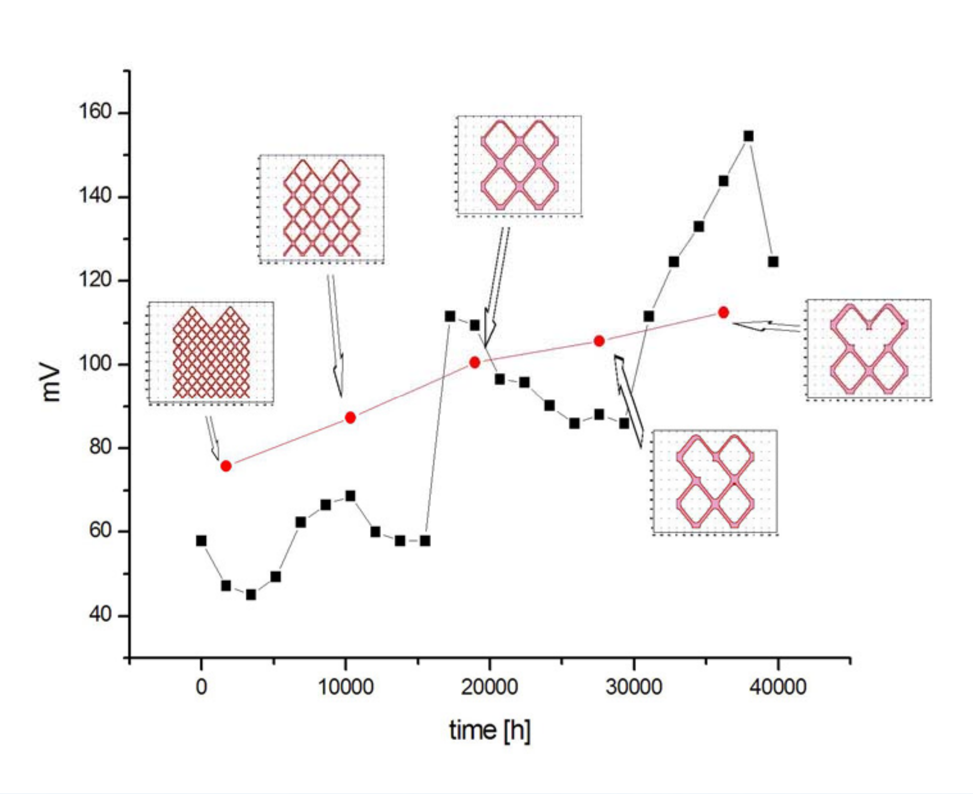


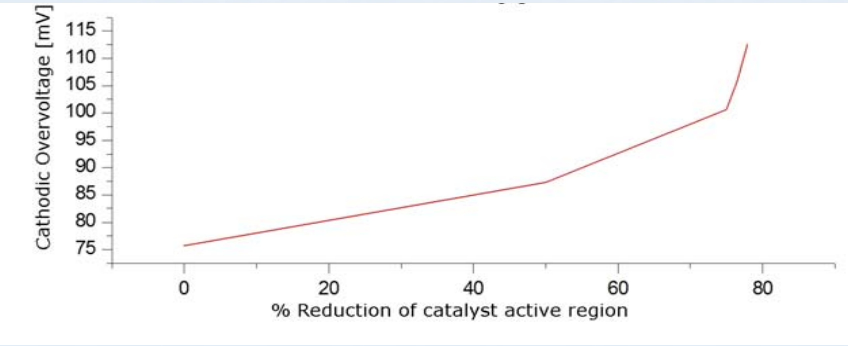


agglomeration↑ ⇒ $i_{L,c}$↓ ∧ O_2 utilisation ↓

Comparison with Long-Term Operation Literature Data

Non-ohmic polarisation contribution of a MCFC cell at 150 mA/cm^2 [Tanimoto 98]





Reduction of catalyst active region, estimated from numerical simulations

Conclusions

✓ We developed a numerical approach, based on the literature agglomerate scheme, able to rationalise changes of electrocatalytic behaviour in terms of morphological variations.

✓ Both positive (lithiation) and negative (agglomeration) electrocatalytic evolutions can be followed.

✓ We found efficient electrochemical conceptual tools able to manipulate the local information provided by COMSOL in order to gain information on the global electrochemical quantities, relevant to fuel-cell development.

✓ We established an approach providing a link between information at material-science level and response of the global electrochemical system.