Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut
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Radiation Grafting: Tailored Ion-conducting Membranes for Electrochemical Applications

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Introducing Antioxidants

- Polymer-bound phenolic antioxidants
- Accelerated stress tests in the fuel cell
- Regeneration strategy PFSA vs. hydrocarbon membranes ?

Beyond Fuel Cells

Conclusion

Acknowledgement

Technical support:

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Jürg Thut

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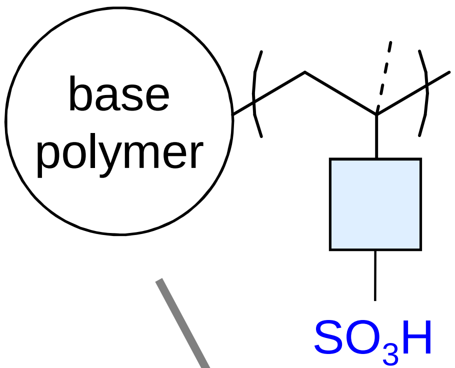
FNSNF
SWISS NATIONAL SCIENCE FOUNDATION

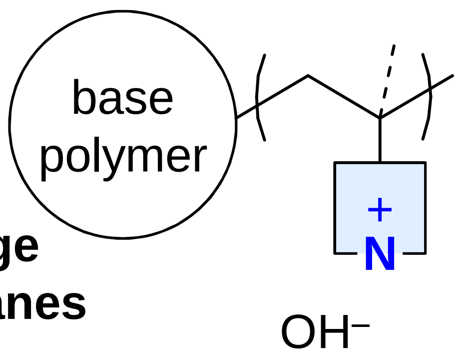
NOVEL

Radiation Grafted Membranes

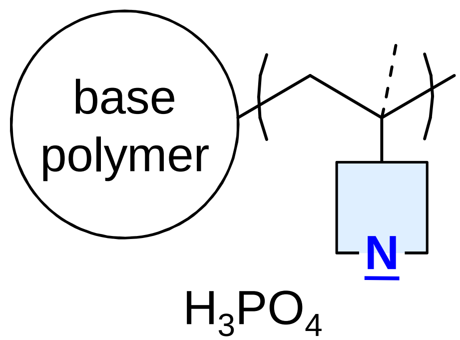
Radiation Grafted Membranes



- 2 dissimilar polymer constituents:
  - **hydrophobic base polymer**
  - **polyelectrolyte**
- connected via **covalent bonds**



anion exchange membranes

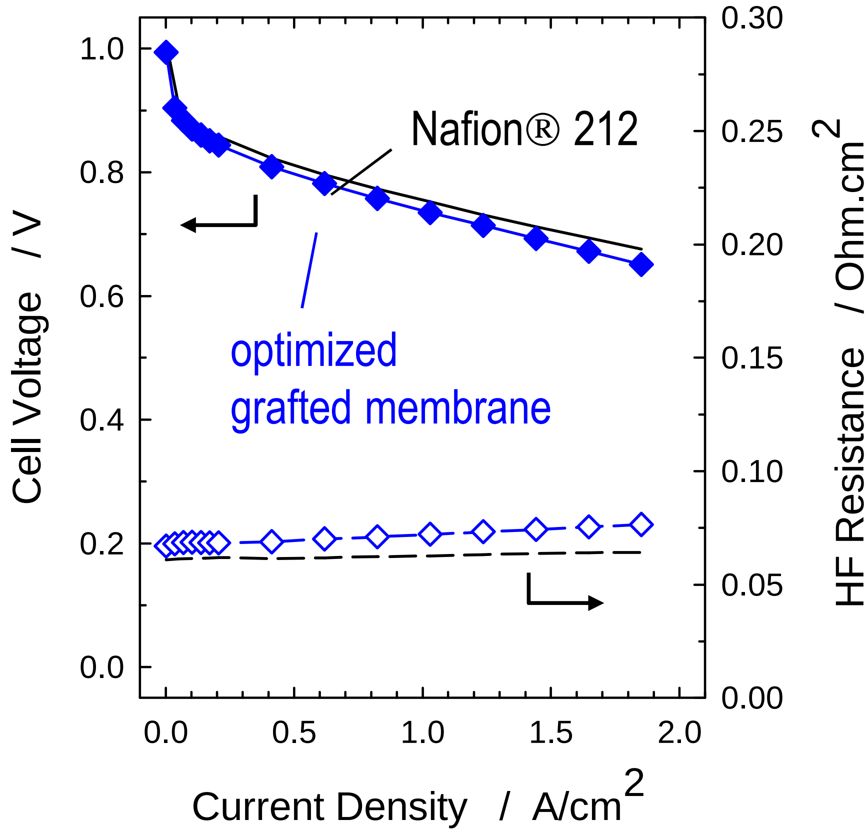


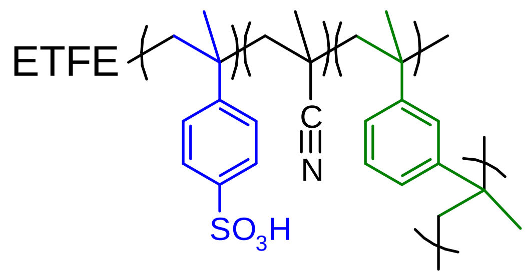
membranes for HT-PEFC (phosphoric acid doped)

L. Gubler, *Adv. Energy Mater.* **4** (2014) 1300827

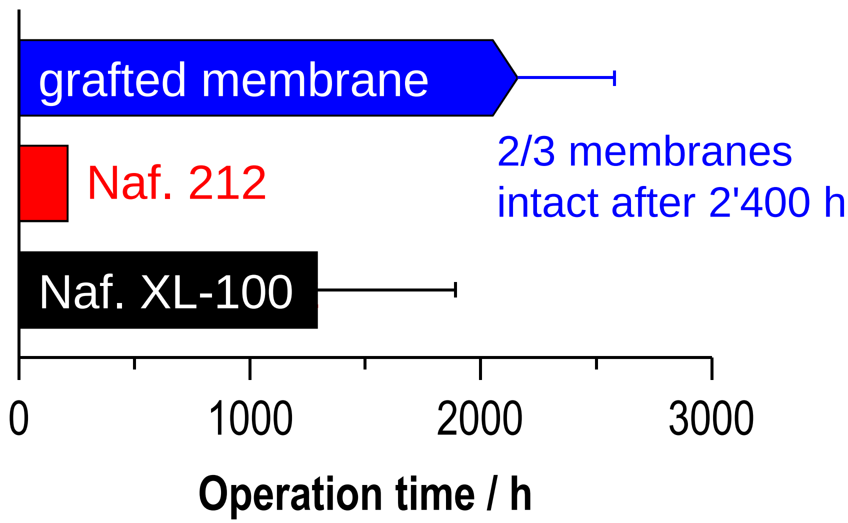
Performance & Durability of Grafted Membranes

T = 80°C, H_2 / O_2, *p* = 2.5 bar_a





durability (accelerated):



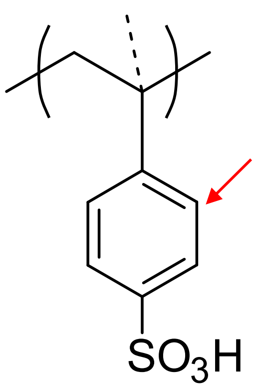
L. Gubler, L. Bonorand, *ECS Transactions* **58** (2013),1, 149

HO• Radical Attack

PFSA ← HO•

$k \approx 10^6\ M^{-1}s^{-1}$ → main chain & side chain degradation

$\tau(HO\bullet) \approx 1\ \mu s$



← HO•

$k = 10^9\text{-}10^{10}\ M^{-1}s^{-1}$ → follow-up reactions, chain fragmentation

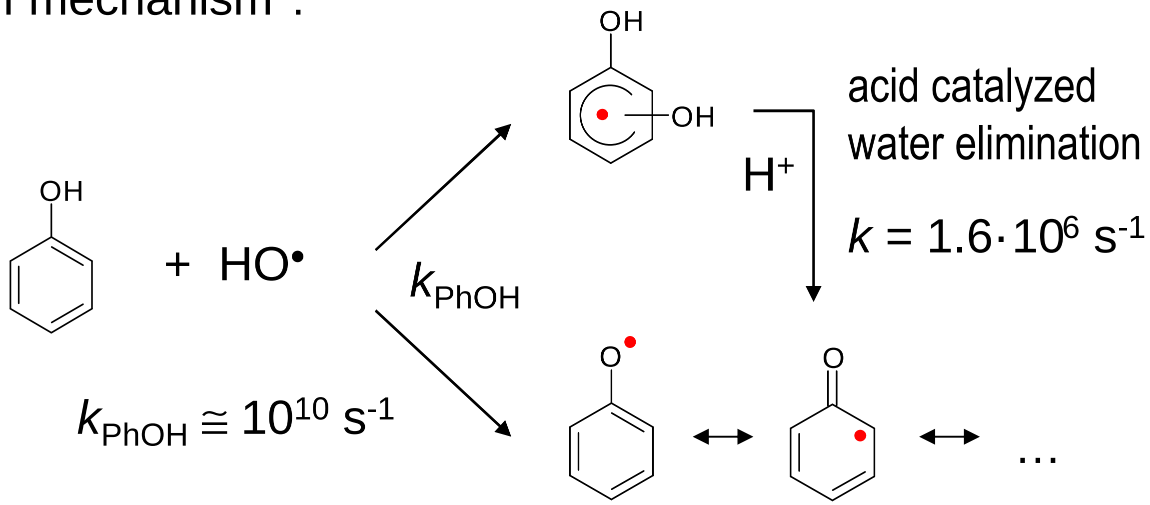
$\tau(HO\bullet) = 10\ ns$

L. Gubler et al., *J. Electrochem. Soc.* **158** (2011) B755
S.M. Dockheer et al., *PCCP* **15** (2013) 4975

Introduction of Polymer-bound Antioxidants

Introducing Antioxidant (HO• Scavenger)

known mechanism*:



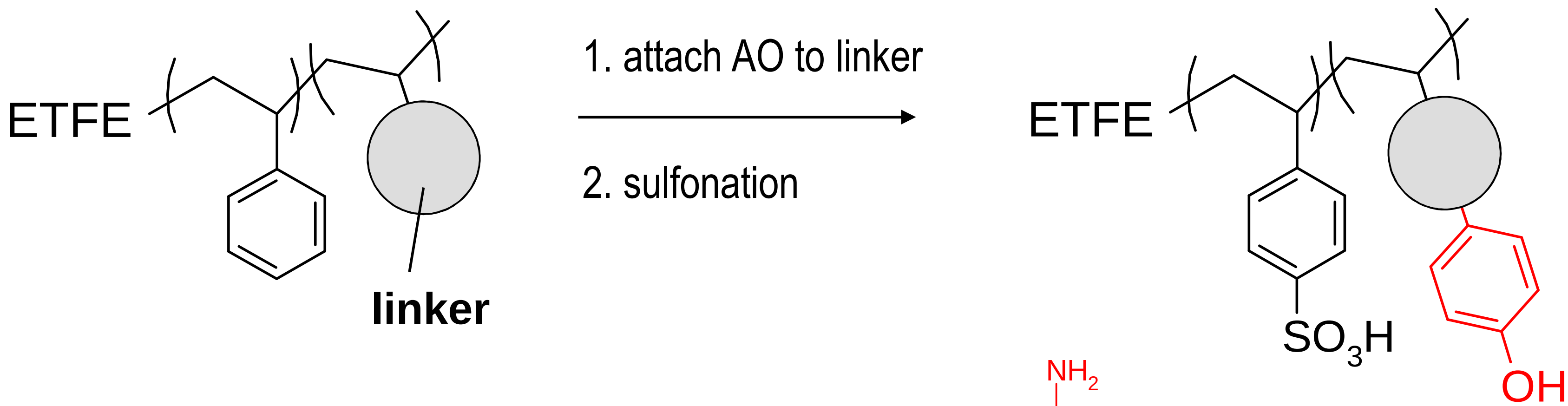
phenoxyl radical

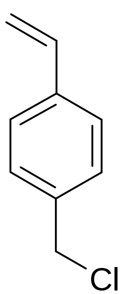
phenoxyl radical:
- relatively stable
- unlikely to attack polymer

*Z. Rappoport, The Chemistry of Phenols, John Wiley & Sons, 2003

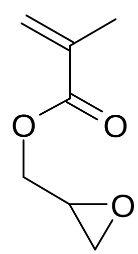
Introduction of Antioxidant Functionality

covalent tethering of **phenol type antioxidant (AO)** to graft copolymer:

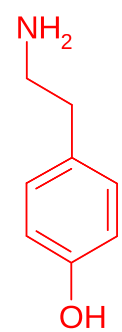




vinylbenzyl
chloride
(VBC)



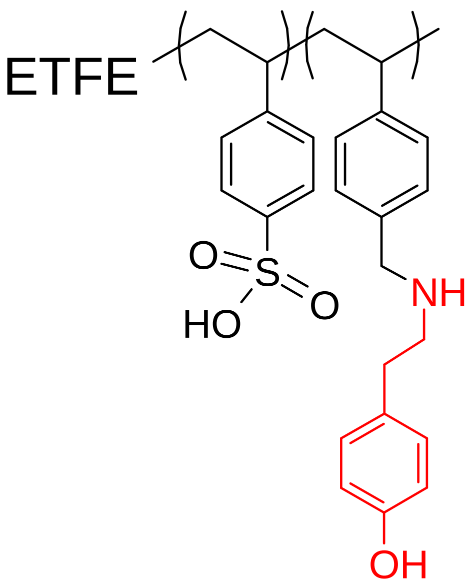
glydidyl
methacrylate
(GMA)



AO:
tyramine

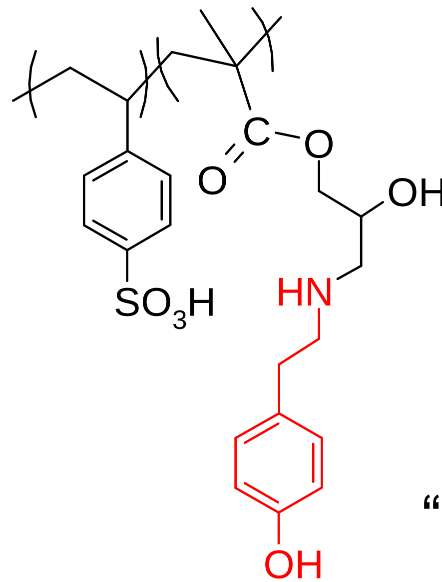
Y. Buchmüller et al., *J. Mater. Chem. A* **2** (2014) 5870

Grafted Antioxidant



VBC
linker

“VBC(Tyr)“



GMA
linker

“GMA(Tyr)“

- poor co-grafting kinetics
- low yield of tyramination of 33% (side reactions)
- poor fuel cell performance

- superior co-grafting kinetics
- yield of tyramination: 56%
- good fuel cell performance (better than pure styrene based)

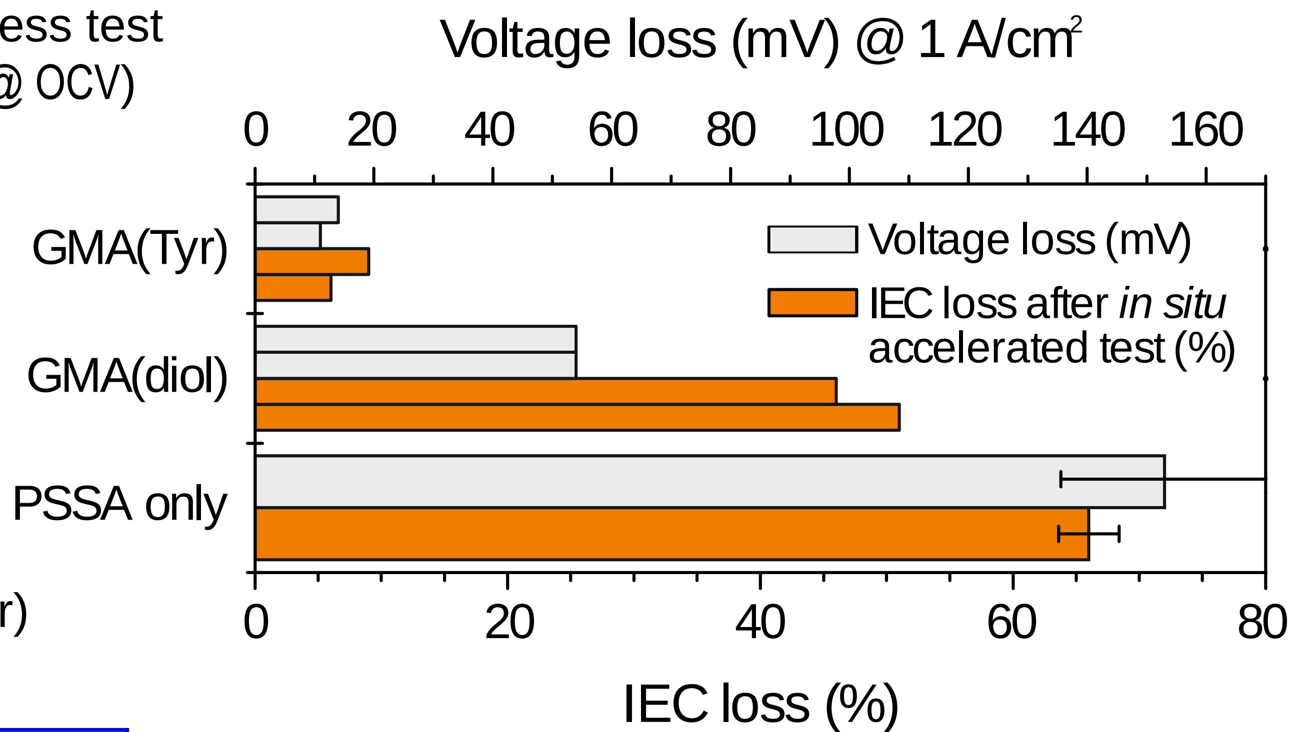
Grafted Antioxidant

in situ accelerated
degradation stress test
(H_2/O_2, 80°C, 4h @ OCV)

w/ antioxidant:

only with linker:

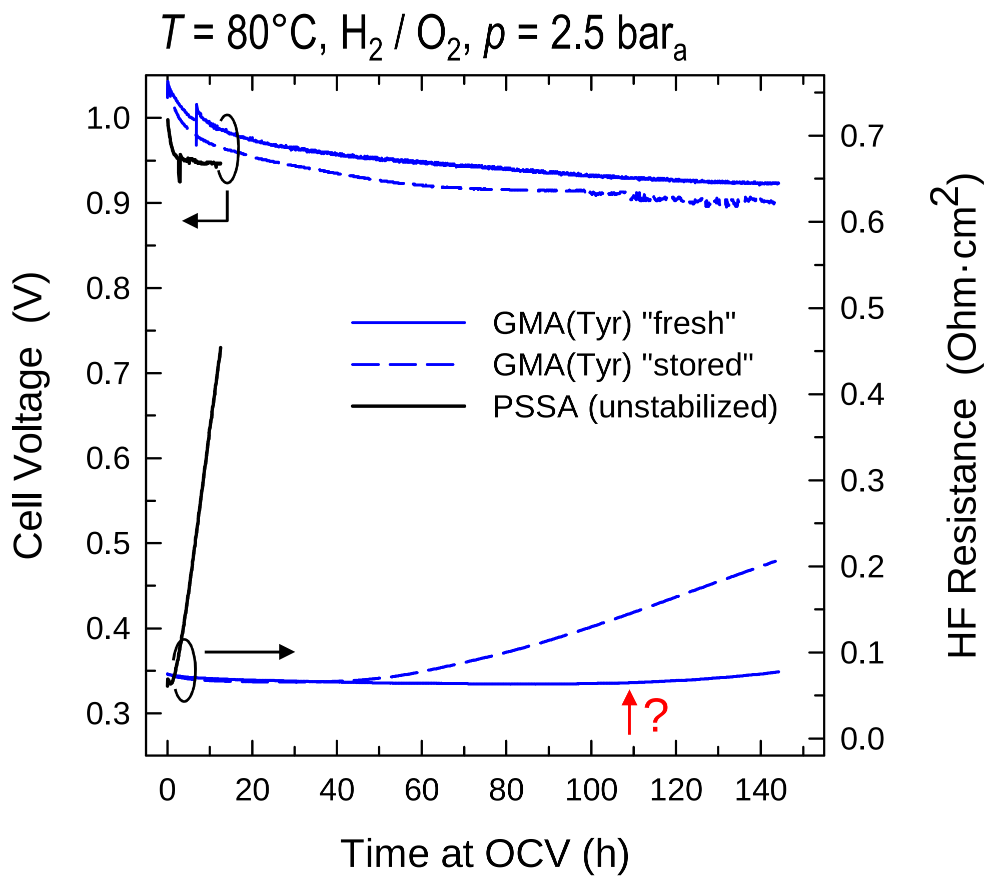
sulfonated styrene
(no co-grafted linker)



concept works

Y. Buchmüller et al., *J. Mater. Chem. A* **2** (2014) 5870

Extended Accelerated Chemical Stress Test



"fresh" membrane:
tested immediately after synthesis of the membrane

"stored" membrane:
kept in fridge (no light) for 7 days before being tested;
sudden increase of resistance suggests depletion of antioxidant (?)

deactivation of the antioxidant

Y. Buchmüller et al., *RSC Adv.* **4** (2014) 51911

Antioxidant Strategies

PFSA

incorporate transition metal redox couples (Mn^{2+}/Mn^{3+}, Ce^{3+}/Ce^{4+}) or corresponding oxides to **scavenge** $HO^{\bullet}$:

e.g.: $Ce^{3+} + HO^{\bullet} + H^{+} \rightarrow Ce^{4+} + H_2O$
$k = 3 \cdot 10^{8}\ M^{-1}s^{-1}$, lifetime of $HO^{\bullet}$ in PFSA ~μs

regeneration of Ce^{3+}:
$Ce^{4+} + H_2O_2 \rightarrow Ce^{3+} + HOO^{\bullet} + H^{+}$
with $[H_2O_2] = 0.5$ mM: $\tau \cong 1$ ms

catalytic $HO^{\bullet}$ scavenging

J. Electrochem. Soc. **159** (2012) B211

Hydrocarbon based

$HO^{\bullet}$ reacts rapidly with aromatic units ($\tau \cong$ ns), need much more effective scavenger, e.g., phenol type H-donor ($k \approx 10^{10}\ M^{-1}s^{-1}$):

$PhOH + HO^{\bullet} \rightarrow PhO^{\bullet} + H_2O$

PhOH is depleted over time.
Could it be regenerated ?

- Regeneration by H_2O_2 unlikely for energetic reasons (thermodynamics, kinetics)
- Repair by reductive power of the anode (~0-50 mV) ?

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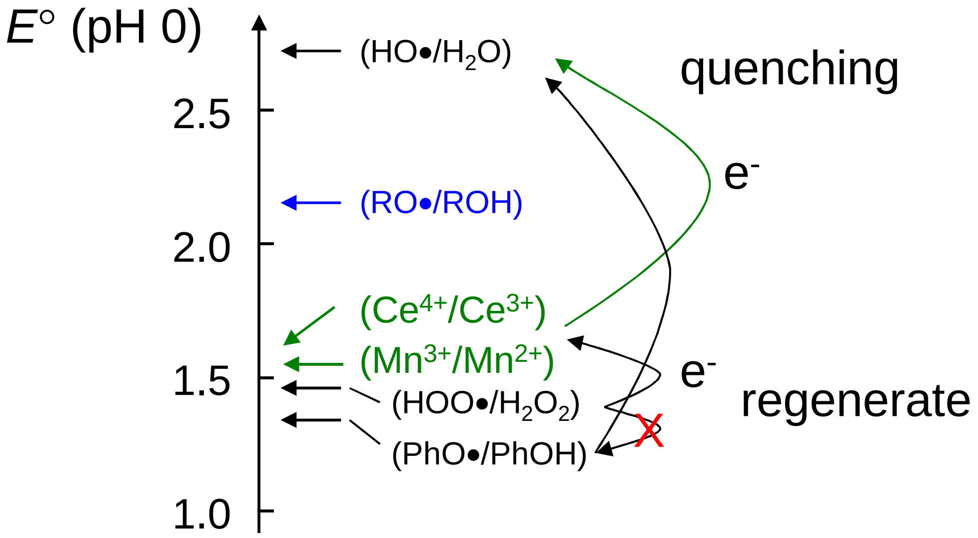
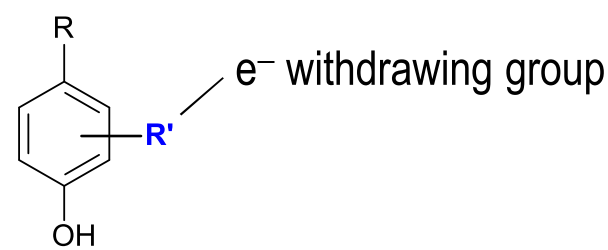
Repair of Spent Phenol Type Antioxidant by H_2O_2 ?

PhO• + H_2O_2 → PhOH + HOO• (mild oxidant)
[H_2O_2] in operating fuel cell ~0.5 mM [1]



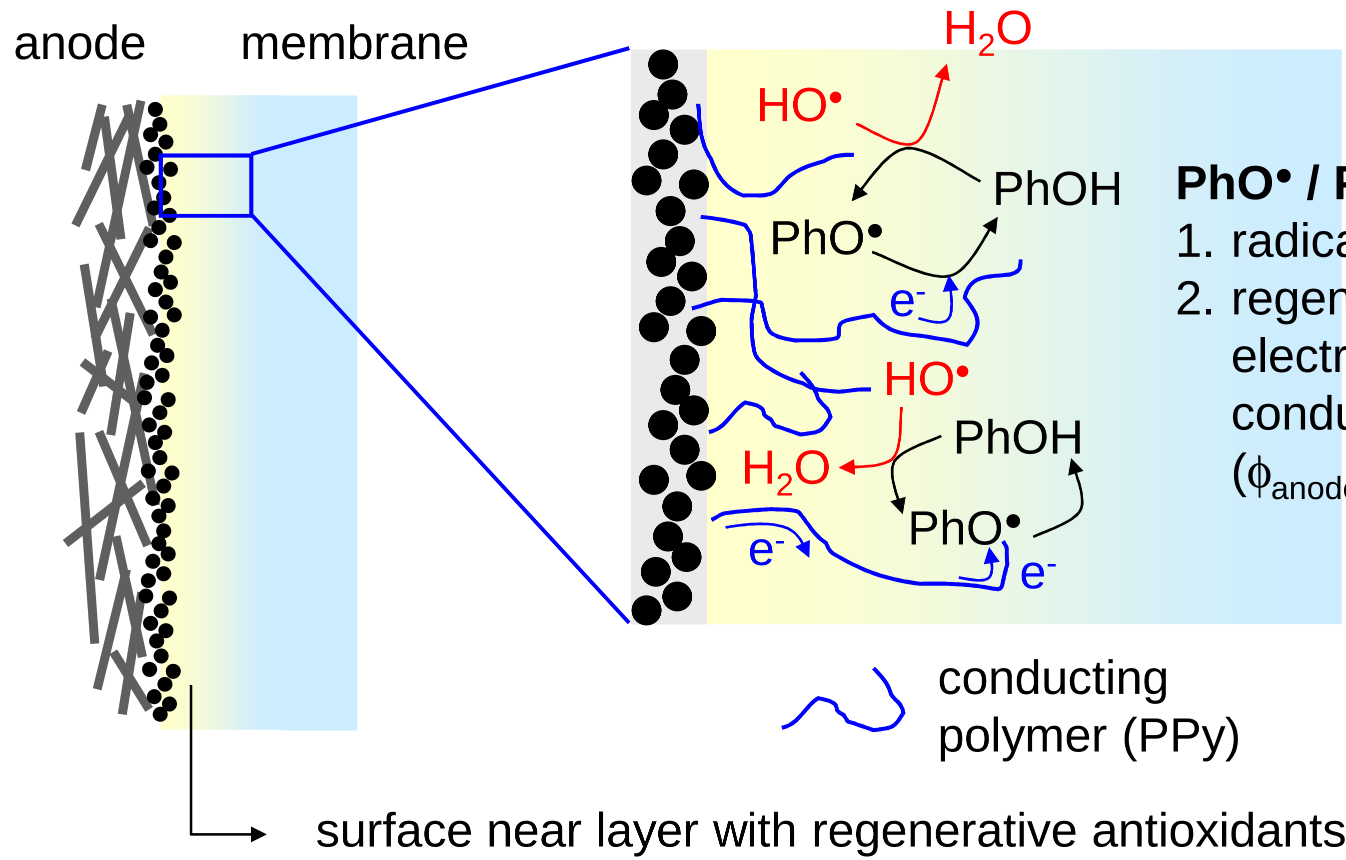
- $E°$(PhO•,H+/PhOH) < $E°$(HOO•,H+/H_2O_2)
  → regeneration by H_2O_2 unlikely
- Increase $E°$(PhO•) by substitution ?



→ yet kinetics expected to be slow

[1] W. Liu, D. Zuckerbrod, *J. Electrochem. Soc.* **152** (2005) A1165

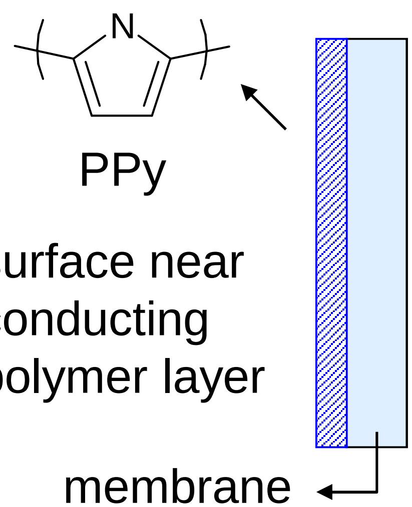
Repair through e⁻ Provided by the Anode ?

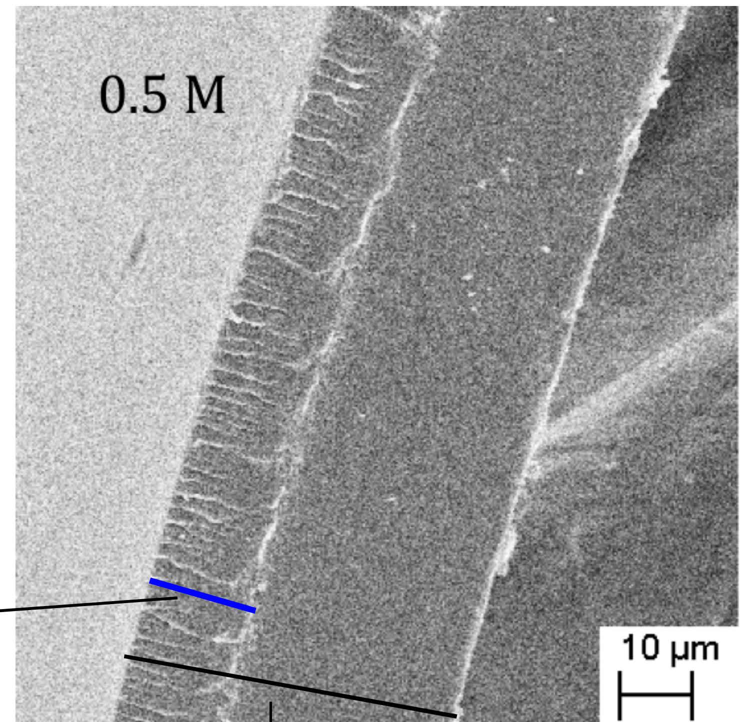


PhO• / PhOH:

1. radical scavenging
2. regeneration (reduction), electron supply via conducting polymer ($\phi_{anode} < \phi_{redox}$)

Polymerization of Pyrrole (Py) into Membrane

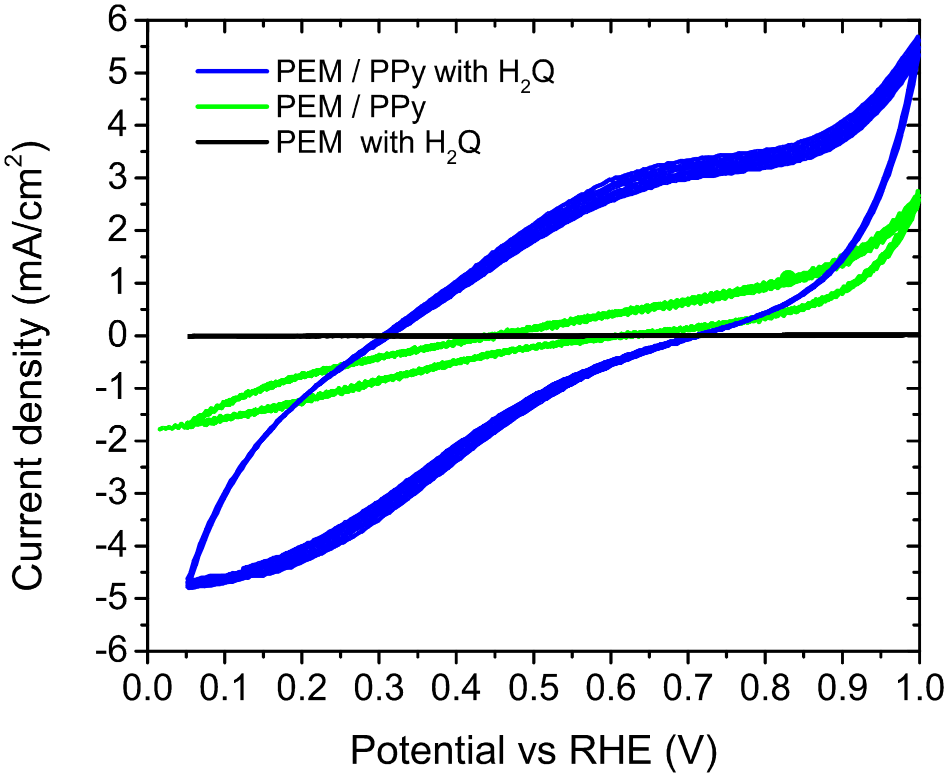




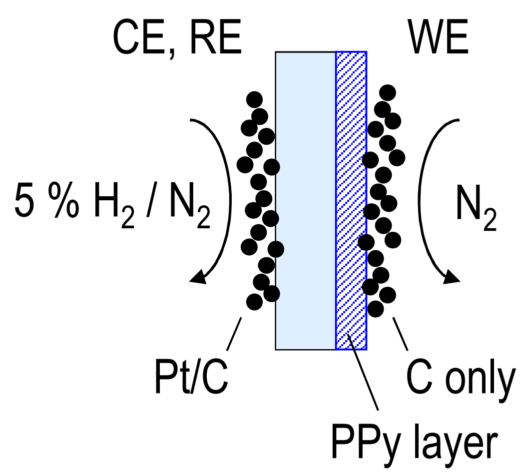
Buchmüller et al., *ChemElectroChem* (2015) in press (doi: 10.1002/celc.201402332)

Electrochemical Response

cyclic voltammetry, using hydroquinone (H_2Q) as redox probe:



fuel cell configuration:



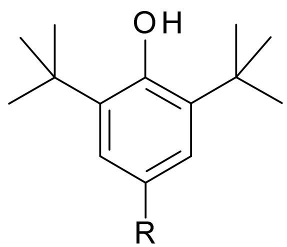
issues:

- membrane resistance increases >2x
- electronic conductivity in PPy phase poor, high transport losses
- PhO• undergoes fast follow-up reactions

Buchmüller et al., *ChemElectroChem* (2015) in press

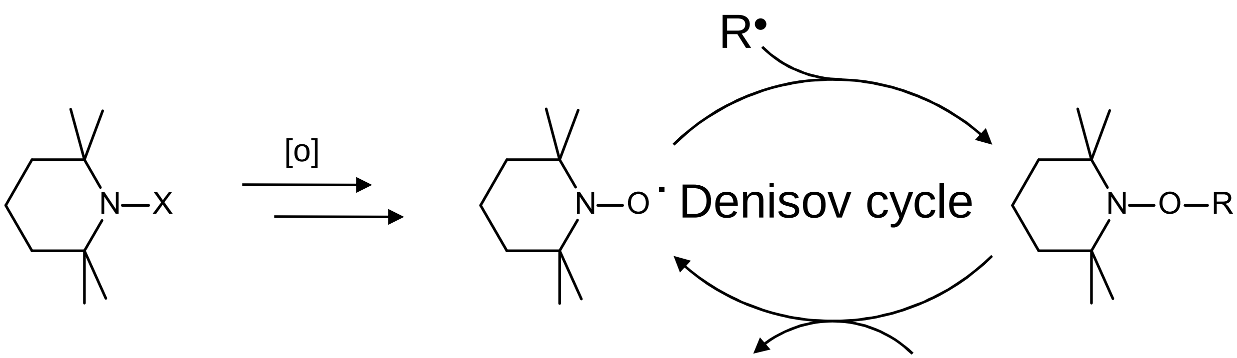
Use Alternative Antioxidant Chemistry ?

- use hindered phenol:



butylated hydroxytoluene (BHT)
well known in plastics industry

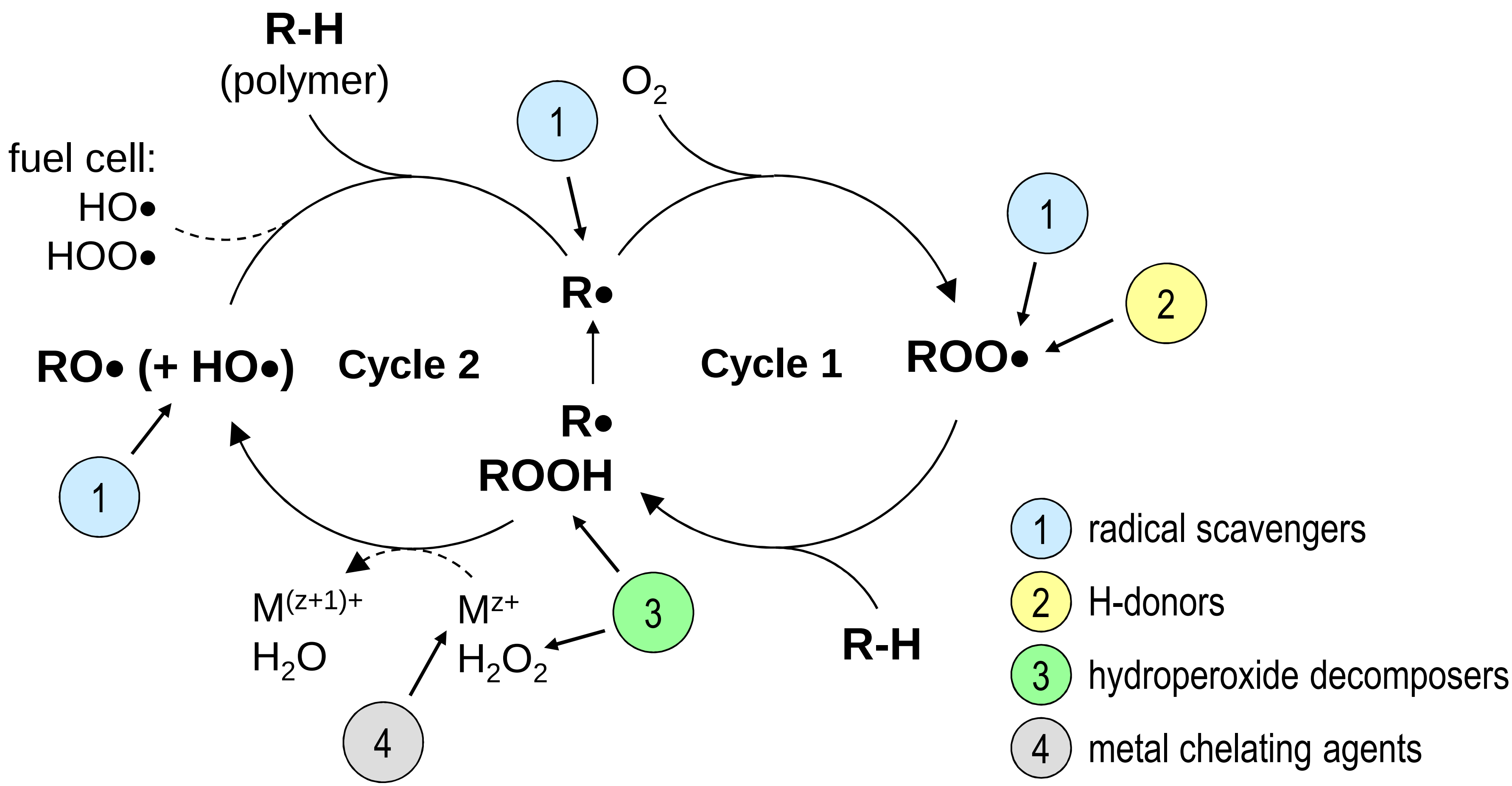
- hindered amine light stabilizers (HALS)* ?



- **target H_2O_2 decomposition**
  (τ >> 1 s) ?

*J.L. Hodgson, M.L. Coote, *Macromolecules* **43** (2010) 4573

Antioxidant Mechanism and Strategy



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Beyond Fuel Cells

Electrochemical Devices with Polymer Electrolytes

Electrolysis

- water electrolysis for high purity H_2 production
- H_2 for fuel cell vehicles
- renewables: storage of excess electricity ("power-to-gas")

Flow batteries

- grid-scale storage of electricity
- decoupled energy and power rating

Lithium batteries

- consumer electronics
- electromobility
- load leveling, peak shaving

Membranes for Water Electrolysis

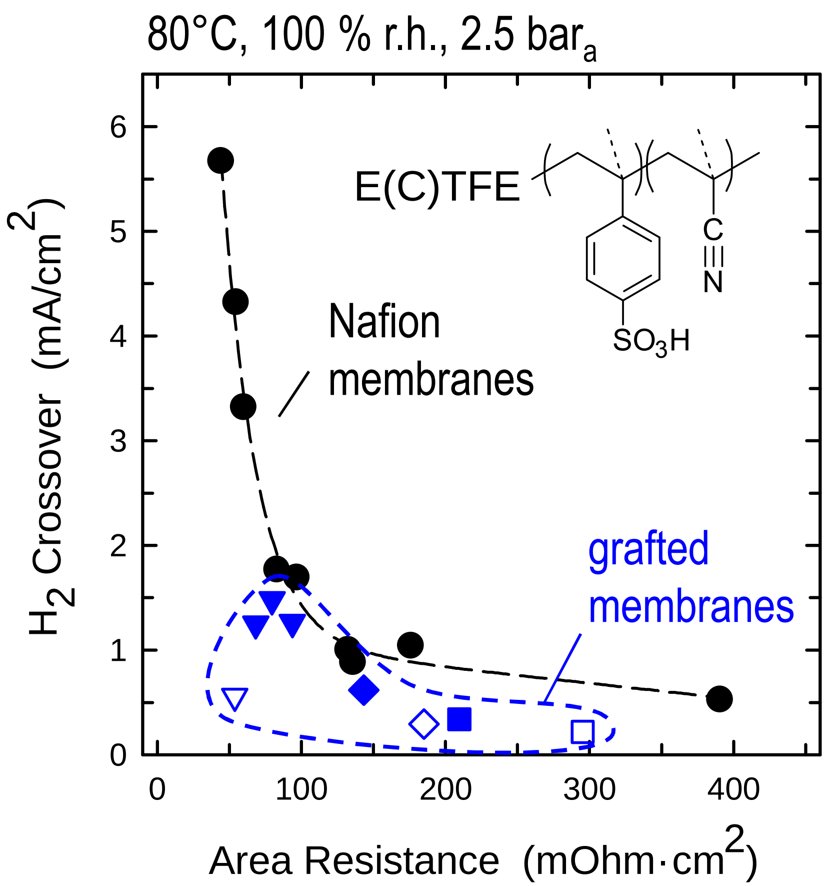


Figure of merit: $\frac{1}{R_\Omega \cdot i_x}$ (in 10^{-3}/V)

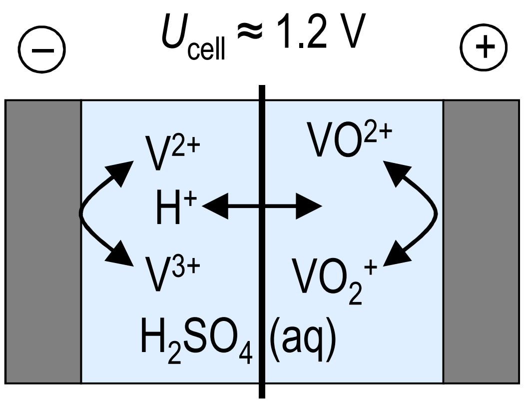
Nafion®: 5.8 ± 1.3
Grafted membranes: 12.6 ± 3.7

- **low-cost**
  (5-10 x cheaper than state-of-the-art)
- **low H_2 and O_2 crossover** through crosslinked polymer architecture
- **mechanically robust** to 100°C and **creep resistant** (semicrystalline polymer, crosslinked graft component)

EU-Project NOVEL

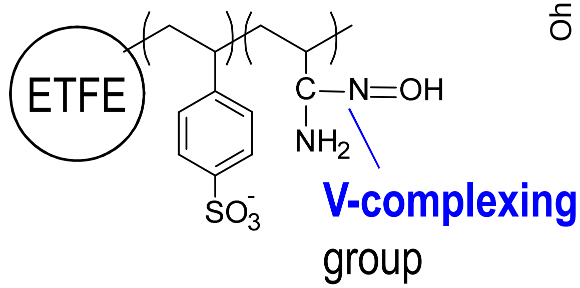
Vanadium Barrier in VRB

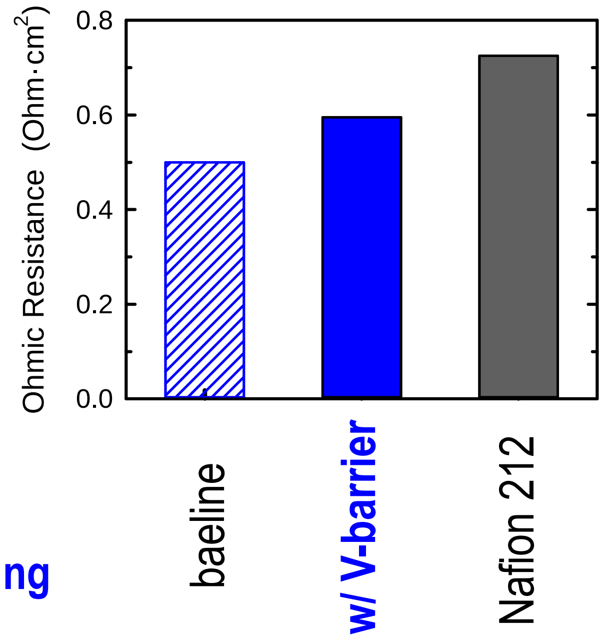
Vanadium redox flow battery (VRB)

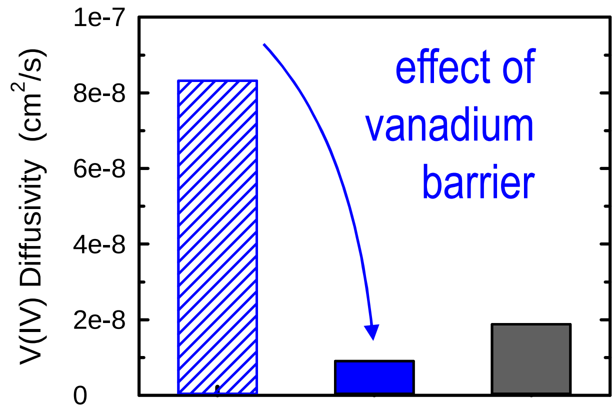


ion-exchange membrane

grafted membrane
with V-barrier:







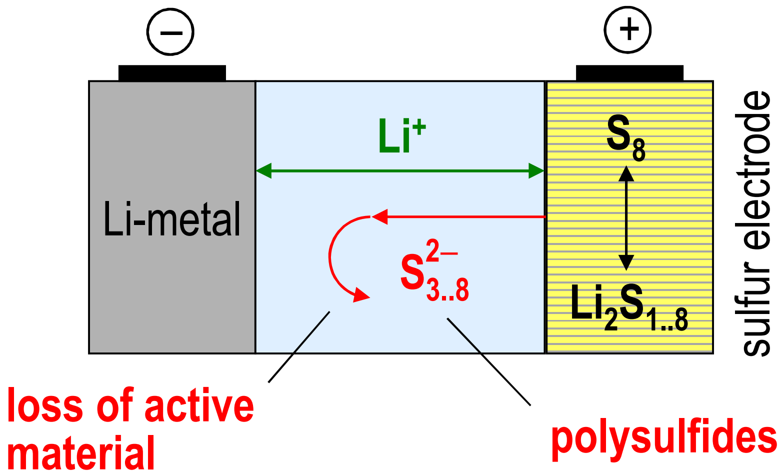
negative electrode: $V^{3+} + e^- \leftrightarrow V^{2+}$

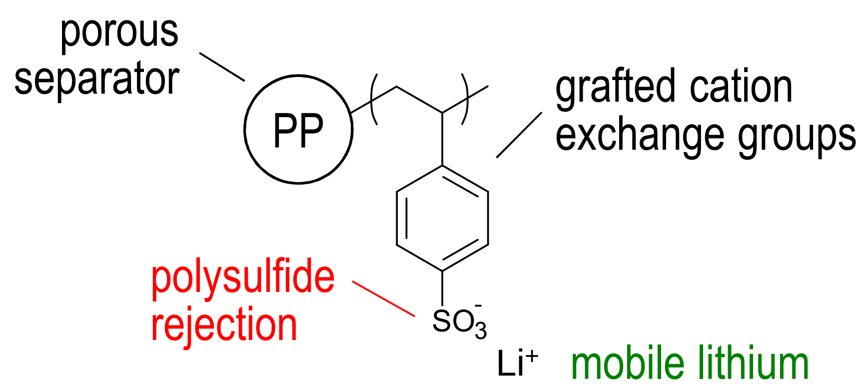
positive electrode: $VO_2^+ + 2\,H^+ + e^- \leftrightarrow VO^{2+} + H_2O$

➔ Poster by Olga Nibel

European Patent Application EP15154151

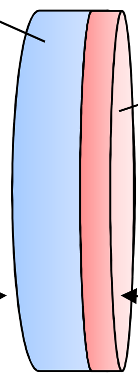
Polysulfide Shuttle in the Li-S Battery



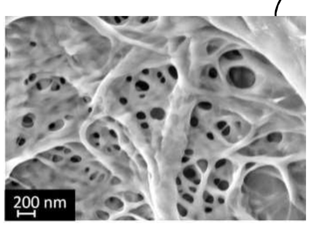


porous support layer (~ 25 µm)

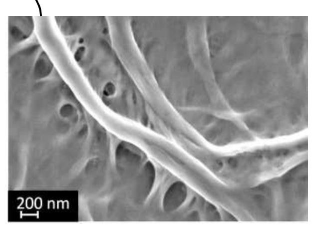
asymmetric porous membrane



dense skin = cation exchange layer (~ 1 µm)

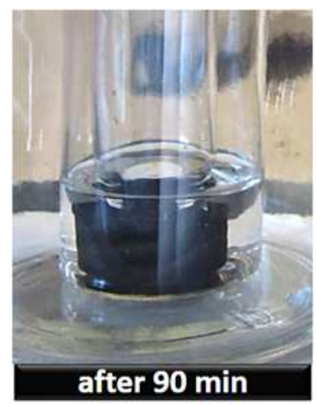


unmodified side



grafted sided

polysulfide diffusion test



grafted separator

pristine separator

J. Conder et al., *J. Mater. Chem. A*, in prep.

Conclusion

- **Radiation grafted membranes** can reach promising performance / durability attributes compared to PFSA membranes
- Membranes with **polymer-bound antioxidants** show considerably improved stability
- However, the phanol type antioxidants are depleted. What **antioxidant strategies** need to be adopted for hydrocarbon membranes ?
- Through adapted design, membranes with improved barrier properties can be synthesized for the **water electrolyzer**, **redox flow cell**, and **lithium-sulfur battery**

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