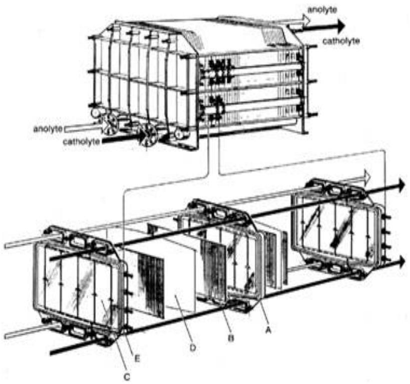
Characterization and optimization of materials for hybrid sulfur cycle electrolyser

CEA Saclay

LECNA
concentrated acids
liquid metals
hot gazes



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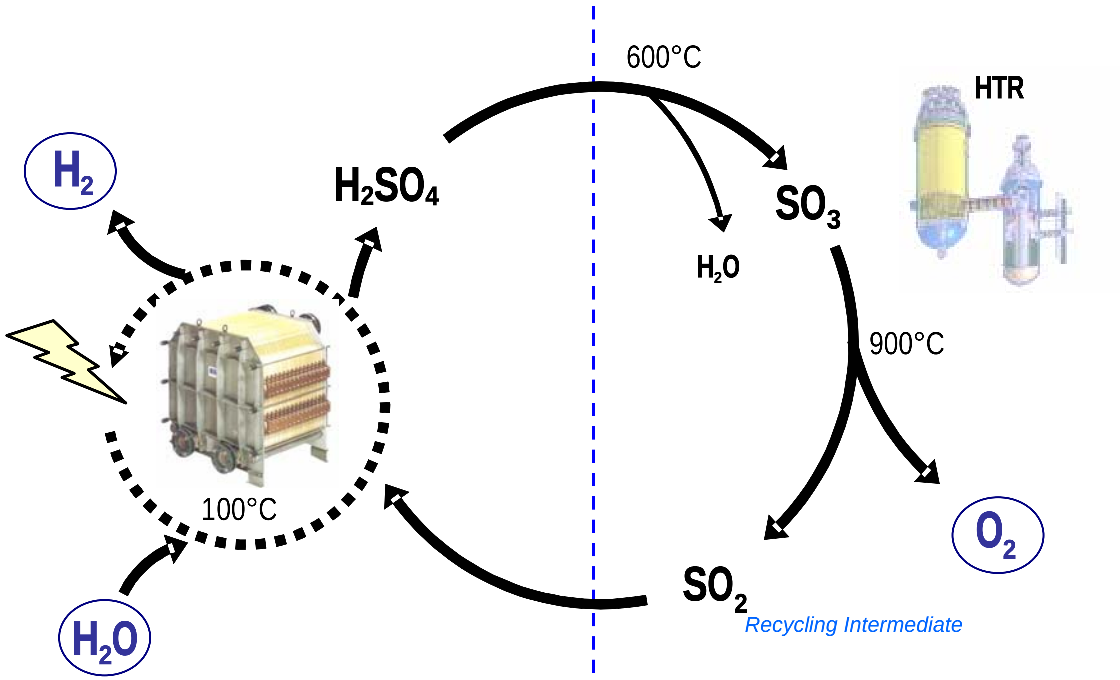
Laboratory of Non Aqueous Corrosion

DEN/DPC/SCCME

Hybrid Sulfur Cycle Electrolyser – Schematic Diagram



- ***Electrochemical Step***

  Oxidation of SO_2 and Reduction of proton

  $SO_2 + 2\,\mathbf{H_2O} \rightarrow \mathbf{H_2} + H_2SO_4$

- ***Thermochemical Step***

  Thermal decomposition of H_2SO_4

  $H_2SO_4 \rightarrow SO_3 + H_2O$

  $\hookrightarrow SO_2 + ½\,O_2$

Hybrid Sulfur Cycle Electrolyzer – Objective

Main objective of the study

Optimize the efficiency of the process → Optimize the electrolyzer section

❖ **To minimize the voltage input for electrolytic hydrogen production**

$$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + H_2$$

$$\mathrm{Ucell} = \underbrace{(E_a^{eq} - E_c^{eq})}_{\text{thermodynamic potentials } (\Delta E^{eq})} + \underbrace{(\eta_a + |\eta_c|)}_{\text{overpotentials (kinetic)}} + \overbrace{\sum RI}^{\text{ohmic drop}}$$

ohmic drop — separator

overpotentials (kinetic) — electrode materials

thermodynamic potentials (ΔE^{eq}), overpotentials (kinetic), ohmic drop — physico-chemical parameters ($[H_2SO_4]$, temperature P_{SO_2})

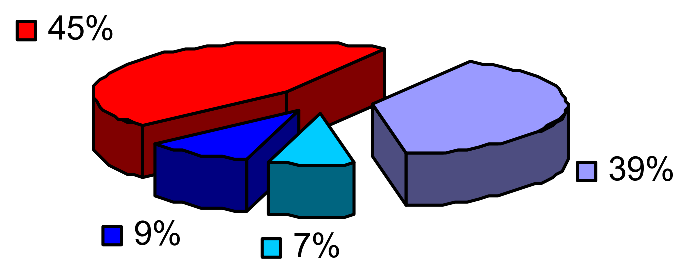
❖ **To maintain long term performances of the cell components**

Hybrid Sulfur Cycle Electrolyzer – bibliographic study

- **Significant advancements in the SO_2-depolarized electrolysis (Westinghouse*)**
  - Feasibility of process on short durations
  - Technical improvements (electrode structures, cell configurations…)
  - **Experimental conditions :**:
    - 50 wt% H_2SO_4 at 50°C & SO_2-saturated under atmospheric pressure
    - anode & cathode : Pt-catalysed carbon plate electrodes (10 mg/cm²)

Ucell = 675 mV for i = 100 mA.cm^{-2} **(the endurance test was terminated after 173 H)**

- **η_a = 265 mV**
- **η_c = 50 mV**
- **ΣRI = 60 mV**
- **ΔE^{eq} = 300 mV**



Electrical efficiency=45% $=100*\eta_F*(\Delta E^{eq}/Ucell)$

With η_F ~1 (quantity of theoric current to produce one mol of H_2/ quantity of experimental current to produce one mol of H_2)

* P. W. T. Lu *et al.*, Int. J. Hydrogen Energy, Vol. 7, No. 7 (1982) 563-575.

Hybrid Sulfur Cycle Electrolyzer – the electrolysis test system

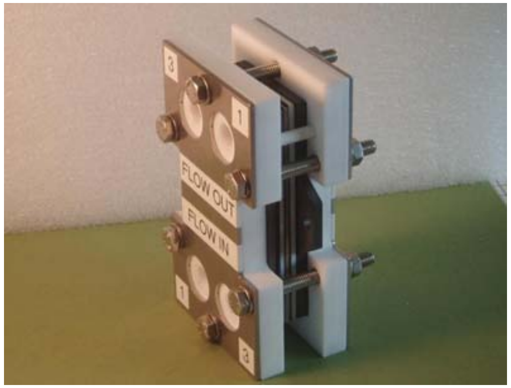
❖ Experimental dispositive

- A filter press electrochemical cell
- Independent flow of anodic & cathodic compartments

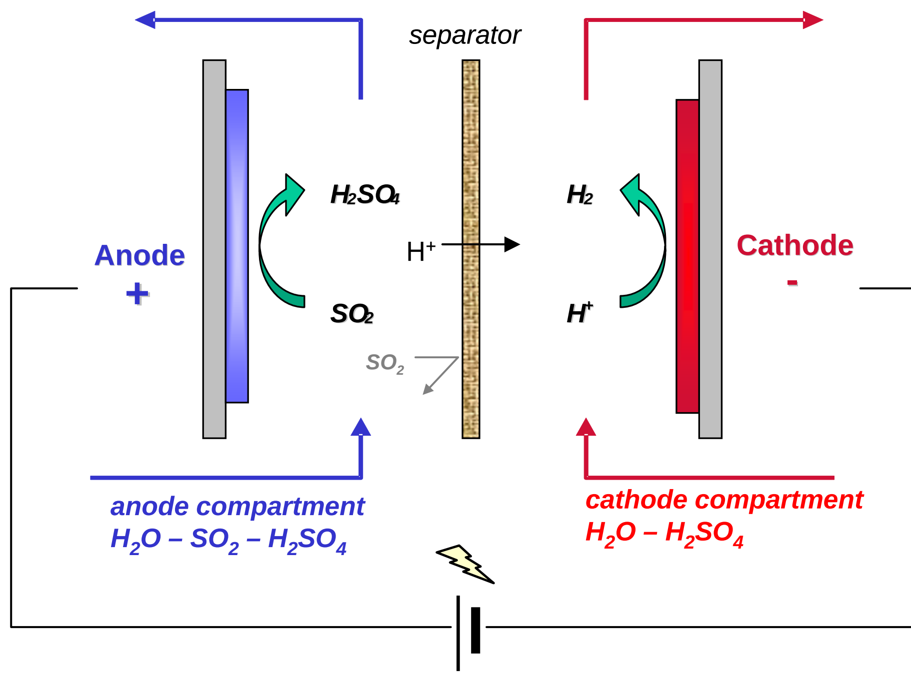
❖ Objectives of this system

- To integrate & to compare the material components versus the cell voltage
  - *electrochemical signal*
  - *ohmic drop of the cell*
- To determine the electrical efficiency
- To evaluate the limitations
- To test the endurance of materials

Hybrid Sulfur Cycle Electrolyzer – Laboratory cell



$SO_2 + 2\,H_2O \rightarrow H_2SO_4 + 2\,H^+ + 2\,e^-$ $\quad$ $2\,H^+ + 2\,e^- \rightarrow H_2$



Scale

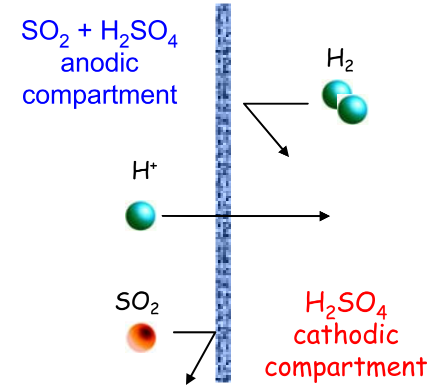
- laboratory — 4 cm
- industrial — 24 cm

Previous Conditions

- temperature : 50 - 100°C
- PSO_2 1 - 10 bar
- $[H_2SO_4]$: 30 - 70 wt%
- $I_{nominal}$ 200 mA/cm²

Hybrid Sulfur Cycle Electrolyzer – Material component : Separator

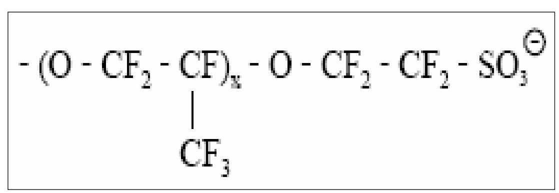
❖ Requirements



- Good stability in concentrated sulfuric acid media
- To prevent the SO_2 migration into the cathodic compartment and the H_2 migration into the anodic compartment
- To allow the H^+ moving through the membrane to maintain a low resistivity

❖ Used material

Cation exchange membrane : perfluorosulfonated ionomer membrane (Nafion®)



The choice of the separator is important for optimize the performances of electrolyzer

Selection criteria for separators

- **Chemical stability in sulfuric acid media :** life duration, long term performance

immersion tests and specific characterizations (optical and electronic microscopy, gravimetric measurements, surface analyses)

- **Resistivity :** resistance of separators (ohmic drop)

electrochemical Impedance Spectroscopy measurements

Nafion®	324	417	424	**117**
R_{cell} (Ω)	0,50	0,35	0,15	**0,10**

- **Choice of ([H_2SO_4], T) couple by abacus**

[H_2SO_4] ~ 30 wt% at high temperature

- **SO_2 selectivity**

currently not study on the SO_2 selectivity

Hybrid Sulfur Cycle Electrolyzer – Material component : material electrode

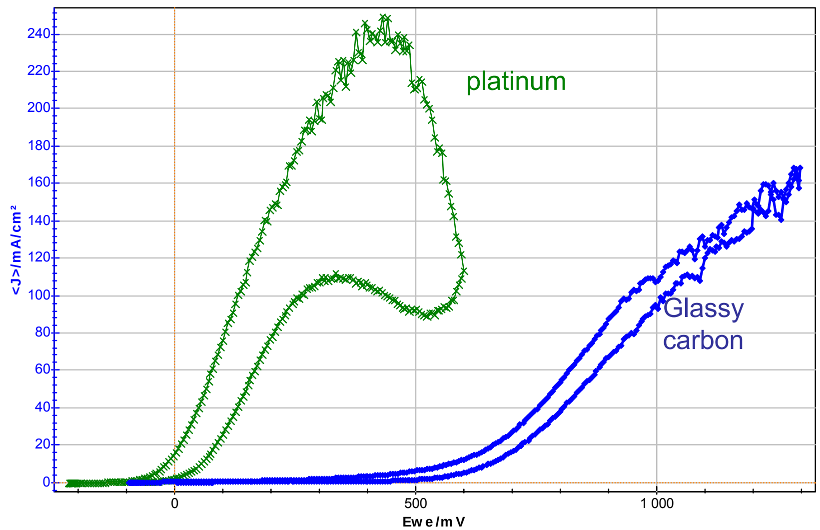
❖ Requirements

- Good stability in concentrated sulfuric acid media
- Good electric conductivity
- To optimize the catalysis of the anodic & cathodic reaction(low overpotentials)

high specific surface area

❖ Choice of material electrode

- Comparison of the catalytic effect of different materials
  - materials electrodes : platinum & glassy carbon
  - experimental conditions : 50 wt% H at 30°C, $(SO_2)_{diss}$ saturated at atmospheric pressure & scan rate = 5 mV.s^{-1}



Validation of platinum as material component of electrodes

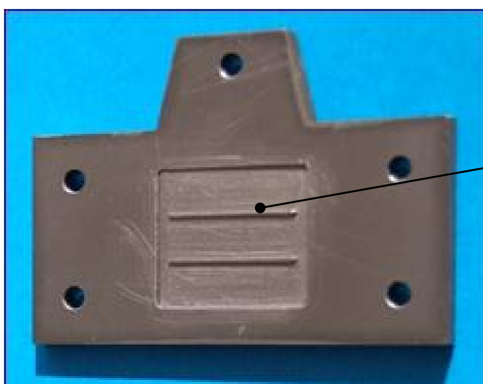
Hybrid Sulfur Cycle Electrolyzer – Material component : material electrode

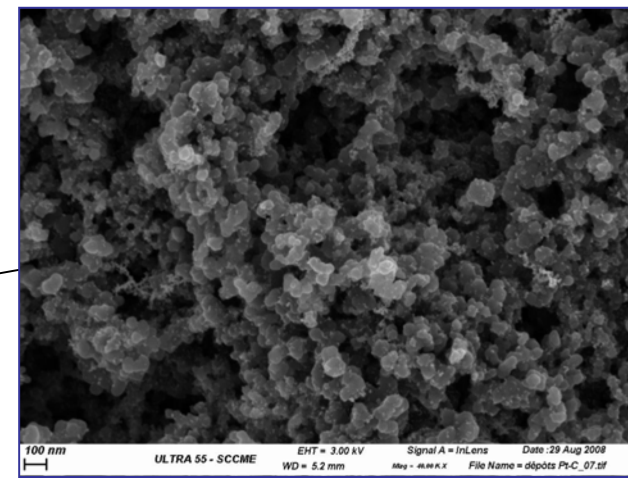
❖ Used material

- Commercial Pt/Ti electrodes
- "PEMFC" type (Proton Exchange Membrane Fuel Cell) electrodes

(collaboration with DRT/LITEN/DTH/LCPEM)

  - Substrate : graphite
  - Deposit : suspensions of Pt/C & Nafion

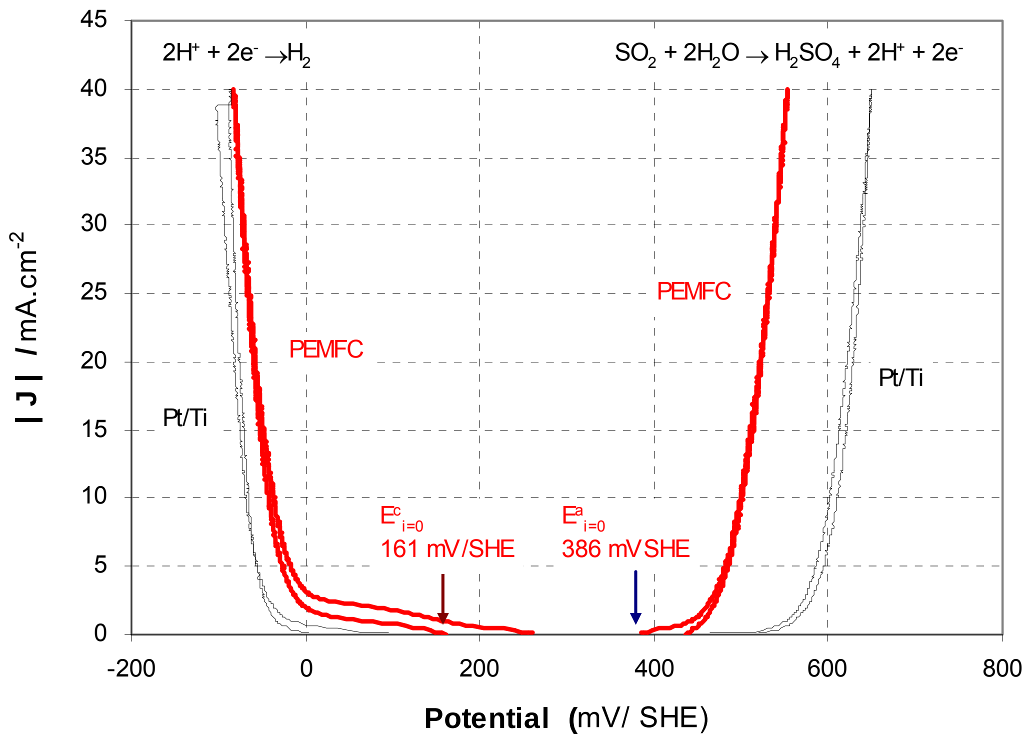




Hybrid Sulfur Cycle Electrolyzer – Performances

Electrochemical measurements on

- Commercial Pt/Ti electrodes
- Pt-C/graphite electrodes ("PEMFC" type)
- Experimental conditions : 30 wt% H_2SO_4 at 50°C, (SO_2)diss saturated at atmospheric pressure & flow rates=0.6 $L.min^{-1}$



Decrease of anodic & cathodic overpotentials with the "PEMFC" type electrodes

❖ Best comprehension of oxidation reaction of SO_2

Oxidation reaction involves two processes[1]

- The first at low overpotentials
  - Process at three steps[2]

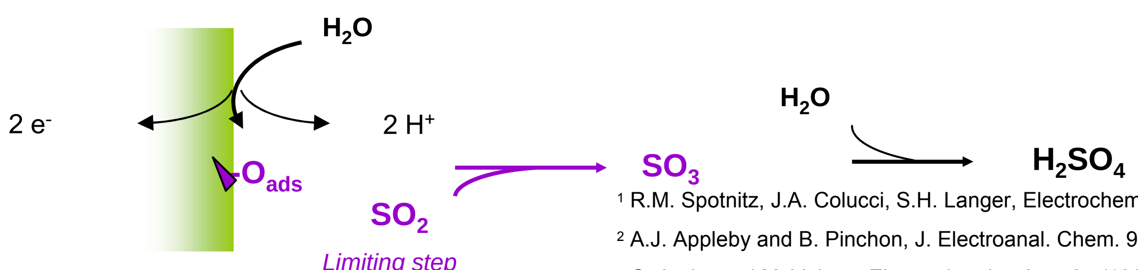
$2\ SO_2 + H_2O \rightarrow 2\ H_2SO_3{}^{+}ads^{*} + 2\ e^-$

$2\ H_2SO_3{}^{+}ads^{*} \rightarrow H_2S_2O_6 + 2\ H^+$ limiting step

$H_2S_2O_6 \rightarrow H_2SO_4 + SO_2$

*Audry and Voinov[3] confirm that this specie is an intermediary specie

- The second at high overpotentials
  - SO_2 oxidation performed by surface oxides MO_{ads}
  - Oxidation kinetic limited by the number / availability of active sites on the electrode surface.



[1] R.M. Spotnitz, J.A. Colucci, S.H. Langer, Electrochemica Acta, 23 (1983) 1053
[2] A.J. Appleby and B. Pinchon, J. Electroanal. Chem. 95 (1979) 59
[3] C. Audry and M. Voinov, Electrochemica Acta 25 (1980) 299
[4] K.I. Rozenthal and V.I. Veselovskii, Zh. Fiz. Khim. 27(1953) 1163.

Hybrid Sulfur Cycle Electrolyzer – Performances

Currently, our experimental conditions are:

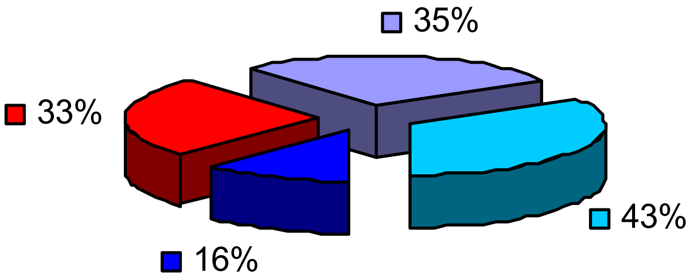
- 30 wt% H_2SO_4 at 50°C, (SO_2)diss saturated at atmospheric pressure & flow rates=0.6 $L.min^{-1}$
- anode & cathode : Pt-C/graphite electrodes ("PEMFC" type)

Pt particles ∅5 nm, C particles ∅50 nm

- separator : Nafion 117

Ucell = 860 mV for i = 100 $mA.cm^{-2}$ (instantaneous measurement)

- **η_a = 233 mV**
- **η_c = 292 mV**
- **ΣRI = 108 mV**
- **ΔE^{eq} = 225 mV**



Electrical efficiency : 33%

Hybrid Sulfur Cycle Electrolyzer – Limitations & problems

❖ **$(SO_2)_{dis} \leftrightarrows [SO_2]$ depends to T**

- Decrease of $(SO_2)_{dis}$
- To control pressure & vacuum

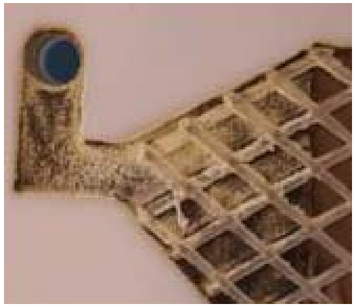
anodic potential can consider the H_2O oxidation at high current densities

❖ **Separator selectivity to SO_2**

- Very bad selectivity

SO_2 diffusion about the cathodic compartment

Pt/Ti cathode : sulfur formation & fouling



❖ **Stability of deposit**

Pt/Ti cathode : substrate (Ti) degradation

under cathodic polarization

➡ **Choice of substrate is important**

Hybrid Sulfur Cycle Electrolyzer –Conclusions & Outlooks

Conclusions

- Ucell-Iapplied values consistent with the literature values
- Advantage of "PEMFC" type electrodes
- Determination of limitations of this system

  the non-selectivity of the membrane at SO_2

Outlooks

- Best comprehension of oxidation process of SO_2

  to determine the limiting parameters
- Endurance tests to confirm:

  performances of the electrolyzer components

  stability of deposits
- Selectivity of membrane at SO_2

  to establish a method to determine the P_{SO_2}
- Determination of efficiencies

  to establish a method to determine P_{H_2}