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Degradation studies of a short-side-chained PFSA material for industrial water electrolysis by MAS and PFG-NMR

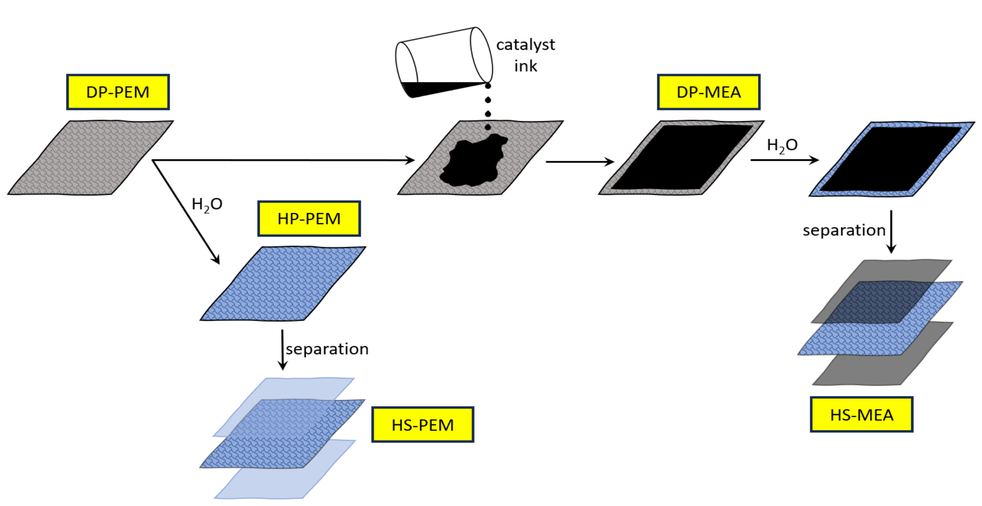
R. Rameker[1,2], M. Plüm[3], S. Jovanovic[1], G. Schmid[3], R.-A. Eichel[1,4], J. Granwehr[1,2]
[1]IEK-9, Forschungszentrum Jülich GmbH, Jülich, Germany , [2]ITMC, RWTH Aachen University, Aachen, Germany,
[3]Siemens-Energy, Erlangen, Germany, [4]IPC, RWTH Aachen University, Aachen, Germany

Motivation

- Proton exchange membrane (PEM) electrolysis considered as promising technique for green hydrogen production.
- Ban of per- and polyfluoroalkyl substances (PFAS) discussed → energy companies forced to use PEMs efficiently → **PEM recycling** can become very important
- Catalyst|PEM separation often based on alcohol for recycling, but influence on PEM structure poorly understood
- NMR based **screening routine** → detect alteration of performance and molecular structure of PEMs including
  - ➢ high-resolution **^{19}F-MAS-NMR** methods → chemical understanding
  - ➢ **80 MHz benchtop ^{1}H-NMR** → industrial quality management

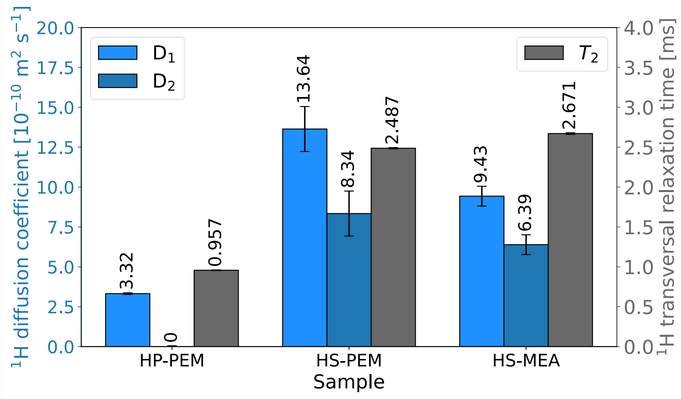
Experimental

Sample preparation



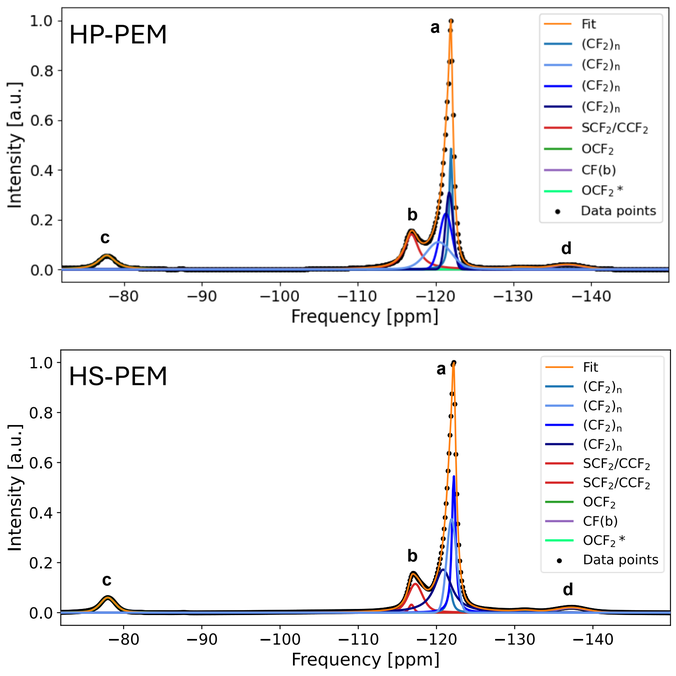
- **HP-PEM → HS-PEM**: simulation of separation procedure to check invasiveness of separation technique, unbiased by possible catalyst residues

Low-field ^{1}H NMR methods



- Correlation of proton mobility (T_2) and proton diffusivity (D_1, D_2)
- **HP-PEM**: fast exchange between bulk diffusion and surface diffusion
- **HS-PEM/MEA**: slow exchange between both diffusion domains; high T_2 → mobile water domains

High-field ^{19}F MAS-NMR methods

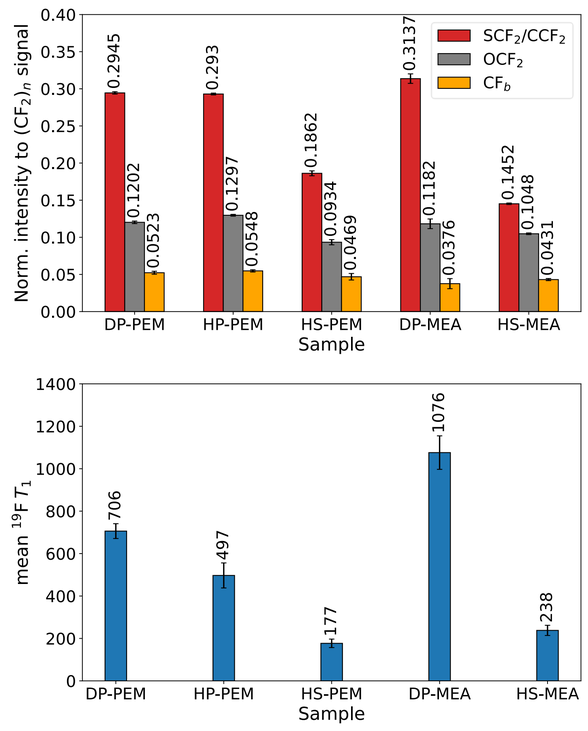


^{19}F spectra

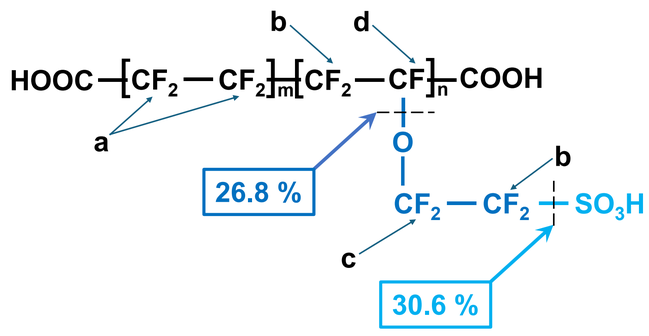
- Alteration of SCF_2/CCF_2 signal → two pseudo-Voigt profiles for **HS-PEM/MEA**
- Decrease of SCF_2/CCF_2 and OCF_2 to $(CF_2)_n$ ratio by separation process → separation of sulfonic acid groups and side chain fragments

^{19}F T_1 relaxation time

- decreased T_1 after hydration (**HP-PEM**)
- significant decrease of T_1 after separation process (**HS-PEM, HS-MEA**)
- Spin diffusion!



Discussion



- Altered signal ratios for **HS-PEM** and **HS-MEA** → **chemical degradation on a molecular level**
- Breakage of the C-S bond during the separation process → possibly starting point for a radical chain reaction:
  - ➢ Side chain unzipped from ionomer backbone
  - ➢ Shift of CCF_2 signal towards the $(CF_2)_n$ signal
  - ➢ Recombination of two chain-terminating -CF_2● groups → possible chain termination reaction
- 30.6% relative loss of sulfonic acid groups and 26.8% relative loss of side chains for **HP-PEM → HS-PEM**
- Breakage of the C-S bond suggested as **rate-determining step** in this reaction mechanism
  - ➢ **Molecular degradation initiated at the side chain**
  - ➢ **Side chain degraded to a greater extent than the backbone**
- Altered T_1 relaxation times due to local rearrangement of spatial ionomer structure induced by ultrasonification

Conclusion

- **^{19}F-MAS-NMR** → precise detection of structural and spatial changes based on the signal ratios and ^{19}F T_1 relaxation time.
- **^{1}H NMR** provides correlated findings → methods less expensive and complex → predestined for fast and reproducible quality control
- Separation mechanism leads to a non-negligible degradation of sulfonic acid groups and also complete side chain fragments.
- Combination of isopropanol and ultrasound considered the main reason for altered signal ratios and T_1 relaxation times.

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