Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supporting Information

Role of Ionic Interactions in Deformation and Fracture Behavior of Perfluorosulfonic-acid Membranes

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1. Comparisons between Mechanical Properties representing the Yield Point

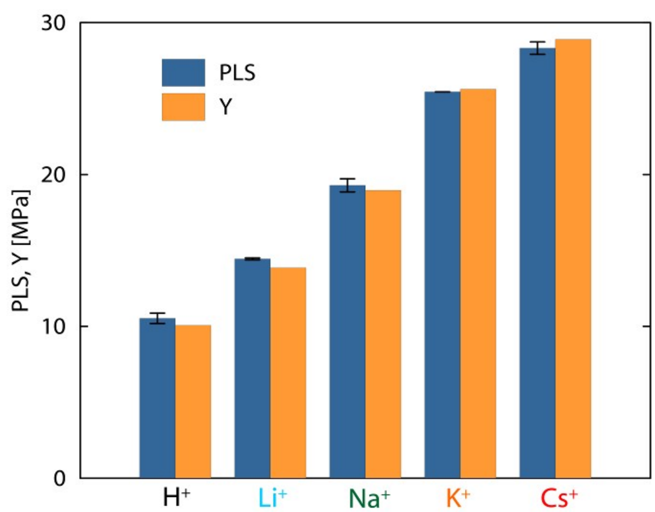

Figure S1 Comparison of PLS and Yield limit from the model.

2. Storage modulus and alpha-relaxation temperature

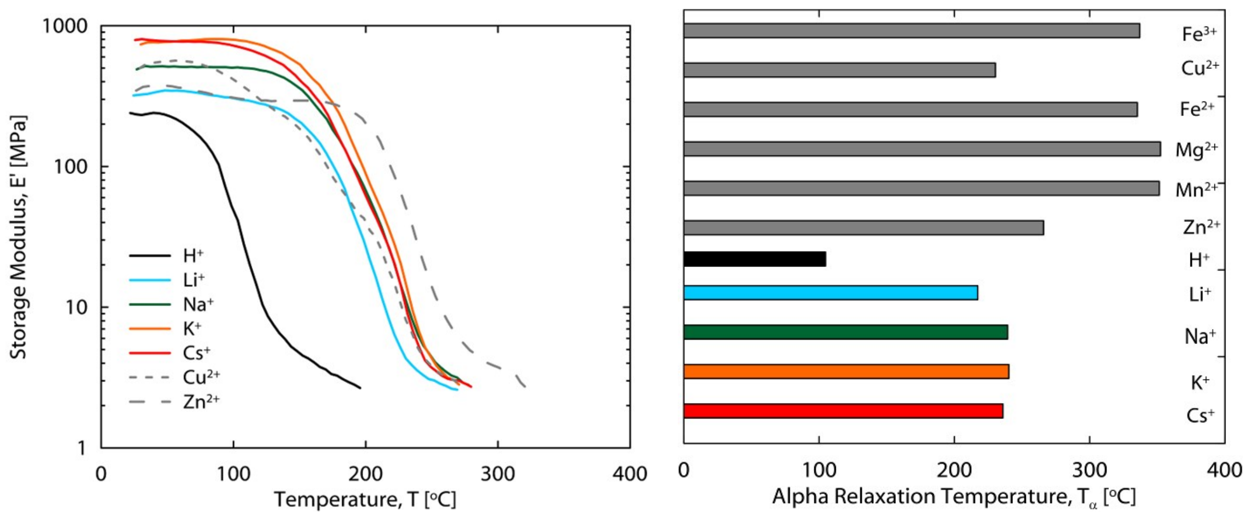

Figure S2 (a) Storage modulus of Nafion membrane in different cation forms as a function of temperature. (b) comparison of alpha-relaxation temperature. Part of data are reproduced from ref [1].

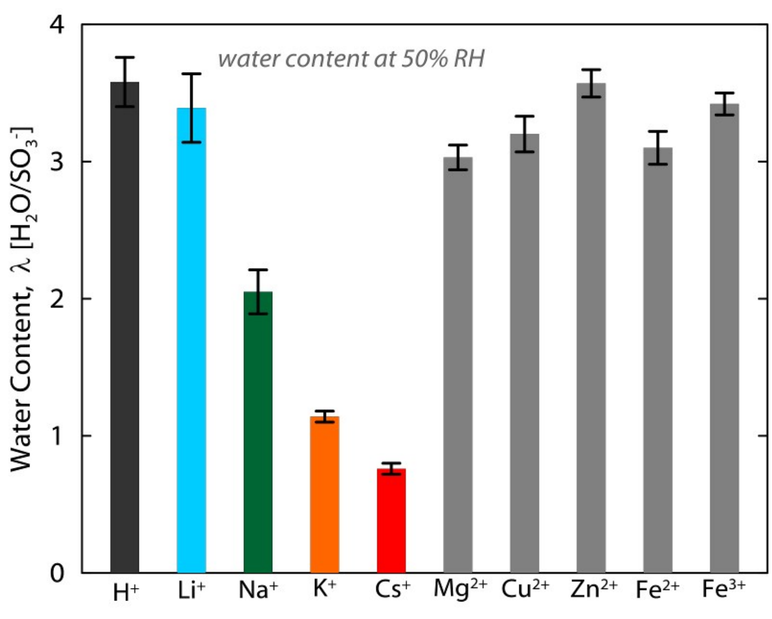

Figure S3 Comparison of water content at 25°C/50% RH, part of data are reproduced from ref [1]. The error bar indicates the average of water content during sorption and desorption.

Table S1 Water content of the ionomer during mechanical testing in various cation forms and the water within the hydration shell of the cations, taken from the literature.[2]

Cation	Weight Change [%]	Water Content [H_2O/SO_3^-]	Water within hydration shell [H_2O/ion][a]
H^+	5.86	3.58	4.8
Li^+	5.54	3.39	4.3
Na^+	3.36	2.05	2.9, 2.8[b]
K^+	1.86	1.14	1.5, 1.4[b]
Cs^+	1.24	0.76	1[b]
Mg^{2+}	4.96	3.03	6.9
Cu^{2+}	5.24	3.20	-
Zn^{2+}	5.84	3.57	-
Fe^{2+}	5.08	3.10	-
Fe^{3+}	5.59	3.42	-

[a] is from E. Glueckauf, Transactions of the Faraday Society, (1955)1235-1244. [b] Okada et al.[3]

3. Additional Information on Constitutive Models

Another model that could describe the large-strain non-linear deformation behavior of polymers is the Ogden model,[4] which derives a constitutive relation from the change in the strain energy density of a chain network upon stretching. For uniaxial tension, the true stress, σ_{true} can be described as:

$$\sigma_{true} = \sum_n \mu_n (\Lambda^{\alpha_n} + \Lambda^{-\alpha_n/2})$$

The fitting results are shown in Figure . where μ_n, α_n are empirical material parameters, and is the stretch ratio, $\Lambda = 1 + \varepsilon$. A least square fit of Ogden's model to experimental data of membranes in different cationic forms is performed using n = 2 in this study, and the fitting parameters as well as fitting results are shown in Table 1 and Figure S2. Good agreement is achieved between Ogden's model and experimental data. It is suggested that for a physically reasonable response, the inequality $\mu_n\alpha_n>0$ must hold,[4] which is satisfied by the obtained fitting parameters (Table 1). For pure shear, Eq. (1) yield $\sum\mu_n\alpha_n=2G$, where G is the shear modulus. Consequently, the elastic modulus of the cationic membranes can be estimated from the fitting parameters using the relation: $E=3(\mu_1\alpha_1+\mu_2\alpha_2)/2$. The estimated moduli are lower than measured Young's modulus, which might be due to the deviation from rubber elasticity theory at small strains. Nevertheless, macroscopic deformation of cation-exchanged Nafion membrane at large strains can be reproduced fairly well using these models.

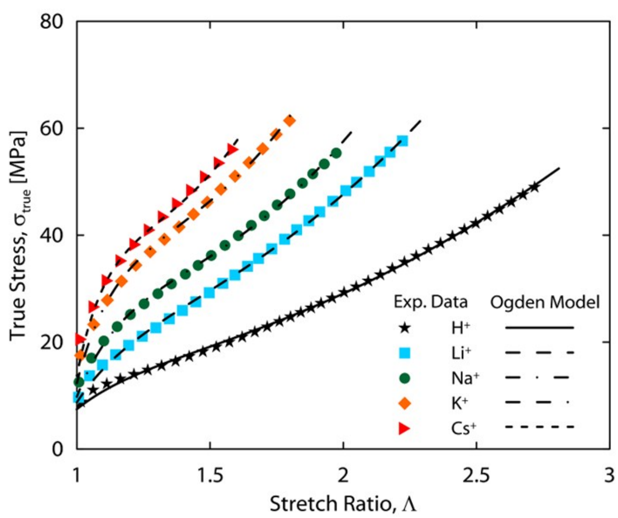

Figure S4 Stress-train response of membranes in different cationic forms measured via uniaxial tensile testing (symbols) and reproduced by Ogden's model (lines).

Table S2 Best-fit material parameters of the constitutive models that can reproduce the stress-strain response of Nafion in different cationic forms at 25°C.

	Ogden Model				Haward-Thackray Model	
Cation	μ_1 [MPa]	α_1	μ_2 [MPa]	α_2	Y [MPa]	G_T [MPa]
H^+	17.94	1.873	-14.21	-3.298	10.07	5.5
Li^+	30.39	2.001	-26.02	-3.478	13.86	9.74
Na^+	38.21	2.53	-33.32	-4.833	18.96	10.73
K^+	48.47	2.967	-42.29	-5.819	25.62	13.33
Cs^+	49.25	3.776	-42.39	-7.584	28.9	14.39

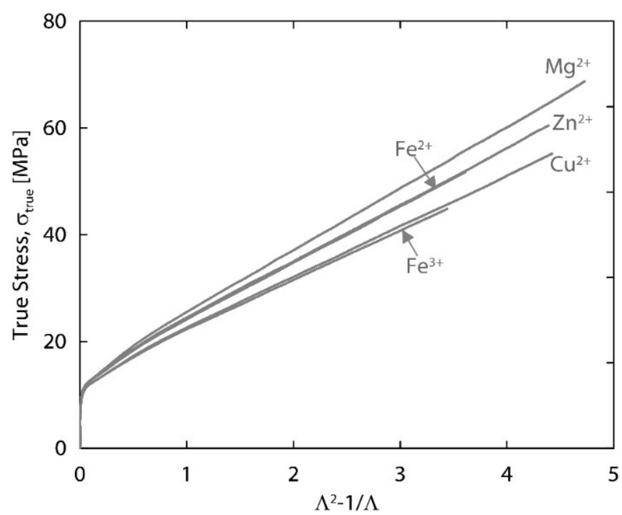

Figure S5 True stress as a function of stretch factor, Λ^2-1/Λ, for (a) monovalent cations and (b) multi-valent cations.

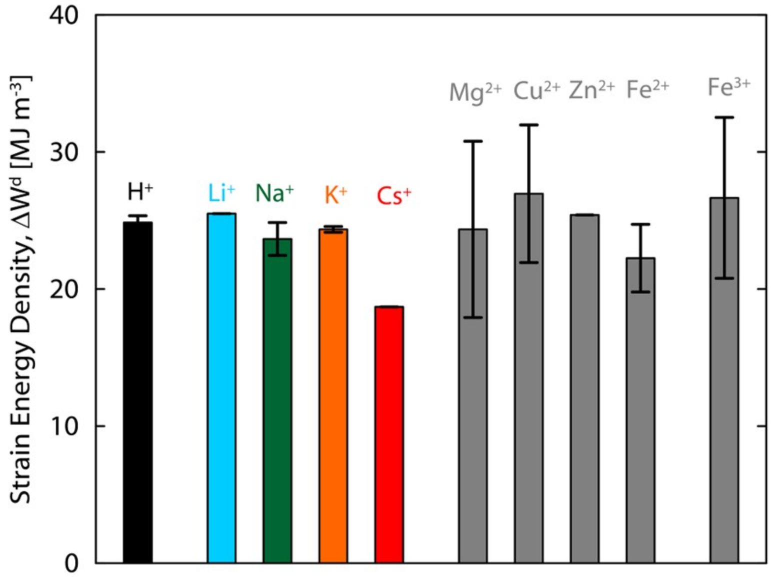

Figure S6 Comparison of strain energy density of Nafion membrane in different cationic forms.

References

1. S. Shi, A. Z. Weber and A. Kusoglu, *Electrochim. Acta*, 2016, **220**, 517-528.
2. E. Glueckauf, *T Faraday Soc*, 1955, **51**, 1235-1244.
3. T. Okada, G. Xie, O. Gorseth, S. Kjelstrup, N. Nakamura and T. Arimura, *Electrochim. Acta*, 1998, **43**, 3741-3747.
4. R. W. Ogden, *Proc R Soc Lon Ser-A*, 1972, **326**, 565-&.