The BBC Membrel^R Process - A Retrospective View 1980-1986

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pem-workshop

Freiburg/Br, Germany
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The situation before and around 1980

- 1972 Club of Rome „Limits of Growth“
- 1973 Oil crisis, Yom Kippur War

Early 1970s

- Awareness of Global Warming
  Prof. H. Flohn, University Bonn
- Decoupling of Gross Domestic Product and Energy Consumption per Capita
  Prof. W. Häfele, KFZ Karlsruhe

N. Nakicenovic, C. Marchetti, IIASA

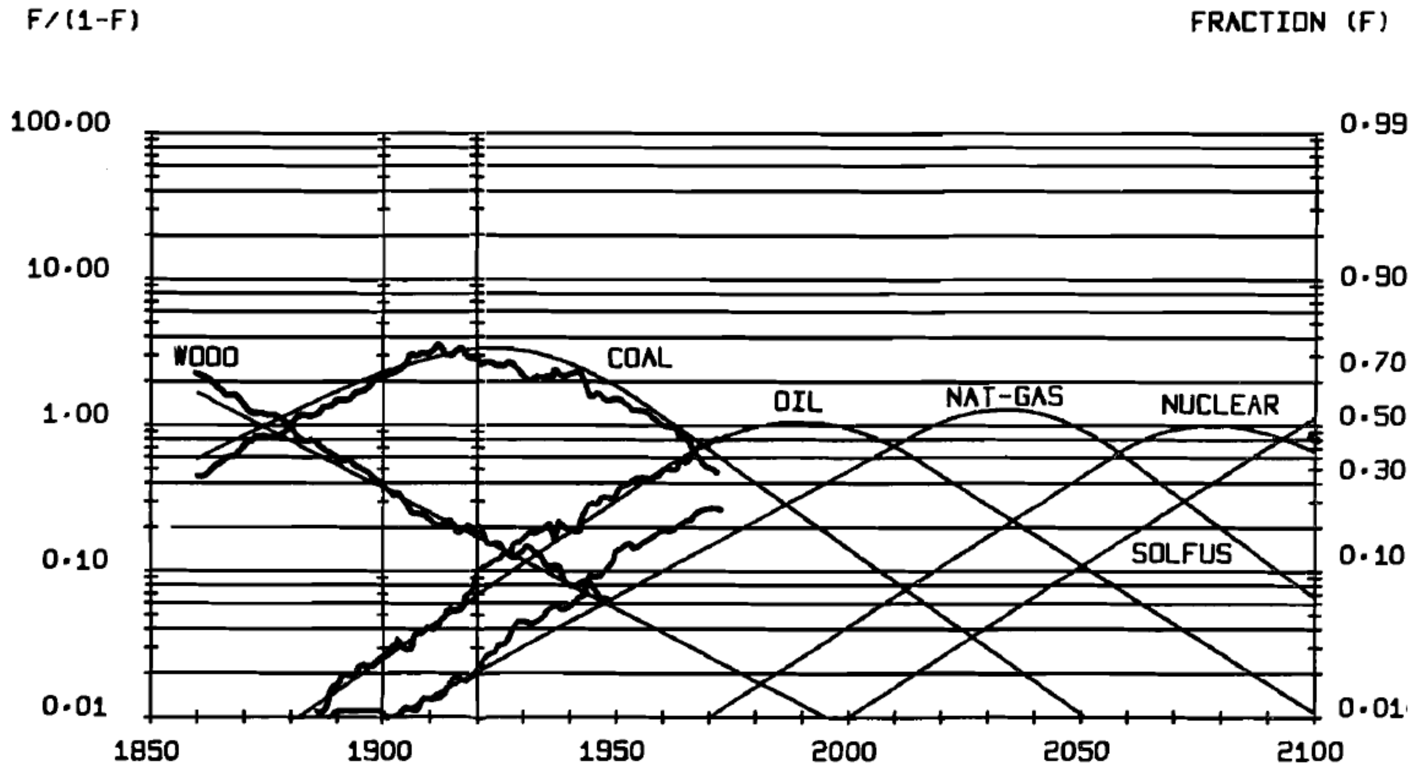


Figure 3. World - Fractional Substitution with Short Data-Base

H_2-promotors: E. Justi, L. Bölkow, J. Bockris, J. Appleby, many others

Drivers towards a Hydrogen Economy

- Brasil Itaipu Hydropower, 1984 (2008: 95 TWh)
- Canada Hydropower Development
- France Nuclear Program
- others

- GE SPE Technology
- DuPont Nafion Development

Brown Boveri & Cie (1891*), Switzerland (now ABB)

- Electricity Generation, Distribution, Storage, Use
- 100.000 employes (20 k in CH, 40 k in D, 40 k rest of world)
- BBC Research Center Baden-Dättwil, Switzerland

- Research on Na/S battery for electromobility (BBC Research Center Heidelberg)

*founded

Interest in H_2-Generation

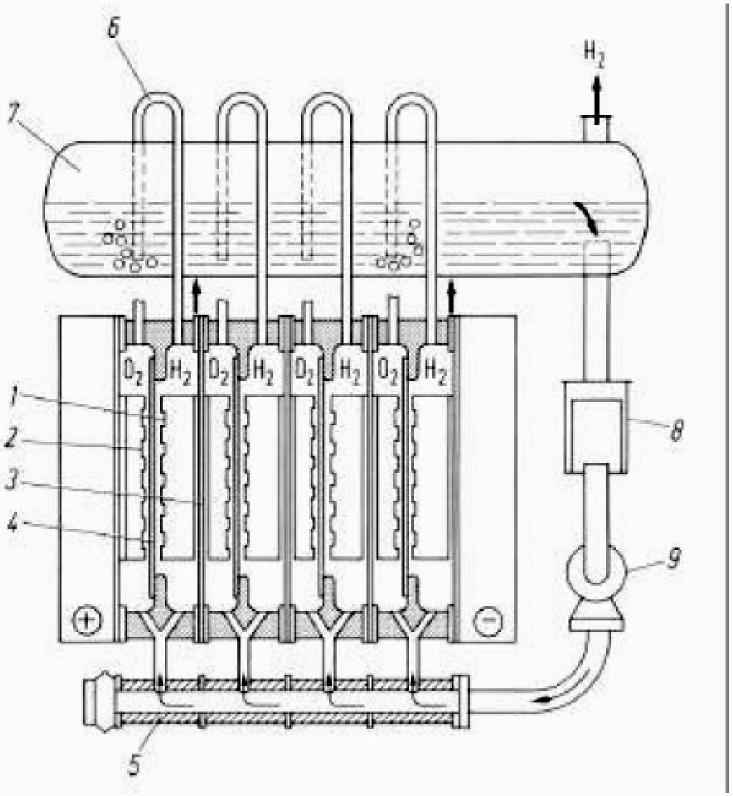
BBC Oerlikon Electrolyser

(MFO)

200 mA/cm^2

1965-70
Aswan, Egypt
33000 m^3 H_2/h
156 MW_e

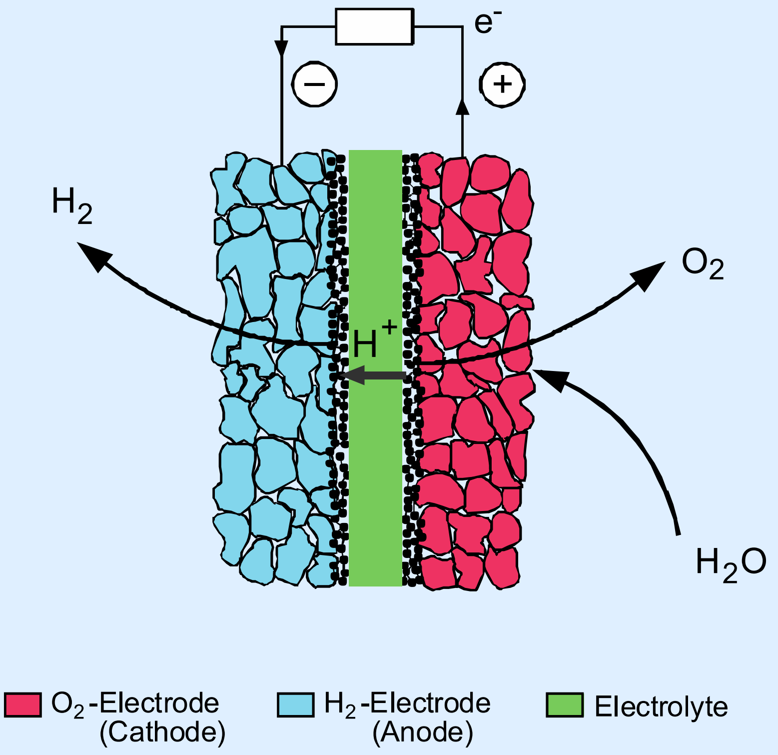
Abbildung 1.2-4: Aufbau eines Elektrolyseurs (Oerlikon)



1 – Kathode, 2 – Anode, 3 – Zellentrannwand, 4 – Diaphragma, 5 – Verteilleitung f. Elektrolyt, 6 – Überlaufrohre (nur für H_2 gezeichnet), 7 – Gasabscheider, 8 – Elektrolytfilter, 9 - Elektrolytpumpe

SPE* water electrolysis

Grubb** 1959, GE Res. Lab.



dual role of acidic electrolyte
operation temperature ≤ 100 °C

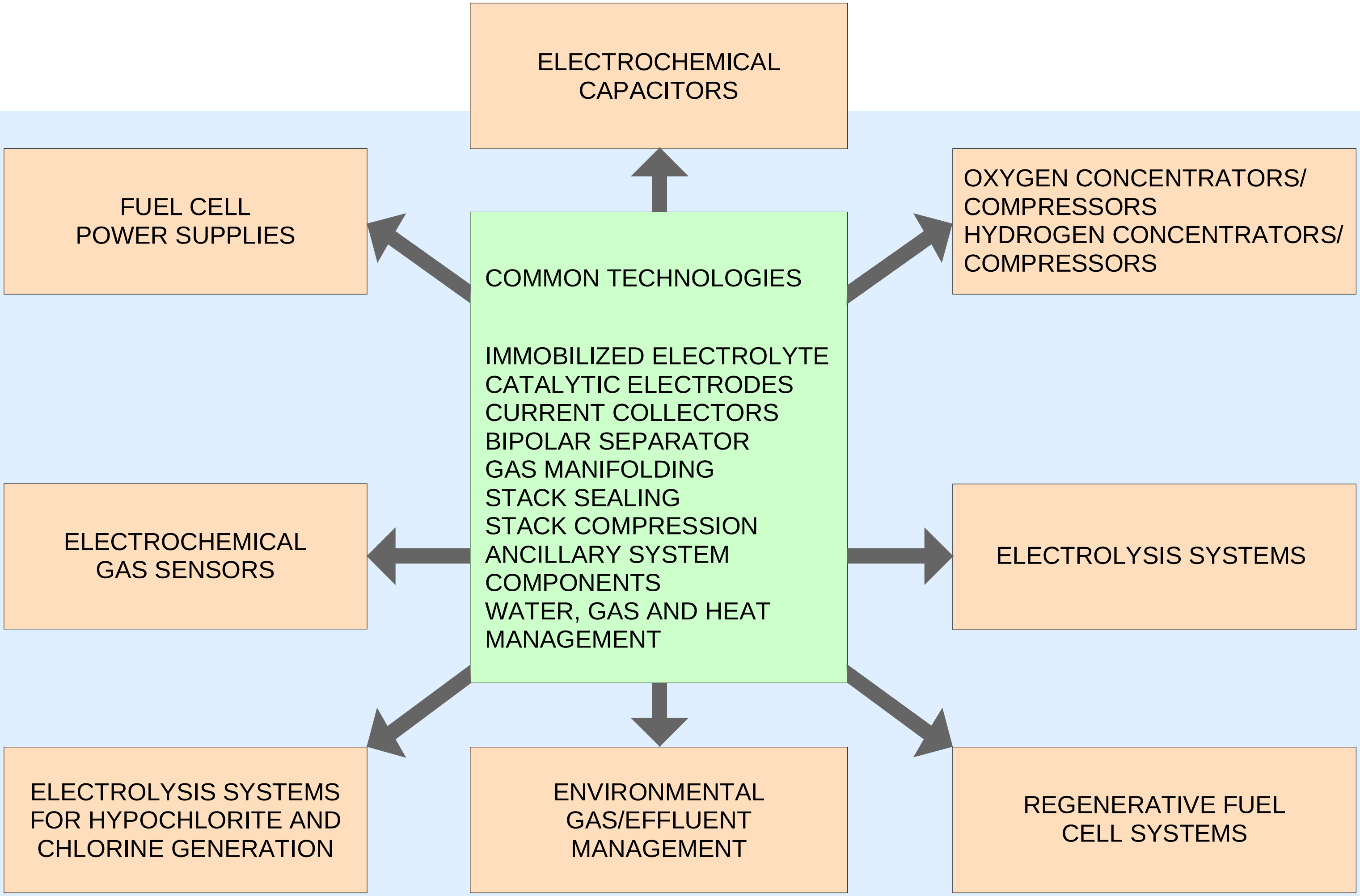
*Trade mark of General Electric Corp.
**W.T. Grubb, “Batteries with Solid Ion Exchange Electrolyte“, JES, 106, 275 (1959)

ANODE : $H_2O \rightarrow 1/2\ O_2 + 2\ H^+ + 2\ e^-$

CATHODE : $2\ H^+ + 2\ e^- \rightarrow H_2$

First free standing polymer membrane: W. Juda, W.A. McRae, US Patent No. 2.636.851 (1953)

Fuel cell know-how, as it exists today, was not available!



ELECTROCHEMICAL CAPACITORS

FUEL CELL POWER SUPPLIES

OXYGEN CONCENTRATORS/ COMPRESSORS
HYDROGEN CONCENTRATORS/ COMPRESSORS

COMMON TECHNOLOGIES

IMMOBILIZED ELECTROLYTE
CATALYTIC ELECTRODES
CURRENT COLLECTORS
BIPOLAR SEPARATOR
GAS MANIFOLDING
STACK SEALING
STACK COMPRESSION
ANCILLARY SYSTEM COMPONENTS
WATER, GAS AND HEAT MANAGEMENT

ELECTROCHEMICAL GAS SENSORS

ELECTROLYSIS SYSTEMS

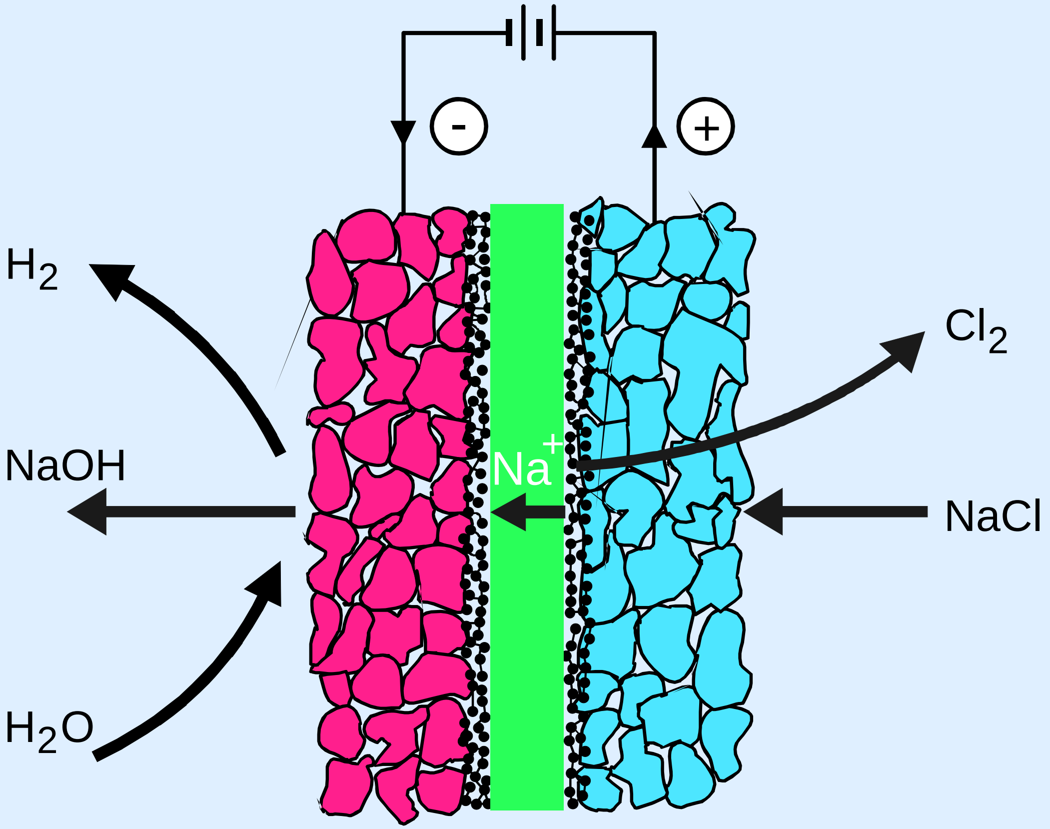
ELECTROLYSIS SYSTEMS FOR HYPOCHLORITE AND CHLORINE GENERATION

ENVIRONMENTAL GAS/EFFLUENT MANAGEMENT

REGENERATIVE FUEL CELL SYSTEMS

A.B. LaConti, Giner Inc., USA

Chlor-alkali electrolysis cell based on the principle of PEFC



🟥 Kathode
🟦 Anode
🟩 Elektrolyt

Solid Polymer Electrolyte

- Fixed concentration of ionic species
- No influence of gas bubbles on electrolyte resistance
- No wetting of electrodes, intimate contact between electrolyte and porous electrode has to be provided
- Small electrolyte gap, low ohmic loss at high current densities
- Bipolar arrangement avoids shunt currents
- Acidic electrolyte requires corrosion resistant electrodes

Zero Gap versus SPE Concept

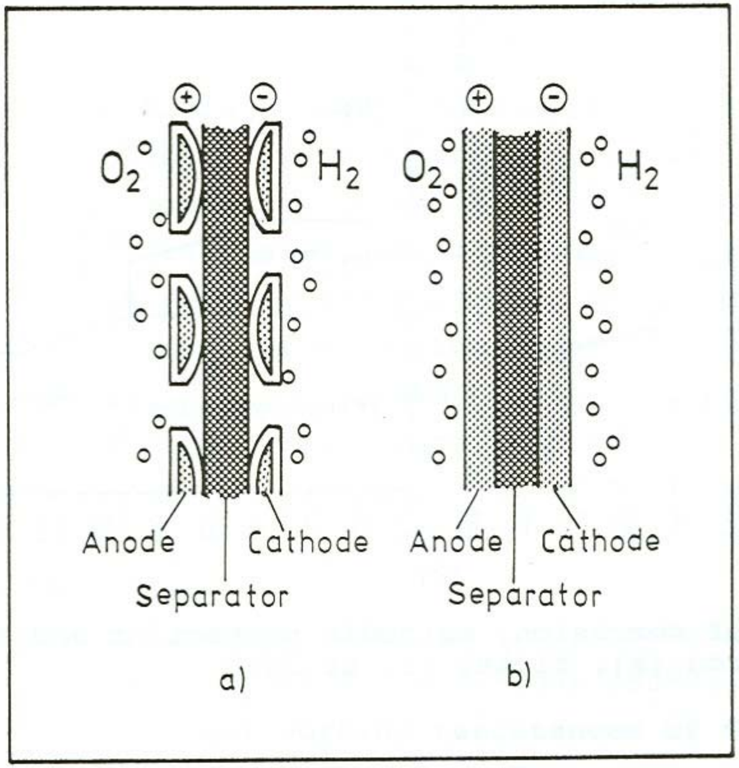
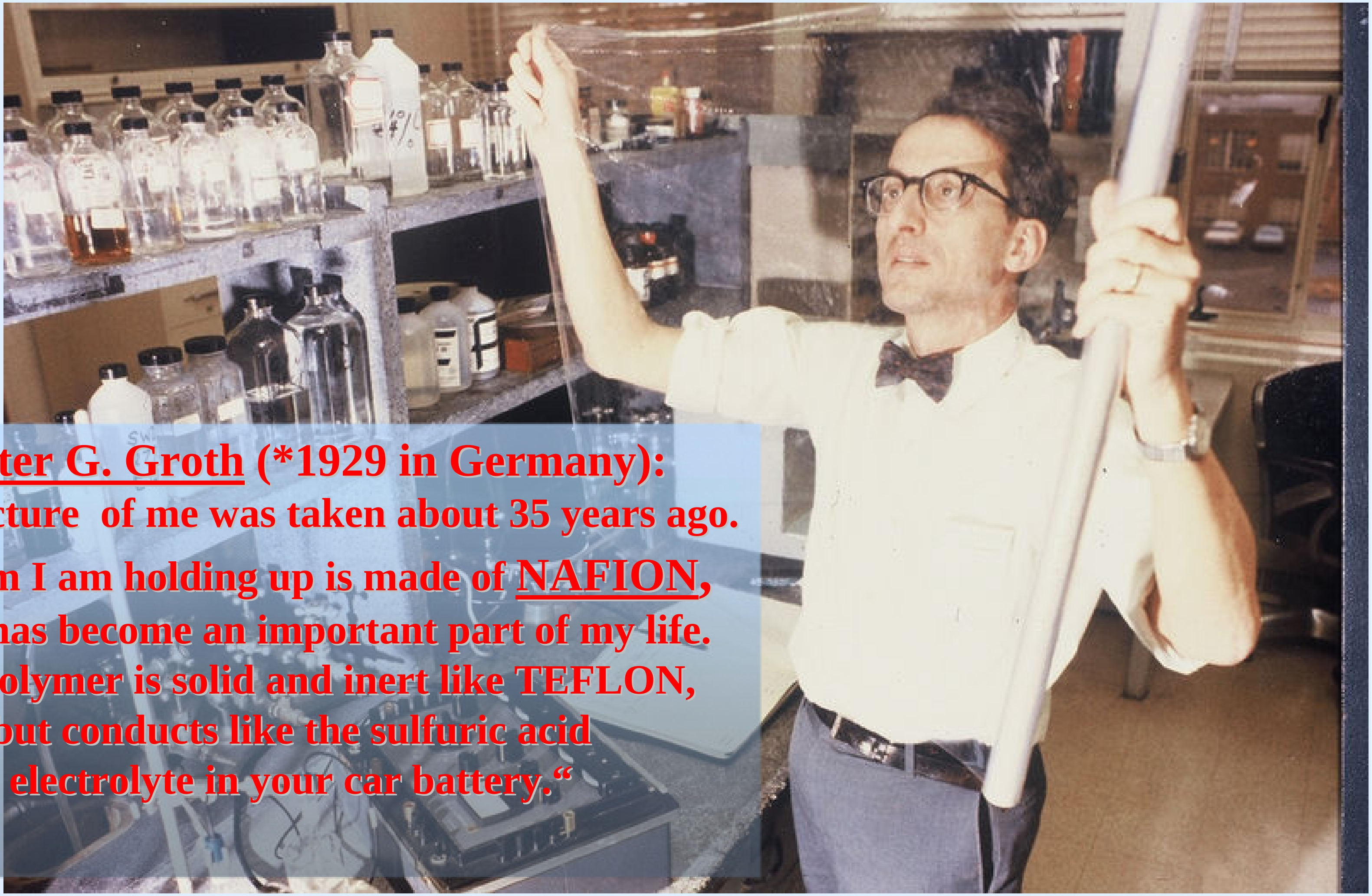


Fig. 8. Zero-gap cell geometry: a: perforated sheet electrodes, b: sandwich technique

Hartmut Wendt, Electrochemical Hydrogen Technologies, Elsevier, 1990

Nafion, a discovery by serendipity



Walter G. Groth (*1929 in Germany):

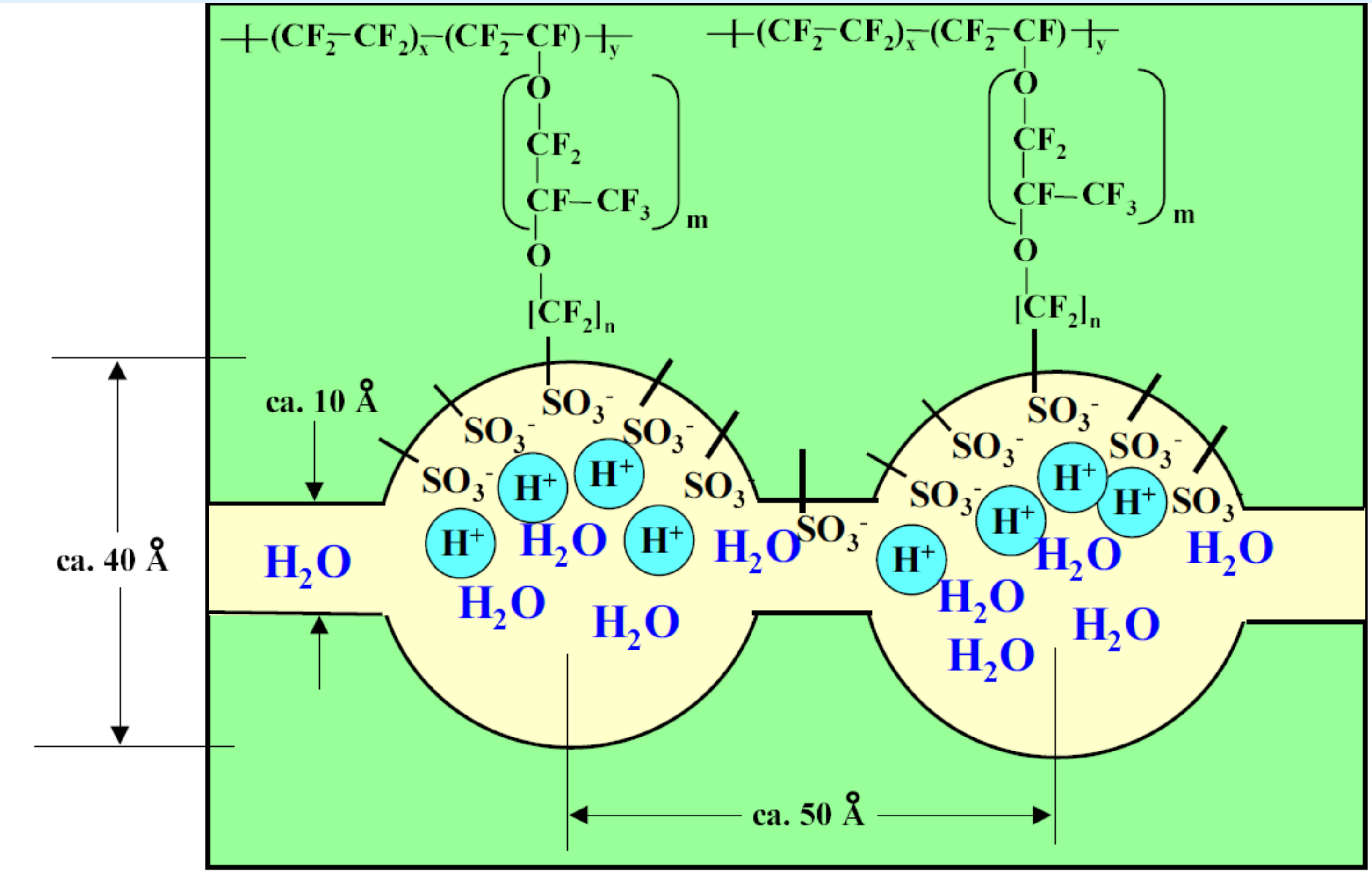
„This picture of me was taken about 35 years ago.

The film I am holding up is made of NAFION,
which has become an important part of my life.
This polymer is solid and inert like TEFLON,
but conducts like the sulfuric acid
electrolyte in your car battery.“

W.G. Grot, Chem. Ing. Techn. 44, 163 (1972), Chem. Ing. Techn. 44, 167 (1972)

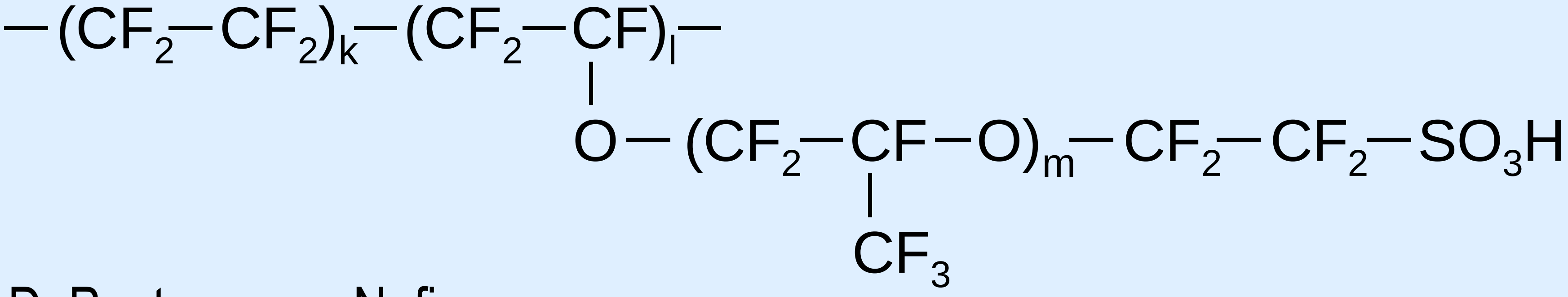
Cluster Network Model

T. Gierke
DuPont



Villard de Lans Ionomer Workshops, organizer M. Pinéri, CEA

Solid polymer electrolyte



$$-(CF_2-CF_2)_k-(CF_2-CF(O-(CF_2-CF(CF_3)-O)_m-CF_2-CF_2-SO_3H))_l-$$

DuPont: Nafion
Asahi Glass: Flemion
Asahi Kasei: Aciplex
3M, Gore, Solvay, Fumatech, others

$m = 1^*$
$l = 1$
$k = 5 - 7$

Other membrane types based on different membrane chemistry are under development

*Scherer, Pfluger, Proc. Electrochem. Soc. 86-13, 52 (1986)

Nafion

- Swelling in combinations of solvents
  (Scherer, Chem. Ing. Techn. 56, 538 (1984))
- Establish Current-Interupt Method as standard for membrane optimization and lifetime indicator, switch 104 A in less than 100 ns (Marek, Scherer)
  (Büchi, Marek, Scherer (J. Electrochem. Soc. 142, 1895 (1995) for PEFC)

NaFlu coating

- Swell Nafion in a combination of solvents in an autoclave to a gel and homogenize (**Stucki**)
  NaFlu Nafion Flüssig (fluid)

  Mix with catalyt powder, brush onto membrane
- Only partly successful!

Radiation grafted membranes tested in water electrolysis cells

1980 -1987

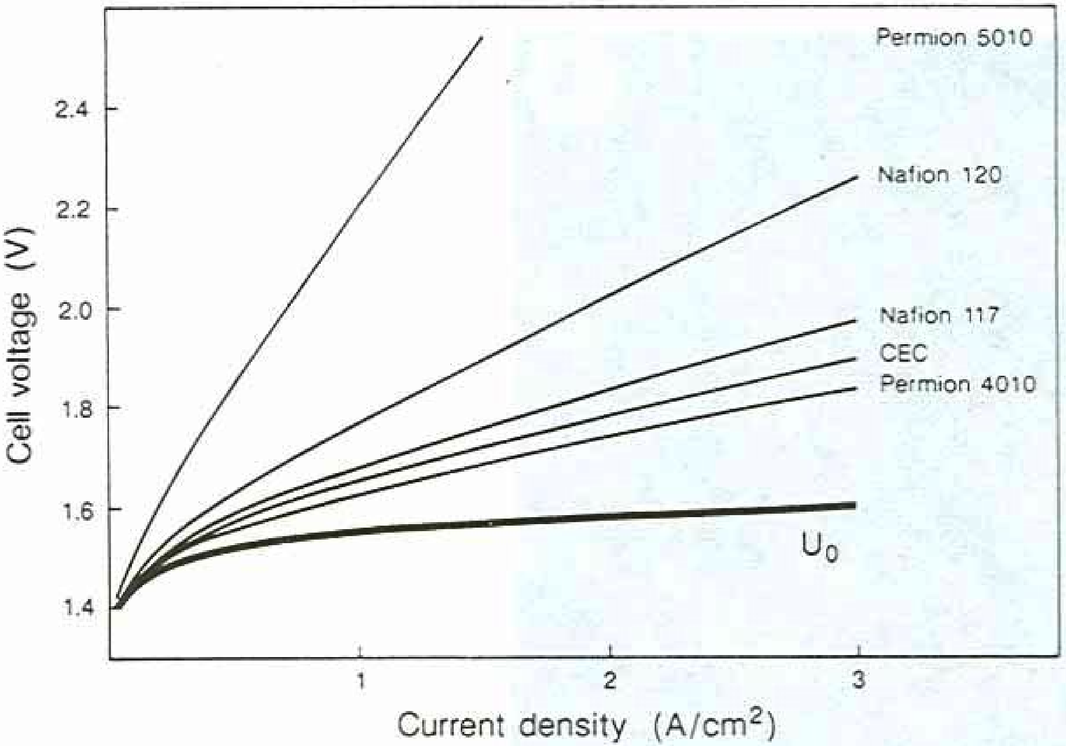


Fig. 6. Current–cell voltage curves for several membranes at 80°C and *iR*-corrected cell voltage U_o.

30 cm^2 cell
80 °C
ambient pressure
Pt cathode
RuIrOx anode

RAI Inc., Permion 5010: PE-styrene grafted; Permion 4010: PTFE-styrene grafted

CEC: Chlorine Engineers Corp., Japan, TFS grafted on perfluorinated substrate

Scherer et al., Int.J. Hydrogen Energy 17, 115 (1992)

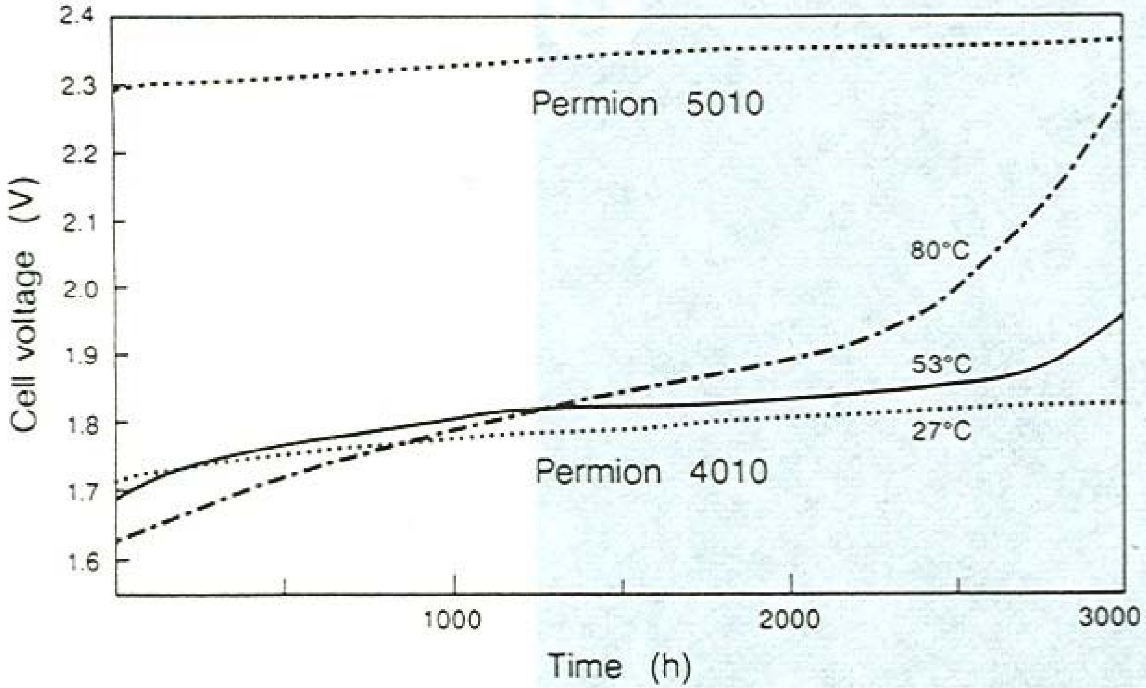


Fig. 7. Cell voltage versus time for Permion 4010 membrane at different temperatures and for 5010 membrane at ambient temperature.

RAI Inc., Permion 5010: PE-styrene grafted; Permion 4010: PTFE-styrene grafted

Scherer et al., Int.J. Hydrogen Energy 17, 115 (1992)

Trifluorostyrene grafted onto perfluorinated substrate

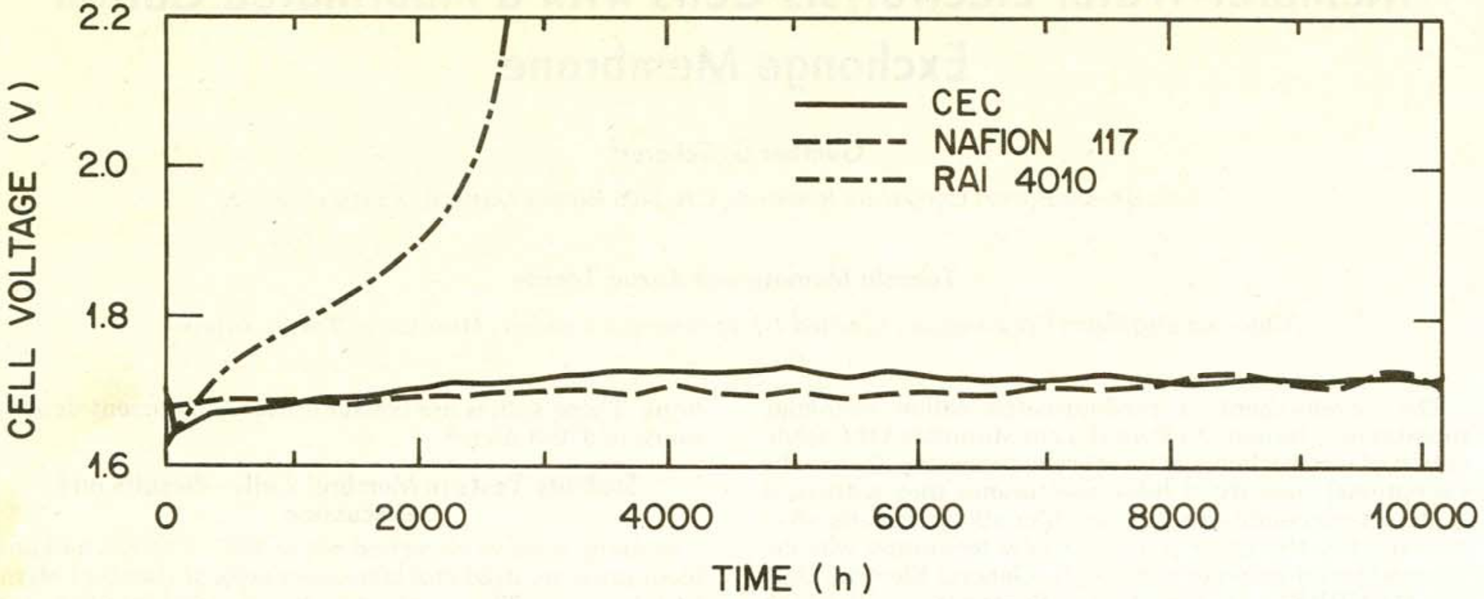


Fig. 2. Cell voltage E_z vs. time for Membrel cells with CEC, Nafion 117, and RAI 4010 membranes. 80°C, 1 A/cm^2, ambient pressure

CEC, Chlorine Engineers Corporation, Japan
Projection: 1/10 of Nafion price

Scherer, Momose, Tomiie, JES 135, 3071 (1988)

Locus of degradation – fuel cell mode

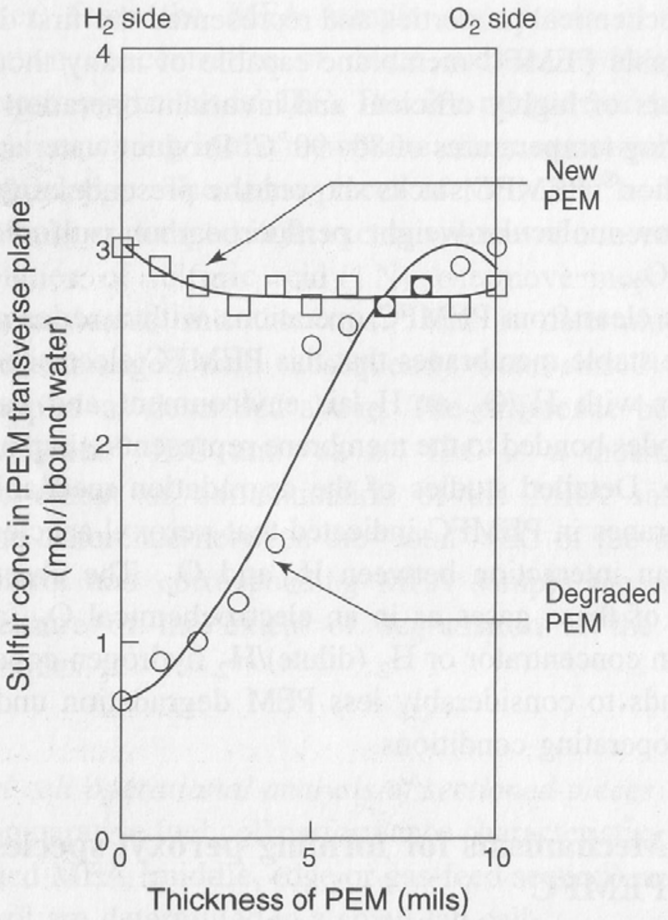


Figure 1. Scanning electron microprobe through 250 µm poly(styrene sulfonic acid) membrane.[10, 11]

- Degradation at H_2 side.
- The presence of H_2 and O_2 are necessary to observe degradation

Hodgon, Boyak, LaConti, GE Laboratories, Direct Energy Conversion Technologies, 1965

A.B. LaConti et al., Fuel Cell Handbook, Chapter 49, Vol. 3 (2003) p. 647

Locus of degradation – water electrolysis mode

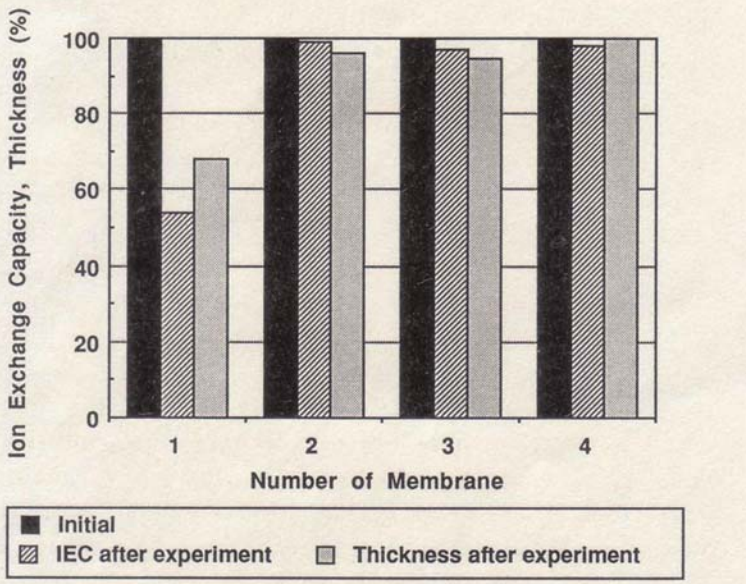


Fig. 11
Ion exchange capacity and thickness of Nafion 117 membranes before and after an electrolysis experiment (>100°C, 1 A cm^{-2}, several thousand hours). H_2-side membrane No. 1, O_2-side membrane No. 4

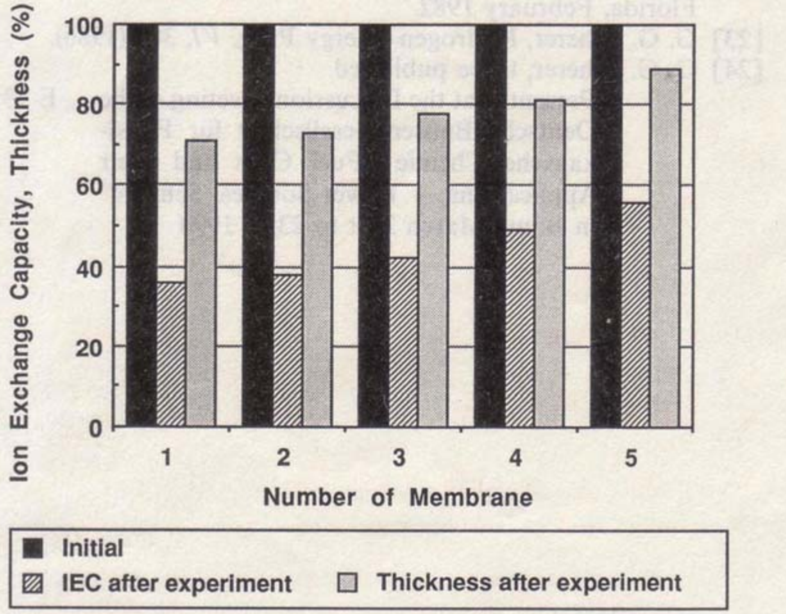


Fig. 10
Ion exchange capacity and thickness of Permion 4010 membranes before and after an electrolysis experiment (80°C, 1 A cm^{-2}, 1000 h). H_2-side membrane No. 1, O_2-side membrane No. 5

Scherer G.G., Ber. Bunsenges. Physik. Chem. 94, 1008, (1990)
Stucki, Scherer, Schlagowski, Fischer, Applied Electrochem. 28, 1041 (1998)

Electrodes

Metal black electrodes:

- Anode RuIrOx
- Cathode Pt

Anode current collector resistant to oxidation and corrosion, platinized porous Ti

Anode catalyst

- RuIrOx
- Ru cheap. Ir expensive (comparable to Pt)
- Preparation according to Adams, Shriver (Degussa)
- Optimized to $Ru_{.80}Ir_{.20}Ox$ (Kötz, Stucki, K. Müller, others (20 plus publications))
- Corrosion mechanism of RuOx via RuO_4
- Spray catalyst plus binder onto anode current collector, subsequent sintering of the binder

Literature

R. Kötz, H.J. Lewerenz and S. Stucki
XPS - Studies of the Oxygen Evolution on Ru and RuO2 Anodes
Journal of the Electrochemical Society 130 (1983) 825

R. Kötz, H.J. Lewerenz, P. Brüesch and S. Stucki
Oxygen Evolution on Ru and Ir Electrodes: XPS - Studies
Journal of Electroanalytical Chemistry 150 (1983) 209

H.J. Lewerenz, S. Stucki and R. Kötz
Oxygen Evolution and Corrosion: XPS Investigations on Ru and RuO2 Electrodes
Surface Science 126 (1983) 463

R. Kötz, S. Stucki, D. Scherson and D.M. Kolb
Identification of RuO4 as the Corrosion Product During Oxygen Evolution on Ruthenium in Acid Media
Journal of Electroanalytical Chemistry 172 (1984) 211

R. Kötz, H. Neff and S. Stucki
Anodic Iridium Oxide Films: XPS Studies of Oxidation State Changes and O2 Evolution
Journal of the Electrochemical Society 131 (1984) 72

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R. Kötz and S. Stucki
Oxygen Evolution and Corrosion on Ruthenium - Iridium Alloys
Journal of the Electrochemical Society 132 (1985) 103
R. Kötz and H. Neff
Anodic Iridium Oxide Films: A UPS Study of Emersed Electrodes
Surface Science 160 (1985) 517
R. Kötz and S. Stucki
Stabilization of RuO2 by IrO2 for Anodic Oxygen Evolution in Acid Media
Electrochimica Acta 31 (1986) 1311
E.R. Kötz and S. Stucki
Ruthenium Dioxide as a Hydrogen Evolving Cathode
J. Applied Electrochemistry, 17 (1987) 1190-1197
A. de Battisti, G. Lodi, M. Cappadonia, C. Battaglin and E.R. Kötz
Influence of the Valve Metal Oxide on the Properties of Ruthenium Based Mixed Oxide Electrodes. Part 2: RuO2/TiO2 Coatings.
Journal of the Electrochemical Society, 136 (1989) 2596

Minimal catalyst loading

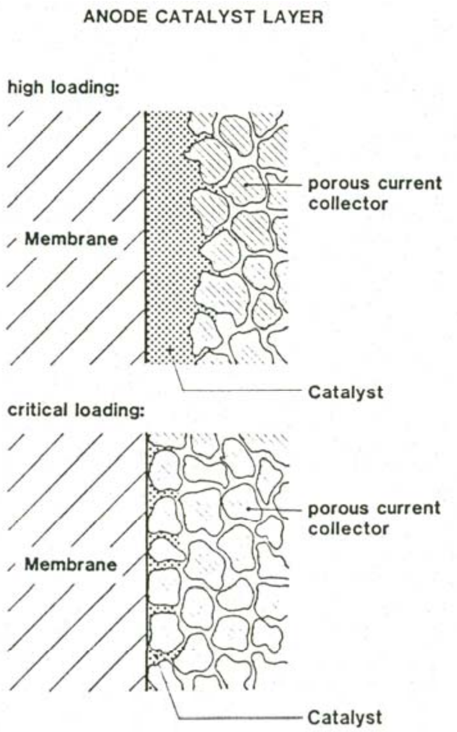

Fig.6
Schematic cross section of the membrane-electrode interface.

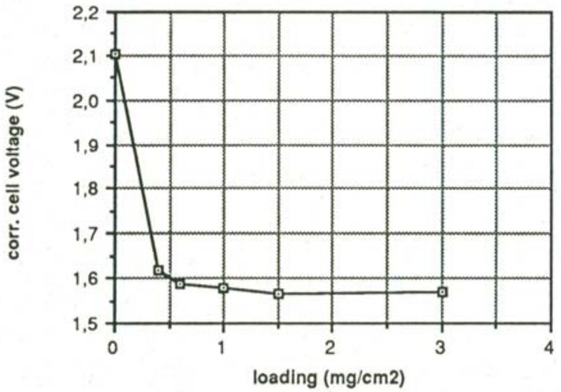

Fig.5
Influence of anode catalyst loading on corrected cell voltage of cells operating at T = 80°C, 1 A cm^{-2}. Loading 0 corresponds to the performance of platinized Ti

Second Symposium on Electrode Materials and Processes for Energy Conversion and Storage. S. Srinivasan, S. Wagner, and H. Wroblowa, editors, PV 87-12, 660 Pages

Sievert, Baumann, Scherer, Stucki, Proc. Electrochem. Soc. 87-12, 367 (1987)

Cathode catalyst

Platinum

Tanaka Method, electroless deposition by impregnation and chemical reduction

Electrochemical deposition of Pt from $Pt(NH_3)_2NO_3$ impregnated membranes

(Stucki, Killer, Scherer, e.g., EP 0120212 B1)

Loading ≤ $1 mg/cm^2$

Problem: Skin effect

Anode Current Collector

Porous Ti-sheets, platinized

Commercial Product from Gould, USA, irregular porosity, thickness, grain size, etc.

Etching and galvanic Pt-deposition

BBC development (H. Devantay), regular porosity, thickness, etc

Challenge particle size distribution of Ti-powder, optimization sinter process

Reduction of Pt-loading ≤ 1mg/cm^2 by post thermal treatment, point contact concept (Scherer, Killer, CHP 649315 A5 , USP 4597846)

Cathode Current Collector

FasPul (C-Fasern (fibres) and C-Pulver (powder), polymer binder)

BBC Development (E. Müller, M. Braun)

Bipolar Plate

Impregnated Electrographite, flow field mechanically machined

BBC Development C-Powder and polymer binder (H. Devantay)
Uniaxial hot pressing leads to graphite particle orientation, anisotropic conductivity

Collaboration with SGL, Meitingen, triggered heat exchanger plate and bipolar plate development for PEFC technology at SGL

State of the art mid 1980s

Laboratory Cells (30 and 100 cm^2)

Nafion 17, 1 A/cm^2, 1.72 V, best 1.64V, at 80 °C, ambient pressure

Test time between 10000 and 20000 h

Tests at current densities up to 15 A/cm^2 for several 1000 h

Short stacks (400 cm^2)

10 to 20 cells operated for several thousand h

Cost model development

(Stucki, Simmrock, U Dortmund)

State of the art mid 1980s

Two 100 kWe electrolyser systems delivered:

Chivaudan, Geneva, continuous operation

Solar Wasserstoff Bayern, Neunburg vorm Wald, intermittend operation*

*Problems with gas purity, thinning of membrane

Stucki , Scherer, Schlagowski, Fischer, J. Appl. Electrochem. 28, 1041 (1998)

Electrolytic Ozone Generation

Ozone generation on PbO_2 anodes (Stucki)

In situ ozone generation for water treatment

S. Stucki, G.Theis, R. Kötz, H. Devantay, H.J. Christen; In-situ Production of Ozone in Water using a Membrel Electrolyzer. J. Electrochem. Soc. 132 (1985) 367

S. Stucki, H. Baumann, H.J. Christen, R. Kötz; Performance of an Electrochemical Ozone Generator. J. Appl. Electrochem. 17 (1987) 773

S. Stucki, D. Schulze, D. Schuster, C. Stark; Ozonization of Purified Water Systems; Pharmaceutical Engineering, 25,1, (2005) 40-56

The End

- 1988 Merger between BBC Switzerland an Asea Sweden to **ABB**
- Termination of Membrel Project, no market developent, no buyer found to take over know-how
- Hydrogen is a Future Technology

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