Combined high field and benchtop NMR studies of catalyst separation techniques on proton exchange membranes

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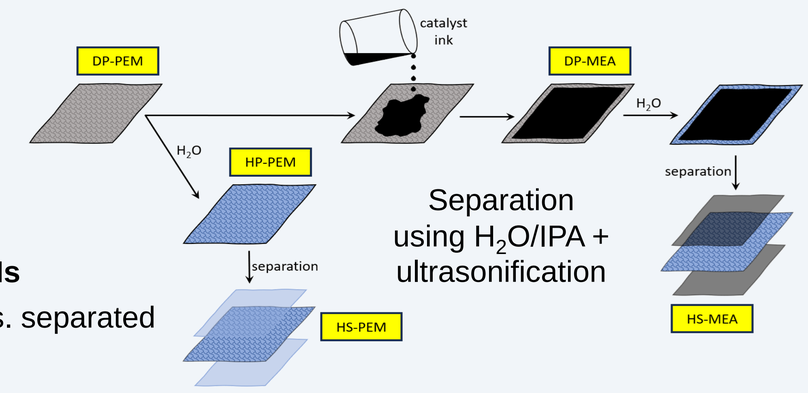
Motivation

- Proton exchange membrane water electrolyzers (PEMWE) are a mature, but not yet widely deployed technology for green H_2 production
- Due to high CRM cost and potential PFAS restrictions, recycling (separation) of both catalysts and PEM in membrane-electrode-assemblies (MEAs) is incentivized
- Development of fast screening technique for industry

Experimental

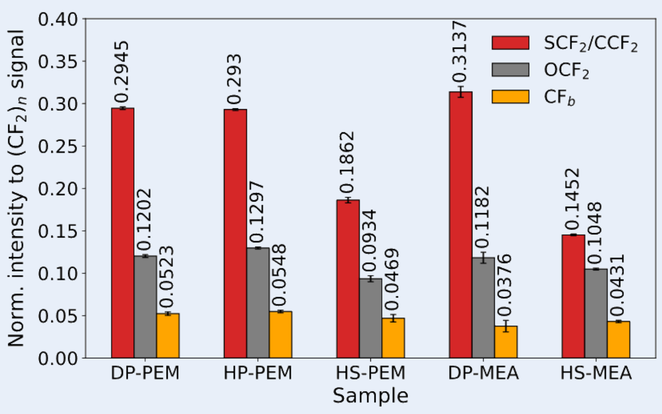
Dry
Hydrated
Pristine
Separated

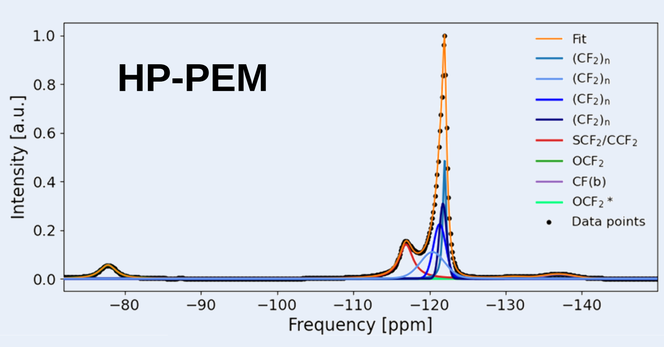


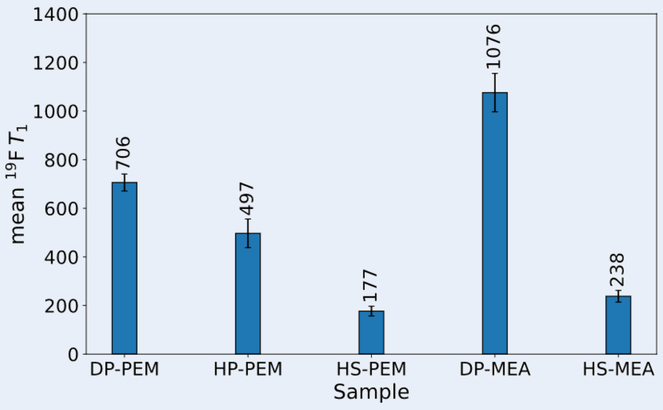
Conditioning of PEMs

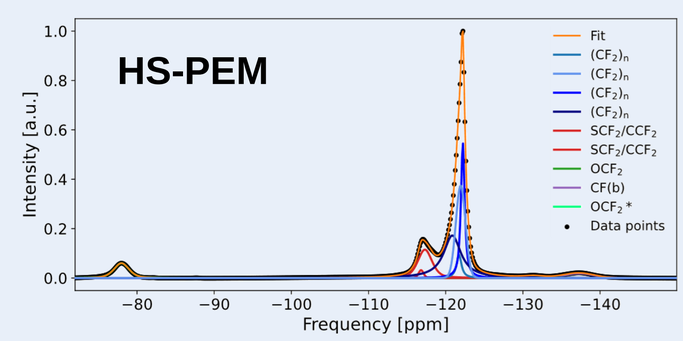
– Dry *vs.* hydrated vs. separated
– PEM *vs.* MEA

High-Field MAS NMR (400 MHz)



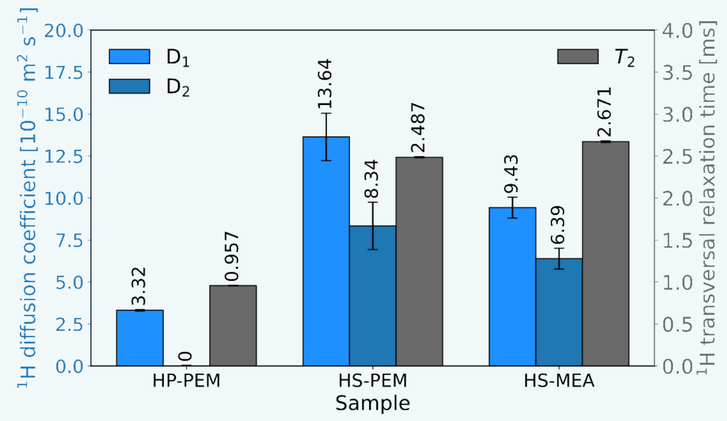






- Separation technique impacts chemical & spatial structure of ionomer
- **^{19}F MAS spectra**
  - Loss of polar side chain after separation, particularly SO_3H group
  - Significant change in SCF_2 peak shape after separation
- **^{19}F T_1 relaxation**
  - Strong spin diffusion for all samples
  - Significant decrease of T_1 after PEM hydration and separation

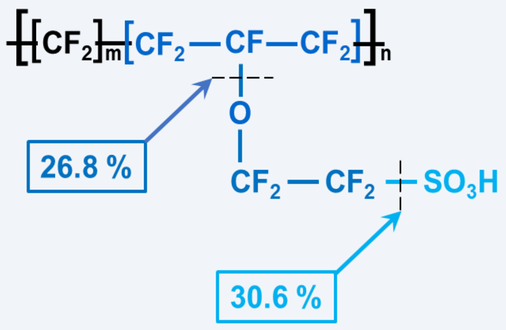
Benchtop NMR (80 MHz)



- **HP-PEM**
  - Single observable diffusion mode
  - Low-medium T_2
- **HS-PEM/HS-MEA**
  - Significantly increased diffusivity
  - Two observable diffusion modes
  - Significantly increased T_2
- Correlation of proton relaxation time (T_2) and proton diffusivity (D_1, D_2)

Discussion

- Separation technique induces chemical bond breakage in the polar side chain
- Side chain loss occurs via chain unzipping starting from SO_3H group,
  - C-S bond breakage as rate determining step
- Change in spatial structure due to side chain loss affects water uptake and transport behavior



Conclusion

- Separation using H_2O/IPA and ultrasonification causes non-negligible degradation of PEM properties via side-chain loss
- **^{19}F high-field MAS NMR**
  - Precise study of PEM chemistry and structure
- **^{1}H benchtop NMR**
  - Correlative findings
  - Low cost and complexity
  - Predestined for industrial screening and quality control

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