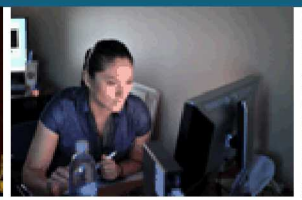
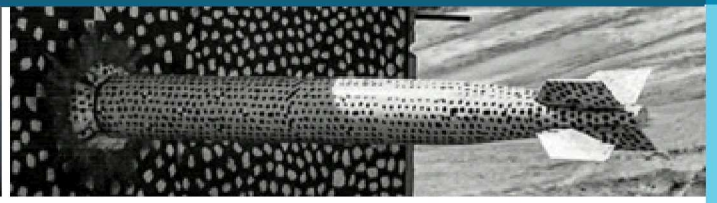
This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2019-11544C

Functionalized Poly(phenylene) membranes for advanced electrochemical applications: Fuel Cells





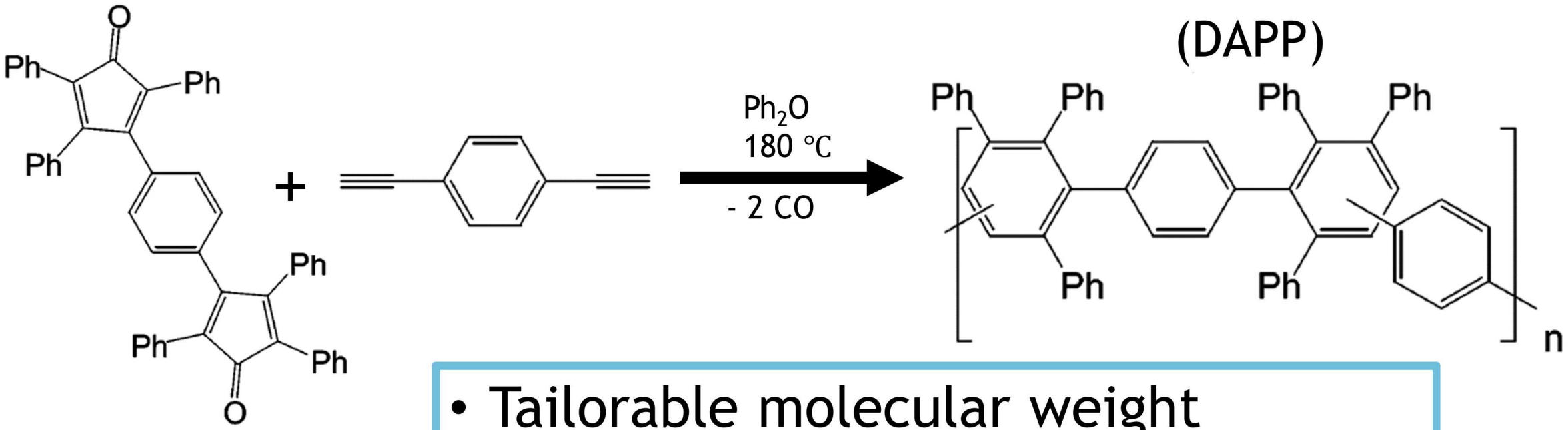
Ehren Baca, Cy Fujimoto, Michael Hibbs, Sandip Maurya, Albert S. Lee, Dongguo Li, Eun Joo Park, Yu Seung Kim

Funding: DOE Office of Electricity

DOE EERE Hydrogen Fuel Cell program

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Diels Alder Polymerization: Poly(phenylene)



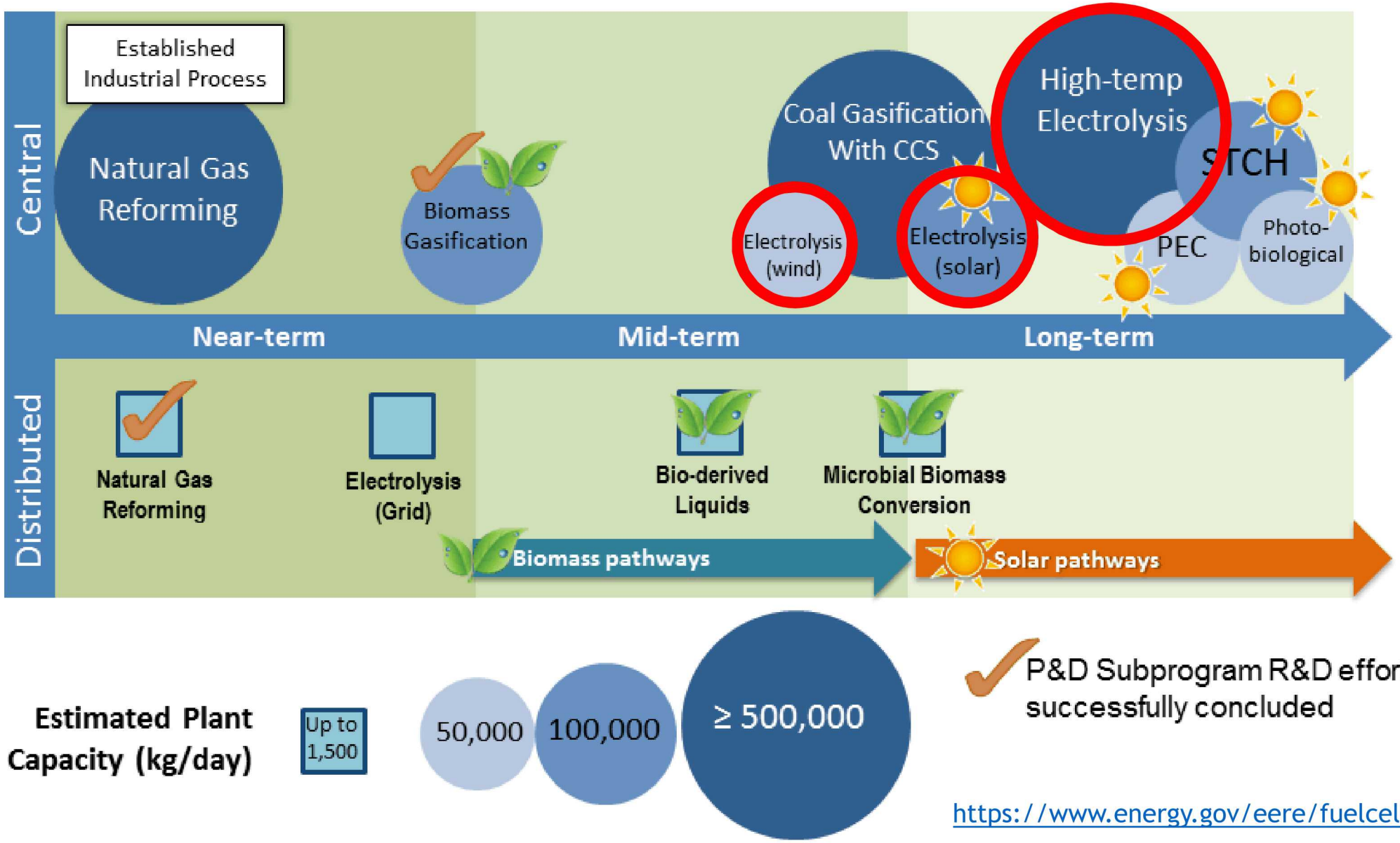
- Tailorable molecular weight
- Highly stable
- *Can be functionalized for different applications*: ex Fuels Cells

Fujimoto, C. H., Hickner, M. A., Cornelius, C. J., & Loy, D. A. (2005). Ionomeric Poly(phenylene) Prepared by Diels–Alder Polymerization: Synthesis and Physical Properties of a Novel Polyelectrolyte. *Macromolecules*, *38*(12), 5010–5016. doi: 10.1021/ma0482720

Economies prepare for hydrogen: Need for IEM's

- "2016, **Japan's Ministry of Economy, Trade and Industry (METI)**, decided that **by 2020** there would be some **40,000 hydrogen fuel-cell vehicles** (FCVs) on Japan's roads, along with **160 fueling stations and 1.4 million residential fuel cells**, known as Ene-Farms" (Hornyak, 2019)
- "**Germany's…hydrogen demand** in the transport and industry sectors is set to **surge 37% by 2030**." (Dazem, 2019)
- "**Renewable hydrogen** costs may fall to as low as **$1.40 a kilogram by 2030** from the current range of $2.50 to $6.80" (Mathis & Thornhill, 2019)

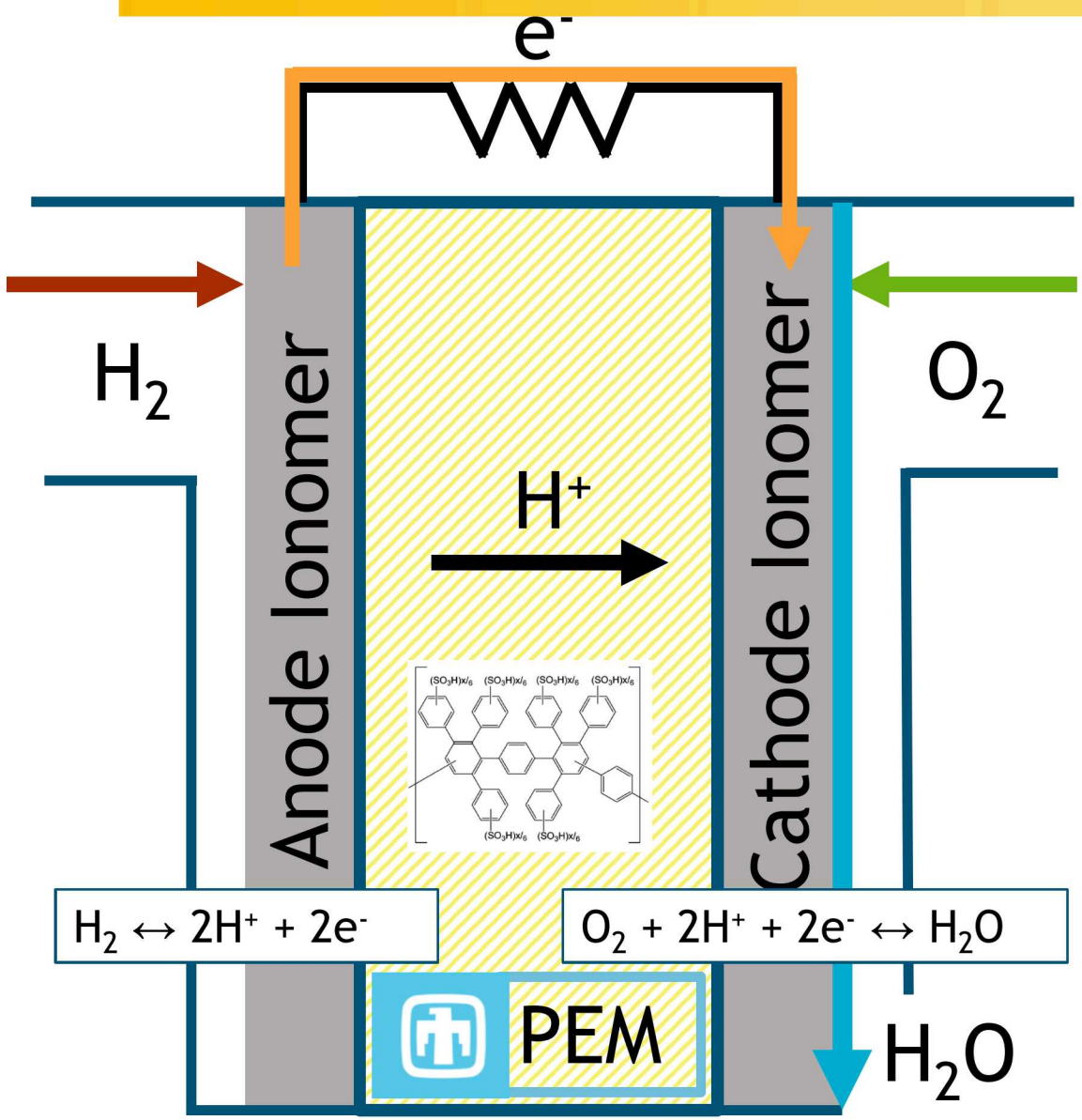
DOE Projected US Hydrogen Economy

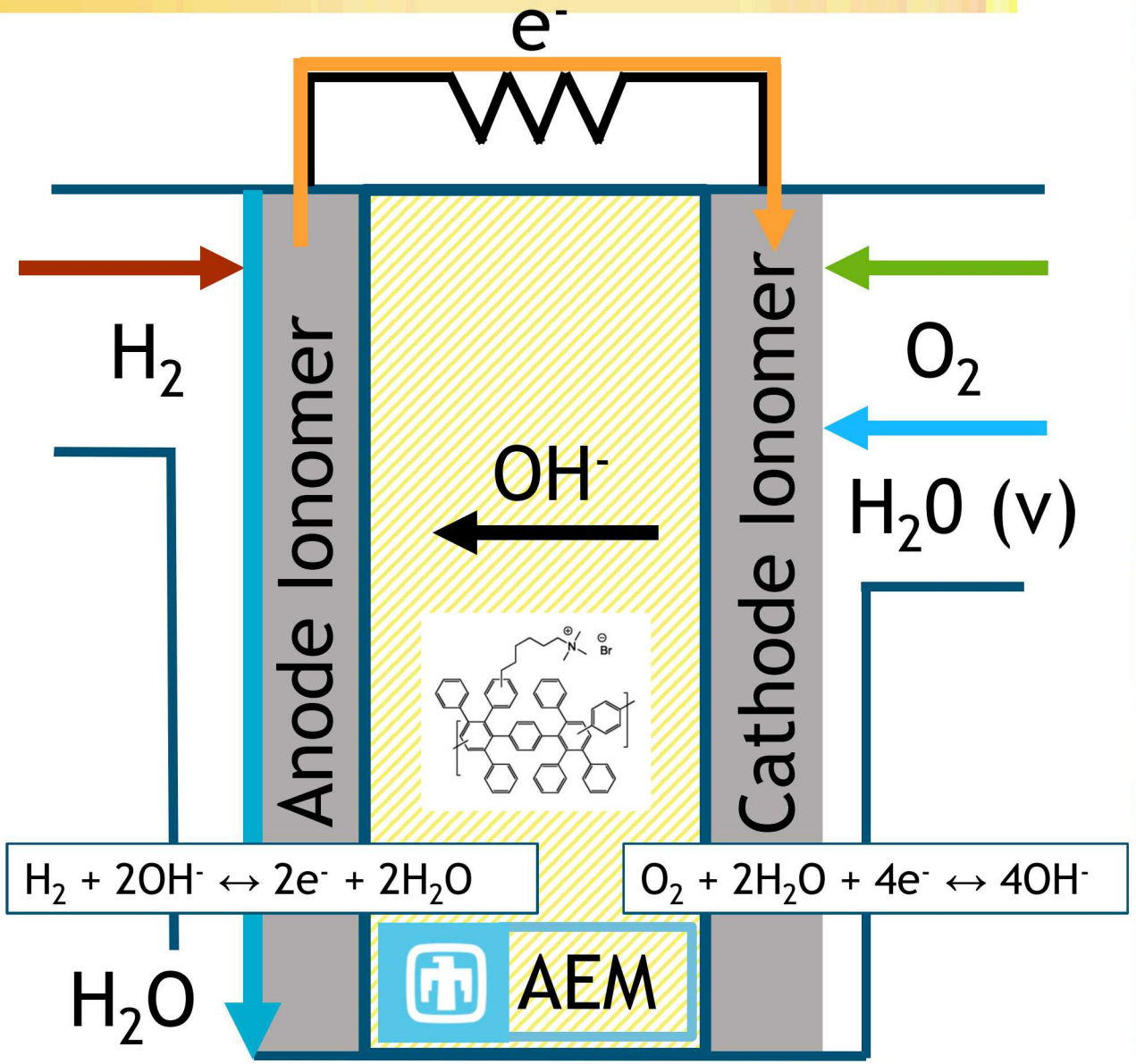


Fuel Cells

https://www.energy.gov/eere/fuelcells/hydrogen-production

Cationic (PEM) and Anionic (AEM) Exchange Fuel Cells

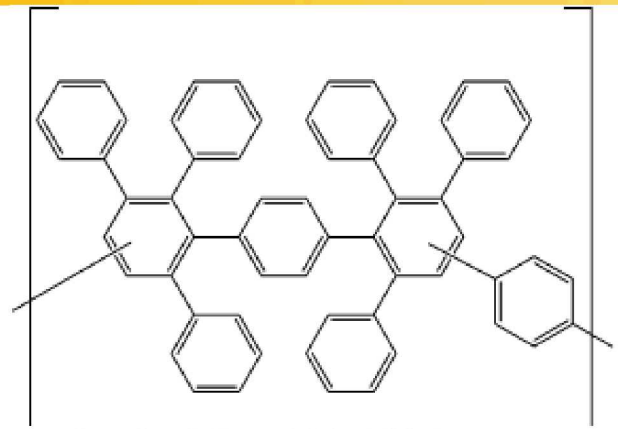




Ion Exchange Membrane Evaluation Metrics

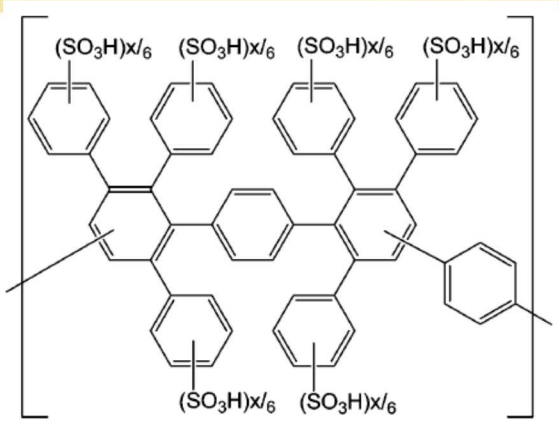
- Ion Exchange Capacity[mmol ion/g]: $\mathrm{IEC} = \frac{V_T C_T}{W_{dry}}$
- Water Uptake[%]: $\left[\frac{W_{wet} - W_{dry}}{W_{dry}}\right] x\ 100\%$
- Ion Conductivity [mS/cm^2]: $k = \frac{L}{Z' A}$

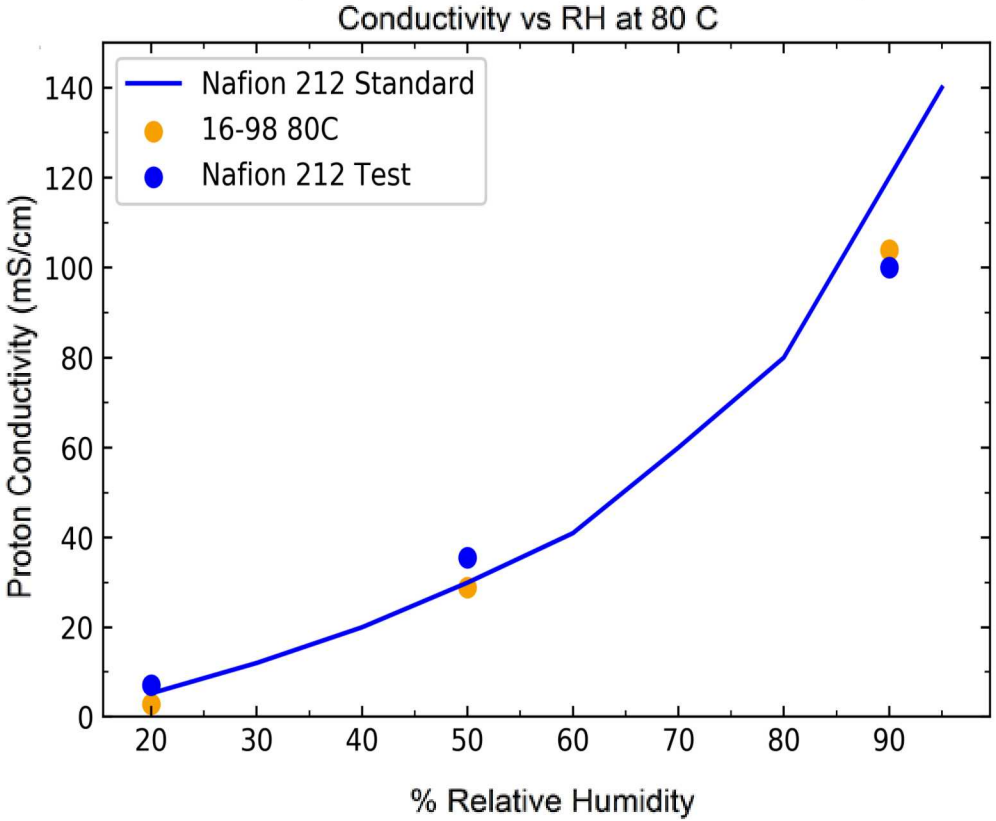
Functionalization: Fixed anionic groups



CH_2Cl_2

$ClSO_3H$





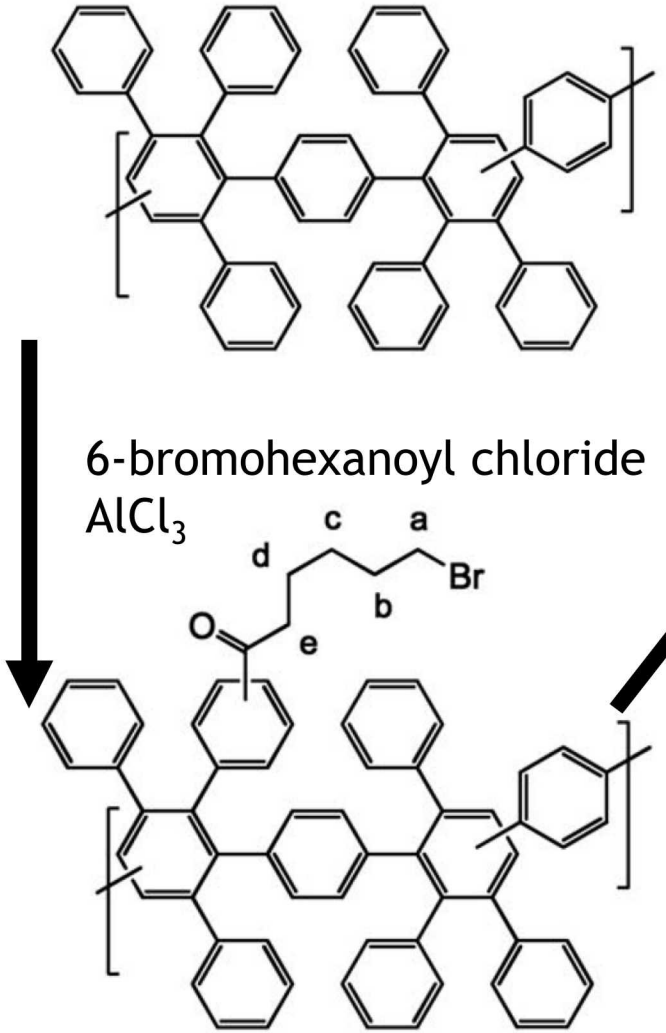
Benefits of PEMFC

- Highly stable
- High TRL
- High performance at high voltage

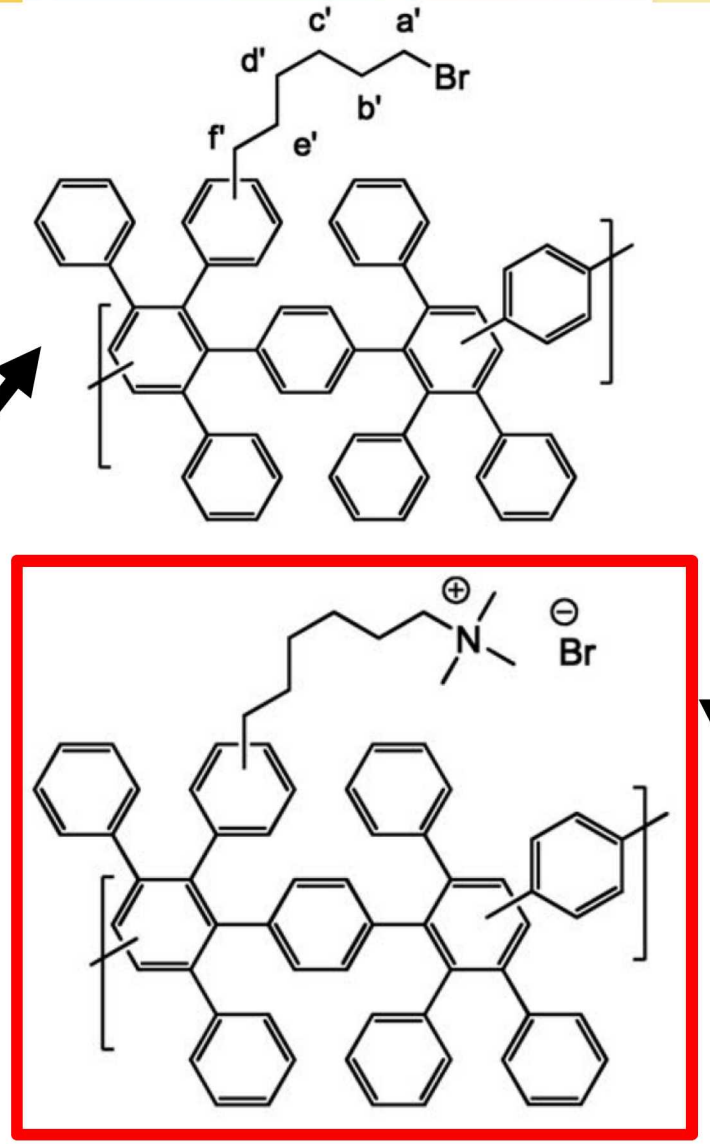
Limitations of PEMFC

- Precious metal catalyst
- Low temperatures
- High hydration

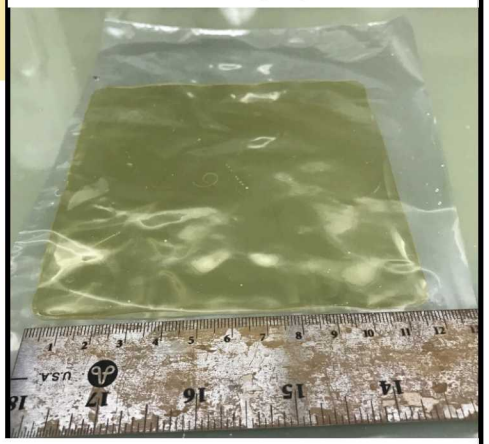
Functionalization: Fixed cationic groups



Keytone Reduction



Pre $N(CH_3)_3$ Soak



12.3 cm x 12.3 cm

1. Casted Film
2. Trimethylamine

Post $N(CH_3)_3$ Soak

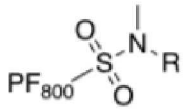
14.9 cm x 14.9 cm

Hibbs, M. R. (2013). Alkaline stability of poly (phenylene)-based anion exchange membranes with various cations. *Journal of Polymer Science Part B: Polymer Physics*, *51*(24), 1736-1742

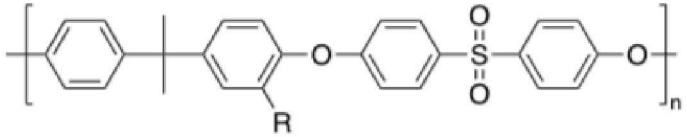
NREL Degradation Test

- 1000h in 1M KOH
- 20% of materials tested passed enhanced aging

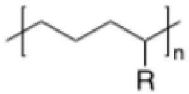
Perfluoro (PF)



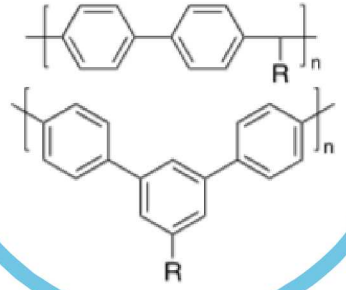
Poly(aryl ether sulfone) (PAES)



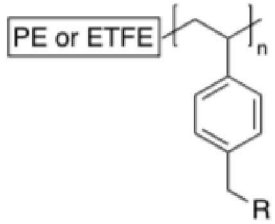
Polyethylene (PE)



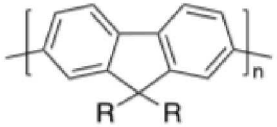
Polyphenylene (PPN)



Polystyrene (PS)



Polyfluorene (PFN)



$R = (CH_2)_m X^+ OH^-$

PF1 Non-degraded (L) and degraded (R):

PF2 Non-degraded (L) and degraded (R):

PAES Non-degraded (L) and degraded (R):

PE1 Non-degraded (L) and degraded (R):

PE2 Non-degraded (L) and degraded (R):

PFN1 Non-degraded (L) and degraded (R):

PPN1 Non-degraded (L) and degraded (R):

PPN2 Non-degraded (L) and degraded (R):

PPN3 Non-degraded (L) and degraded (R):

PPN4 Non-degraded (L) and degraded (R):

PPN5 Non-degraded (L) and degraded (R):

PPN6 Non-degraded (L) and degraded (R):

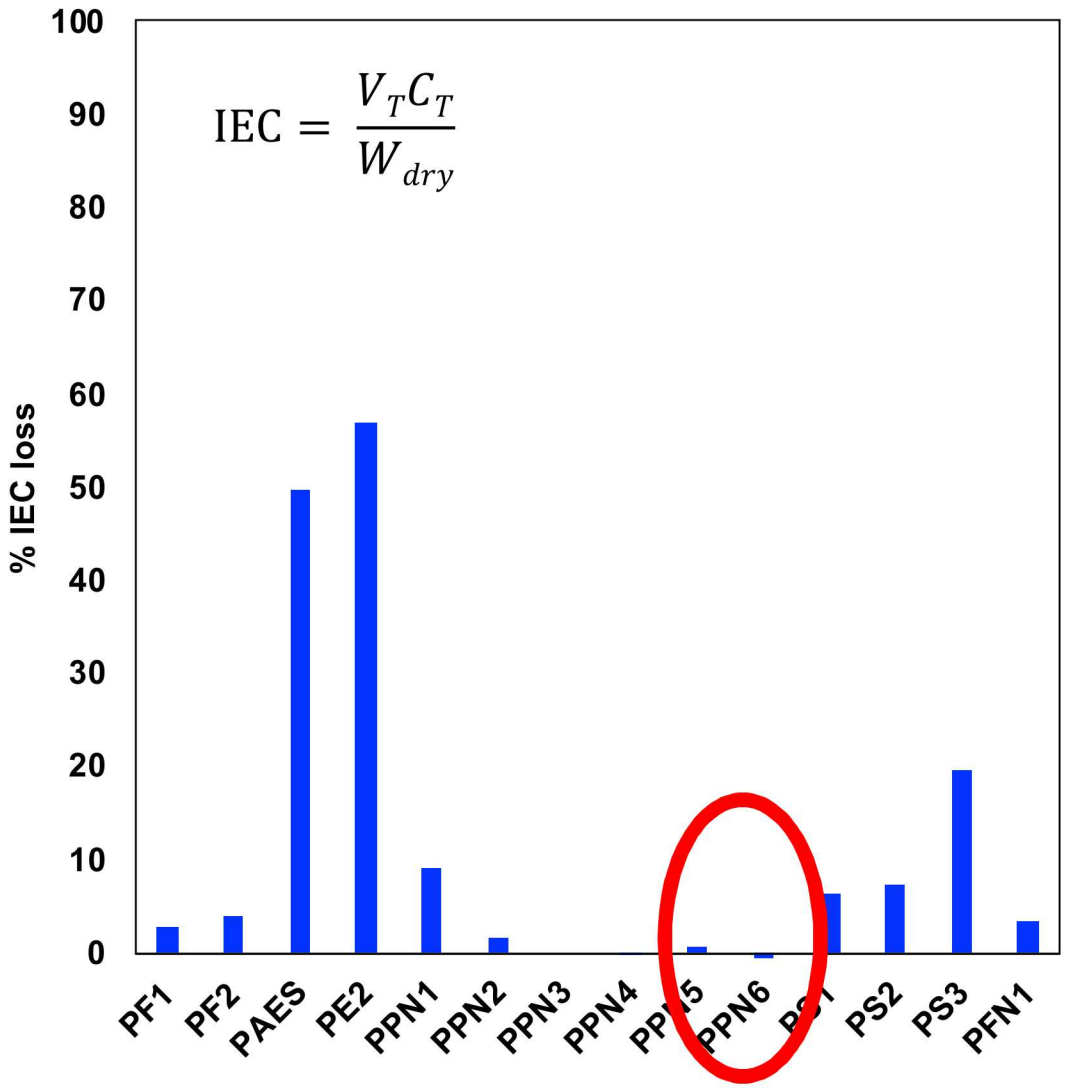
PS1 Non-degraded (L) and degraded (R):

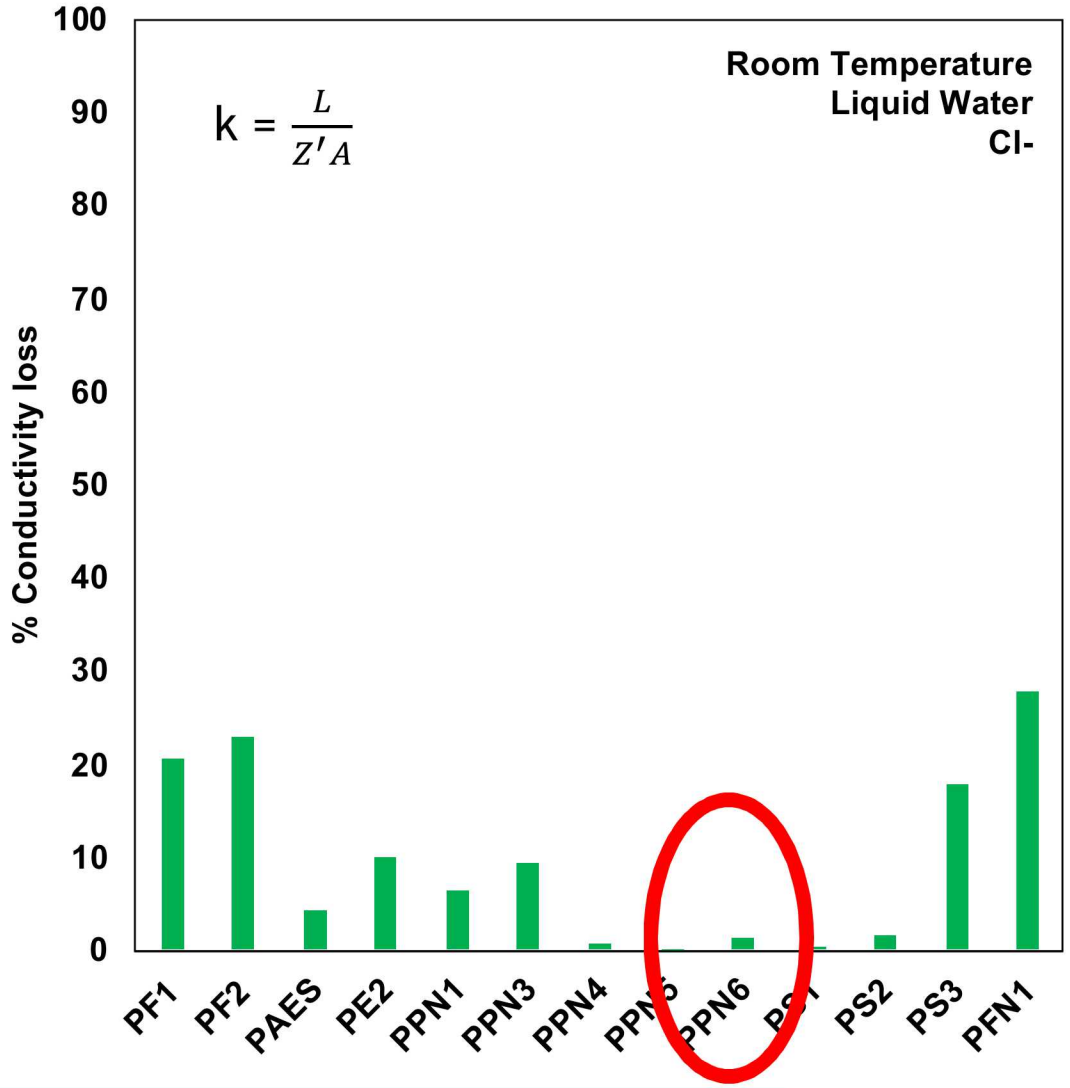
PS2 Non-degraded (L) and degraded (R):

PS3 Non-degraded (L) and degraded (R):

Study Credit: Kelly M. Meek and Brian S. Pivovar from NREL

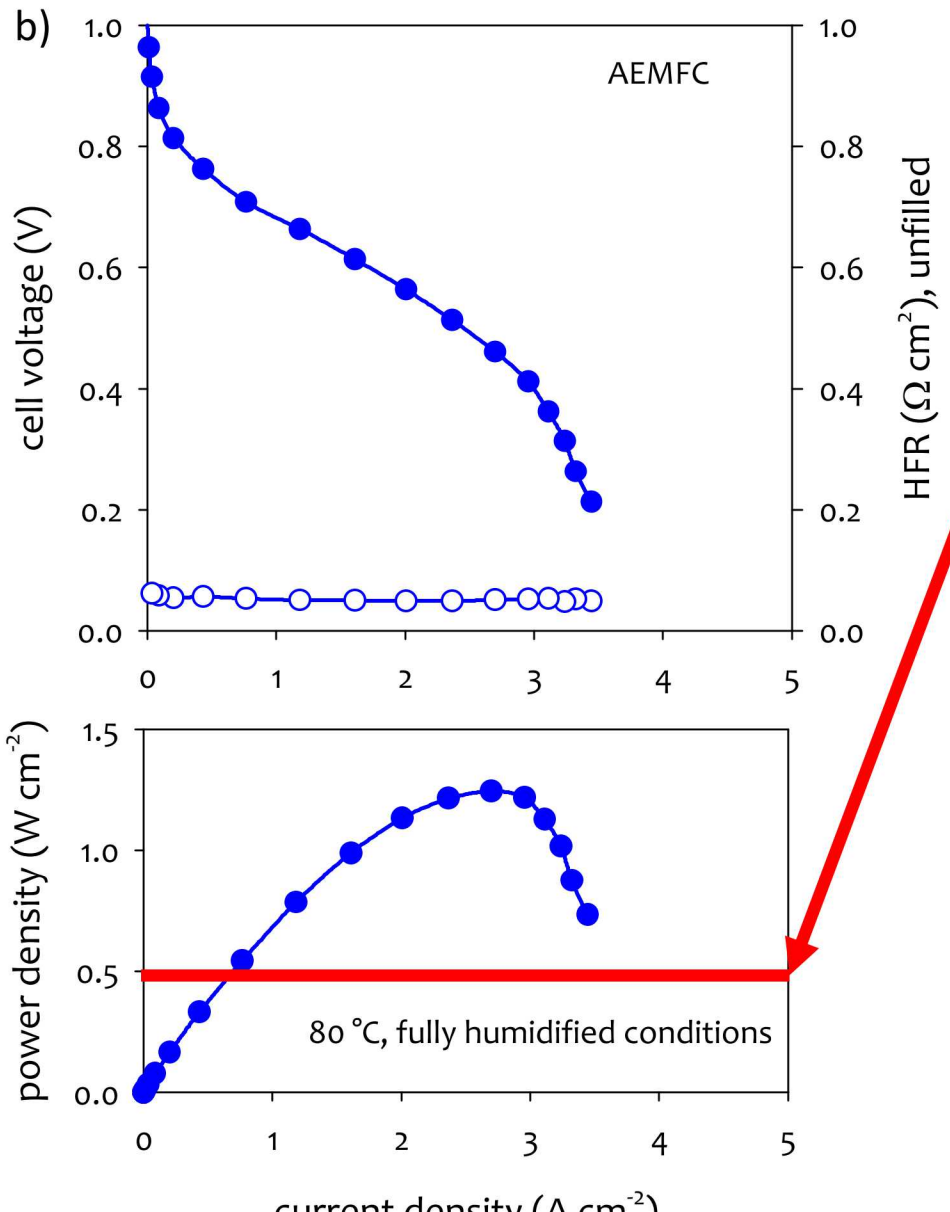
Post Degredation IEC and Conductivity





Study Credit: Kelly M. Meek and Brian S. Pivovar from NREL

AEMFC Polyphenylene performance



Benefits of AEMFC

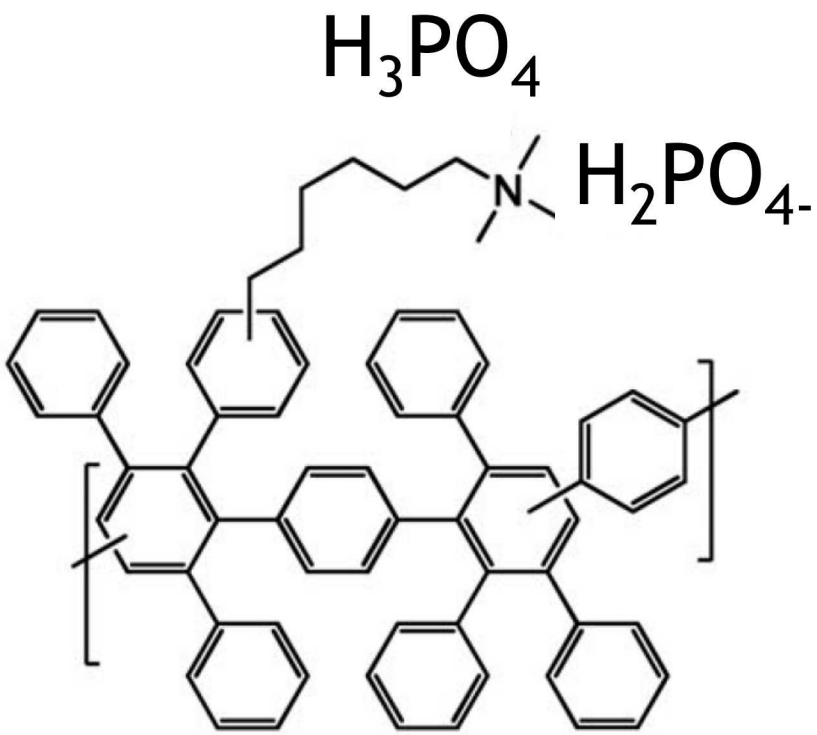
- 1 W/cm^2 PEMFC Standard, 1.2 W/cm^2
- 200-300 mW/cm^2 standard for AEMFC[8]
- Alkaline environment may accept non-PGM catalyst

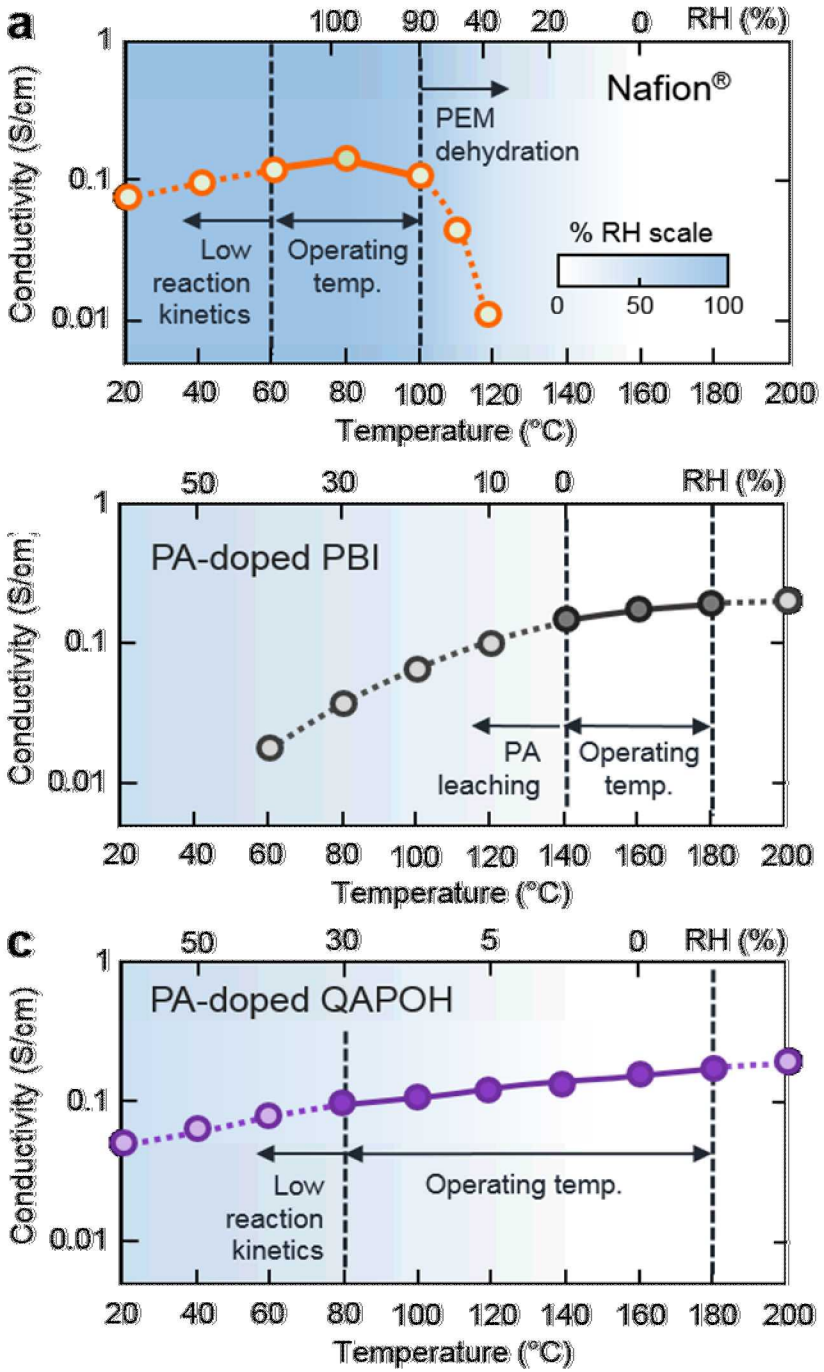
Limitations of AEMFC

- Degradation due to CO_2
- Requires high humidity (90%) which complicates engineering

Test Credit: Yu Seung Kim (LANL)

High Temperature PEMFC: PA-DAPP





Benefits of PA-DAPP

- More stable than PEMFC
- Wide operating window

- TRL higher than AEMFC
- TRL lower than PEMFC
- May not be able to use non-PGM catalyst

Lee, K.-S., Spendelow, J. S., Choe, Y.-K., Fujimoto, C., & Kim, Y. S. (2016). An operationally flexible fuel cell based on quaternary ammonium-biphosphate ion pairs. *Nature Energy*, *1*(9). doi: 10.1038/nenergy.2016.120

Conclusions

- Fujimoto's material shows promising results in enhancing fuel cell operation
  - Continuing work with LANL
  - Investigating commercialization interest
- Solutions in other sectors
  - LANL high temperature electrolysis
  - University partner for water treatment
  - Flow battery research at SNL
  - Industrial companies for process implementation

Citations

1. Hornyak, T. (2019, February 26). How Toyota is helping Japan with its multibillion-dollar push to create a hydrogen-fueled society. Retrieved from https://www.cnbc.com/2019/02/26/how-toyota-is-helping-japan-create-a-hydrogen-fueled-society.html

2. Dazem , V. (2019, February 26). Retrieved from https://www.bloomberg.com/news/articles/2019-08-02/germany-turns-to-hydrogen-in-quest-for-clean-energy-economy

3. Mathis , W., & Thornhill , J. (2019, August 21). Retrieved from https://www.bloomberg.com/news/articles/2019-08-21/cost-of-hydrogen-from-renewables-to-plummet-next-decade-bnef

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5. Hibbs, M. R. (2013). Alkaline stability of poly (phenylene)-based anion exchange membranes with various cations. *Journal of Polymer Science Part B: Polymer Physics*, *51*(24), 1736-1742.

6. Fujimoto, C. H., Hickner, M. A., Cornelius, C. J., & Loy, D. A. (2005). Ionomeric poly (phenylene) prepared by Diels− Alder polymerization: synthesis and physical properties of a novel polyelectrolyte. *Macromolecules*, *38*(12), 5010-5016.

7. Park, E. J., Maurya, S., Hibbs, M. R., Fujimoto, C. H., Kreuer, K. D., & Kim, Y. S. (2019). Alkaline Stability of Quaternized Diels–Alder Polyphenylenes. *Macromolecules*, *52*(14), 5419-5428.

8. Lee, K.H., Cho, D. H., Kim, Y. M., Moon, S. J., Seong, J. G., Shin, D. W., …Lee, Y.M. (2017). Highly conductive and durable poly(arylene ether sulfone) anion exchange membrane with end-group cross-linking. Energy & Environmental Science, 10(1), 275-285.

Questions?

Thanks for listening.

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