Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

A Magnetic Resonance and Electrochemical Study of the Role of Polymer Mobility in Supporting Hydrogen Transport in Perfluorosulfonic Acid Membranes

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Supplemental Information

S1: Calculation of H_2 permeability from the crossover current

Based on Faraday's Law: $I = nFJA$

where n is the number of electrons transferred in the hydrogen oxidation reaction, F [C mol^{-1}] is the Faraday constant , J [mol s^{-1}m^{-2}] is the flux of reactant and A [m^2] is the active area.

$$J = \frac{I}{nFA} \qquad \left(\text{unit calculation: } \frac{\left[C/s\right]}{\left[C/mol\right]\left[m^2\right]} = \frac{mol}{s \cdot m^2}\right)$$

$$\Rightarrow P_{H_2} = \frac{J \cdot d_{PFSA}}{p_{H_2}} \qquad \left(\text{unit calculation: } \frac{\left[\frac{mol}{s \cdot m^2}\right]\left[m\right]}{\left[Pa\right]} = \frac{mol}{s \cdot m \cdot Pa}\right)$$

where P_{H_2} is H_2 permeability, p_{H_2} is the H_2 pressure at the preset conditions, d_{PFSA} is the thickness of the PFSA membrane.

*MEA active area is not involved in the calculation because it will be cancelled out during the derivation.

S2: ^{19}F DQ NMR pulse sequences and normalization process

R26$_4^{11}$ pulse sequence with Bruker Avance III system. Interleaved pseudo 2D experiment.

```
; PARAMETERS
;-----------------------------------------------
;d1  : recycle delay
;d20 : delay b/w presaturation pulses
;l20 : number of presaturation pulses


;p1  : 90 deg pulse (F1)
;pl1  : 90 deg pulse power (F1)

;cnst31 : spinning frequency (in Hz)
;l1 : N symmetry number
;l2 : n symmetry number
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;l3 : nu symmetry number
;p11 : length of R element 90 pulse
;p12 : length of R element 270 pulse
;pl11 : R sequence power level (F1)
;l11 : no. pairs of R elements in excitation and reconversion for first slice
;l10 : increment step size for l11 in next slices
;d11 : length of excitation and reconversion periods
;d10 : Z-filter delay
;d31 : rotor period


; CALCULATIONS
;-----------------------------------------------
;calculate length of one rotor period
"d31 = 1.0s/cnst31"

;calculate length of excitation and reconversion periods
"d11 = 2*l11*d31*l2/l1"

;calculate the 90 and 270 pulse lengths for R element
"p11 = 0.25*d31*l2/l1"
"p12 = 0.75*d31*l2/l1"

;calculate the R element phases (phi=nu/N*pi)
"cnst1=(180.0*l3)/l1"              ; phi
"cnst2=cnst1+180"                  ; phi+180
"cnst3=-1*cnst1"                   ;-phi
"cnst4=-1*cnst1+180"               ;-phi+180

"acqt0=-p1/2"
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```
define loopcounter nfid
"nfid=td1/2"


; PULSE SEQUENCE
;-------------------------------------------------

; DQ spectrum (uses ph31 phase list for receiver)
;-------------------------------------------------
1 ze
  d11
  d31

;PRESATURATION (on F1)
2 d20
  (p1 ph20 pl1):f1
  lo to 2 times l20

;RECYCLE DELAY
  d1 pl11:f1

;DQ EXCITATION (on F1)
3 p11 ph11+cnst1
  p12 ph11+cnst2
  p11 ph11+cnst3
  p12 ph11+cnst4
 lo to 3 times l11

;DQ RECONVERSION (on F1)
4 p11 ph12+cnst1
  p12 ph12+cnst2
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```
  p11 ph12+cnst3
  p12 ph12+cnst4
 lo to 4 times l11

;Z-FILTER
  d10

;OBSERVE PULSE (on F1)
  (p1 pl1 ph13):f1

;ACQUISITION
  go=2 ph31
  30m wr #0 if #0 zd   ;save data to disk and reset phase lists


; REFERENCE spectrum (uses ph30 phase list for receiver)
;------------------------------------------------

;PRESATURATION (on F1)
12 d20
  (p1 ph20 pl1):f1
  lo to 12 times l20

;RECYCLE DELAY
  d1 pl11:f1

;DQ EXCITATION (on F1)
13 p11 ph11+cnst1
  p12 ph11+cnst2
  p11 ph11+cnst3
  p12 ph11+cnst4
```

```
 lo to 13 times l11

;DQ RECONVERSION (on F1)
14 p11 ph12+cnst1
  p12 ph12+cnst2
  p11 ph12+cnst3
  p12 ph12+cnst4
 lo to 14 times l11

;Z-FILTER
  d10

;OBSERVE PULSE (on F1)
  (p1 pl1 ph13):f1

;ACQUISITION
  go=12 ph30
  30m wr #0 if #0 zd    ;save data to disk and reset phase lists

;INCREMENT LOOP COUNTER
15 1m iu11
  lo to 15 times l10

;LOOP BACK TO BEGINNING
  lo to 2 times nfid

exit

;PHASE LISTS
ph20 =  0
ph11 =  0
```

ph12 = 1 2 3 0

ph13 = 0 0 0 0 1 1 1 1 2 2 2 2 3 3 3 3

ph31 = 0 2 0 2 1 3 1 3 2 0 2 0 3 1 3 1

ph30 = 0 0 0 0 1 1 1 1 2 2 2 2 3 3 3 3

Normalization process

During the pseudo 2D experiment, a reference spectrum (REF) and a double quantum spectrum (DQ) with the same dipolar recoupling time τ_{DQ} were collected in an alternating fashion. Please refer to the pulse sequence above.

The normalized double quantum term (nDQ) was calculated based on $nDQ = DQ / \Sigma MQ$, where $\Sigma MQ = DQ + REF$ at each recoupling time. The normalization of the DQ term follows a point-by-point style where absolute signal intensities were used during this process.