Air gas-diffusion electrodes for operation in saline electrolytes

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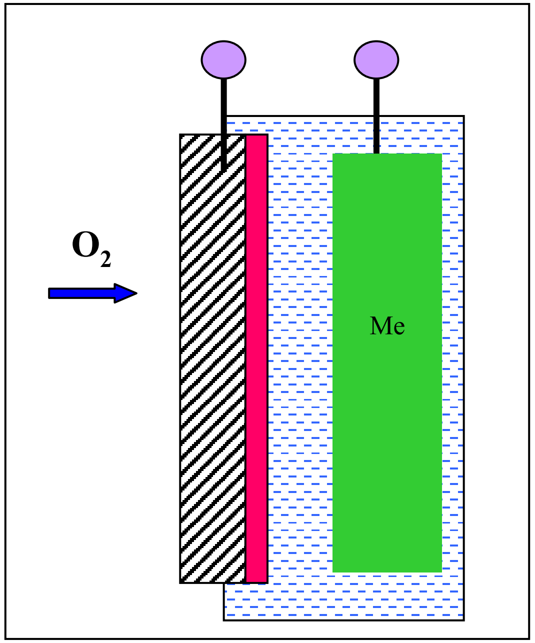
AIR GAS-DIFFUSION ELECTRODES IN METAL-AIR CELL

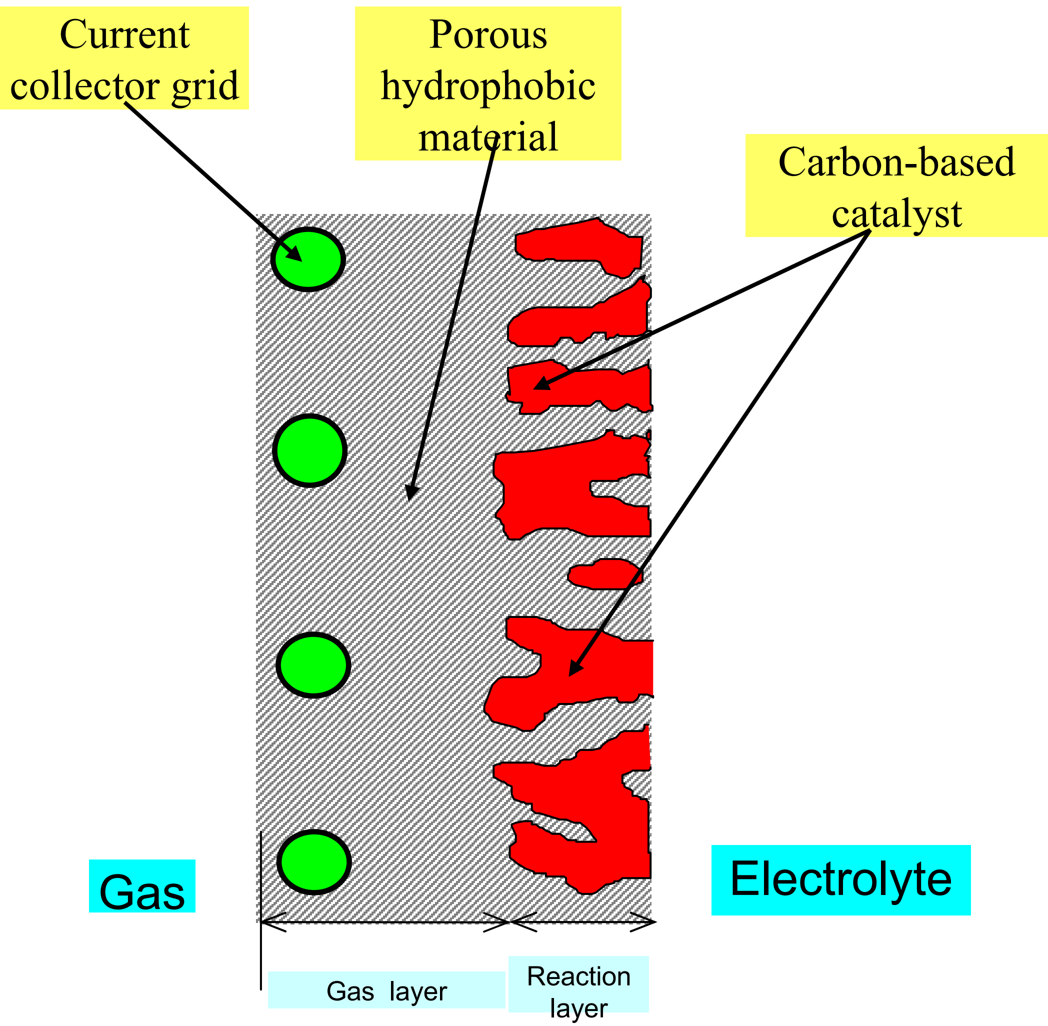
wall of the cell - separates electrolyte from surrounding air



REQUIREMENTS:

- **No leakage** of electrolyte through the electrode
- **High porosity** – effective oxygen supply
- **Electronic conductivity**
- **Catalyst** for electrochemical oxygen reduction
- **Mechanical strength** (hydrodynamic shocks, etc.)
- **Stability** with time of operation
- **Low price**

THE CONCEPT FOR AIR ELECTRODE DESIGN



Effective oxygen supply for the catalyst

Catalyst zones – no hydrophobic or binding agents

Various catalysts can be applied without changing the overall structure of the electrode

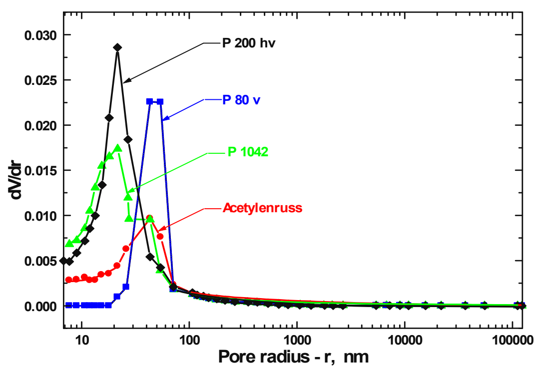
FREE VARIATION OF THE STRUCTURE PARAMETERS:

- **thickness of the reaction layer**
- **thickness of the gas layer**
- **catalyst/hydrophobic material in the reaction layer**

POROUS HYDROPHOBIC MATERIAL
produced from acetylene black and PTFE

The material is produced in a powder form

Porous tablets of various thickness and shapes can be prepared from the material by pressing



Tablets from the hydrophobic material:

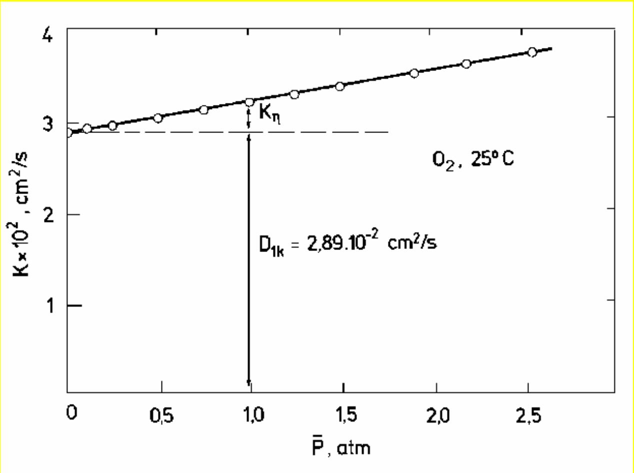
- **high porosity 0.7–0.9 cm²/g**
- **high hydrophobicity Θ_{eff} = 118–124°**
- **electronic conductivity 1.0–2.0 $\Omega^{-1}.cm^{-1}$**
- **nanopores ř = 10–100 nm**

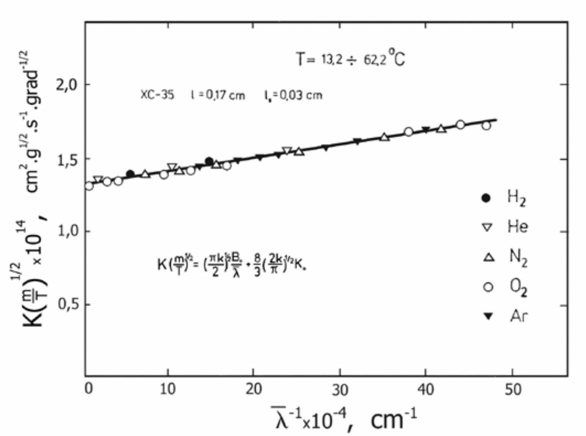
The properties of the hydrophobic material depend to a great extent on the properties of the carbon material used for its production:

Air electrodes containing hydrophobic material with smaller pores show longer life-time

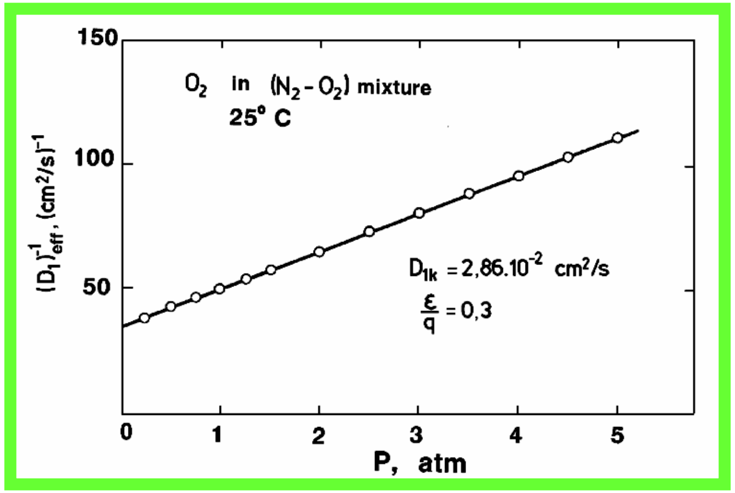
Investigation of the mechanism of gas-transport through the porous hydrophobic material: KNUDSEN DIFFUSION

GAS FLOW
total pressure gradient





GAS DIFFUSION
partial gas pressure gradient
constant total gas pressure

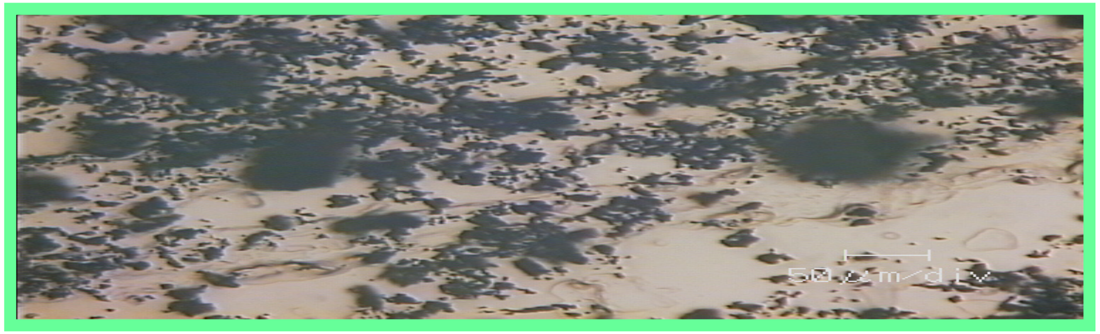


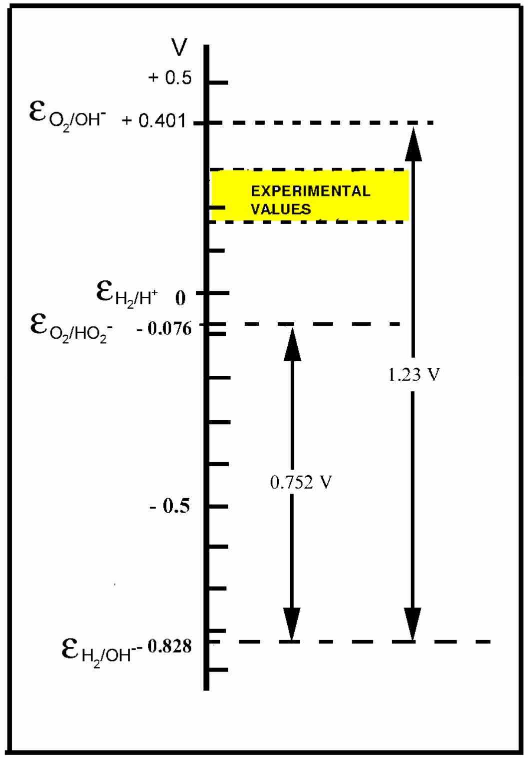
Bosanquet

$$(D_i)^{-1}_{eff} = D^{-1}_{ik} + (D_{12})^{-1}_{eff}$$

$$(D_i)^{-1}_{eff} = D^{-1}_{ik} + \left[\frac{\varepsilon}{q}.D^{(1)}_{12}\right]^{-1}.P$$

CATALYSTS FOR ELECTROCHEMICAL REDUCTION OF OXYGEN





CARBON MATERIALS

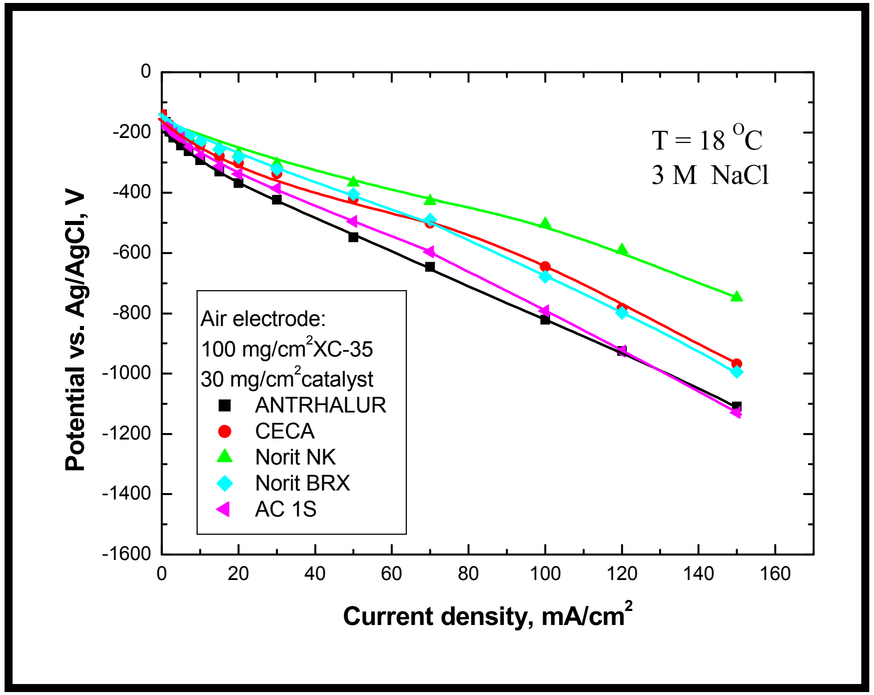
- highly developed surface area
- oxygen adsorption capability
- suitable morphology
- chemical stability
- electronic conductivity
- low price

CATALYSTS

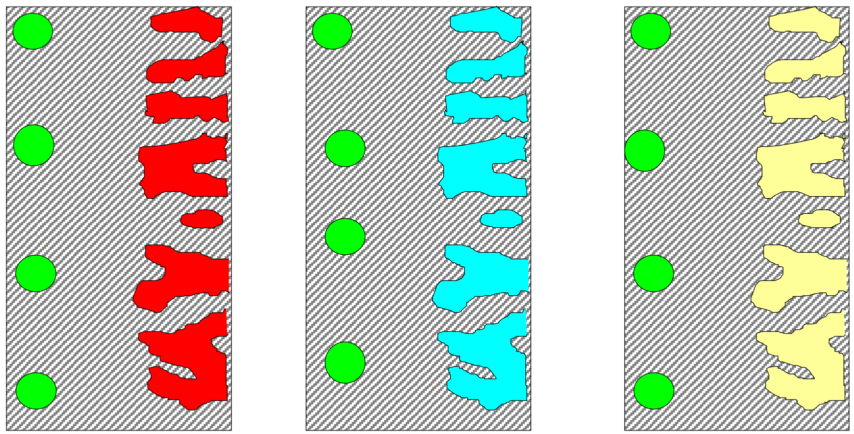
ACTIVE CARBON - various types

- ACTIVE CARBON PROMOTED
  - with Ag
  - with combinations of Co and Ni
- pyrolyzed CoTMPP

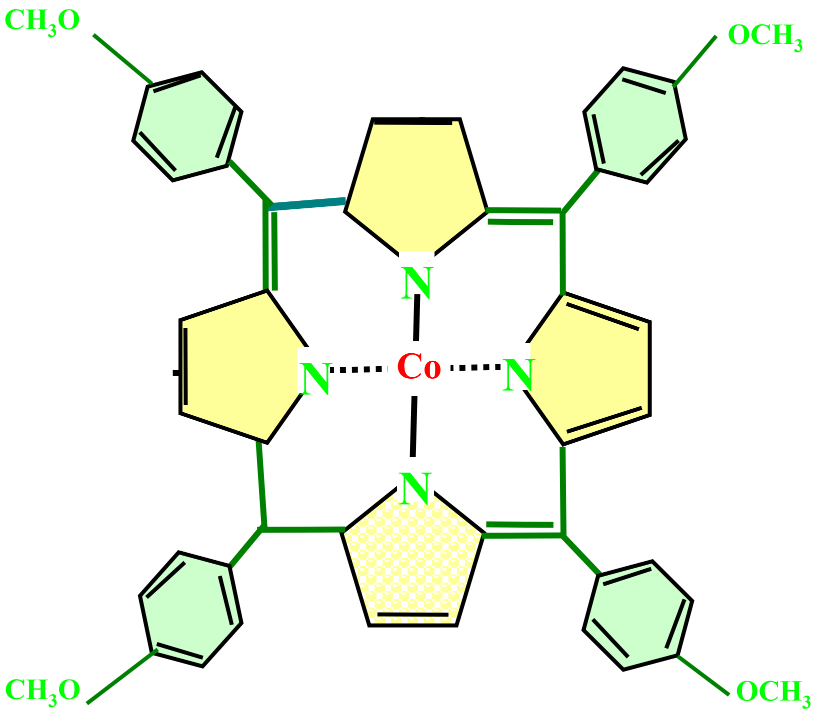
Polarization curves of air electrodes with different types of active carbon catalysts

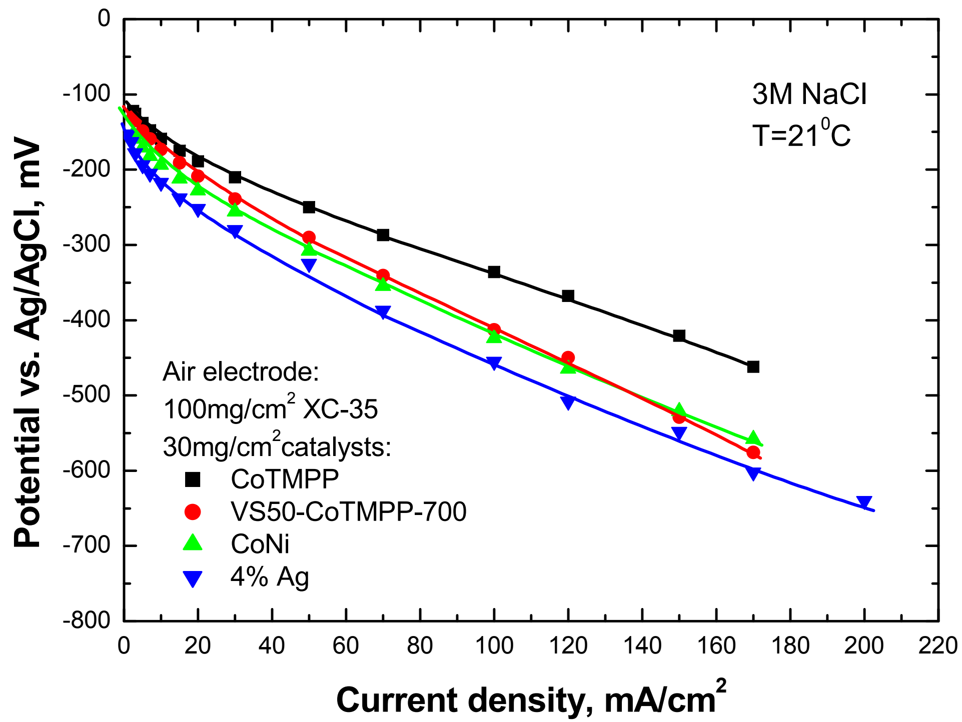


The observed differences in electrode characteristics are due to differences in the properties of the catalyst only



Air gas-diffusion electrode with different catalysts

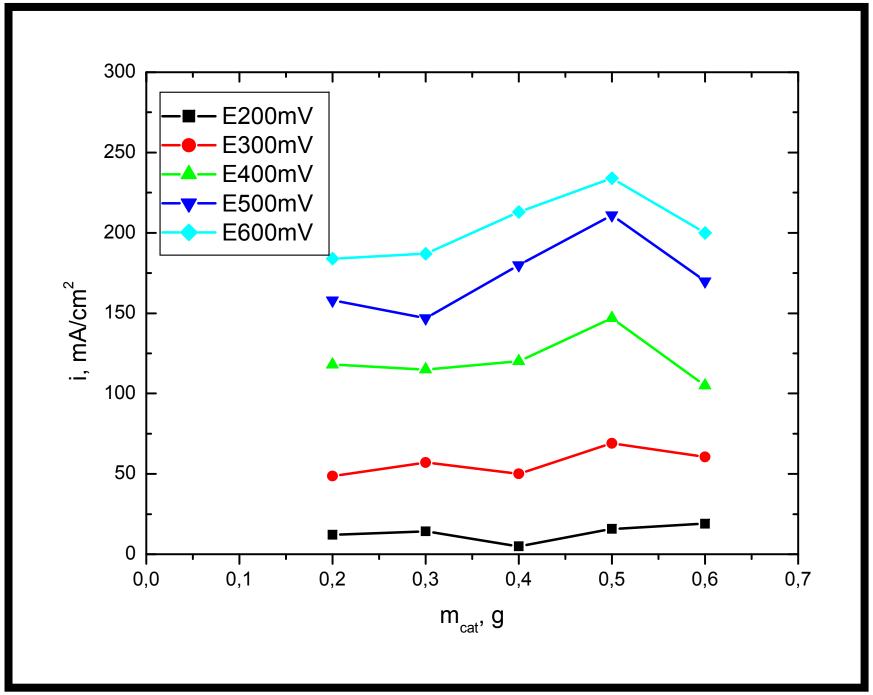




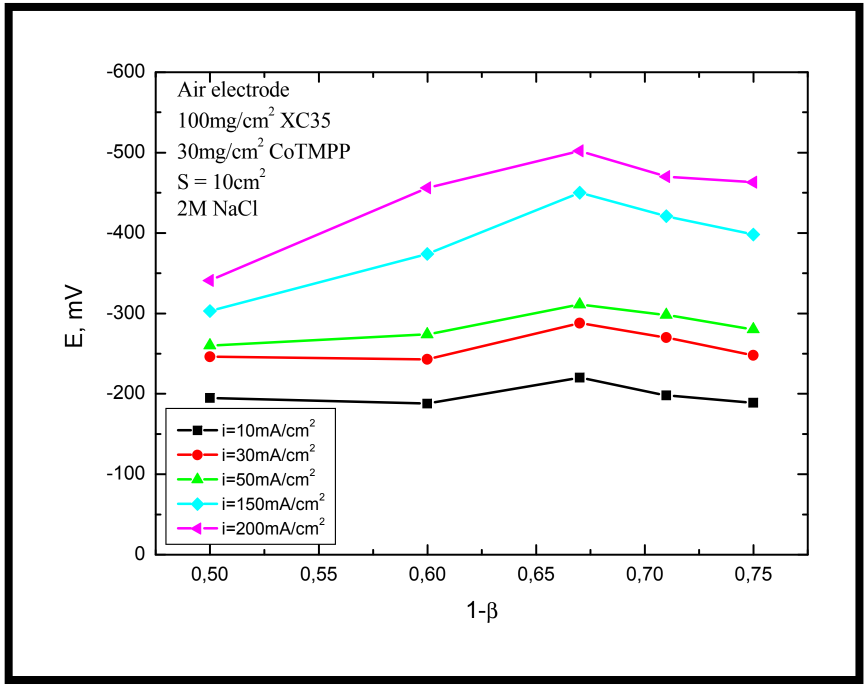
Polarization curves of air electrodes with

- CoTMPP
- VS50-CoTMPP-700
- CoNi
- 4% Ag

OPTIMIZATION OF THE AIR ELECTRODE STRUCTURE



Current of the air electrode as a function of the catalytic layer content at constant potential



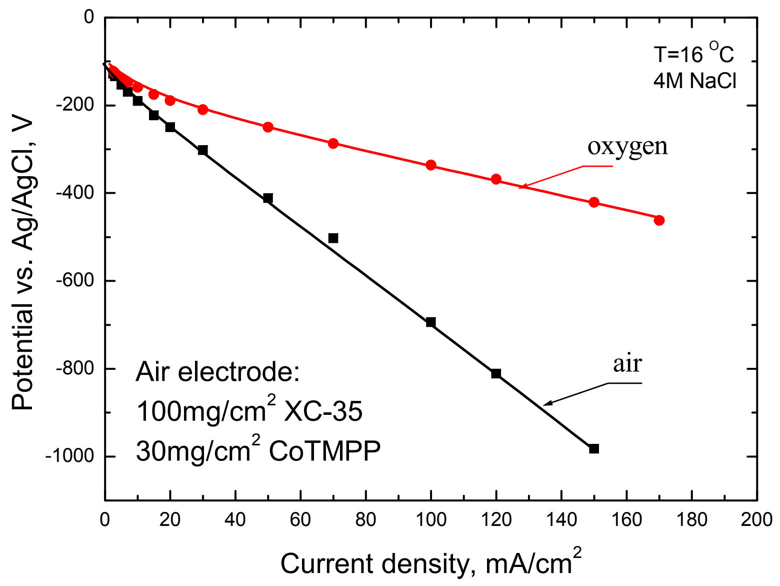
Current generated from the air electrode at constant potential as a function of the ratio catalyst/hydrophobic material in the active layer

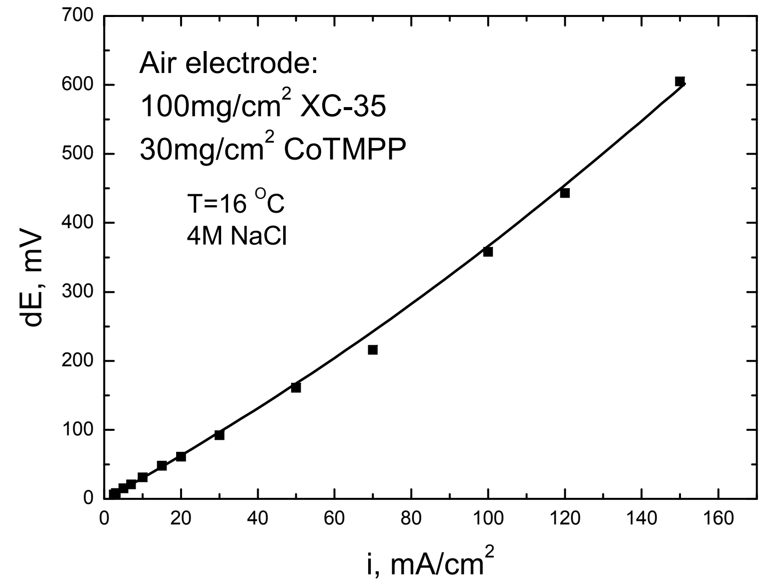
METHOD FOR ESTIMATION OF TRANSPORT HINDRANCES

IDEAL ELECTRODE
no hindrances

REAL ELECTRODE:
activation hindrances
transport hindrances
IR drop

$$\Delta E = E_{O_2}(I) - E_{air}(I)$$





LONG-TERM OPERATION OF AIR ELECTRODES

Electrochemical reduction of oxygen:

$$O_2 + H_2O + 2e^- \longleftrightarrow HO_2^- + OH^-$$

$$HO_2^- \longrightarrow 1/2O_2 + OH^- \quad \text{(cat)}$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

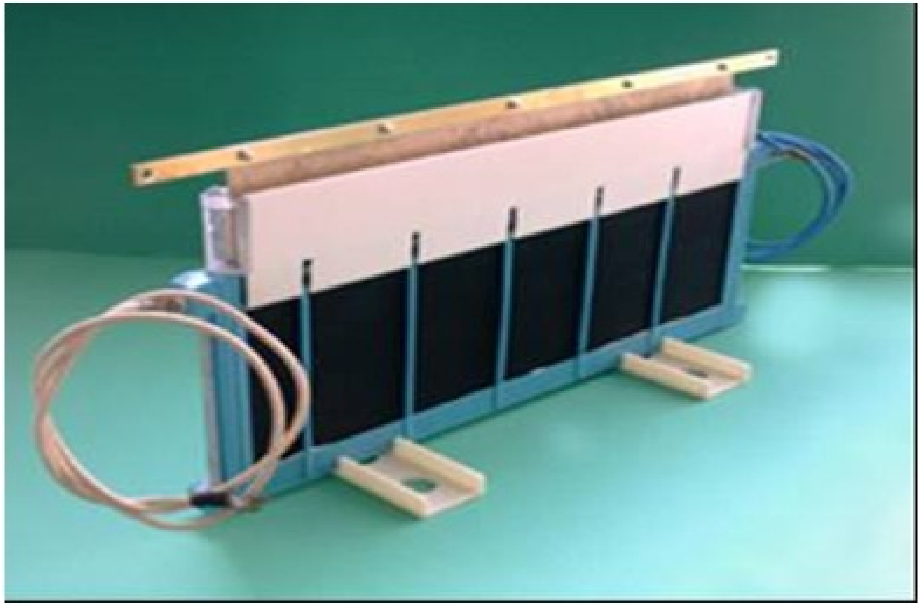
During operation the generated H_2O_2 oxidizes the carbon surface and makes it hydrophilic:

- ☞ **the tiny hydrophobic gas-pores in the carbon grains are gradually soaked with electrolyte**
- ☞ **the hindrances in the transport of oxygen increase**

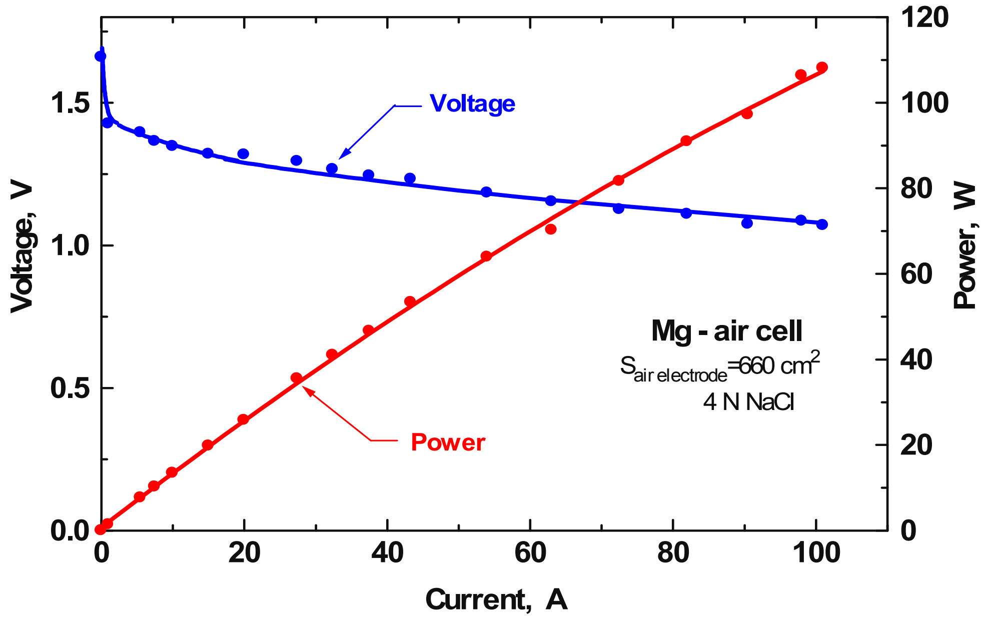
ENLARGEMENT OF THE LIFE-TIME OF THE CARBON AIR ELECTRODES

- ☞ **Increase of the hydrophobic gas-pores volume in the active carbon grains by suitable treatment**
- ☞ **Selection of catalysts with high activity for the heterogeneous H_2O_2 destruction**

GAS-DIFFUSION ELECTRODES
For fuel cells and metal-air cells and batteries

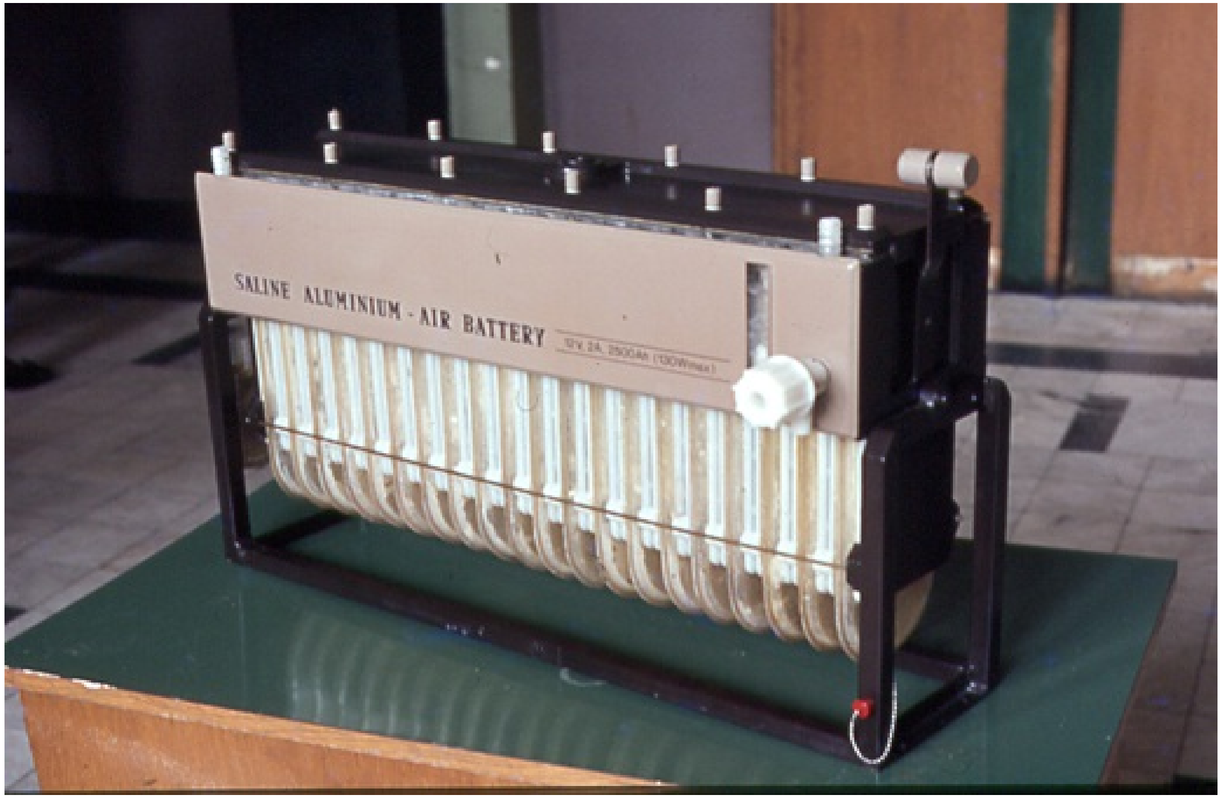


Experimental Mg-Air cell with 2 air electrodes (total working area of the air electrodes is 660 cm^2)



Current-voltage and power characteristics of the Mg-Air cell

ALUMINIUM-AIR BATTERY



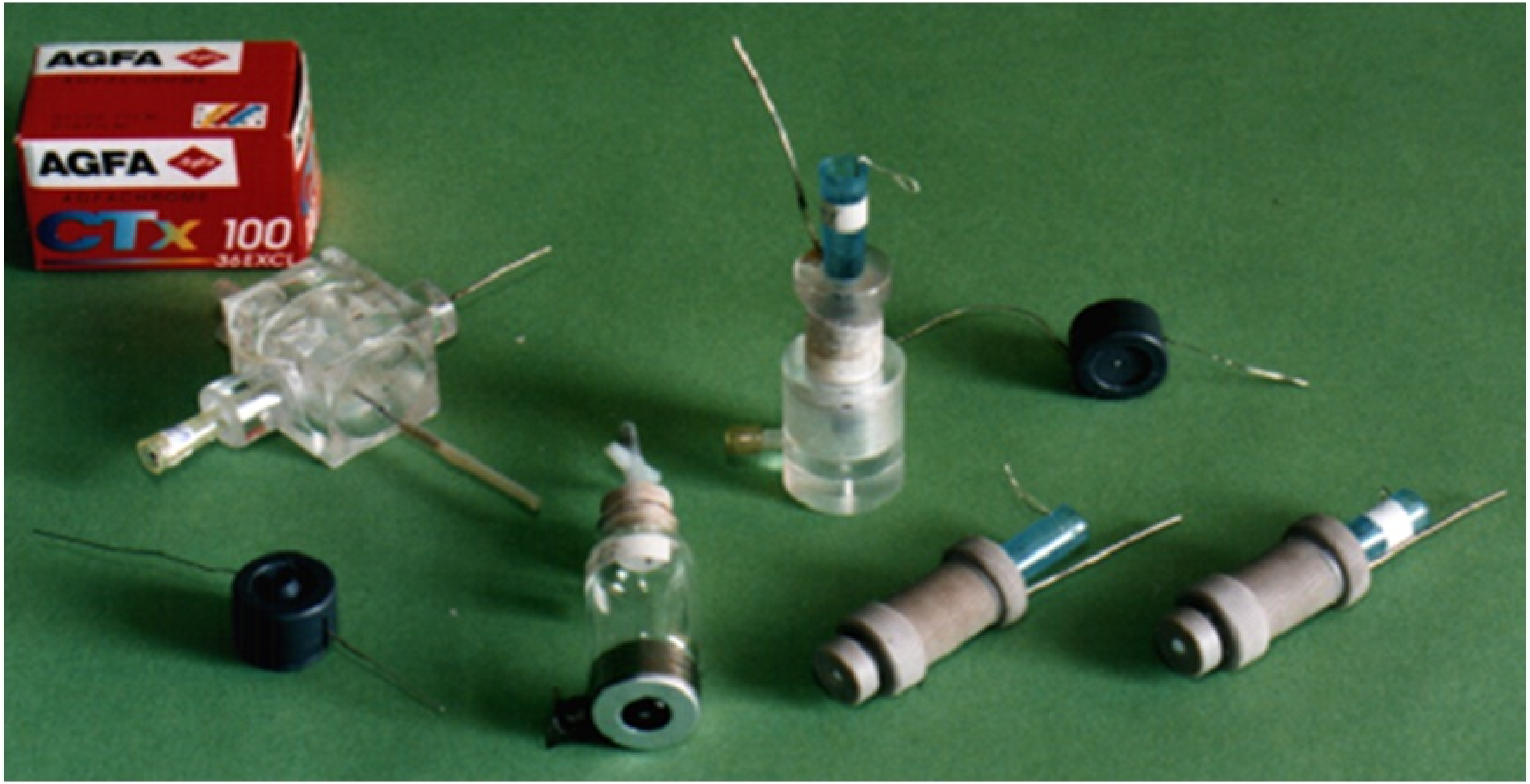
12 V, 2.5 A,
2500 Ah

Electrolyte - sea water

The electrolyte is changed after 8 hours of operation.

BIOSENSORS

- glucose
- lactate
- phenol in water solutions
- volatile phenolic compounds in gas mixtures (air)



THANK YOU