ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for *Adv. Funct. Mater.,* DOI: 10.1002/adfm.202008778

Anion Exchange Ionomers: Impact of Chemistry on Thin-Film Properties

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Thin-Film Preparation

Table S1 Ion exchange thin-film spin-cast parameters

Sample Name	wt%	Solvent
1-Fuma (Br-)	0.52	IPA/H_2O(1:1)
2-Fuma (Br-)	0.84	IPA/H_2O(1:1)
3-Fuma (Br-)	2.05	IPA/H_2O(1:1)
DMBPN	1	EtOH/ IPA (1:1)
N2-25	1	EtOH/ IPA (1:1)
1-QS	1.5	DMF
2-QS	2.58	DMF
3-QS	4.09	DMF
1-PFAEM	0.95	IPA/H_2O(1:1)
2-PFAEM	1.51	IPA/H_2O(1:1)
3-PFAEM	2.78	IPA/H_2O(1:1)
1-Nafion	0.82	IPA/H_2O(1:1)
2-Nafion	1.71	IPA/H_2O(1:1)
3-Nafion	3.03	IPA/H_2O(1:1)
1-PSS	0.5	H_2O

Table S2. The impact of solvent on Fumion® thin-film casting

Sample Name	Casting Solvent	Castability
Fumion (Br^-)	NMP	×
Fumion (Br^-)	NMP_DMSO	×
Fumion (Br^-)	NMP_DMF	×
Fumion (Br^-)	NMP_MeOH	√
Fumion (Br^-)	NMP_IPA/H2O	√
Fumion (HCO_3^-)	NMP_IPA/H2O	×

As listed in Table S2, multiple solvents have been used for film casting, only MeOH and IPA/H_2O were able to form nice Fumion thin-films. The reason could be due to the AEI ionomers solubility in solvent varied among different polymer-solvent systems. In general, Fumion was found to be more difficult to dissolve in the solvent than that of Nafion. Much longer of the sonication process needed. PTFE syringes and filters (0.45 µm pore size, VWR) were used to void dissolving by organic solvent during filtration procedure. We tried to obtain similar counter-ions for all thin-films using the following ion-exchange procedure. Thin-film was ion-exchanged to HCO_3^- form by soaked in 0.5 M $NaHCO_3$ for 1 h, however, the film is delaminated from the substrate.

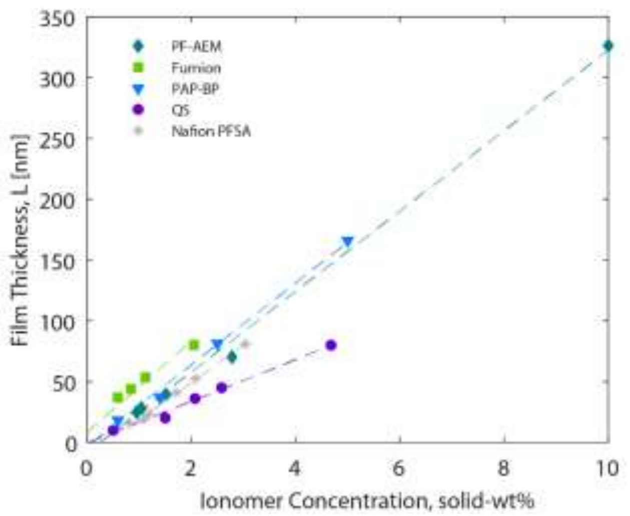

Figure S1 Correlation between the thickness of spun-cast thin-films and concentration of ionomer dispersion. The thickness of the films correlated fairly well with the ionomer solid content with a linear relationship, confirming the film-forming capability of AEIs, similar to PFSAs. Compared to perfluorinated ionomer, hydrocarbon ionomers are observed to be more difficult to cast into uniform films, which could be due to their higher surface energy or IEC lowering their adhesion force to a substrate. [46]

Morphology and Density

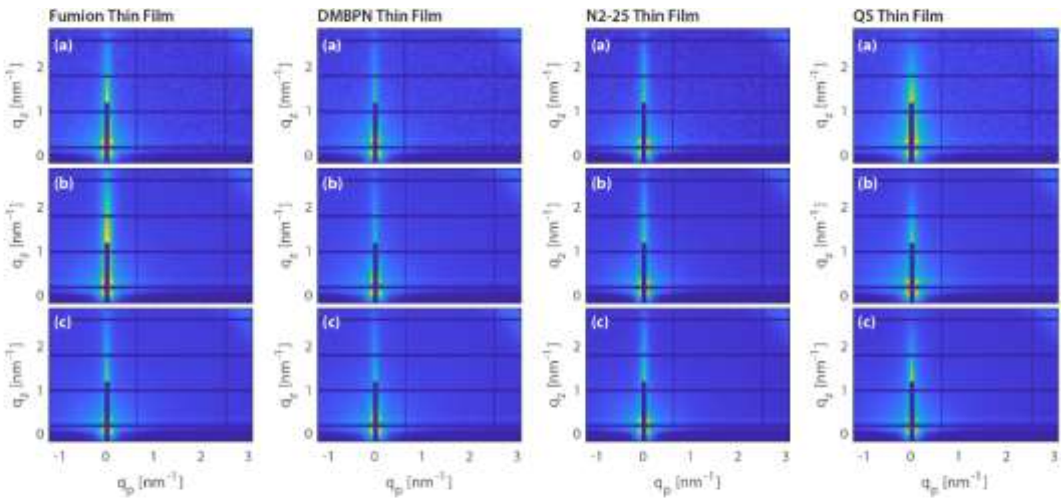

Figure S2 (a) to (c) the impact of thin-film thickness on 2D GISAXS patterns for Fumion, DMBPN, N2-22 and QS ionomer thin films in saturated conditions.

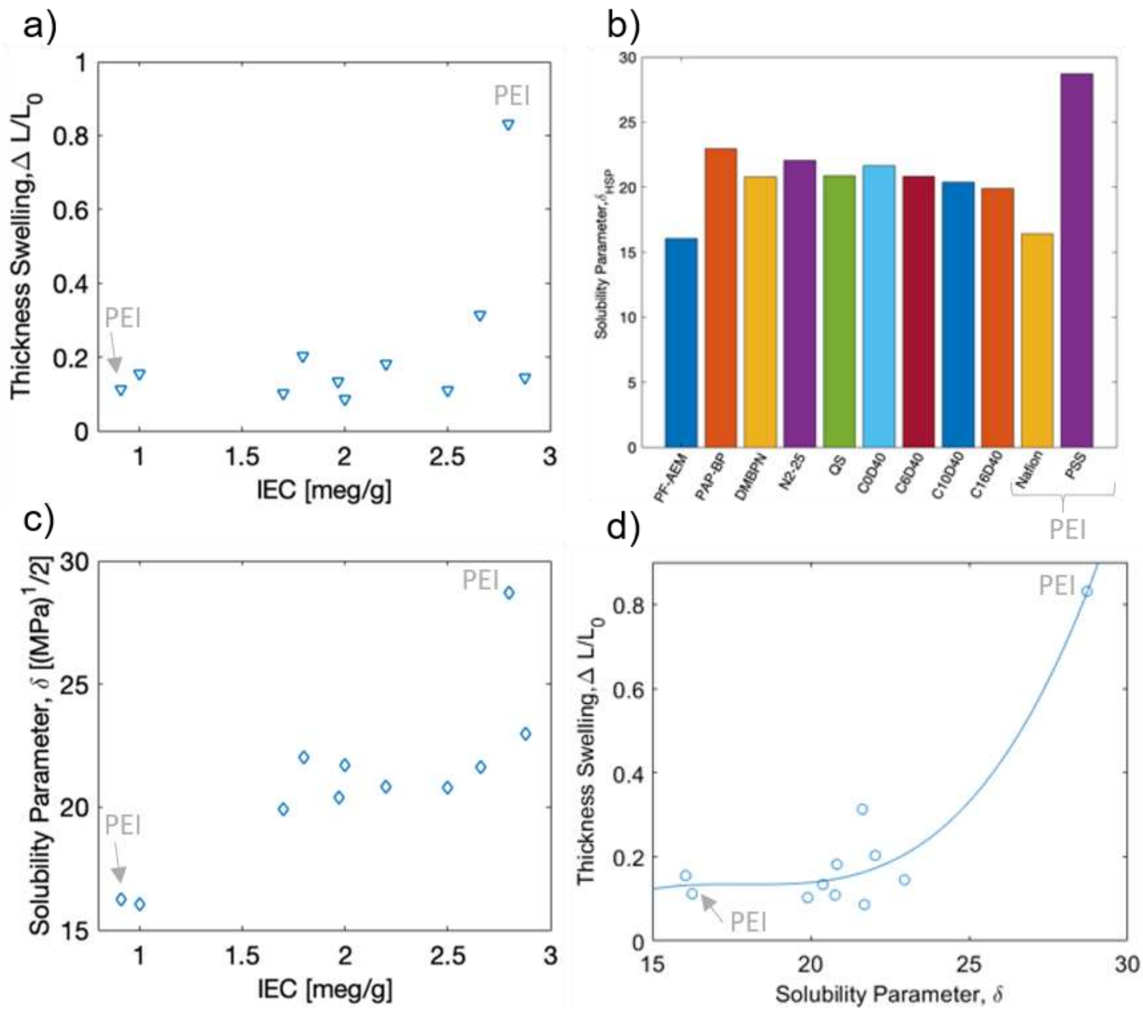

Figure S3 (a) Thickness swelling ratio at water-saturated condition as a function of IEC; (b) solubility parameters of ionomers, calculated from group contribution theory; (c) solubility parameter as a function of IEC and (d) thickness swelling as a function of solubility parameter.

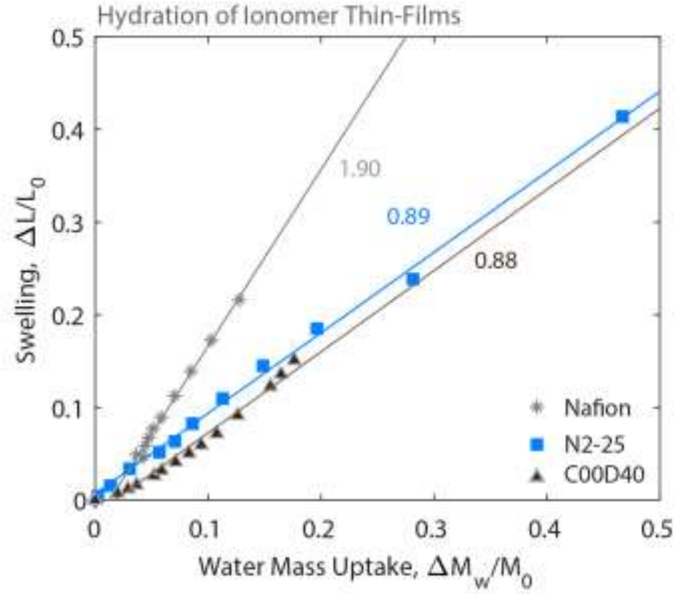

Figure S4 Thickness swelling of thin-film (ellipsometry) vs. its water mass uptake (QCM) measured simultaneously in a humidity-controlled environmental cell.

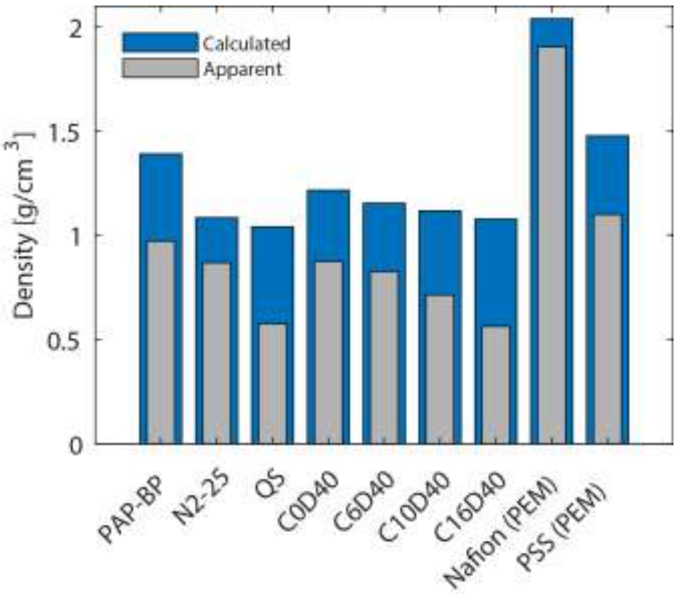

Figure S5 The comparison of measured density vs. calculated density of ionomers.

Confinement Effect: Additional Correlations

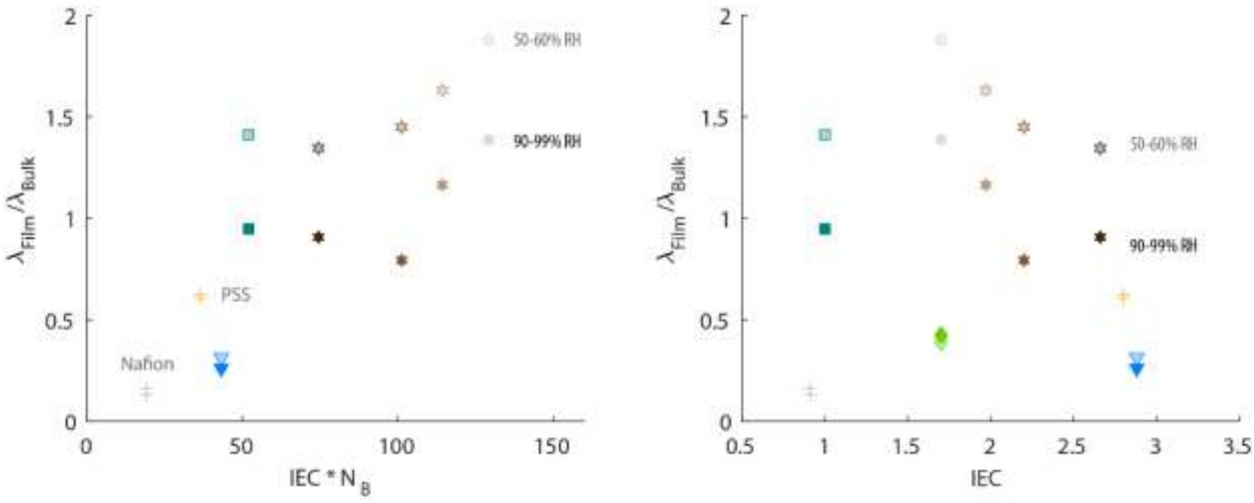

Figure S6 Confinement impact in water content between bulk and thin-film as a function of left) Combined values of IEC (ion exchange capacity) *N_B (bond number of side-chain). Empty symbols: 50-60% RH and filled symbols: 90-99%RH; right) IEC at various relative humidity conditions, which indicates $\lambda_{Film}/\lambda_{Bulk}$ does not correlate well with IEC.

Table S3 Bond number on the side-chain of ionomers.

Ionomers	Bond #
PFAEM	52
Nafion	20
PSS	15
PAP-BP	24
C0D40	28
C6D40	46
C10D40	58
C16D40	76
N2-25	96
QS	75
Fumion	N/A