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JÜLICH FORSCHUNGSZENTRUM

Mobility and distribution of phosphoric acid in high-temperature polymer electrolyte fuel cells

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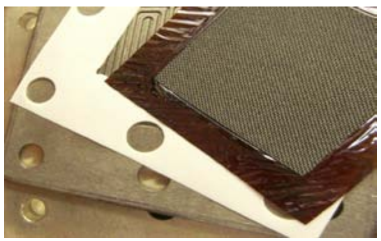
Outline

- Introduction
- Phosphoric acid
- In-situ characterization
- Conclusion

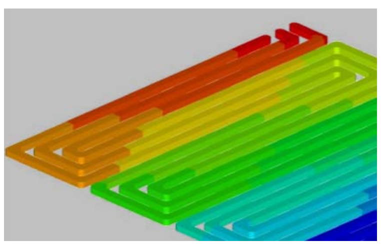
Area of HT-PEFC research and development

Focus on three topics:

Stacks up to 5 kW_{el} (power density, lifetime)



Electrodes (lifetime, performance, acid mobility)

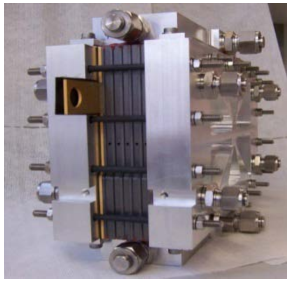


Modeling and Simulation (develop. tool, basic research)

HT-PEFC stack development

power

2009



14 cells, 200 cm²/cell
liquid or air cooling
616 W

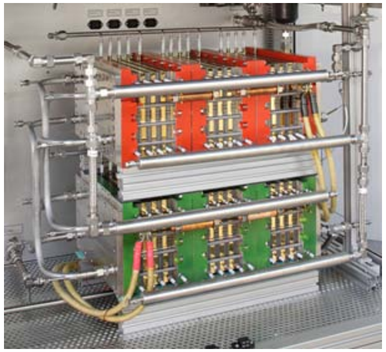
2010

30 cells, 320 cm²/cell
modular concept
liquid cooling

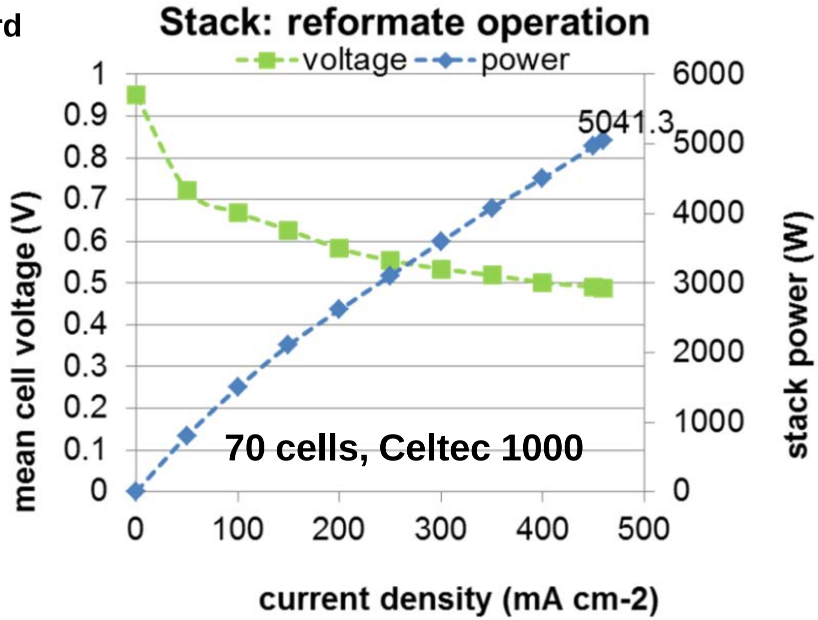
2011

36 cells, 320 cm²/cell
in 3 Modules
oil cooling every 3rd cell, 2000 W

2012



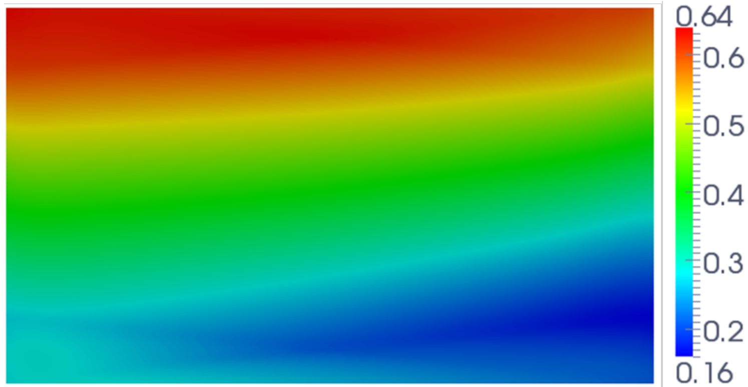
synthetic reformate:
(41% H_2, 58% N_2, 1% CO)
λ=2/2
Liquid cooling:
T_{in}: 160 °C, T_{out}: 170 °C



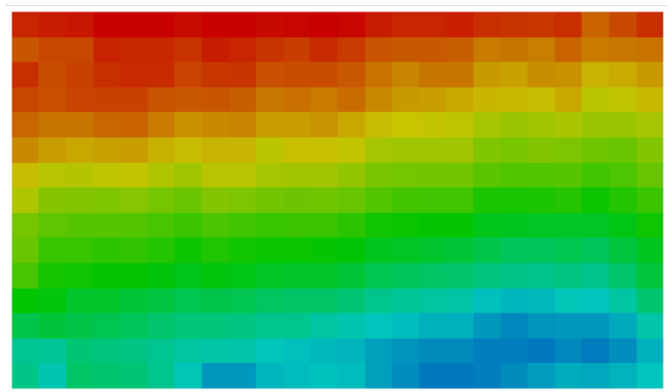
Details will be presented at ASME 2012, November 9-15, 2012, Houston, Texas, USA

Modeling/simulation

Simulation

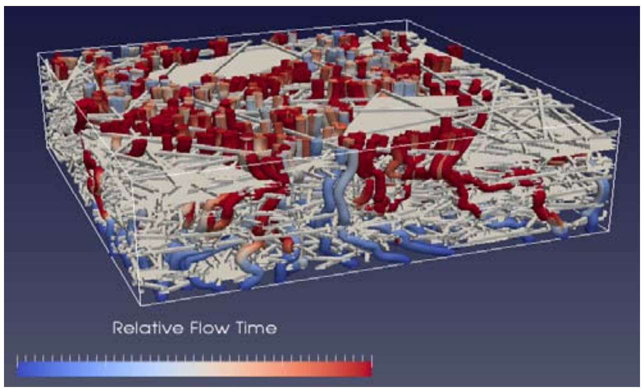


Experiment



current density / A cm^{-2}

T= 160°C, co-flow
λ= 1.2 / 2.0
V_{CFD}=0.501 V,
V_{EXP}=0.486
synthetic reformate:
40% H_2, 1% CO



- **CFD**
- **Lattice-Boltzmann**
- **Analytical models**

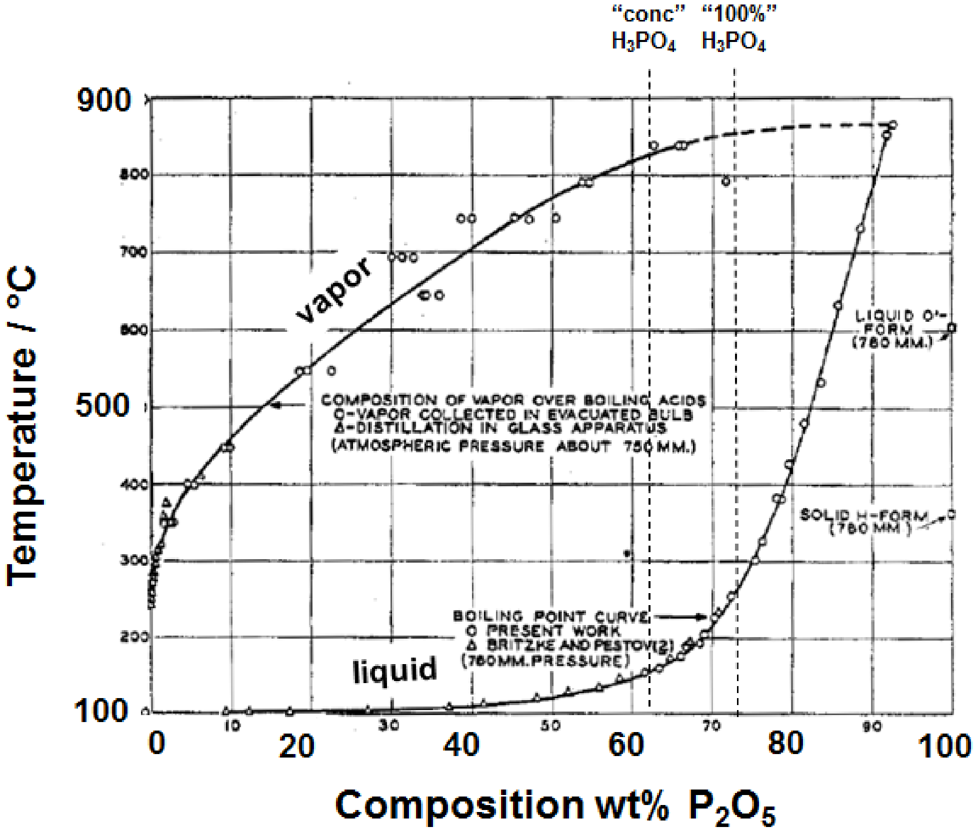
- **A much better understanding of processes in membrane and electrodes is necessary in order to improve the MEAs and the MEA model (stationary and transient operating conditions)**

Elektrolyte / MEA

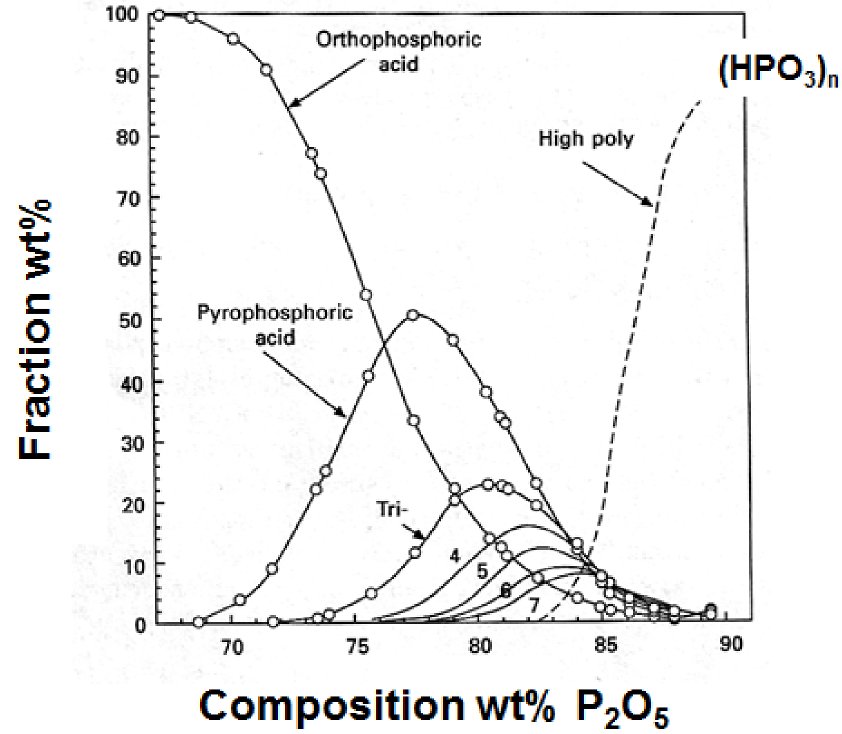
Phosphoric acid

Phosphorpentoxid: $P_2O_5 \Rightarrow P_4O_{10}$

Formation of phosphoric acid: $P_4O_{10} + 6\ H_2O = 4\ H_3PO_4$



Liquid vapour phase diagram at ambient pressure (1 bar)



Condensation of phosphoric acid, forming of polyphosphoric acids

$2\ H_3PO_4 = H_4P_2O_7 + H_2O$

$H_3PO_4 + H_4P_2O_7 = H_5P_3O_{10} + H_2O$

$H_3PO_4 + H_5P_3O_{10} = H_6P_4O_{13} + H_2O$

$H_3PO_4 + H_6P_4O_{13} = H_7P_5O_{16} + H_2O$

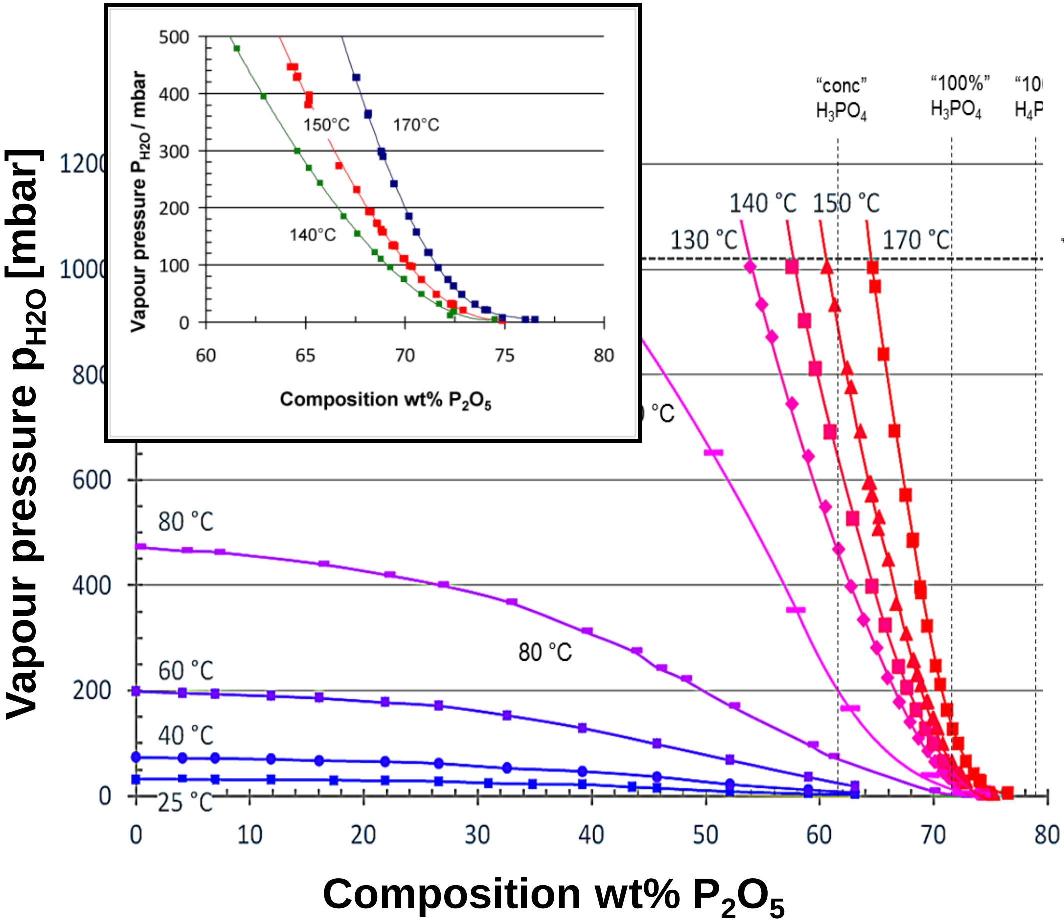
....

(Taking into account only unbranched chains)

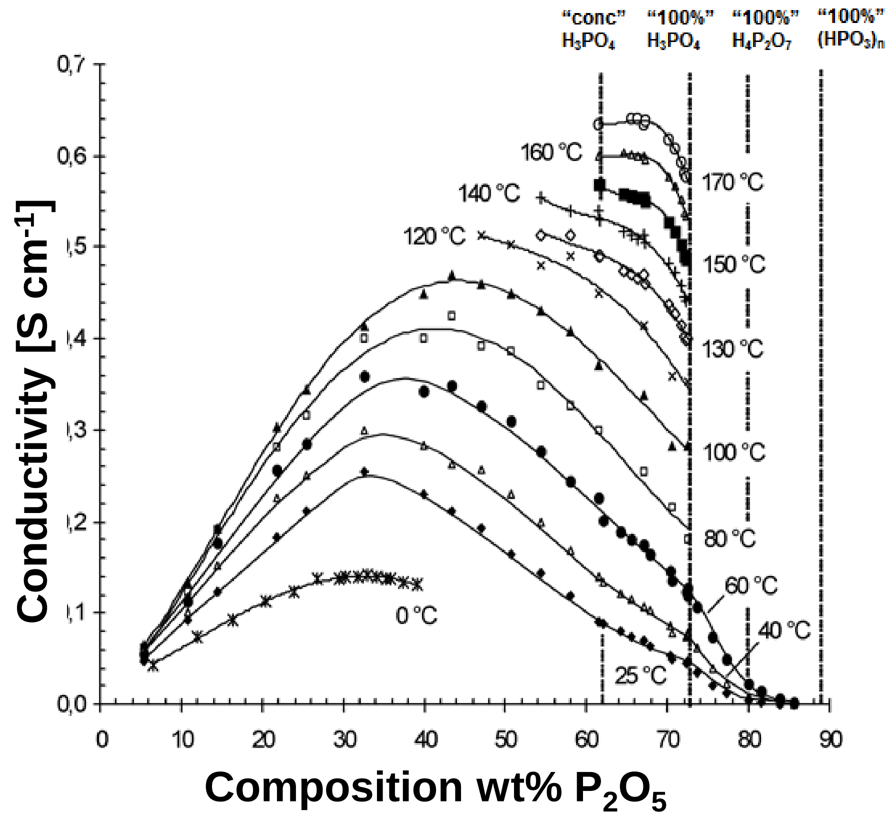
Data: R.F.Jameson, J. Chem. Soc 1 (1959) 752-759
Figure: T.F. Fuller, K.G. Gallagher, Phosphoric Fuel Cells, in: Materials for Fuel Cells, Ed. M. Gasik, Woodhead Publishing Limited, 2008, p 209-247

E.H. Brown, C.D. Witt, Ind. Eng. Chem. 44 (1952) 615-618

Phosphoric acid



Vapour pressure p_{H2O} of the system P_2O_5 – H_2O as function of composition and temperature

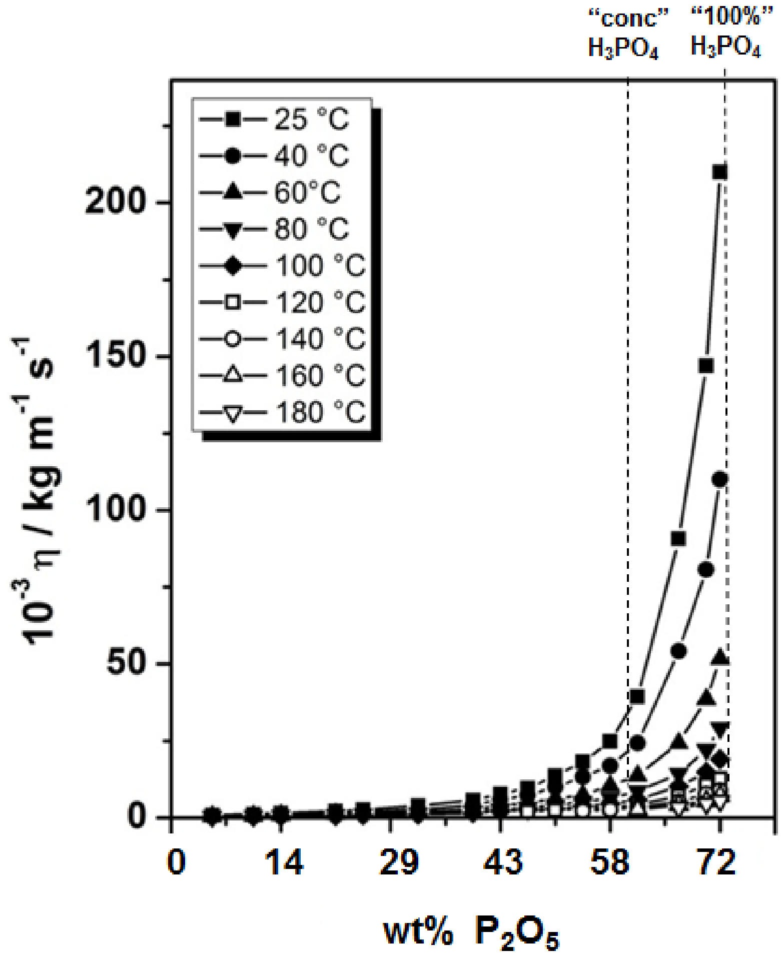


Conductivity as function of composition and temperature

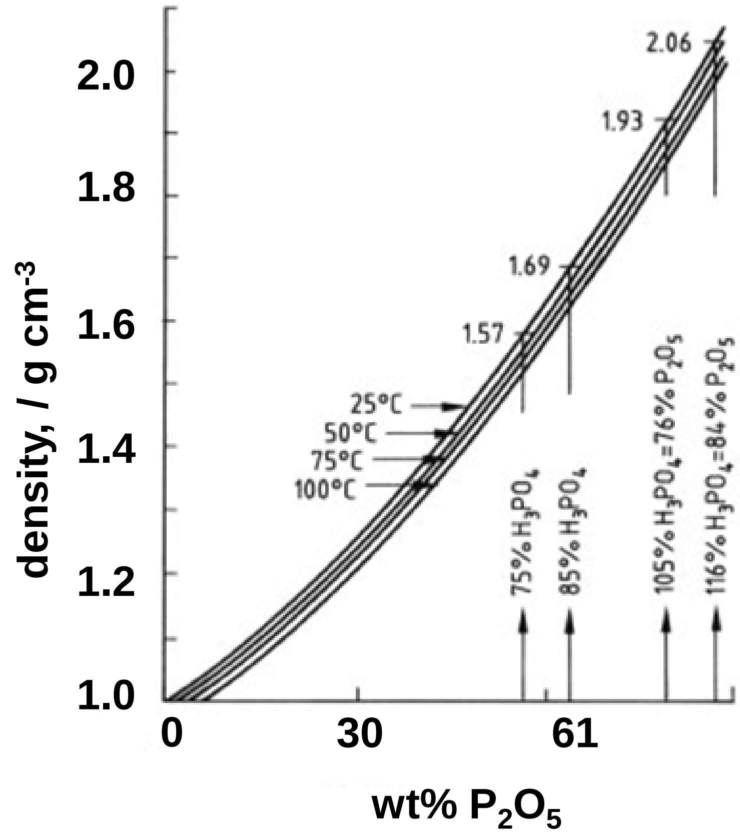
wt% P_2O_5	wt% H_3PO_4	
61,56	85	"conc. H_3PO_4"
72,42	100	"100% H_3PO_4"
79,76	109,79	"100% $H_4P_2O_7$"
88,74	122,52	"100% $(HPO_3)_n$"

Source: C. Korte, Phosphoric Acid, an Electrolyte for Intermediate-Temperature Fuel Cells –Temperature and Composition Dependence of Vapor Pressure and Proton Conductivity, in: D. Stolten, B. Emonts, Eds, Fuel Cells Science and Engineering, Wiley VCH 2012

Phosphoric acid



Dynamic viscosity of the system $P_2O_5 - H_2O$ as function of composition and temperature



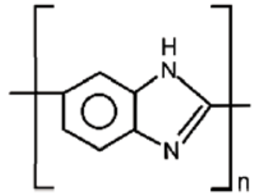
Density of Phosphoric acid

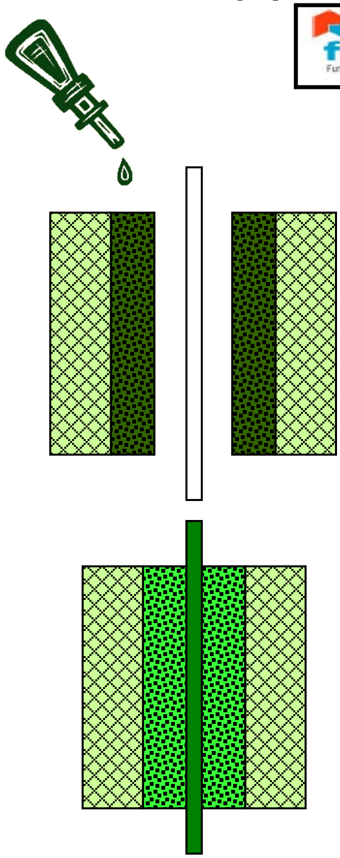
Data: Ullmann's Encyclopedia of Industrial Chemistry, Phosphoric Acid and Phosphates, Schrödter, Bettermann, Staffel, Wahl, Klein, Hofmann, Wiley VCH 2008

Mobility and distribution of phosphoric acid

Poly (2,5-benzimidazole)

fumatech



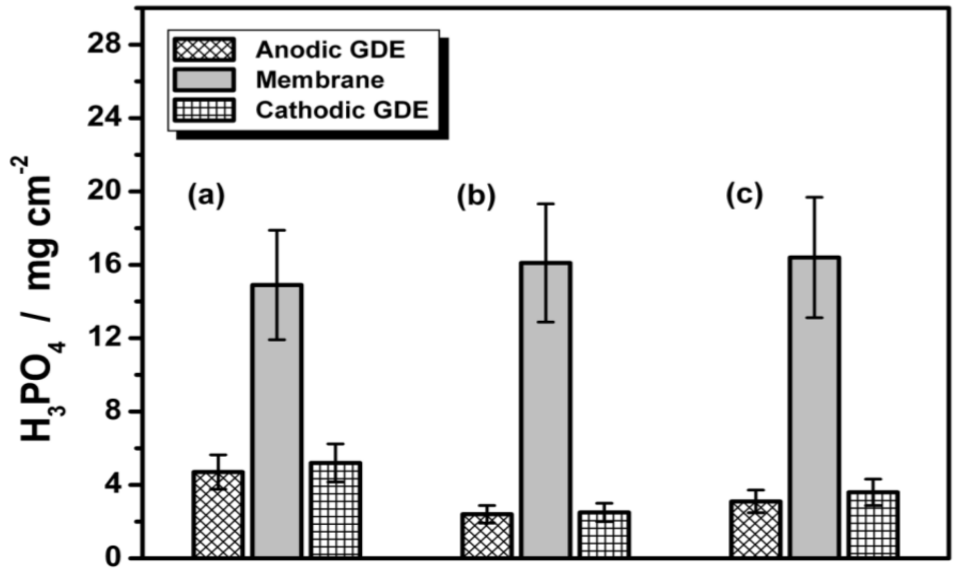


- Different doping procedures

➢ Same distribution after 100 h

➢ Rapid start up possible after ~ 10 min

➢ Max. power after ~ 70 h



Acid distribution in MEAs as determined from disassembled MEAs after ~100 hours of service

(a): dry membrane and both GDEs impregnated with 20 mg cm^{-2} of H_3PO_4 prior to cell assembly

(b): membrane pre-doped in 8M phosphoric acid and both GDEs loaded with 10 mg cm^{-2} of H_3PO_4

(c): membrane pre-doped in 8M phosphoric acid and only the anode impregnated with 20 mg cm^{-2} of H_3PO_4.

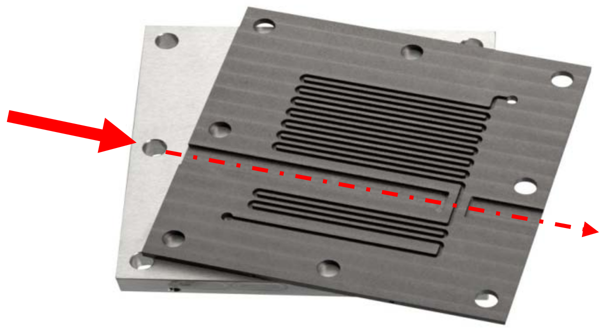
Two regions:

- **Membrane: ABPBI – Phosphoric acid**
- **Electrodes: Pt/C, PTFE – Phosphoric acid**

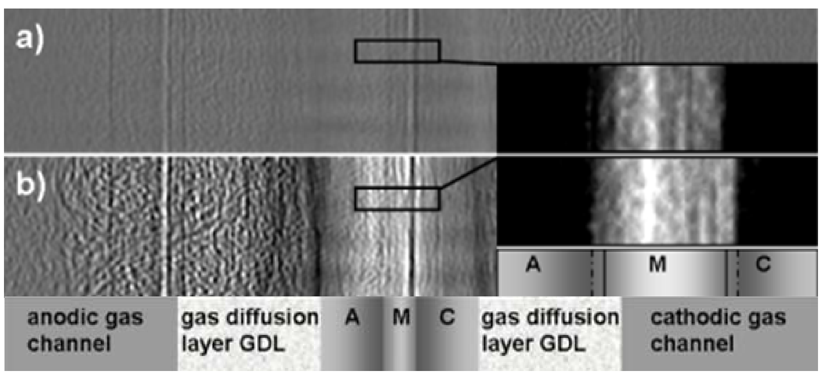
C. Wannek, I. Konradi, J. Mergel, W. Lehnert
Int. J. Hydrogen Energy 23 (2009) 9479

C. Wannek, W. Lehnert, J. Mergel
J. Power Sources 192 (2009) 258-266

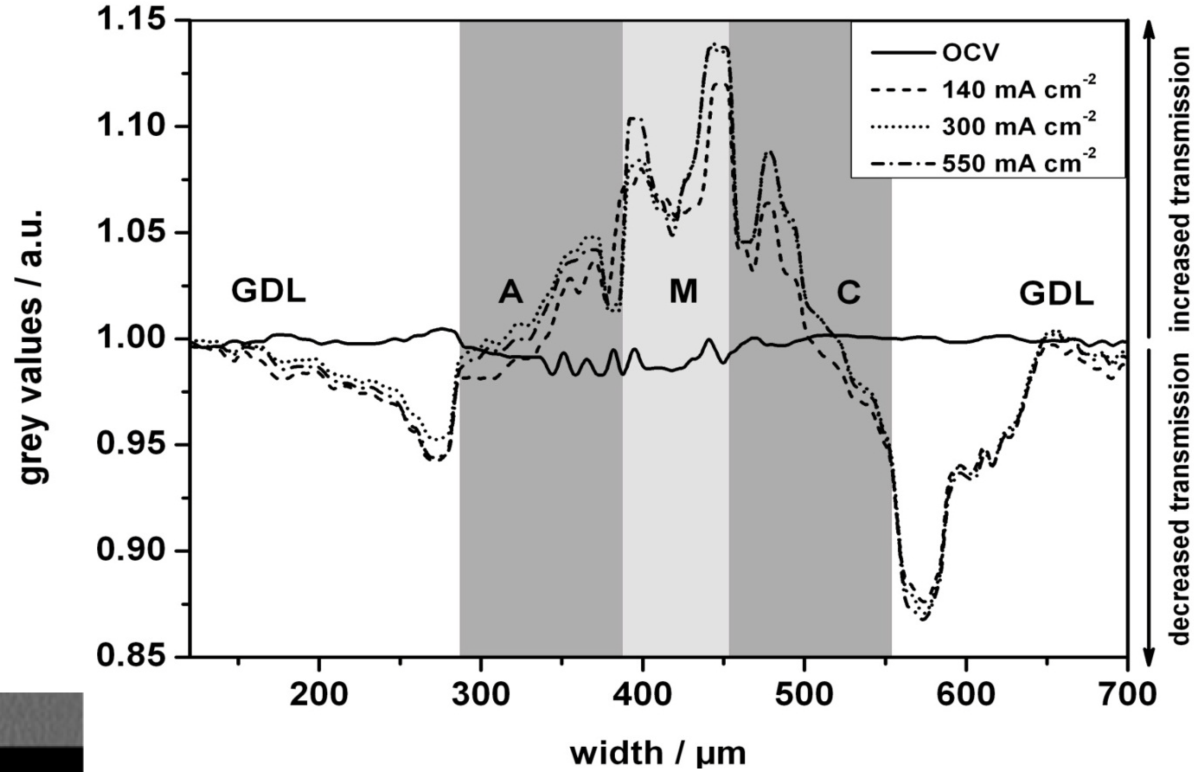
In-situ measurement of phosphoric acid distribution



In-plane synchrotron X-ray radiography



Normalized radiographs at load-cycles

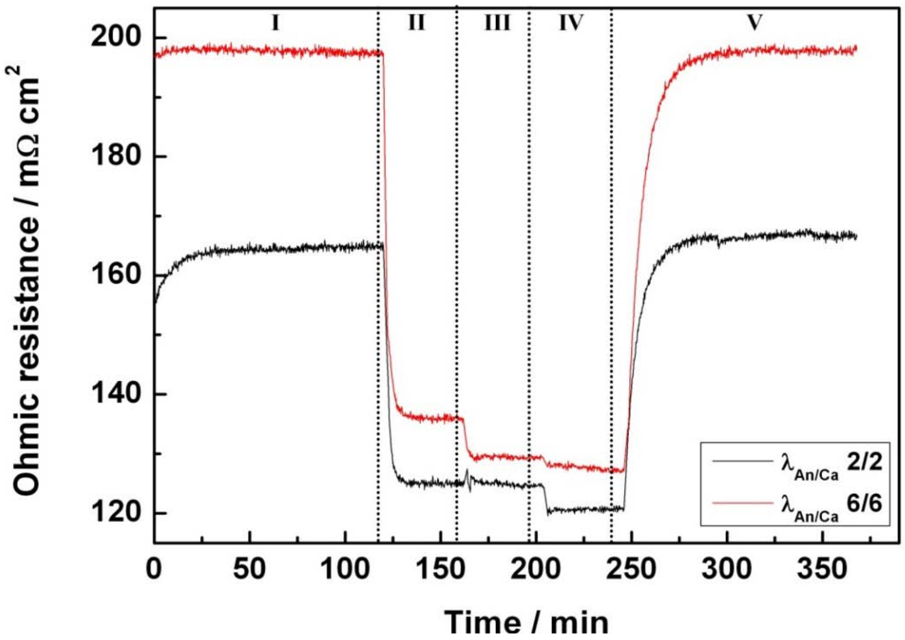


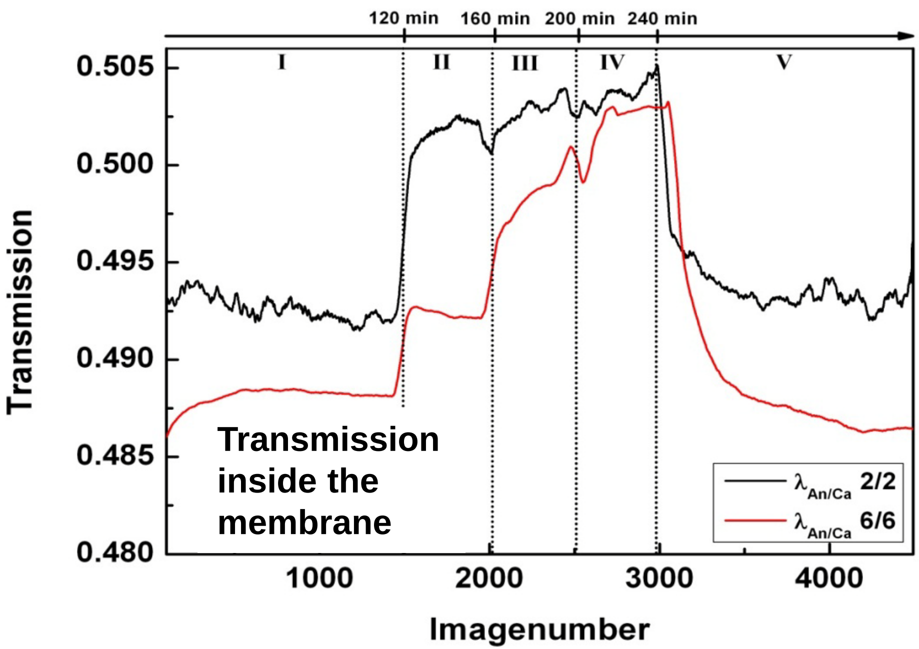
- **Increased transmission in membrane due to hydration of phosphoric acid by product water**
- **Decreased transmission at electrode-GDL-interface due to filling of pores**
- **Swelling of the membrane: undoped 30 µm, at OCV 55 µm, under load 65 µm**

similar cell see: R. Kuhn, J. Scholta, Ph. Krüger, Ch. Hartnig, W.Lehnert, T. Arlt, I. Manke, J. Power Sources 196 (2010) 5231

W. Maier, T. Arlt, Ch. Wannek, I. Manke, H. Riesemeier, Ph. Krüger, J. Scholta, W. Lehnert, J. Banhart, D. Stolten, Electrochemistry Communications 12 (2010) 1436

Dynamic behaviour during load change

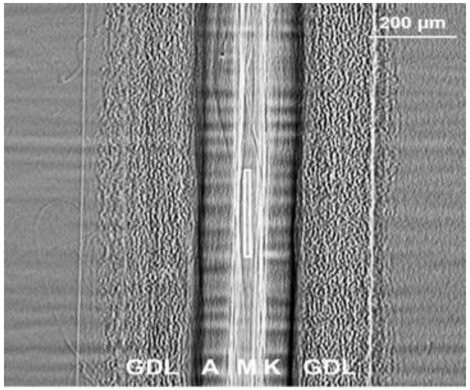




Areas	
I	OCV
II	140 mA cm^{-2}
III	350 mA cm^{-2}
IV	600 mA cm^{-2}
V	OCV

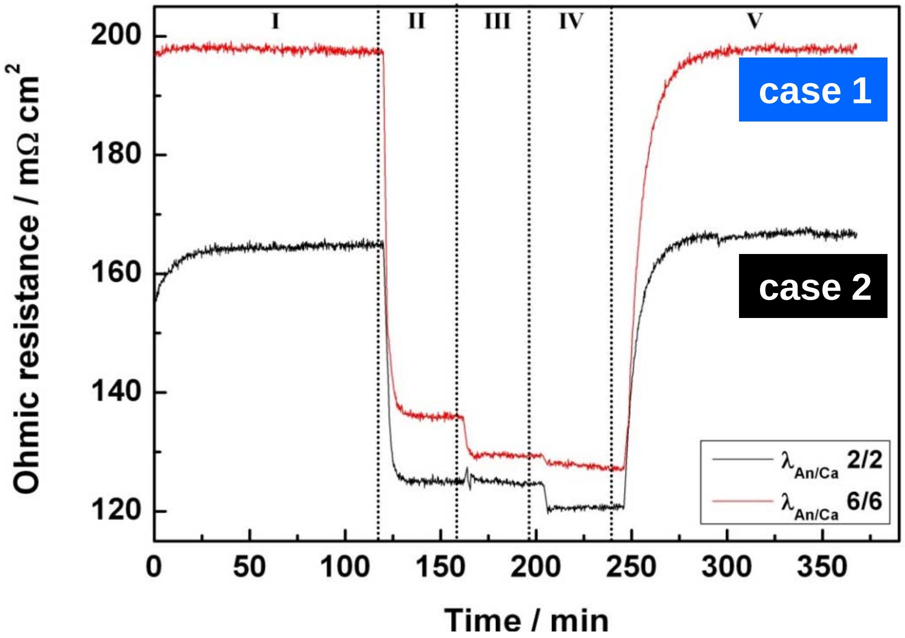
same gas flow at 140 mA cm^{-2} and OCV

- **Correlation between resistance and transmission**
- **Gas flow rate influences resistance and transmission**
- **Stationary conditions after:**
  OCV – load: ~ 20 min (water production)
  load – OCV: ~ 40 min (transport limitation)
- **Two phase system with high dynamic**



W. Maier, T. Arlt, K. Wippermann, C. Wannek, I. Manke, W. Lehnert, D. Stolten
J. Electrochem. Soc **159** (2012) F398-F404

Different operating conditions



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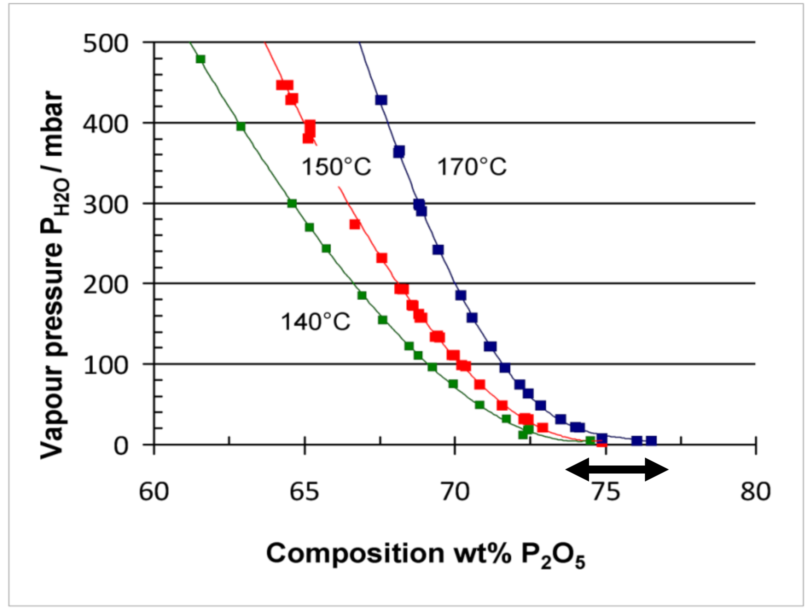

- dry gas at inlet (dewpoint -40 °C)
- most of the produced water will exit on cathode
- cross over current $I_{cross} \leq 5 mA/cm^2$
- equilibrium between acid and vapour

Water vapour partial pressure at exit
case 1: p_{water} : ~ 3 mbar
case 2: p_{water} : ~ 8 mbar

This rough estimation shows that acid composition changes drastically in this water vapour partial pressure region
=> large difference at OCV due to gas cross over. Not taken into account the interaction between acid and membrane

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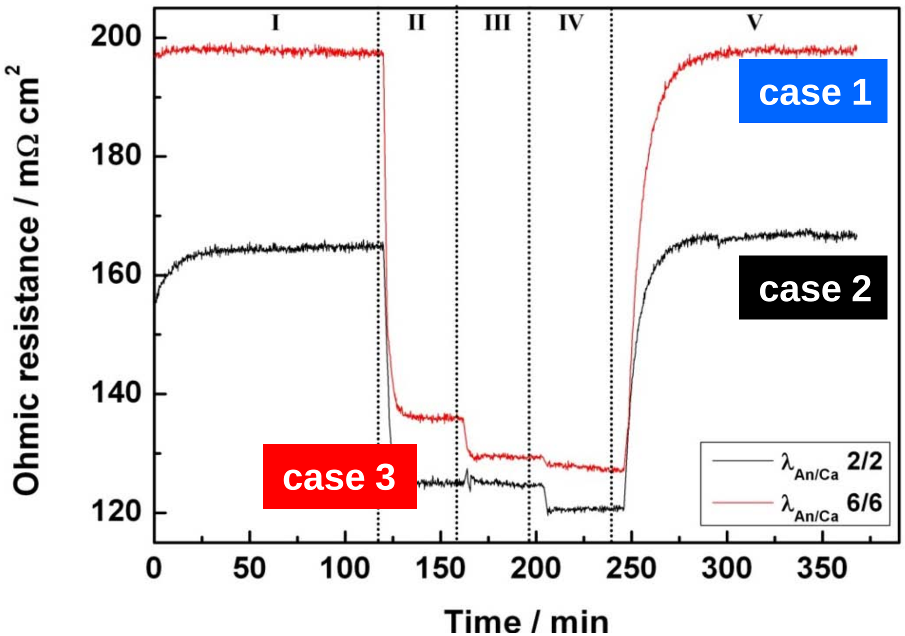

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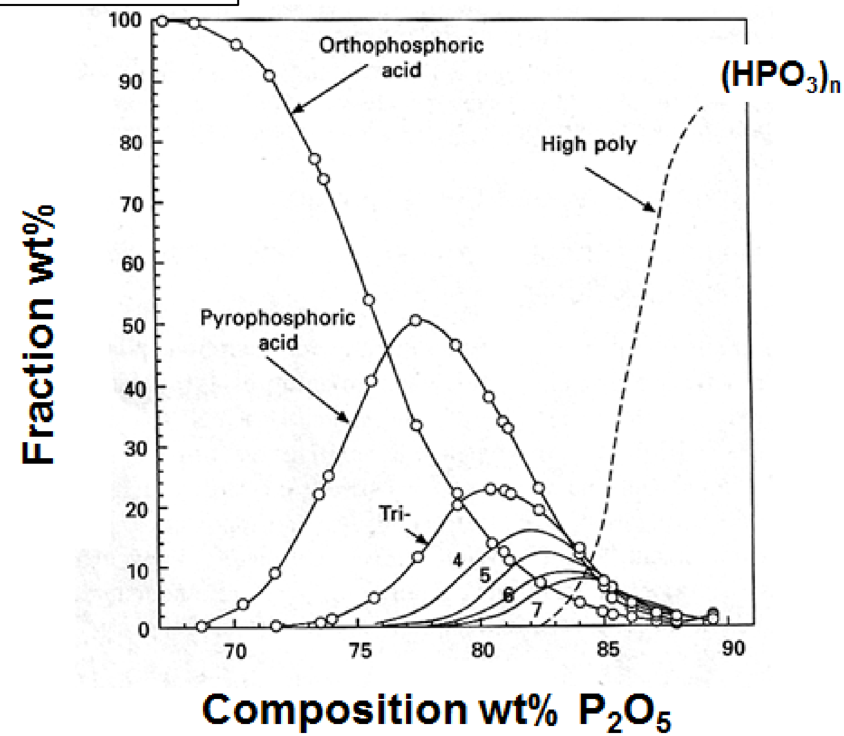

Water vapour partial pressure at exit:

case 3: p_{water} : ~ 190 mbar => 70 wt% P_2O_5 (upper limit)

High current density :

⇒ **concentration gradient of water vapour between electrode and gas channel**

⇒ **composition of P_2O_5 shifted to lower values**

Rough estimation:
Not taken into account the interaction between acid and membrane

This estimation is in general agreement with analyzed data from in-situ synchrotron X-ray radiography

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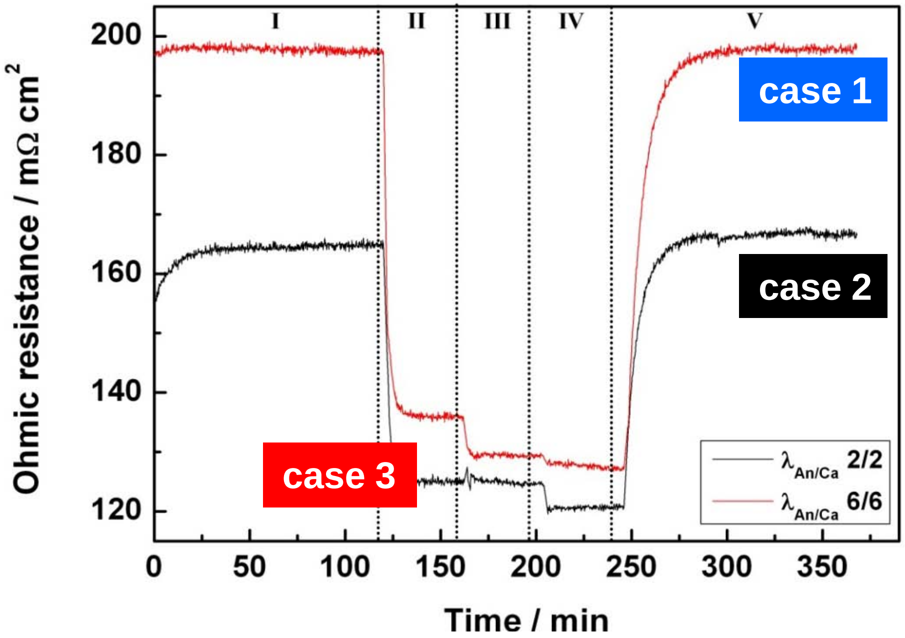
(W. Maier, Dis RWTH Aachen 2012)

Different operating conditions



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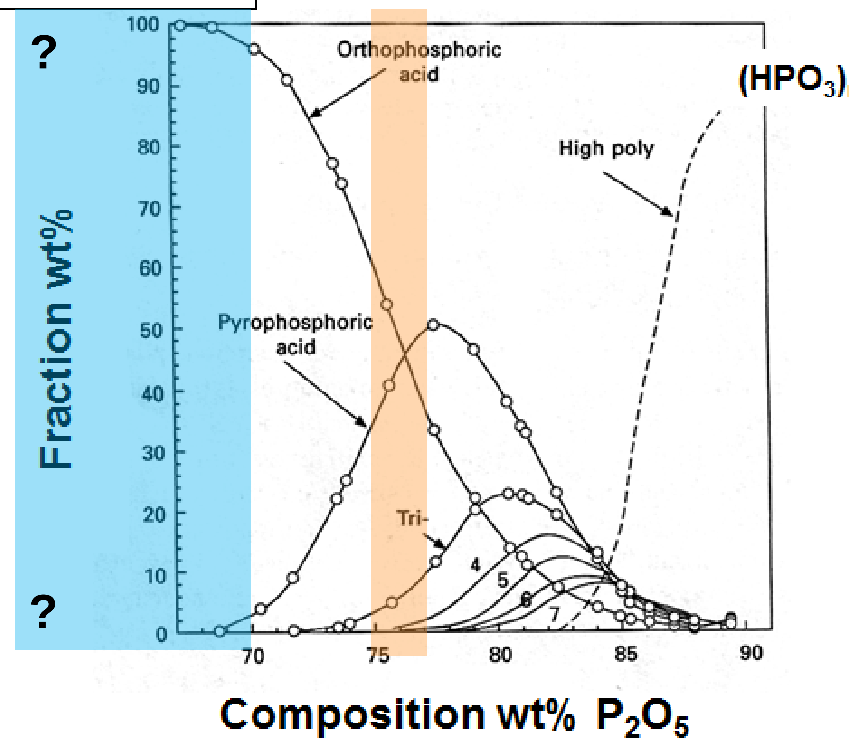
same gas flow at 140 mA cm^{-2} and OCV



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current region **OCV region**

Rough estimation:
Not taken into account the interaction between acid and membrane

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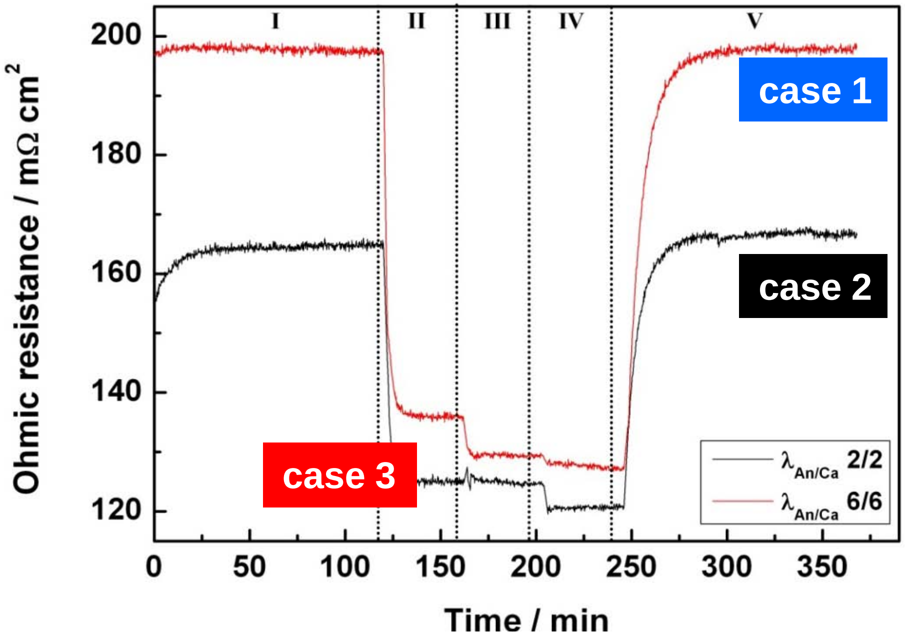
Different operating conditions



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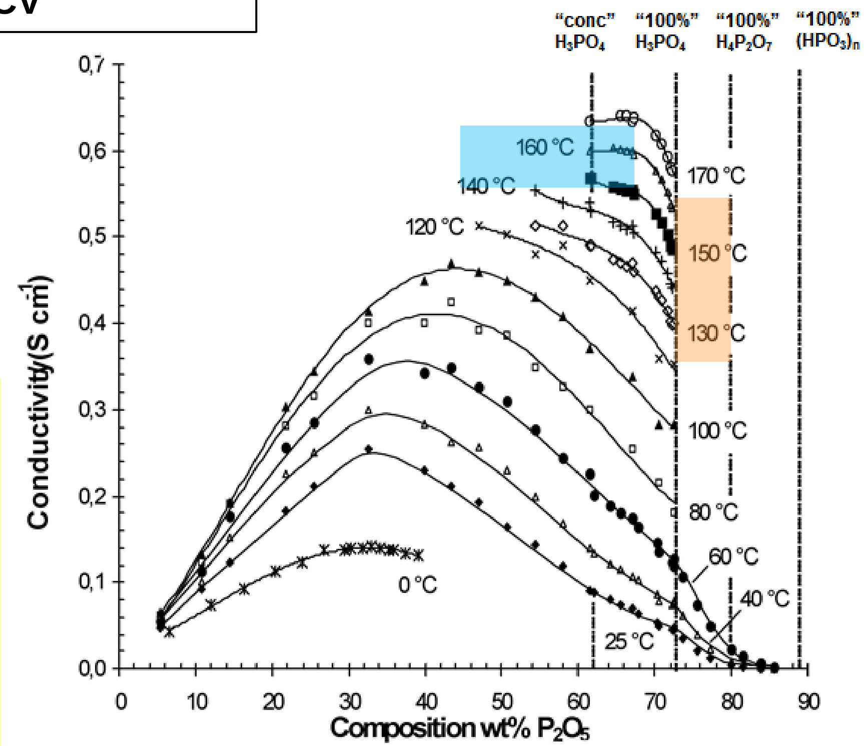

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current region **OCV region**

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Conclusion

- Two phase system with high dynamic
- Composition and distribution change of phosphoric acid in MEA
- Swelling of membrane

Experimental in-situ data available which allow to modify and verify membrane and MEA models

➢ Much more in-situ and ex-situ data necessary in order to understand and optimize MEAs

Thank you for your attention