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HTMWG – CARISMA Meeting

Strategy for Aging Tests of Fuel Cell Membranes

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Outline

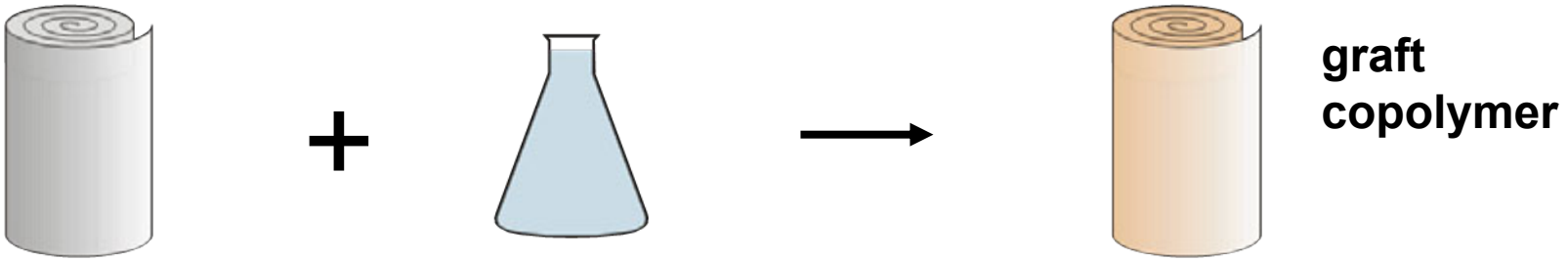
- Intro: **Radiation Grafted** Fuel Cell Membranes
- Probing Membrane 'Health State'
- How to Get More and Better Information in Shorter Time:
  - **Cell Design** Considerations
  - **Accelerated Aging** Tests
  - Advanced ***Post Mortem*** **Analysis**
- Concluding Remarks

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Radiation Grafted Fuel Cell Membranes

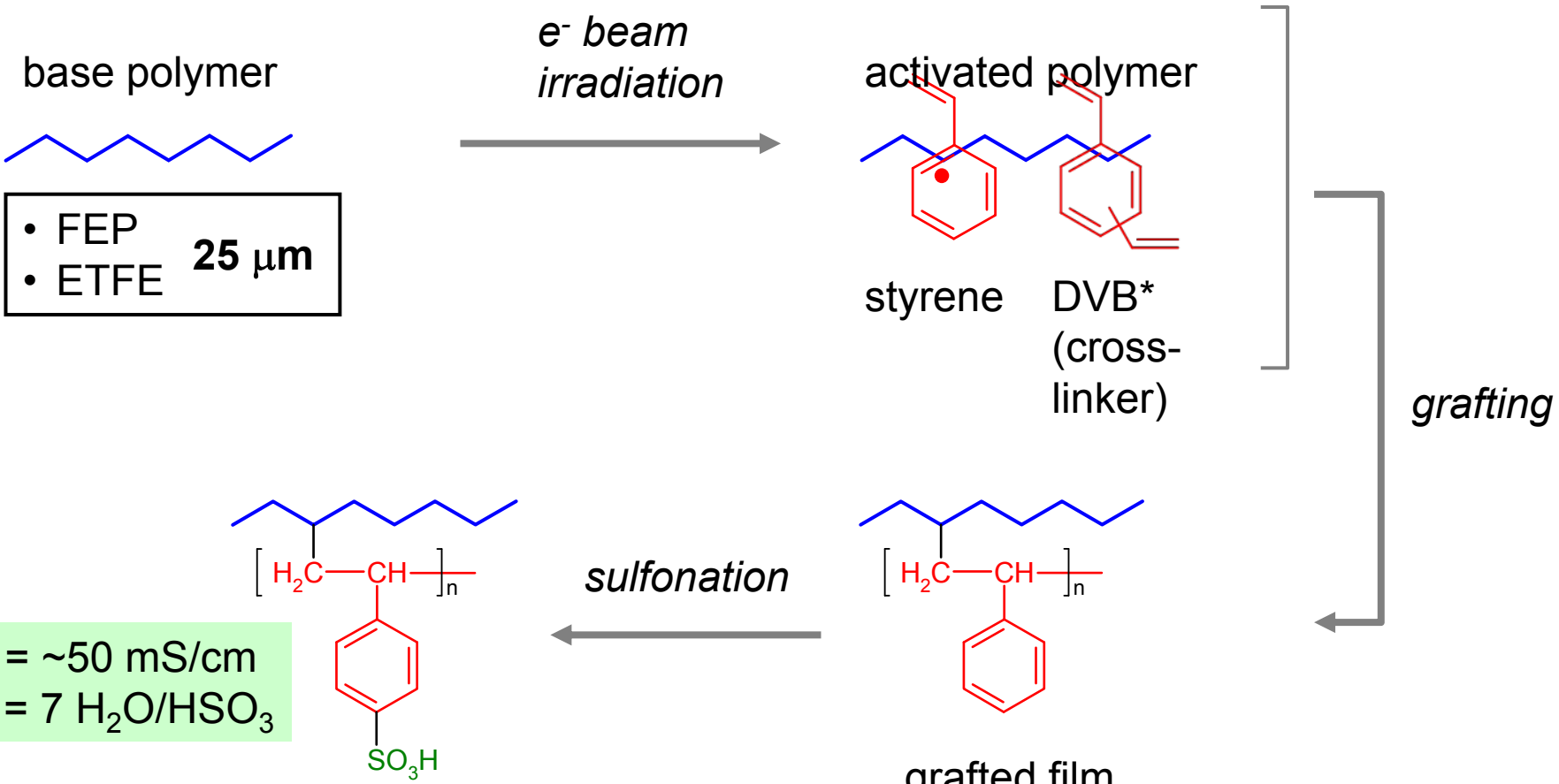
Merits of Graft Copolymerization

- **tailoring of the membrane composition** to the required application (e.g. low methanol crossover for the DMFC)
- potentially **cost effective** process due to cheap base materials



base polymer film + **functional monomers** → **functional membrane**

Pre-Irradiation Grafting Process



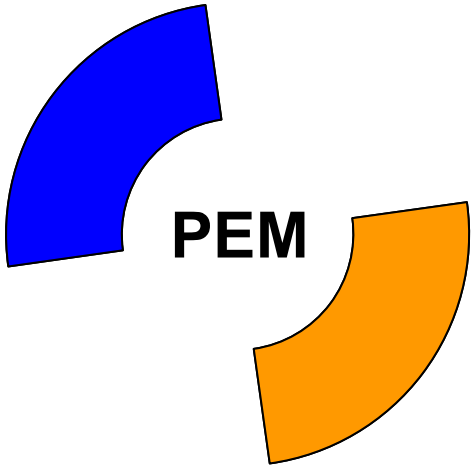
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Probing Membrane 'Health State'

Review Primary Membrane Functionalities

H^+ transport

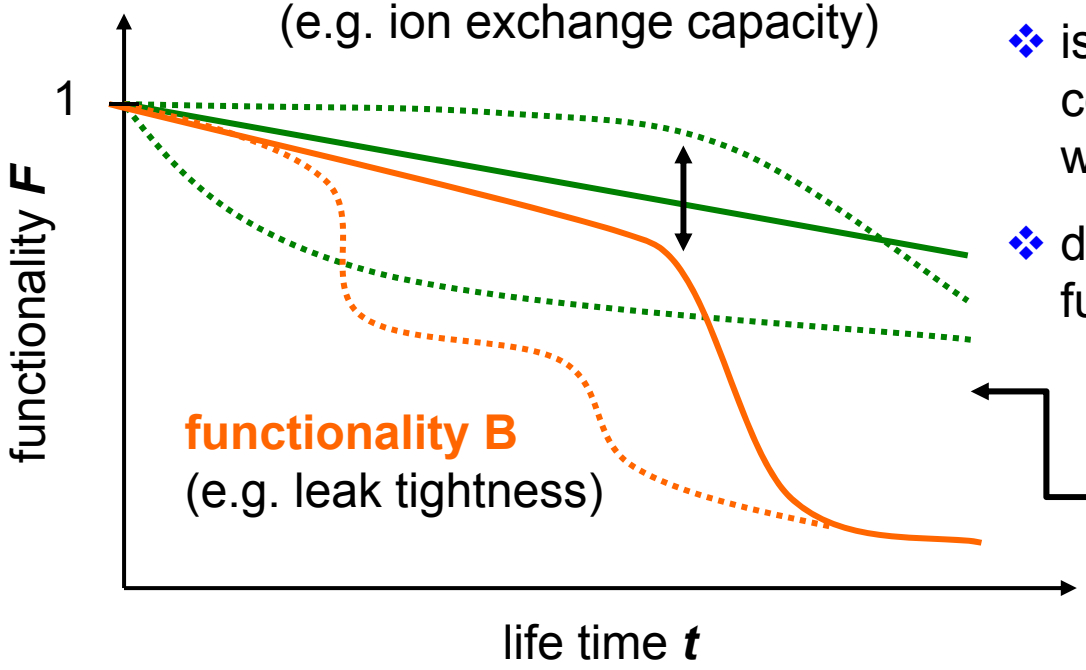
- membrane thickness
- hydration state
- water management
- membrane-electrode interface



separator

- separate electrons
- separate reactants
- mechanical integrity

Time Evolution of Membrane State

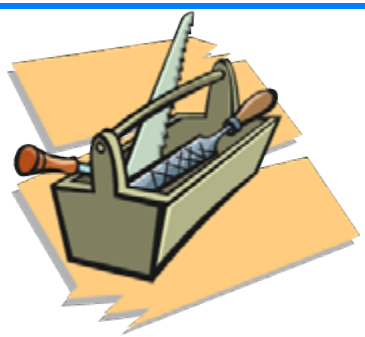


- how do the **functionalities *F*** change as a function of time ?
- is the **degradation rate -d*F*/d*t*** constant, increasing, decreasing with time, or discontinuous ?
- does the degradation of one functionality **affect** the other ?

failure criteria for A, B

can we measure the different membrane functionalities continuously ?

Monitoring Membrane Health State



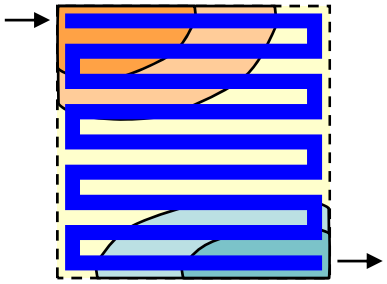
property	phenomenon	test method
ohmic resistance	H^+ transport	current pulse (time domain) high frequency resistance (frequency domain)
MEA integrity	mixed potential, gas crossover / permeation	measure OCV
gas permeation	membrane thinning and pinhole / crack	electrochemical H_2 permeation measurement; tracer gas ?

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Cell Design Considerations

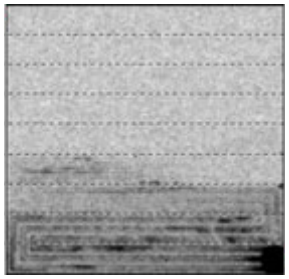
Serpentine Flow Fields

serpentine flow field



- Δp relatively high
- inhomogeneous operating conditions likely
- non-uniform degradation

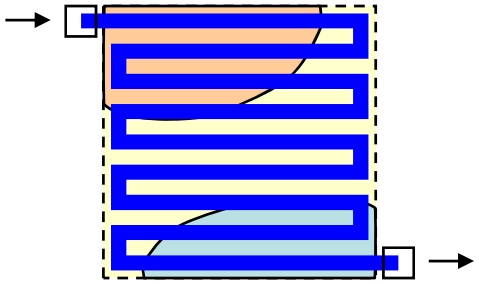
neutron radiogram*



membrane at end of test



protected gas inlets

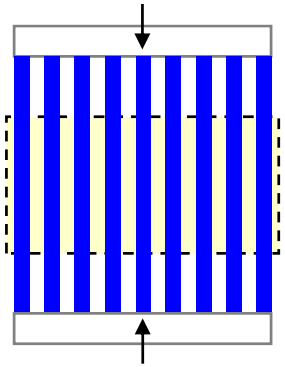


- tendency towards pinhole formation in gas inlet areas alleviated, but not eliminated

* Schneider et al., *Electrochem. Commun.* **7** (2005) 1393

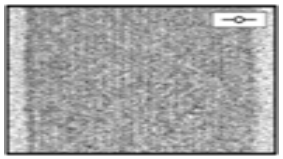
Differential Flow Fields

parallel flow field



- short channels, Δp relatively small
- high gas flows → "differential cell"
- (more) uniform conditions & degradation

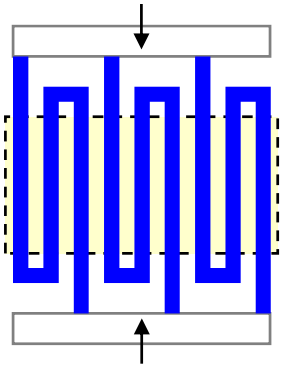
neutron radiogram*



membrane at end of test



flow field with forced cross-land flow

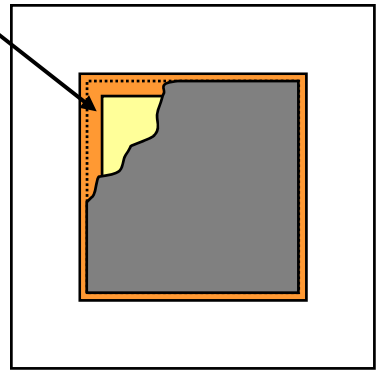


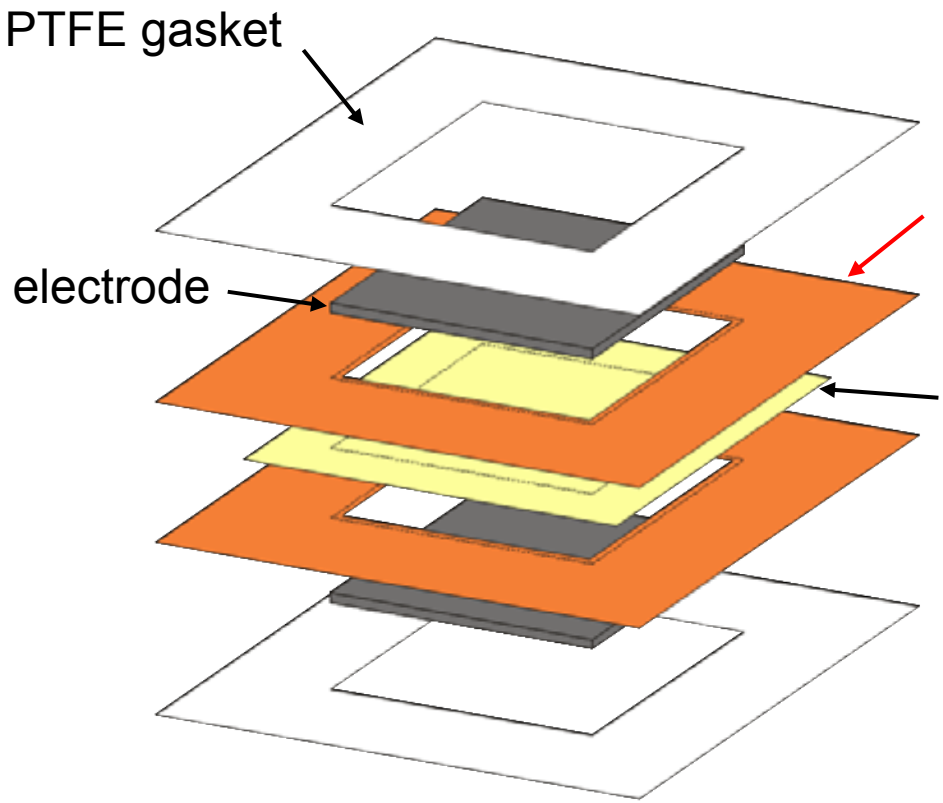
- flow forced under lands due to Δp
- reduce channel-land partitioning ?

* Zhang et al., *Electrochim. Acta.* **51** (2006) 2715

Avoiding Edge Effects

electrode – sub-gasket
overlap 1.5 mm



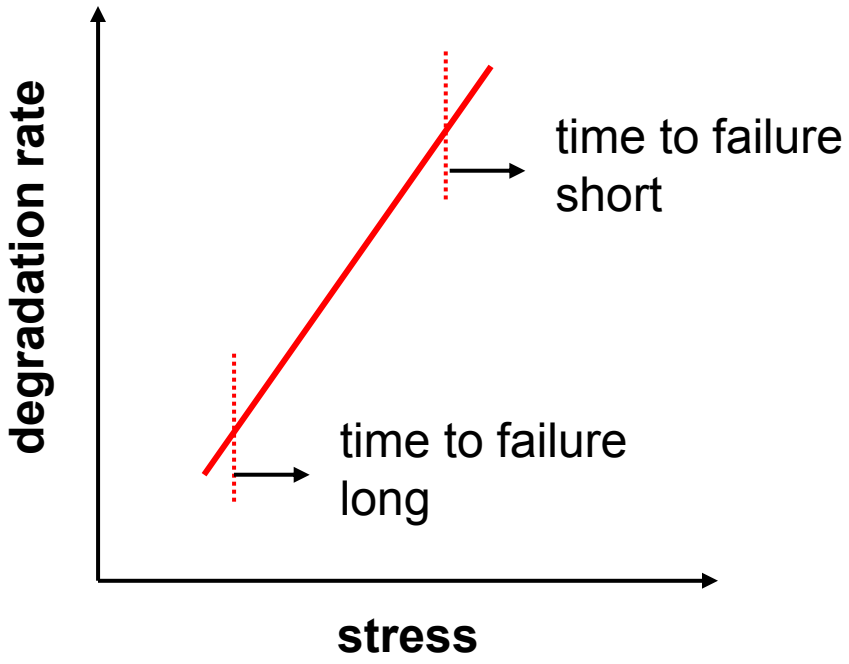


subgasket prevents exposure of membrane in edge region of the active area

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Accelerated Aging Tests

Increasing Throughput via Accelerated Aging



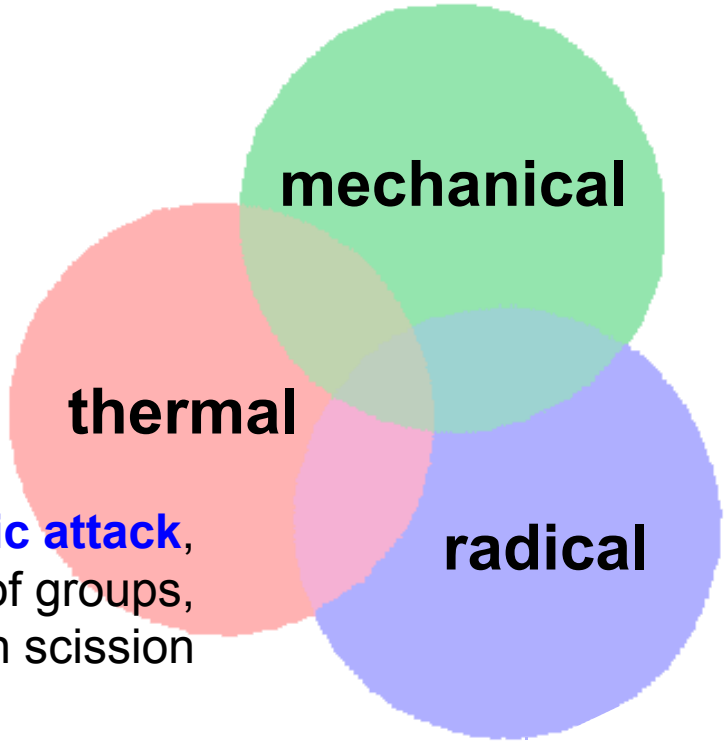
identify **stress factors**:
T, **r.h.**, ***p***, ***U*** , other ?

- how does the **rate of degradation** depend on the **stress factors** ?
- how do the stress factors **cross-correlate** ?
- how do the stress – degr. rate relations **depend on materials** ?

so far, very little is known !

increasing the stress factor(s) will accelerate degradation and yield shorter time to failure

Membrane Degradation Mechanisms



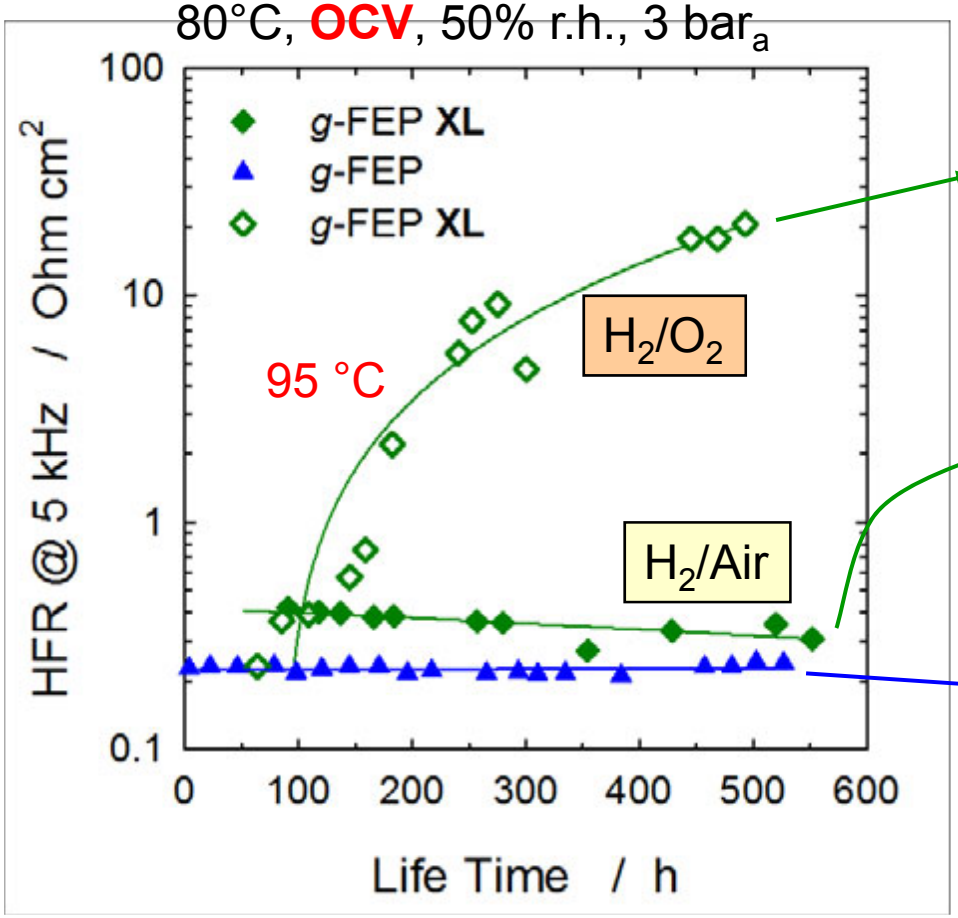
crack formation due to **r.h. cycling fatigue**

pinhole formation / puncturing by electrode as a consequence of **compressive creep**

thermo-hydrolytic attack, loss of groups, chain scission

chain scission / membrane consumption caused by attack of **free radical species** ($HO^{\bullet}$, $HOO^{\bullet}$, $H^{\bullet}$?)

Chemically Induced Degradation



96 %

12 %

72 %

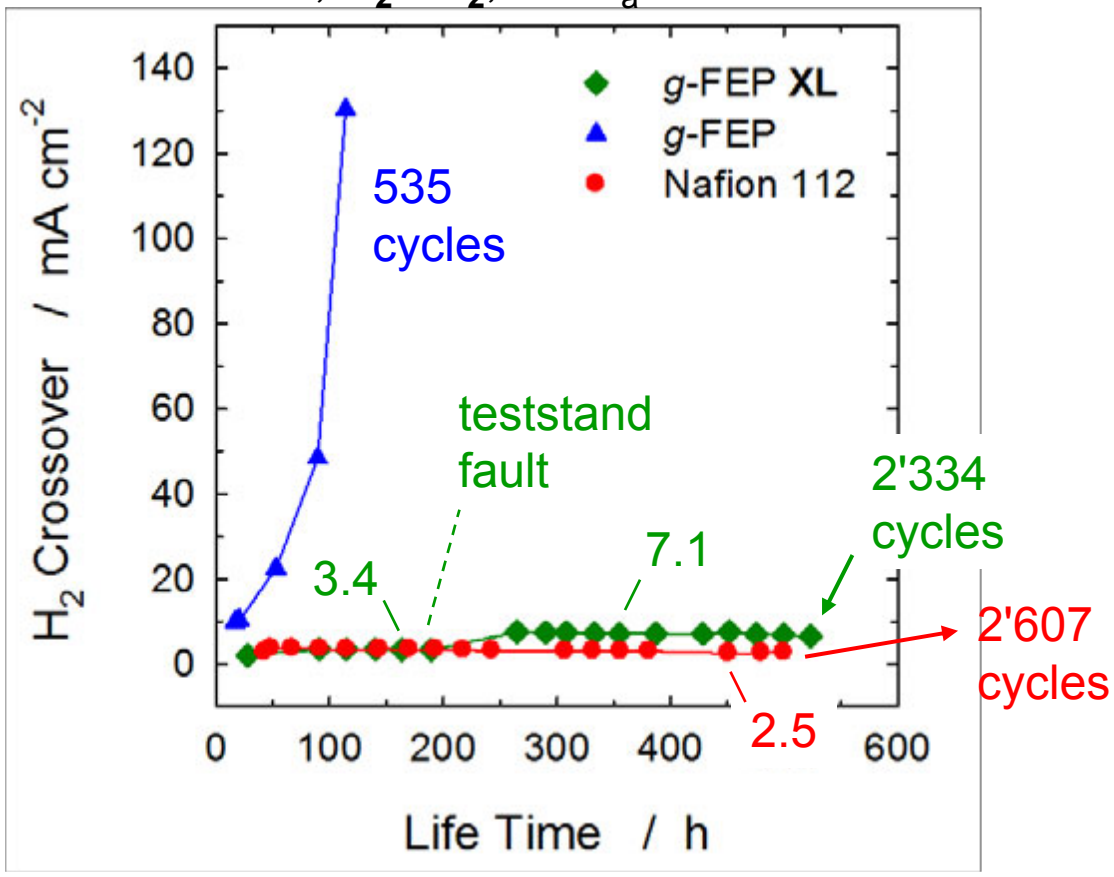
fuel cell environment:
(H_2, O_2, H_2O, H^+, Pt)

HO• / HOO• / H•

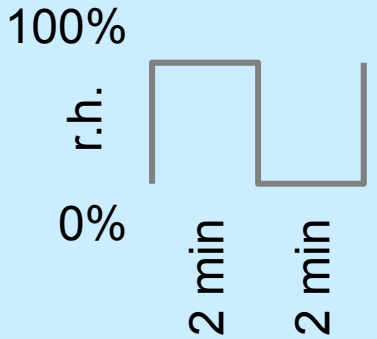
chemical degradation
(ionic site loss)

Mechanically Induced Degradation

80°C, H_2 / N_2, 3 bar_a



r.h. cycling

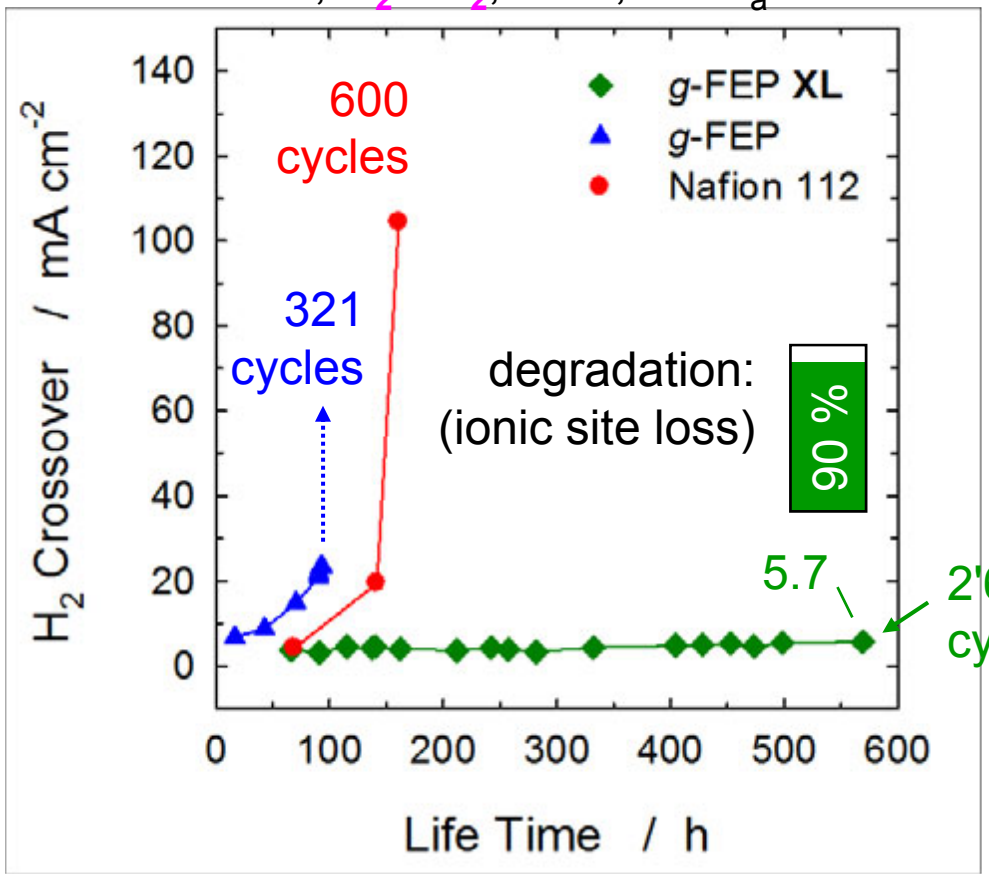


r.h. cycling induces visco-elastic creep of the polymer and causes fatigue

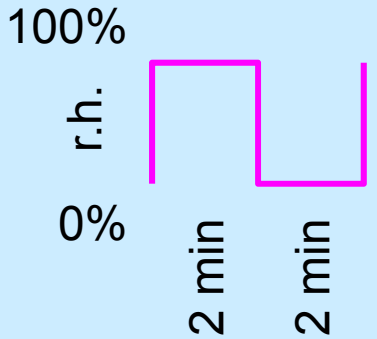
→ gradual loss of membrane integrity

Combined Mechanical / Chemical Mode

80°C, H_2 / O_2, OCV, 3 bar_a



r.h. cycling

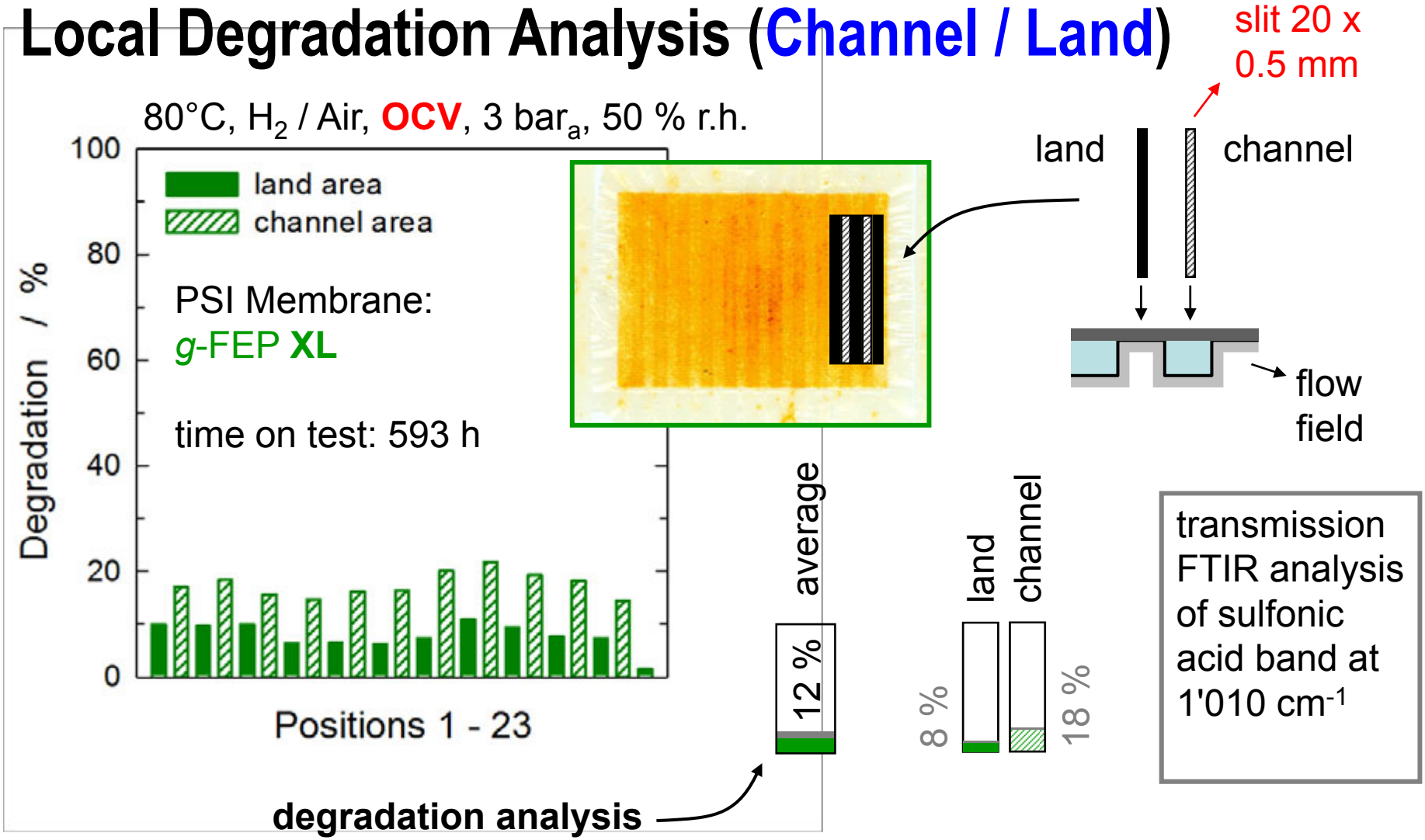


how do mechanical and chemical degradation interact ?

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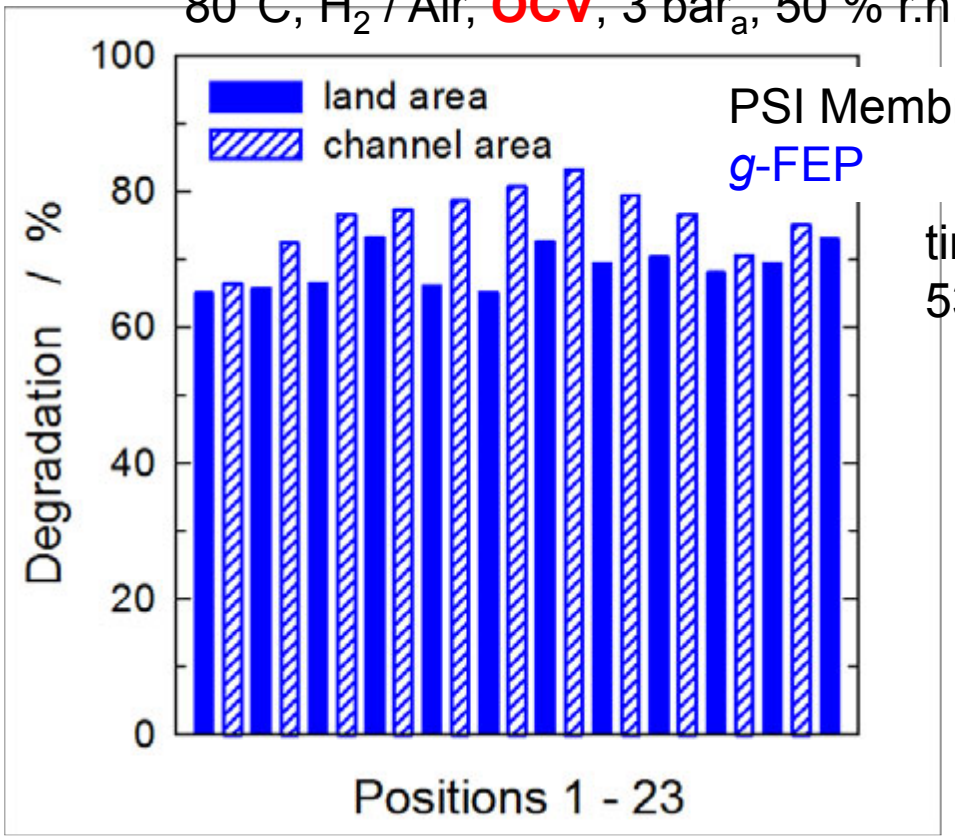
Advanced *Post Mortem* Analysis

Local Degradation Analysis (Channel / Land)



Local Degradation Analysis (Channel / Land)

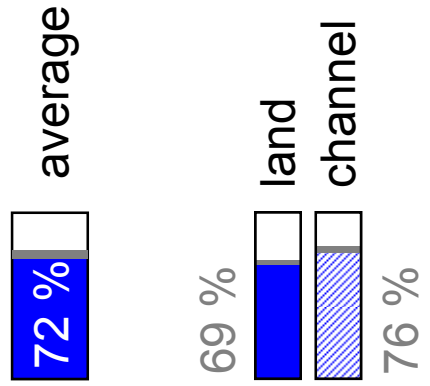
80°C, H_2 / Air, **OCV**, 3 bar_a, 50 % r.h.



PSI Membrane:
g-FEP

uncrosslinked membrane

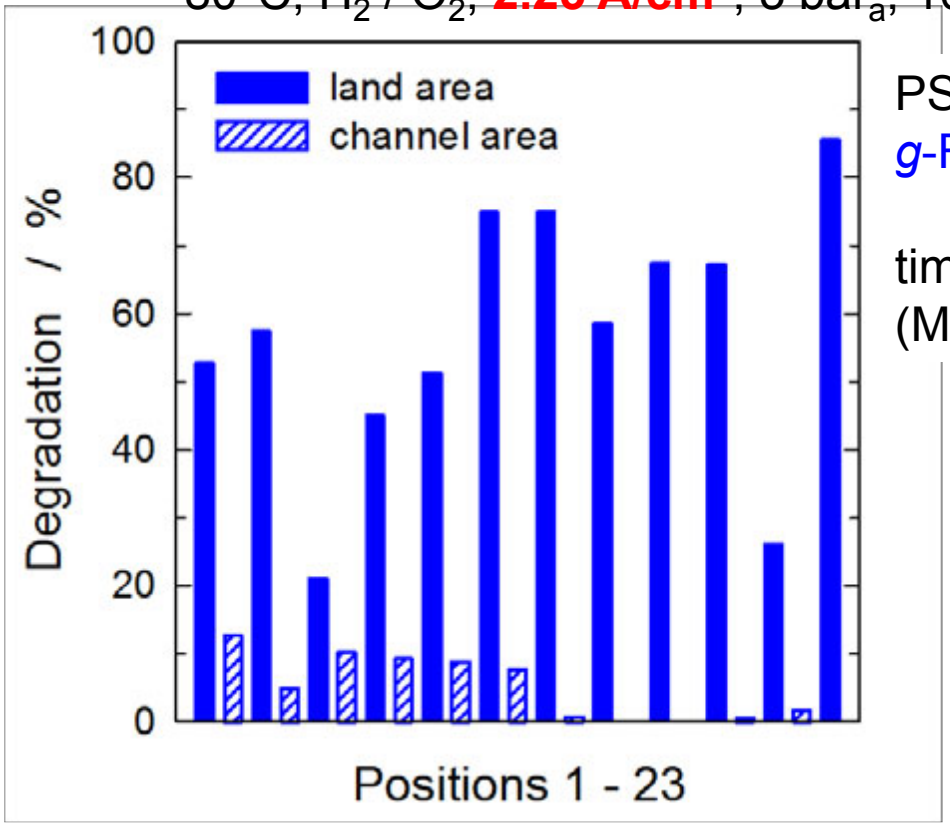
time on test:
531 h



degradation analysis

Local Degradation Analysis (Channel / Land)

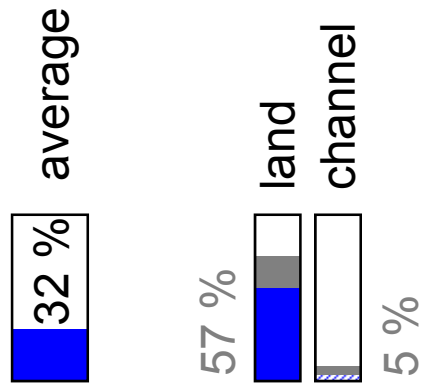
80°C, H_2 / O_2, **2.25 A/cm²**, 3 bar_a, 100 % r.h.



PSI Membrane:
g-FEP

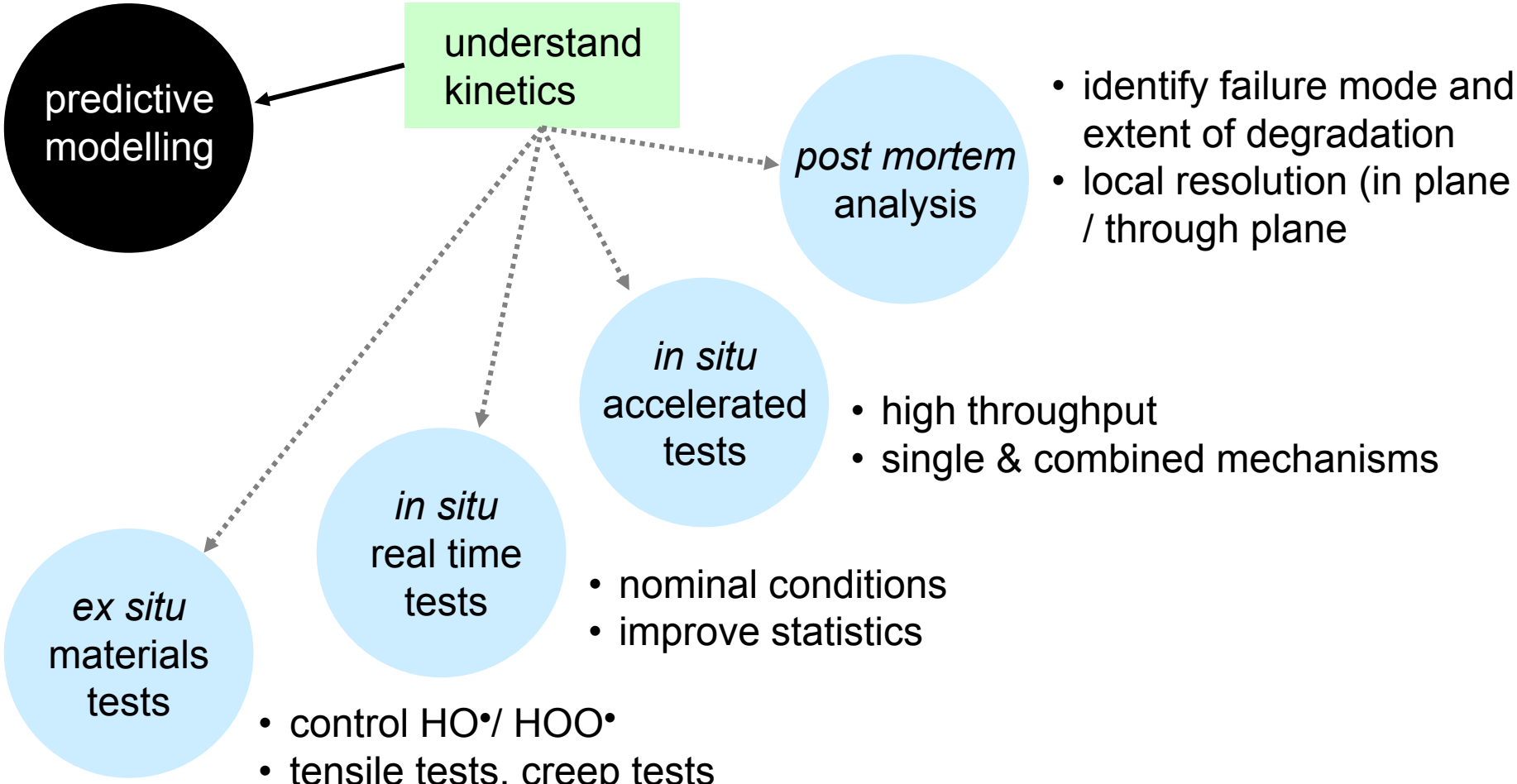
uncrosslinked membrane

time on test: 142 h
(MEA failure)



degradation analysis

Concluding Remarks – Understanding Aging



- identify failure mode and extent of degradation
- local resolution (in plane / through plane

- high throughput
- single & combined mechanisms

- nominal conditions
- improve statistics

- control $HO^{\bullet}$/ $HOO^{\bullet}$
- tensile tests, creep tests