

MODELING AND PILOT SCALE STUDIES OF THE HYS CYCLE ELECTROLYZER

CEA-Marcoule

S. Charton, D. Ode , J.J. Ramadier, P. Rivalier

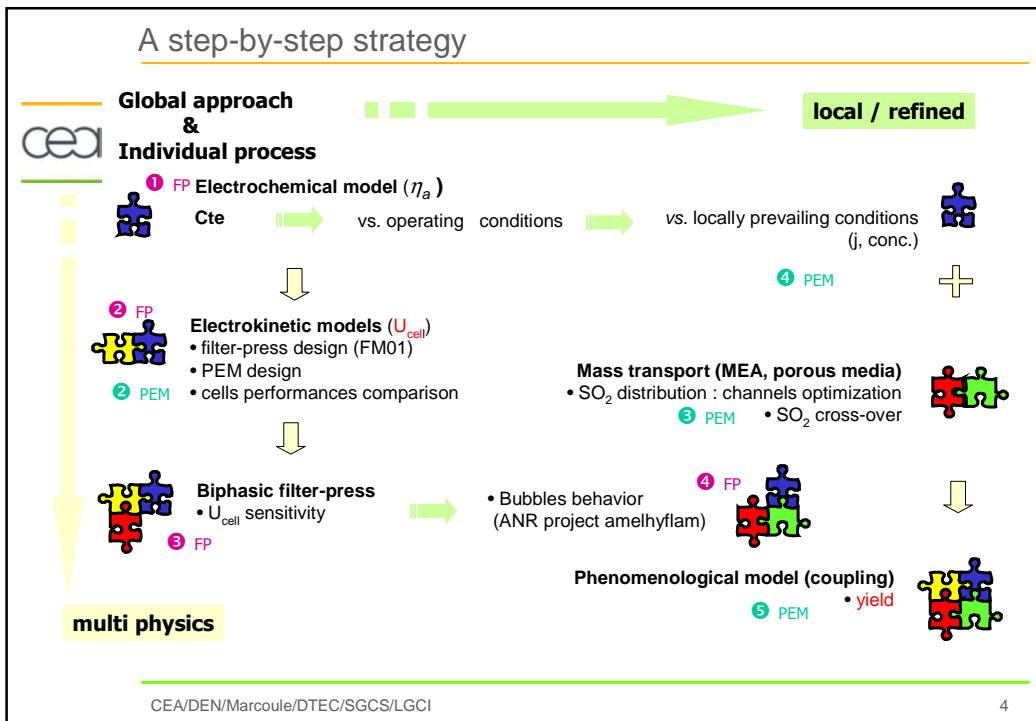
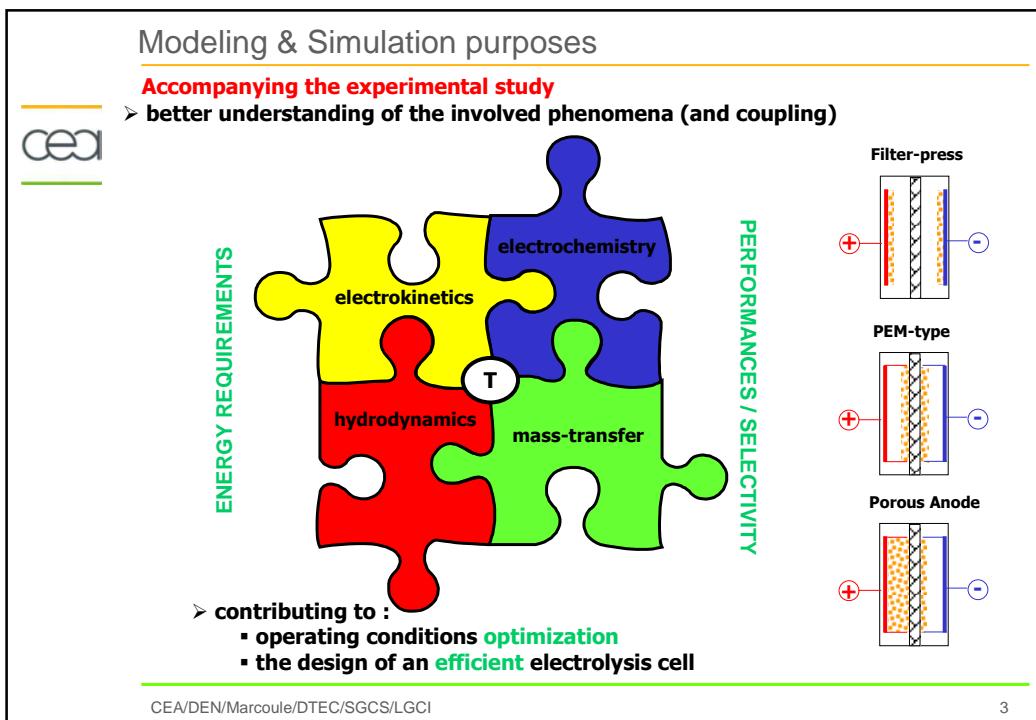


With the collaboration of :
CEA Saclay (LECNA) N. Gruet, (P. Pleurdeau) R. Robin
CNRS Grenoble (LEPMI) J.P. Caire, E. Chainet, (J. Janvier), T. Michaud
CEA Grenoble (LITEN) N. Guillet, E. Mayousse

Overview

- 1- Electrochemical step modeling :
 - a. objectives and methodology
 - b. results (filter-press design)
 - c. future works

- 2- Pilot test facility :
 - a. brief description
 - b. Filter-press and PEM electrolyzers results
 - c. future works



Overview



1- Electrochemical step modeling :

- a. objectives and methodology
- b. results (filter-press design)
- c. future works

2- Pilot test facility :

- a. brief description
- b. Filter-press and PEM electrolyzers results
- c. future works

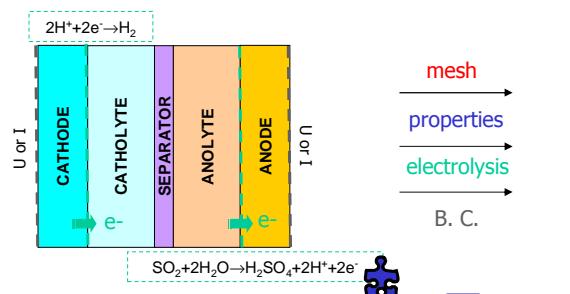
Electrokinetic Model (1/5)



1- Model assumptions (FM01)

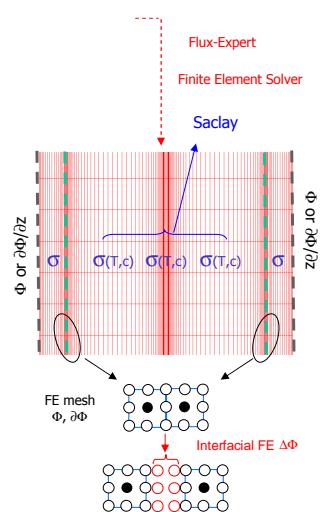
Potential distribution : solved variable Φ

Uniform fluid repartition (1D or 2D model)



Scope :

- preliminary design
- sensitivity analysis (geometry, operating conditions)

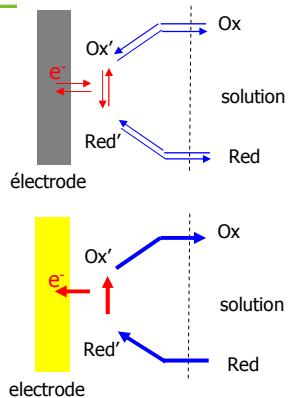


Electrokinetic Model (2/5)

2.1- Principle of the « overall » electrochemical model



✓ Need for a numerical expression $\eta_a = j/(op. cond.)$



at equilibrium : $i = 0$

$$E_{electrode} = E_{Red/Ox}^{eq}$$

$i \neq 0$ « kinetics »

$$+ \eta$$

$$\eta_{activation} + \eta_{concentration} = f(i)$$

Charge Transfer

Mass Transfer

Design of Experiments (voltammetry ; 3-electrodes cell)
(coll. CNRS-LEPMI, Grenoble)

3 factors :

- 3 levels T : 20°C, 45°C et 70°C
- 3 levels [H₂SO₄] : 20 %wt, 40 %wt, 60 %wt
- static or rotating disk electrode

NB: SO₂ saturation

CEA/DEN/Marcoule/DTEC/SGCS/LGCI

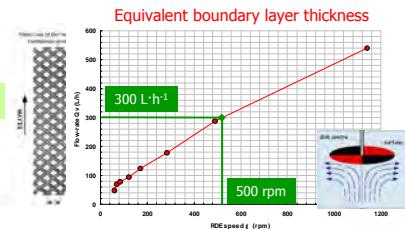
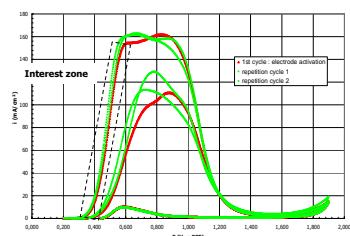
7

Electrokinetic Model (3/5)

2.2 – Electrochemical model derivation



1- hydrodynamic analogy between FM01 and RDE



2- domain exploration / reproducible procedure determination

Sweep rate :	10^{-3} to 5×10^{-2} V/s
RDE speed :	0 to 2000 rpm
Initial potential :	0.2 to 0.35 V _{ecs}
Maximum potential :	1.2 to 1.9 V _{ecs}
Concentration:	20%, 40% and 60%
Temperature:	20°C, 45°C and 70°C

(~ 300 experiments (including 22 DOE runs))

3- data processing

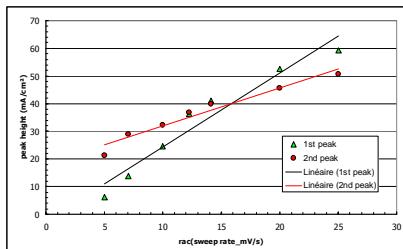
✓ thermodynamics $\rightarrow E_0$

$$\eta_a(j) = E - E_0 \text{ with } E = a(T, w\%) + b(T, w\%) \cdot j + c(T, w\%) \cdot j^2 + d(T, w\%) \cdot j^3$$

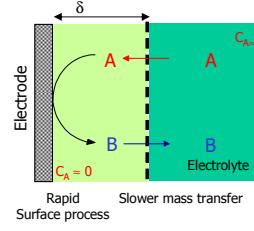
CEA/DEN/Marcoule/DTEC/SGCS/LGCI

8

Mass transfer limitation ?

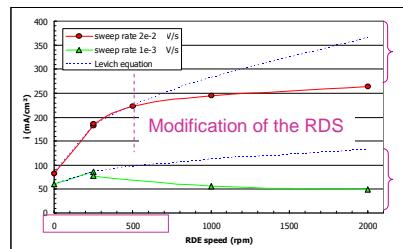


Evidence of mass transfer limitation (Cottrell)

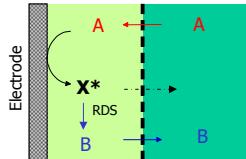


$A \rightarrow B$
If δ decreases :
Apparent rate \uparrow

$A \rightarrow X^* \rightarrow B$
If δ decreases :
 X^* desorption \uparrow



Deviation from Levich model



CEA/DEN/Marcoule/DTEC/SGCS/LGCI

9

Electrokinetic Model (4/5)



2.2 – Electrochemical model derivation

⇒ Matrix of Experiment (2×3^2 design)

- ✓ not in random order
- ✓ no noticeable effect of RDE speed
- ⌚ response surface achieved for j_{max} and OCV
- ⌚ a,b,c,d ⇒ lack of fit



Tabulated values of a,b,c,d

✓ AIChE conference (Philadelphia, 2008)

run	Acid wt.%	Temperature (°C)	RDE speed (rpm)
1	20	20	0
2		500	500
3		0	0
4		45	500
5		70	0
6		500	500
7	40	20	0
8		500	500
9		0	0
10		45	500
11		70	0
12		500	500
13	60	20	0
14		500	500
15		0	0
16		45	500
17		70	0
18		500	500
R1	40	45	0
R2		500	500
R3		0	0
R4		500	500

CEA/DEN/Marcoule/DTEC/SGCS/LGCI

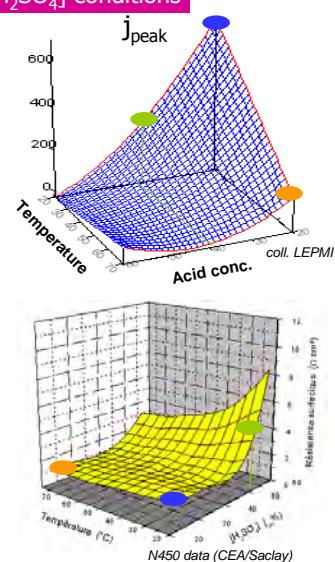
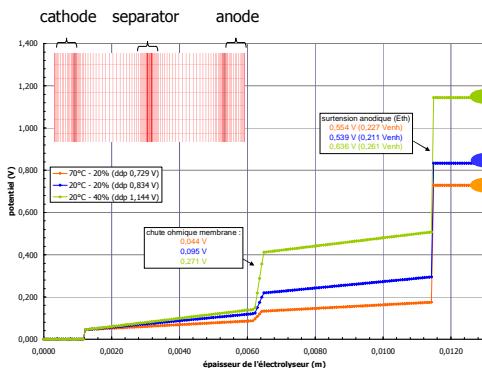
10

Electrokinetic Model (5/5)



3- Application to FM01 sensitivity vs. T and $[H_2SO_4]$ conditions

Flux-Expert – JNF 1000A/m²



✓ GPE-EPIC conference (Venice, June 14-17)

CEA/DEN/Marcoule/DTEC/SGCS/LGCI

11

Coupled Fluid Mechanic / Electrokinetic Simulation (1/3)

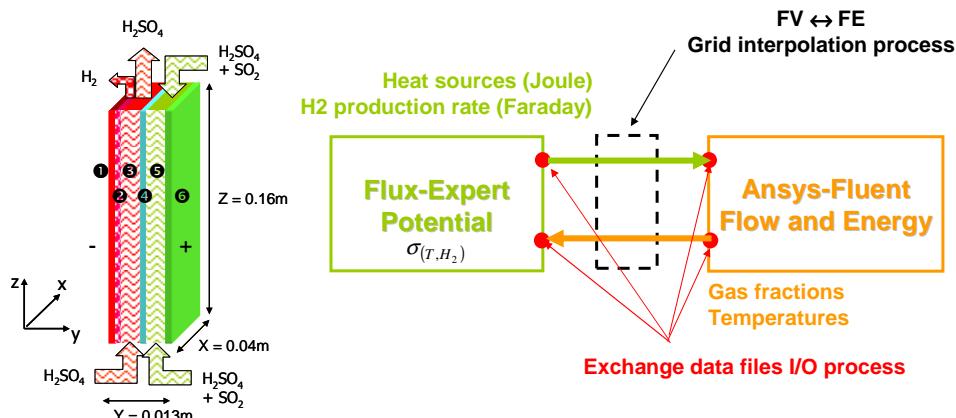


1- Model assumptions

$$\sigma_{(T,\alpha_{H_2})} = \sigma_{T,0} (1 - \alpha_{H_2})^{1.5}$$

Potential distribution

Biphasic (Euler-Euler) and turbulent ($k-\epsilon$) flow



✓ F. Jomard et al., J. Appl. Chem., 308 (08) pp. 297

CEA/DEN/Marcoule/DTEC/SGCS/LGCI

12

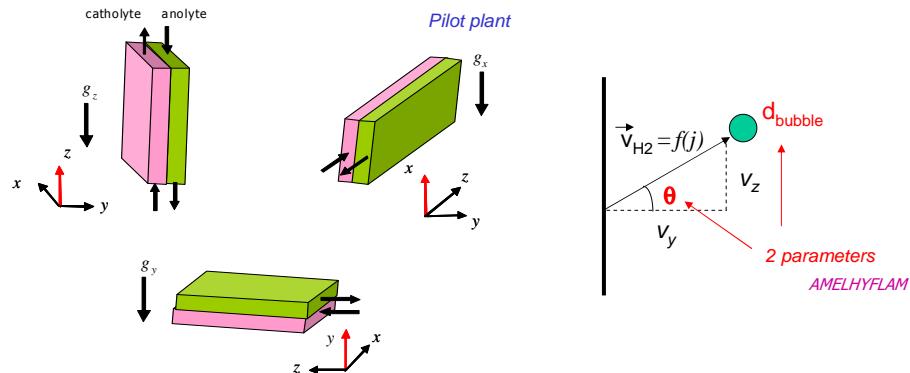
Coupled Fluid Mechanic / Electrokinetic Simulation (2/3)

2- Sensitivity study



U_{cell} sensitivity towards :

- operating parameters : cell orientation & catholyte flow-rate
- « unknown » parameters of the Eulerian model (θ and d_{bubble})



CEA/DEN/Marcoule/DTEC/SGCS/LGCI

13

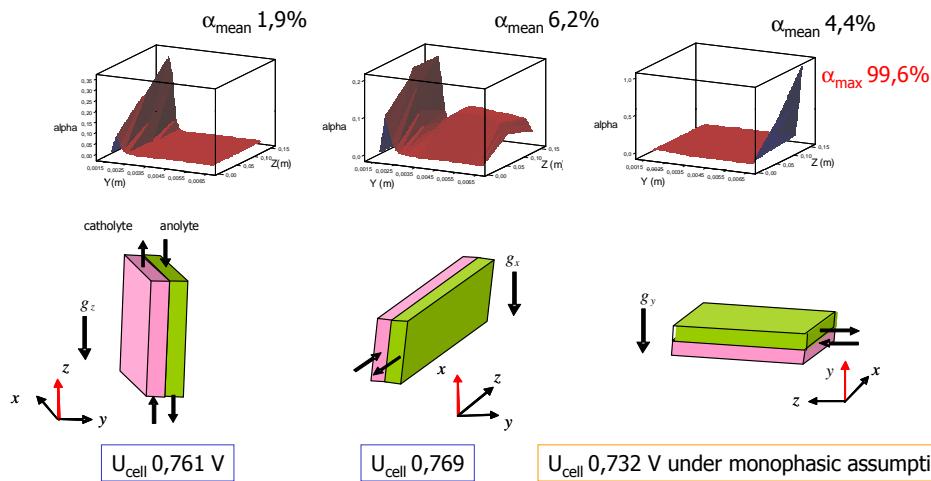
Coupled Fluid Mechanic / Electrokinetic Simulation (3/3)

3- Example of simulation results

✓ ELECTROCOR conference (Bologna, June 24-26)

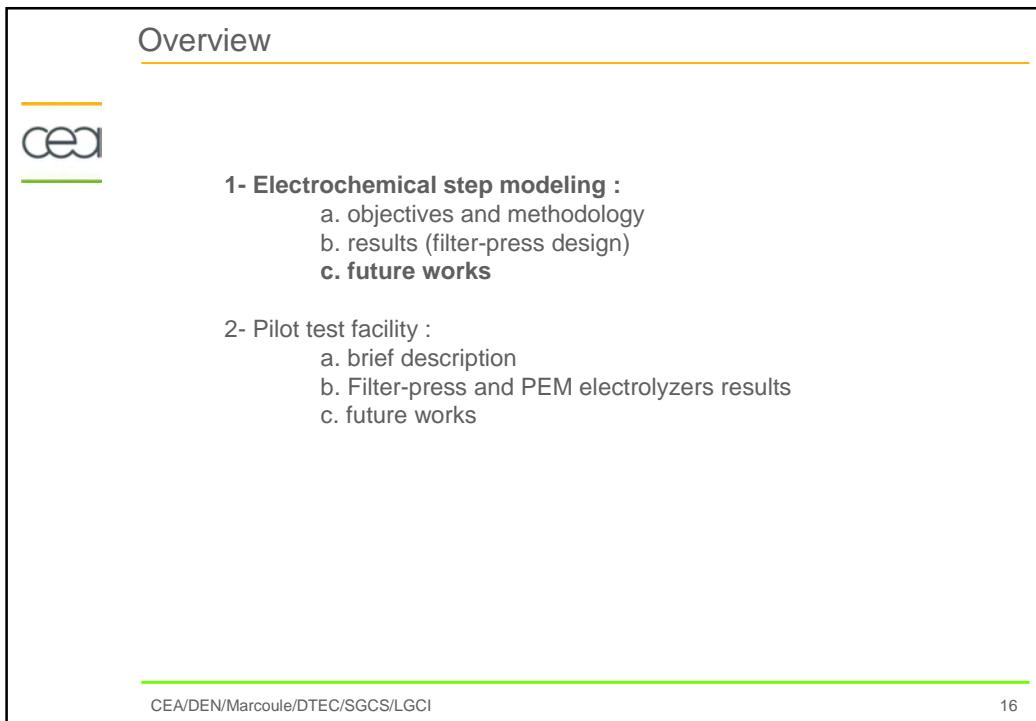
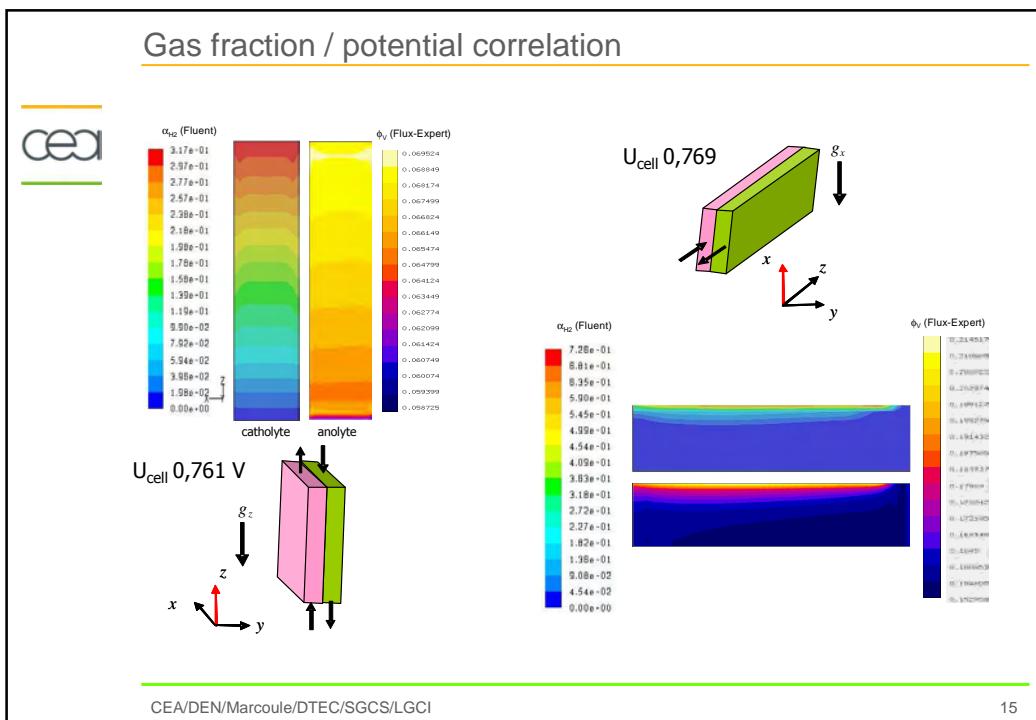


⇒ Influence of the cell orientation on H₂ repartition and hold-up



CEA/DEN/Marcoule/DTEC/SGCS/LGCI

14

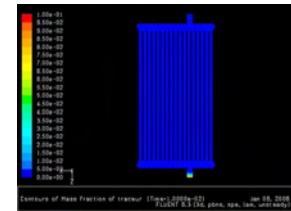
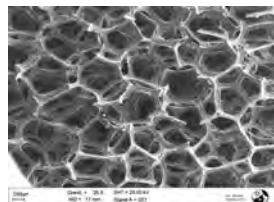
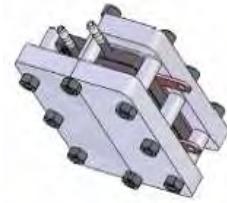


Current and future works



Focus on PEM-like configuration

- Electrokinetic modeling
 - sensitivity analysis
- Phenomenological modeling of the MEA
 - mass, charges and ionic transport
 - “true” electrochemical model required
- Hydrodynamic study and optimization
 - tracer and RTD experiments (PEM channels, porous anode)
 - CFD (Ansys Fluent)



CEA/DEN/Marcoule/DTEC/SGCS/LGCI

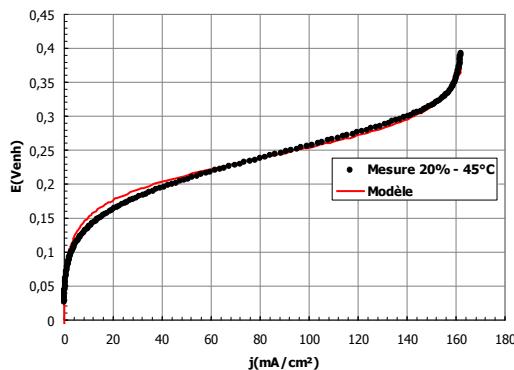
17

Current and future works

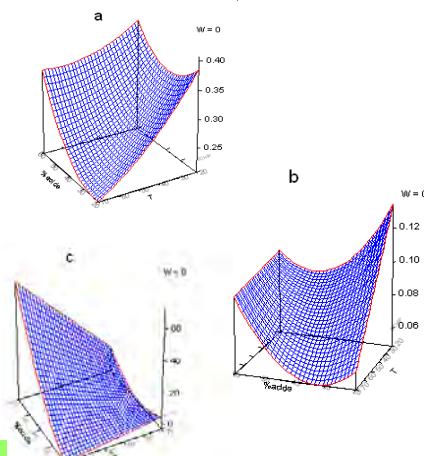


DOE data reprocessing

⇒ new $E = f(j)$ numerical model



- ✓ 3 parameters A,B,C (instead of 4)
- purely empirical numerical law (based on physical models)
- encouraging results obtained (static data)



CEA/DEN/Marcoule/DTEC/SGCS/LGCI

18

Overview



- 1- Electrochemical step modeling :
- objectives and methodology
 - results (filter-press design)
 - future works

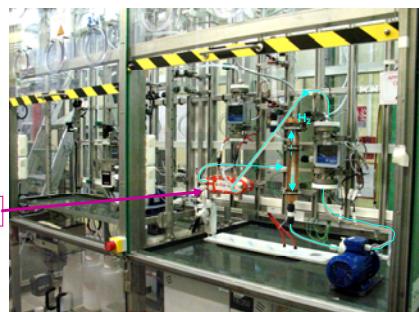
- 2- Pilot test facility :
- brief description
 - Electrolyzer tests early results
 - future works

CEA/DEN/Marcoule/DTEC/SGCS/LGCI

19

Pilot Plant Overview

✓ P. Rivalier and al., Proceedings of ICONE16, May 11-15, 2008, Orlando



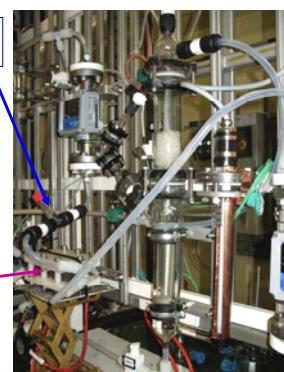
Available in May 08
Since Jul. 08 in automatic way
Reproducible results achieved early 09

- Capacity 100 NL_{H2}/h Today : 10 L/h
- adjustable operating parameters :
 - I ≤ 300 A 2000 A/m²
 - flow-rate up to 1 m³/h 200 L/h
 - acid concentration up to 60wt% 20 %
 - T (RT to 100°C) and soon P (up to 10 bars)

Closed catholyte loop (SO₂ accumulation)

Electrodes potential measurement available since march 09

Flow-cell (Ea measurement)



CEA/DEN/Marcoule/DTEC/SGCS/LGCI

20

