

Supporting Information

In Situ Growth and Characterization of Metal Oxide Nanoparticles Within Polyelectrolyte Membranes

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A. MATERIALS AND EXPERIMENTAL METHODS

A.I. Materials:

Nafion-117 ionomer membrane with an equivalent weight of 1100 g/SO₃H was purchased from Ion Power, Inc. Salt reagents zinc nitrate (98%), cobalt(II) nitrate (98%), iron(III) nitrate (98%), nickel(II) nitrate(98.5%), magnesium(II) nitrate (98%), and sodium hydroxide (>97%) were purchased from Sigma-Aldrich.

A. II. Membrane Preparation:

For standard MONP-Nafion composite films, Nafion membranes were cut into 0.5 x 0.5 inch films about 200 μm in thickness, and soaked in 10 mL of an aqueous 0.05 M metal salt solution for 24 h at room temperature (RT). The membranes were then removed, rinsed in DI and placed in 0.5 M aqueous NaOH solution for a period of 6 h at 60 °C to promote hydrolysis towards the metal hydroxide. After 6 h, the films are removed from the NaOH solution and rinsed briefly in DI. The films are then placed in an empty vial for 24 h at 100 °C. The above procedure was repeated for the synthesis of the bulk metal oxide nanoparticles without the membrane by mixing equal volumes of 0.05 M metal salt with 0.5 M aqueous NaOH solution for 6 h at 60 °C. The particles are then filtered and rinsed and placed in the furnace for 24 h at 100 °C to induce oxidation of the MONP.

A. III. Characterization:

Scanning electron microscopy: Cleaved cross sections of the membranes were obtained by dipping them in liquid nitrogen for 30 sec prior to cutting. TEM was performed using a JEOL 1200EX transmission electron microscope. About 10 mg of metal-oxide powder was added to 1 mL of ethanol and sonicated for 5 minutes. After sonication, one drop of ethanol/MONP solution was added to a TEM copper grid (FORMVAR, 400 Mesh, carbon film coated copper grid, or FCF400-Cu from Electron Microscopy Sciences) and was left to air-dry. Analysis on TEM was done afterwards. SEM was performed with the Zeiss Sigma Field Emission SEM with Oxford EDS. X-ray diffraction patterns were obtained by using a wide angle Philips XPert system. The same procedure was used for the HAADF-STEM images, albeit lacey carbon TEM grids were employed and was performed using a Nion UltraStem equipped with an aberration corrector,

which allows us to obtain spatial resolution down to $\sim 1 \text{ \AA}$ at an operating voltage of 60 kV. The condenser lens system was set to produce an illumination probe semi-angle of 35 mrad and a beam current of $\sim 10\text{--}20 \text{ pA}$.

WAXRD patterns were obtained by the Philips XPert system. For the XRD analysis, a baseline correction was applied to each pattern, limited to the range involving the three primary peaks. Baseline corrections were applied at the base of each peak. Absorption and transmission measurements were performed using a Photonics CCD Array UV-vis spectrometer

A large broad peak at low angles, spanning several tens of angles can be seen that is attributed to instrumental effects. At angles of 2Θ between 25 to 55 degrees, the observed broadening is attributed to the amorphous polymer host. These factors somewhat affect the heights of the 3 primary peaks corresponding to the dominant surface planes of zinc oxide. In addition, broadening of individual peaks is also observed throughout the XRD pattern arising from a convoluted number of factors such as lattice strain, particle size, orientation, and possible dislocations and stacking faults.¹

Absorption and transmission measurements were performed using a Photonics CCD Array UV-vis spectrometer and using the model of Pesika et al.² Briefly, the authors use an effective mass model for spherical particles with a Coulomb interaction term³ where the bandgap E^* [eV] can be approximated by:

$$E^* \cong E_g^{Bulk} + \frac{\hbar^2 \pi^2}{2er^2} - \left(\frac{1}{m_e m_0} + \frac{1}{m_h m_0} \right) - \left(\frac{1.8e}{4\pi\epsilon\epsilon_0 r} \right) \quad (1)$$

Where E_g^{Bulk} is the bulk bandgap, r is the particle radius, m_e is the effective mass of the electron, m_h is the effective mass of the holes, m_0 is the free electron mass, ϵ is the relative permittivity, ϵ_0 is the permittivity of free space, \hbar is Plank's constant, and e is the charge of the electron. Parameters for ZnO are given by: $E_g^{Bulk} = 3.2 \text{ eV}$, $\epsilon = 8.5$, $m_e = 0.26$, and $m_h = 0.59$.

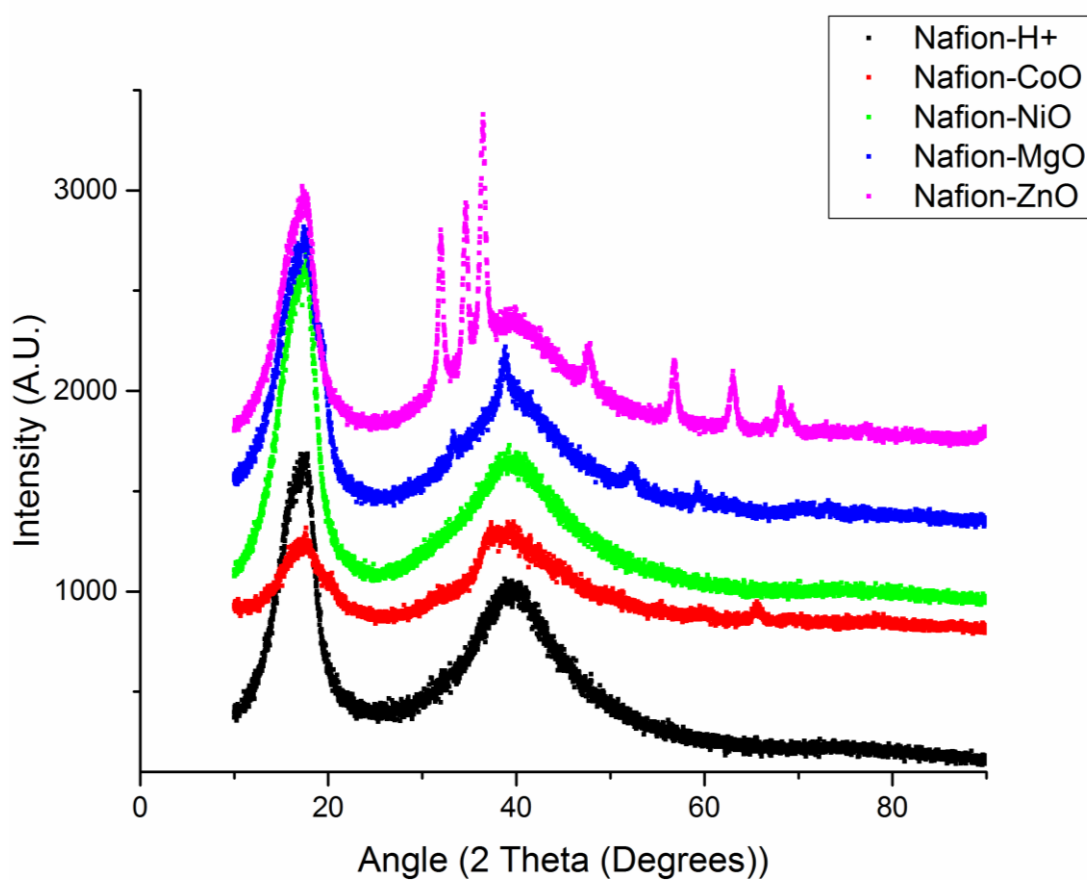
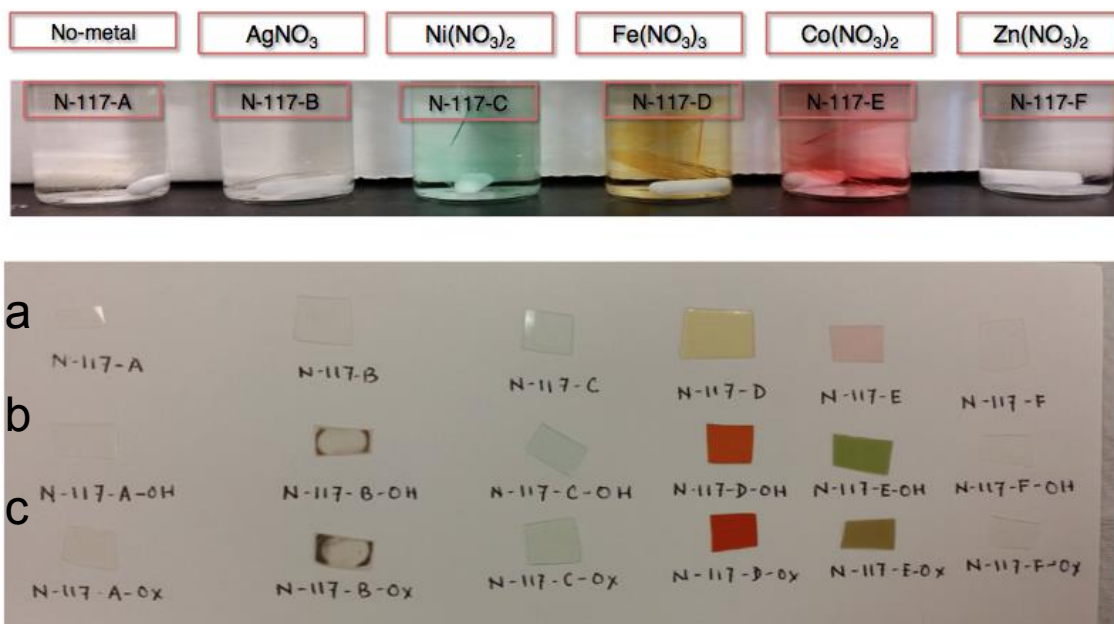


Figure S1: Top image: Top row: impregnated Nafion films in different metal nitrate salts. (a) Nafion membranes after ion exchange step. (b) Nafion membranes after hydrolysis step. (c) Nafion membranes after condensation step. Suffix -OH and -OX stand for metal hydroxide and metal oxide, respectively. Bottom Graph: XRD pattern of different metal oxides synthesized in situ.

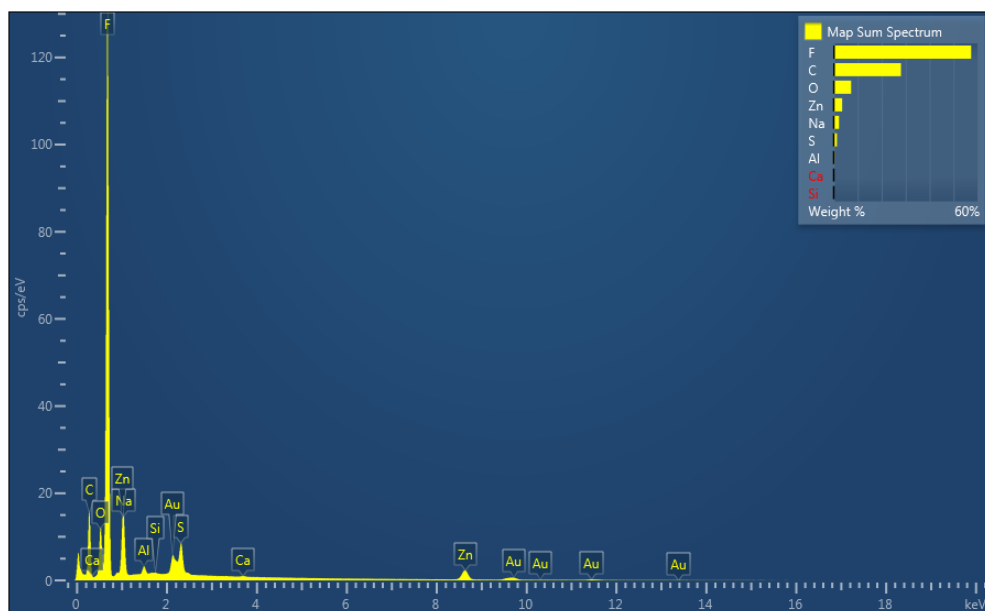


Figure S2: Electron diffraction spectroscopy (EDS) of a Nafion cross section displayed in Figure 2c in the manuscript.

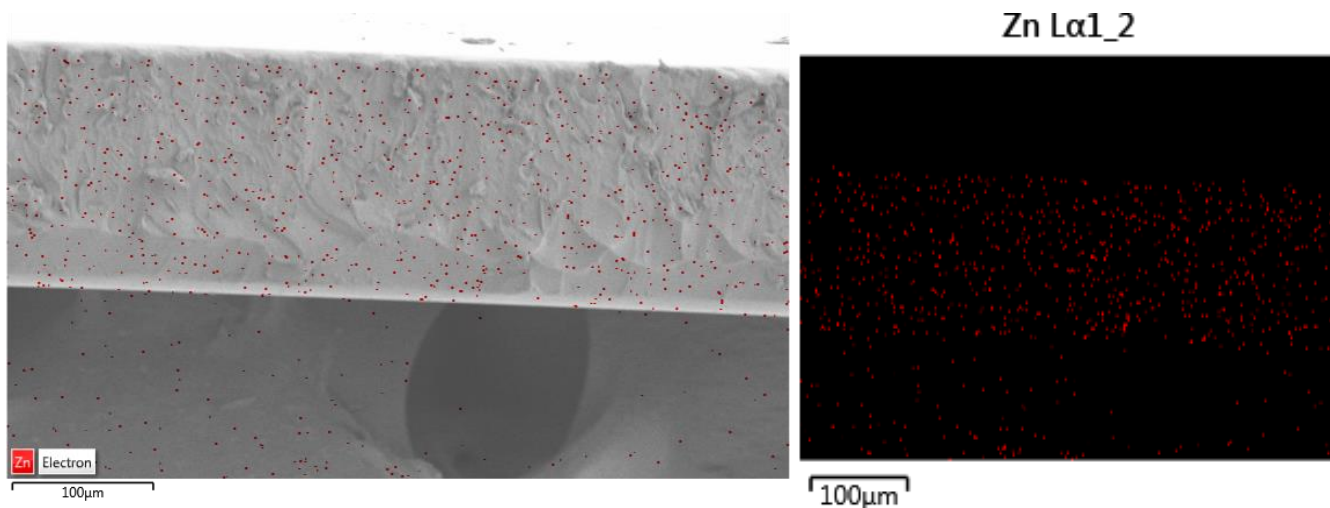


Figure S3: SEM/EDX of the ZnO/Nafion membrane edge uncut. (Left) The edges lack the high concentration of Zn that results from deformation upon cutting. (Right) EDX mapping only. Zinc seen on the carbon tape arises from ZnO particles on the surface of the ZnO/Nafion composite that were transferred during specimen preparation.

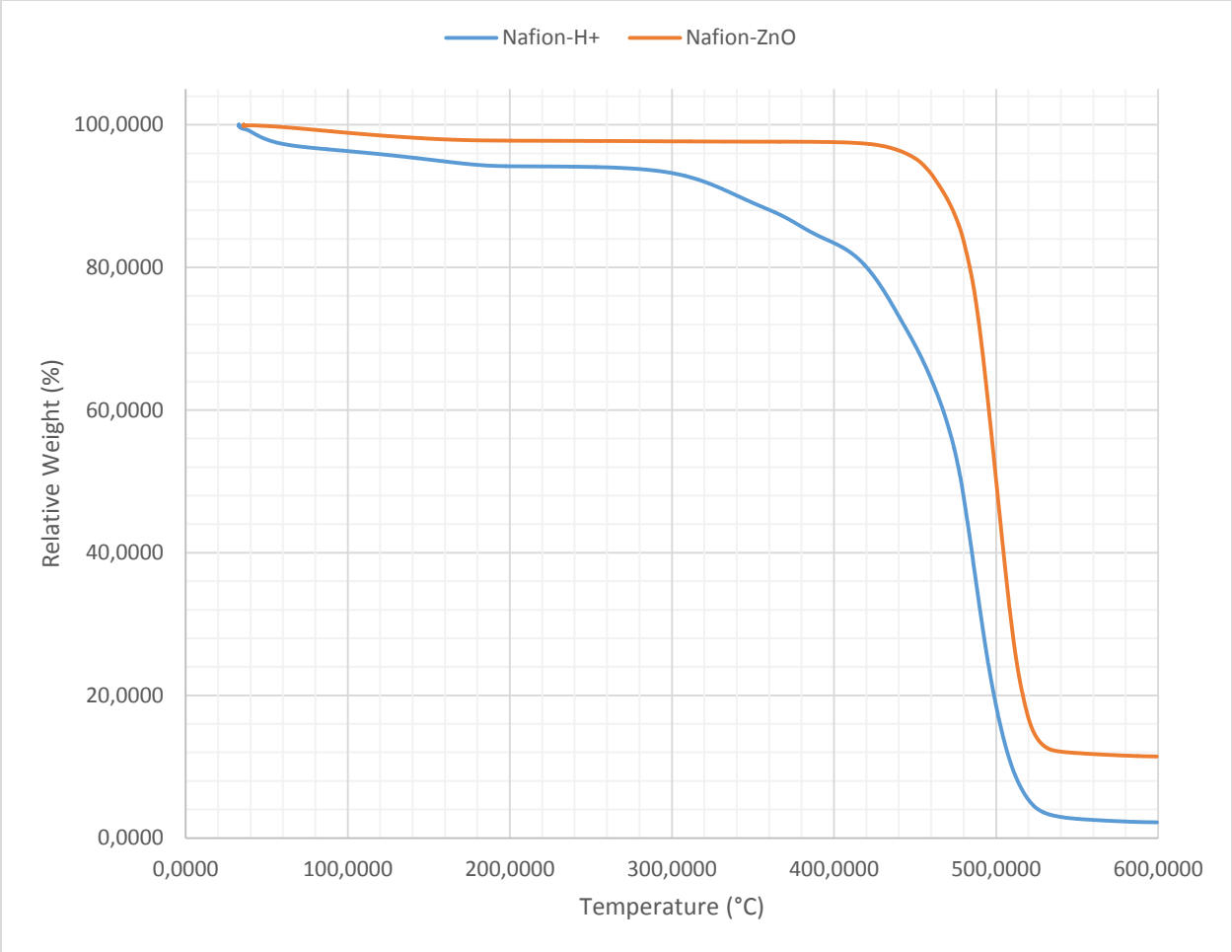


Figure S4: Thermogravimetric analysis (TGA) traces of the ZnO-Nafion films grown from a 0.05 M Zn(NO₃)₂ solution.

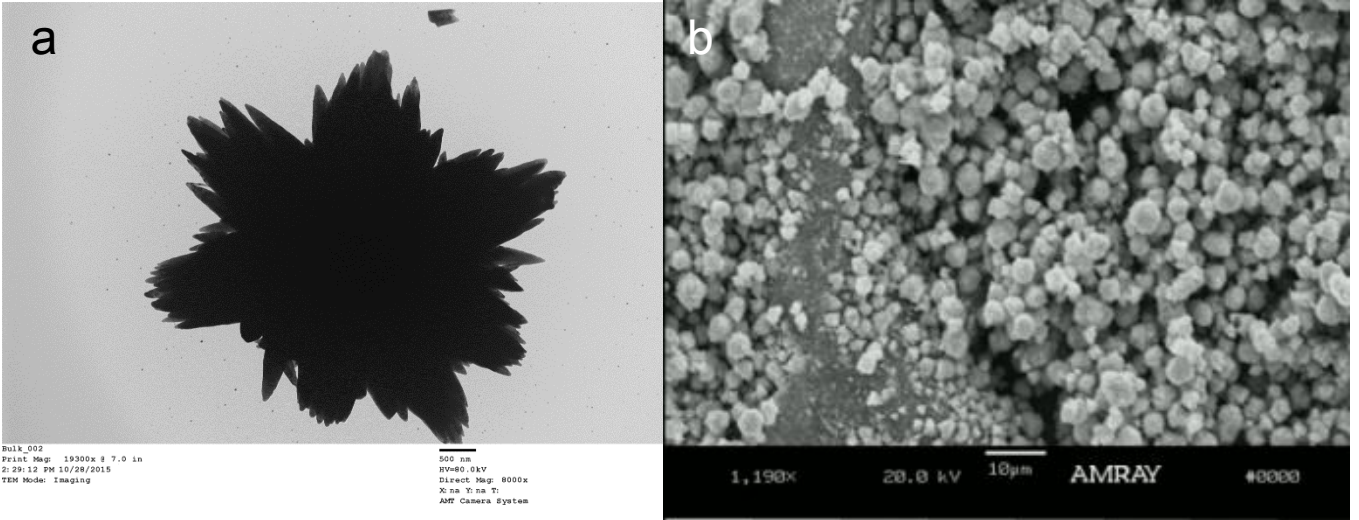


Figure S5: (a) TEM image of zinc oxide nanoparticle prepared in bulk and without the Nafion-117 host membrane. (b) SEM image of the bulk nanoparticles.

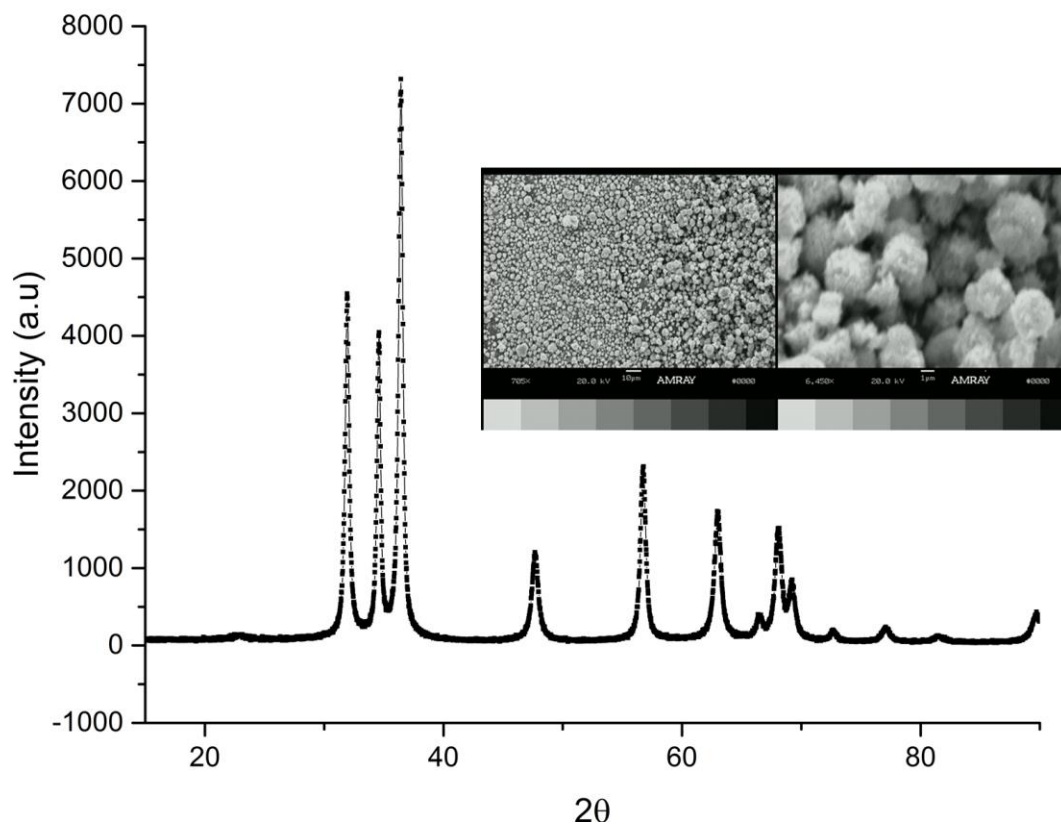


Figure S6: XRD of the bulk zinc oxide prepared without the Nafion-117 membrane. Inset shows the SEM images of the zinc oxide powder.

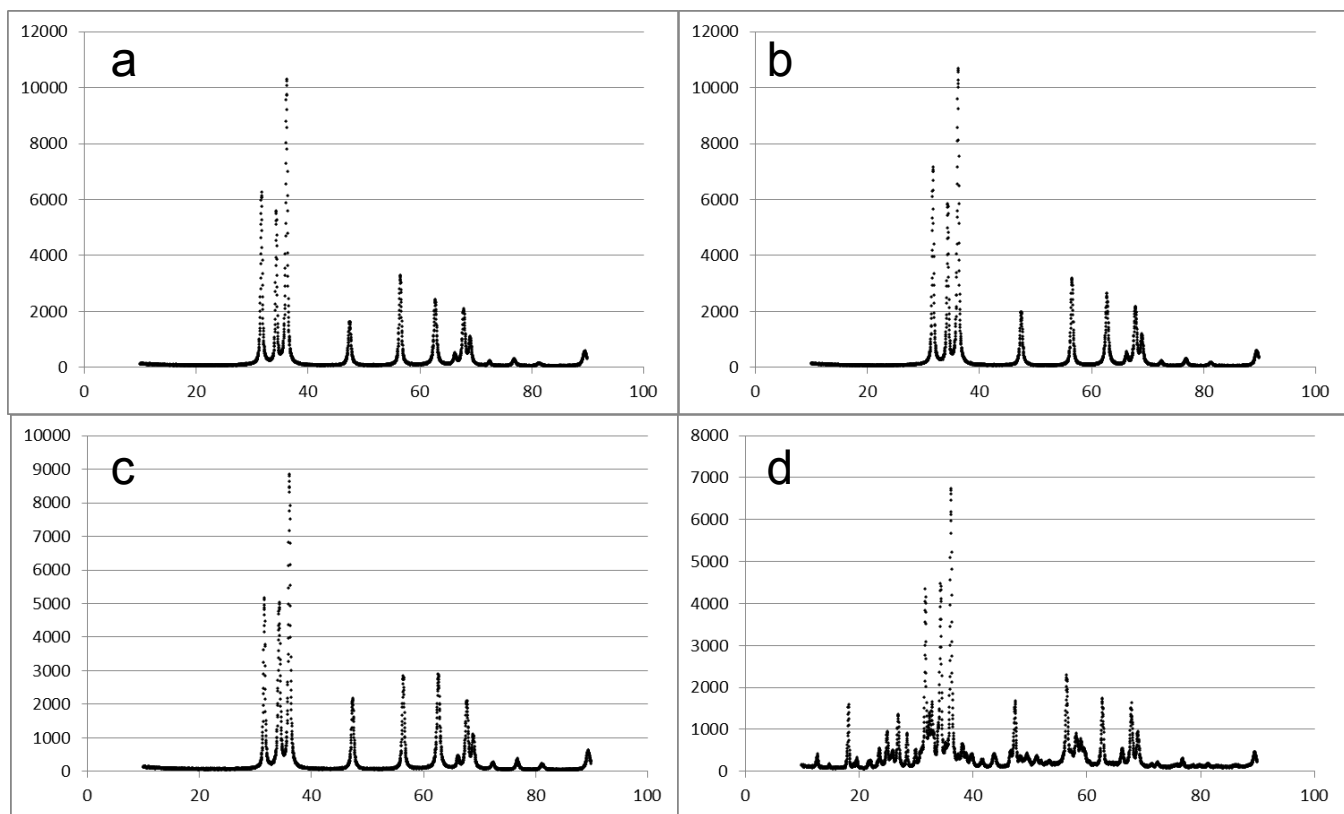


Figure S7. Bulk synthesis of ZnO with 2-propanol. (a) 20% (b) 40% (c) 60% and (d) 80%. Y-axis is intensity (a.u.) and X-axis is 2θ .

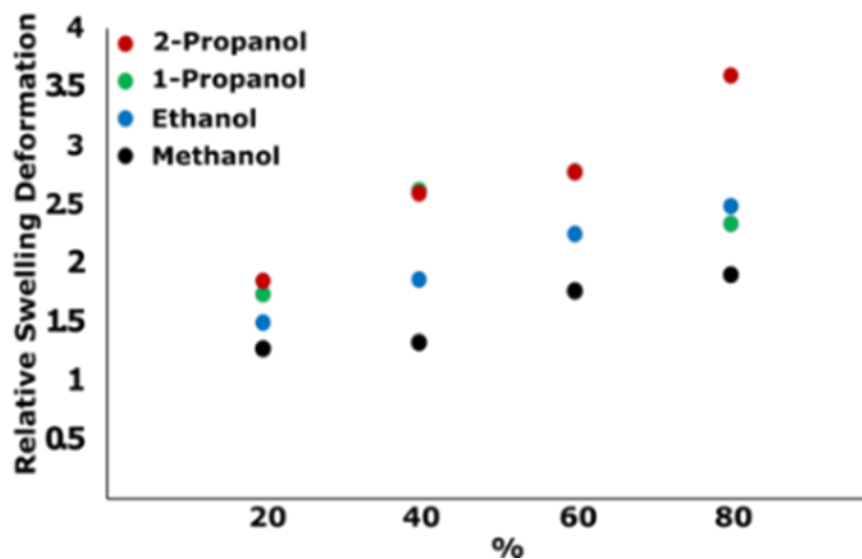


Figure S8: Swelling behavior of Nafion-117 film prepared in different alcohols at different concentrations. Film dimensions were measured after the impregnation of the metal salt.

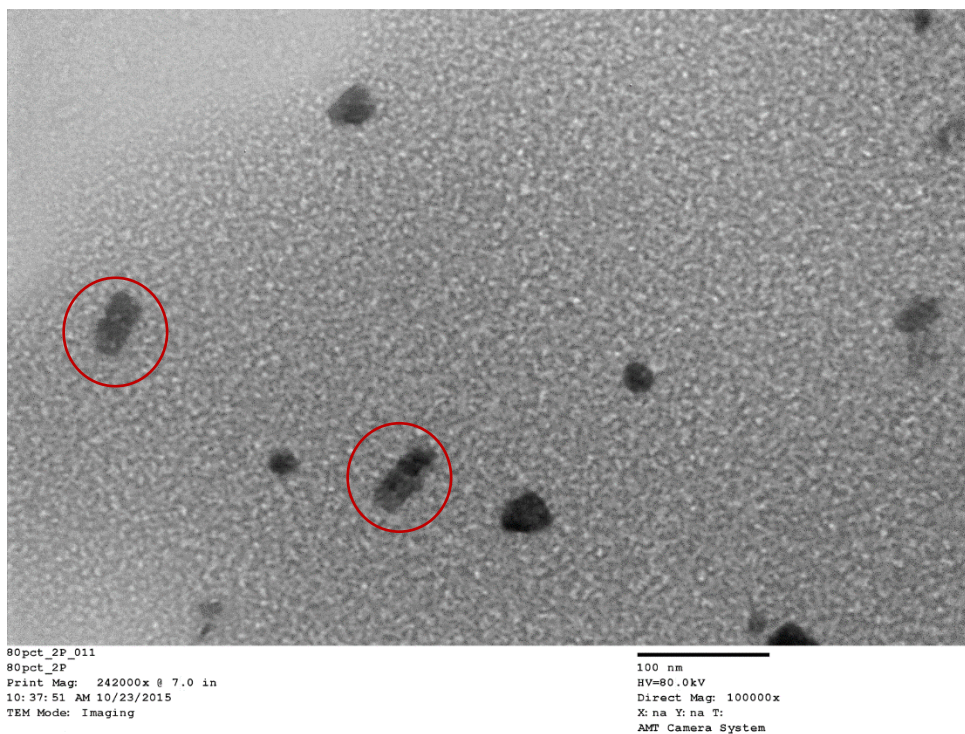


Figure S9: TEM images showing the twinning of two particles grown in adjacent hydrophilic domains in Nafion 117 membrane. Films were prepared in a 80% 2-propanol/water binary mixture.

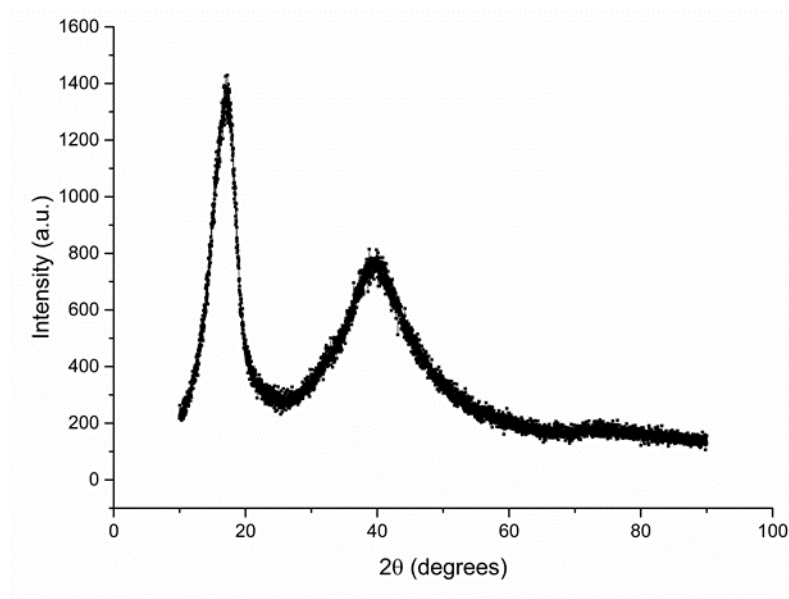


Figure S10: XRD pattern of MONP-Nafion composites synthesized without the inclusion of water.

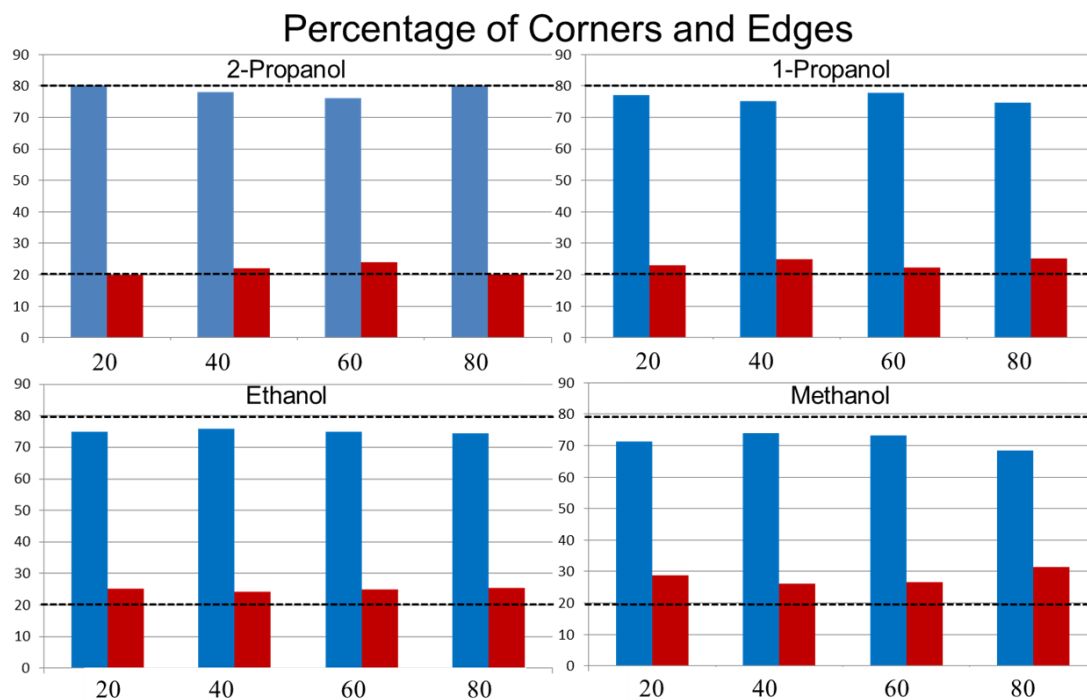


Figure S11: XRD analysis of films prepared with different alcohols at different concentrations. Blue column represents the accumulated peak intensities for the {100}, {002} and {100} planes. Red column represents the peak intensities for the {102}, {110}, {103} and {112} planes. The top dotted line marks the 80% mark for the cumulative portion while the bottom dotted line marks 20%.

B. SIMULATIONS METHODS:

Dissipative particle dynamics (DPD) simulations were performed in accordance with procedures followed in ref⁴

B. I. Relative volumes of the beads

Table S1.

Bead	W	C	E	S	S [□]
Fragment	(H ₂ O) _{4.5}	(-CF ₂ -) ₄	-O-CF(CF ₃)-	(-CF ₂ -) ₂ SO ₃ K	(-CF ₂ -) ₂ SO ₃ ⁻

			CF2-O		
Σr_i ^(a)	4.14	4.04	3.67		
Representative compound ^(b)	H ₂ O	H(CF ₂) ₄ H	CF ₃ OCFOCF ₂ H	H(CF ₂) ₂ SO ₃ K	H(CF ₂) ₂ SO ₃ ⁻
V_{COSMO}	29.1	141.1	112.7	124.2	140.7
Effective volume, Å ³	134.5	131.3	117.1	119.3	136.5

(a) sum of volume parameters r_i for the functional group forming the fragment

(b) molecule, for which the COSMO volume was calculated using PQS ab-initio; correspondingly V_{COSMO} is the volume of the molecule, rather than the bead volume

B. II. Details of MD simulations for DPD parameter fitting

The simulation procedures were similar to those employed in refs. ⁵ We used MDynaMix ⁶ software package. In the initial configuration, molecules were arranged in a lattice order at a low density of 0.005 g/cm³. The system was then gradually contracted in a series of constant-temperature MD simulations at $T = 303\text{K}$ maintained by a simple velocity scaling. After the density of 1.0g/cm³ (aqueous solutions) or 1.7 g/cm³ (perfluorohexadecane) was achieved, the simulation proceeded at a constant pressure $P = 1\text{atm}$. T and P were maintained by the Nose-Hoover thermostat. ⁷ System equilibration was performed for 200 ps followed by additional 10 to 1 ns MD simulation, over which the system configuration was periodically saved to disc for analysis. The distribution of distances between the beads in DPD simulations were fitted to the distances between the centers of mass of the corresponding fragments (see Table 1 in

the main text and Table S1). In order to maintain symmetry in Nafion model, we assumed that some fluorocarbon groups were divided between the two neighboring beads. In particular, the location of bead C1 from the MD trajectories of the Nafion fragment shown in Figure S1(a) was calculated as

$$\mathbf{r}_{C1} = (\mathbf{r}_3 * M_{CF} + \mathbf{r}_2 * M_{CF2} + \mathbf{r}_4 * M_{CF2} + 0.5 * \mathbf{r}_1 * M_{CF2} + 0.5 * \mathbf{r}_5 * M_{CF2}) / (M_{CF} + 4 * M_{CF2})$$

The indexes of fluorocarbon groups are also shown in the Figure.

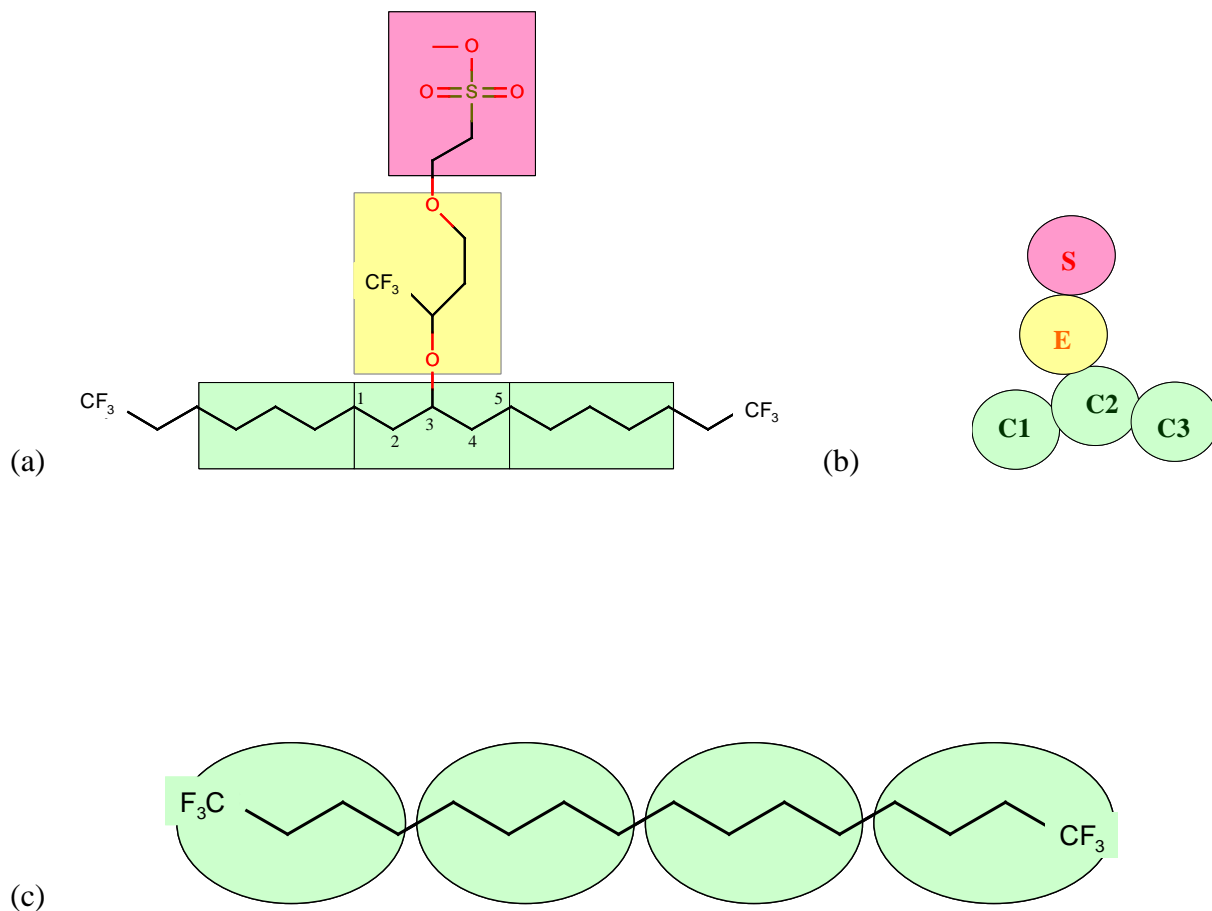


Figure S12. (a) Nafion fragment modeled in aqueous solution by molecular dynamics in order to obtain distribution of distances between the bead centers (b) coarse-grained model of Nafion fragment simulated by DPD (3) molecular and coarse-grained models of perfluorohexadecane.

B. III. Details of DPD simulations.

Nafion was presented by oligomers each containing 20 monomers. Bead density $\rho^*R_c^3$ in the system was set to 3, a common choice for aqueous solutions. The random force, which accounts for thermal fluctuations, is taken proportional to the conservative force that is also acting along the vector between the bead centers: $\mathbf{F}_{ij}^{(R)}(r_{ij}) = \sigma w^R r_{ij} \theta_{ij}(t) \mathbf{r}_{ij}$, where $\theta_{ij}(t)$ is a randomly fluctuating in time variable with Gaussian statistics. The drag force is velocity-dependent: $\mathbf{F}_{ij}^{(D)}(\mathbf{r}_{ij}, \mathbf{v}_{ij}) = -\gamma w^D(r_{ij}) (\mathbf{r}_{ij} \cdot \mathbf{v}_{ij})$, where, $\mathbf{v}_{ij} = \mathbf{v}_j - \mathbf{v}_i$, \mathbf{v}_i and \mathbf{v}_j are the current velocities of the particles. We assume the common relationship between the drag and random force parameters $w^D(r) = [w^R(r)]^2$. σ and γ are parameters that determine the level of energy fluctuation and dissipation; they are related as $\sigma^2 = 2\gamma kT$ that allows to maintain constant temperature in the course of simulation. We assumed $\gamma = 4.5$, a common value fitted to the diffusion coefficient of water. In the initial configuration, all beads were assigned random locations in the box. Starting from this random configuration, we performed a steepest descent energy minimization taking in account only harmonic bond and short-range conservative forces. The minimization was followed by 10000 step preliminary MD simulation ($\gamma = 0$, no drag or random forces) at temperature fixed by velocity scaling on each step. DPD simulations started from the final configuration obtained in that preliminary MD run. In-house DPD program was used.

B. III.A. Simulations of Nafion fragments employed in forcefield fitting.

The systems exactly mimicked the MD simulations (Table S2). Simulations were 150000 DPD steps long, time step in reduced time units was $0.02(m_w R_c^2/kT)^{1/2}$. First 50000 steps were discarded. After that the coordinates of all beads except solvent beads were dumped to disk every 100 steps. The distributions of intramolecular distances and angles were calculated from this trajectory. In first simulations, we used reasonable bond parameters approximately evaluated from average distances and dispersions obtained in MD simulations. Then, the bonds were optimized from one simulation to another in order to improve the agreement with the MD results similarly to ref ⁸

B. III.B. Simulations of hydrated Nafion

Nafion was presented by oligomers each containing 20 monomers. Simulations were conducted in cubic boxes of $30R_c$ (22.3nm) in size, the total number of beads was around 81000 in each simulation. The total numbers of beads of each type is given in the table at the bottom of this section. On the minimization and preliminary scaled-velocity MD stages, all beads were uncharged. Before DPD simulations started, S beads were converted to S- (at low hydration, the beads for conversion were chosen randomly), and randomly chosen W beads were converted to M+ beads, according to the targeted system composition. The total number of DPD steps was 800000 in each simulation. The initial configuration was created by placing all beads at random coordinates within the simulation box. Then the energy was minimized using a primitive steepest descent algorithm, which led to a segregated system with small hydrophilic clusters of several W, S and M beads. The minimization was followed by 10000 step preliminary MD simulation ($\gamma = 0$, no drag or random forces) at temperature fixed by velocity scaling on each step. DPD

simulations started from the final configuration obtained in that preliminary MD run. DPD simulations were started from these configurations. First 200000 DPD steps were performed with no long-range correction (electrostatic interactions were cut off at $5R_c$), and after that, Ewald summation was turned on to account for the long-range electrostatics. The structural evolution was characterized using the number of overlapping pairs of mobile (W and M+) beads as a criterion. The initial portions of each trajectory characterized by a persistent upward trend (about 400000 steps) were discarded. Over the last 400000 steps, the system configuration was dumped to disk every 1000 steps. In so doing, we collected 400 configurations for structural analysis and the calculation s of chemical potentials of water via Widom insertions.

Table S2. Numbers of beads of different types in each simulation. The number of M⁺ (hydrated counterion) beads equals the number of S⁻ beads. There were no W beads in all simulations for $\lambda=2.24$

$\lambda =$	2.2			4.5			6.8		
PEW	S-	S	C	S-	W	C	S-	W	C
945	11172	6284	52371	15511	3447	46532	17153	12388	51459
1145	9191	5170	57447	13018	2893	52071	14155	10223	56621
1345	7807	4392	60994	11215	2492	56077	12050	8702	60248
1745	6000	3375	65625	8783	1952	61482	9287	6707	65006

9.0			13.5			18.0		
S-	W	C	S-	W	C	S-	W	C
15511	18957	46532	13018	28929	39054	11215	36138	33646
13018	15911	52071	11215	24923	44862	9851	31743	39405
11215	13708	56077	9851	21892	49257	8783	28301	43916
8783	10735	61482	7924	17609	55467	7218	23257	50525

III. C. Electrostatic interactions: comparison between smeared and point charges.

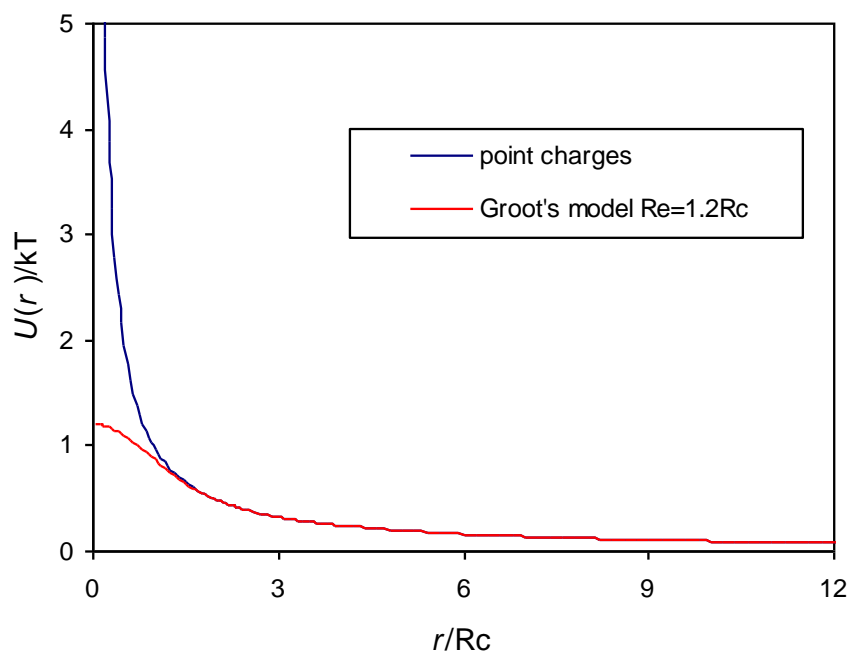


Figure S13. Comparison of electrostatic potential between two $+e$ point charges and linearly smeared charges with smearing radius of $R_e=1.2R_c$ in a dielectric medium of $\epsilon_r = 78$, which corresponds to water at room temperature.

B. IV. Water sorption and diffusion in hydrated Nafion

Table S3. Main results.

$\lambda =$	9			13.5			18		
PEW	$m_W/m_{pol}, \%$	$\phi_W, \%$	D_W/D_{pure}	$m_W/m_{pol}, \%$	$\phi_W, \%$	D_W/D_{pure}	$m_W/m_{pol}, \%$	$\phi_W, \%$	D_W/D_{pure}
945	16.5	28.6	0.12	24.7	37.5	0.11	32.9	44.4	0.04
1145	13.7	25.0	0.014	20.5	33.3	0.009	27.4	40.0	0.002
1345	11.7	22.2	0.0009	17.6	30.0	0.0002	23.4	36.4	0
1745	9.1	18.2	0	13.6	25.0	0	18.2	30.8	0
$\lambda =$	2.24			4.5			6.75		
PEW	$m_W/m_{pol}, \%$	$\phi_W, \%$	D_W/D_{pure}	$m_W/m_{pol}, \%$	$\phi_W, \%$	D_W/D_{pure}	$m_W/m_{pol}, \%$	$\phi_W, \%$	D_W/D_{pure}
945	4.1	9.1	0.001	8.2	16.7	0.011	12.3	23.1	0.062
1145	3.4	7.7	0	6.8	14.3	0.0029	10.3	20.0	0.0087
1345	2.9	6.6	0	5.9	12.5	0.0002	8.8	17.6	0.0019
1745	2.3	5.2	0	4.5	10.0	0.0001	6.8	14.3	0.0006

m_W/m_{pol} are calculated assuming K^+ as cation

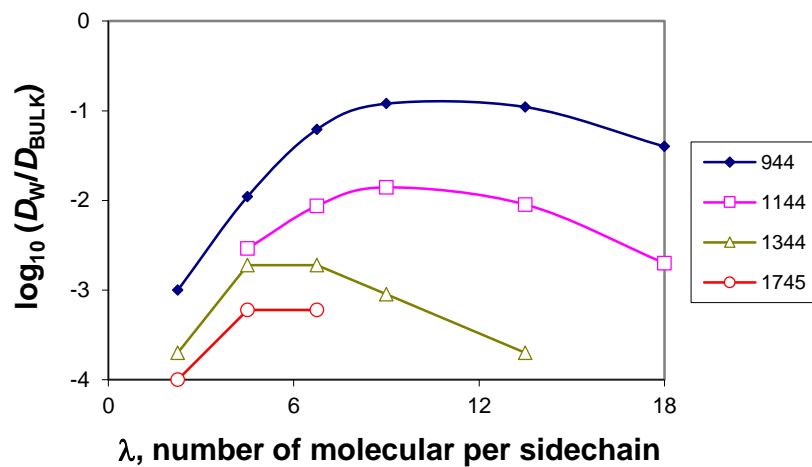


Figure S14. Self-diffusion coefficient of water in hydrated Nafion reduced to the diffusion coefficient of pure water for polymers of hydration level λ .

C. LITERATURE REVIEW OF WORKS DEMONSTRATING THE IN SITU GROWTH OF AN INORGANIC PHASE WITHIN NAFION AND RELATED POLYMERS

First Author	Inorganic Phase	Comments	Precursor	Recommended Application	
Ai	Pt np			H ₂ O ₂ sensor	9
Alberti				PEMFC	10
Amiinu	Silica			PEMFC	11
Amjadi	TiO ₂		Tetraethylortotitanate	PEMFC	12
Amjadi	SiO ₂			PEMFC	
Babu	PbS			Quantum dots	13
Baradie	SiO ₂		Tetraethoxysilane (TEOS)	PEMFC	14
Cele		Review Paper		PEMFC	15
Chalkova*	ZrO ₂ , SiO ₂			PEMFC	
Chaundhury	SiO ₂	Studied the IEC, water upatake and ion exchange isotherms of Na ⁺ & Cs ⁺ and Na ⁺ & Ba ²⁺ binary systems	Tetraethoxysilane (TEOS)		16
Chen	SiO ₂		Tetraethylorthosilicate	PEMFC	17
Chen	Zeolite Beta	Hydrothermal crystalization		DMFC	18
Chi	ZnO nanorods	Grown ZnO rods first, then cast Nafion, then etched away ZnO.		PEMFC	19
Choi	MWNT/ZnO		Tris(2,2'-bipyridyl) ruthenium(II)	Chemiluminescence sensor	20
Choi	ZrO ₂	Proton transport properties		PEMFC	21
Choi*		Review		DMFC	22
Chowdhury		POM filtration		Filtration membranes	23
Colicchio	SPEEK/PWA			DMFC	24
Cui	Chitosan/heteropol yacid			DMFC	25
Daiko	TiO ₂ /SiO ₂		Si(OC ₂ H ₅) ₄ and Ti(OC ₄ H ₉) ₄		26

Daiko		Hygroscopic oxides	Si(OC ₂ H ₅) ₄ and Ti(OC ₄ H ₉) ₄	DMFC	27
Daiko	phenylsilsequioxane	Nafion/PDDACl			28
Damay	SiO ₂ , ZrP	H ₃ PO ₄ , H ₃ PW ₁₂ O ₄₀ Transport properties		PEFC	29
Deng	SiO ₂		Tetraethoxysilane (TEOS)		30
Deng	SiO ₂		Tetraethoxysilane (TEOS) & diethoxydimethylsilane (DEDMS)		31
Deng	SiO ₂	SAXS studies			32
Deng	SiO ₂	Fluorescence probe investigations			33
Deng	SiO ₂				34
Deng	SiO ₂	TGA studies	Tetraethoxysilane & diethoxydimethylsilane		35
Doyle***	SWNT/Fe ₂ O ₃	Redox and oxygen evolution studies		Redox	36
Dresch	SiO ₂	SAXS/Neutron; prepared in different solvents		PEMFC	37
Dupuis		Review		PEMFC	38
Hill	ZrP	disulfonated poly(arylene ether sulfone)		DMFC	39
Huang	Pt			Non-enzymatic glucose sensing	40
Ingle (2014)	Pt nanorods	Pt(NH ₃)(4)(NO ₂)(2)		Catalysts for electrochemical devices	41
Jalani	ZrO ₂ , SiO ₂ , TiO ₂			High Temp. PEMFC	42
Jiang	SiO ₂		Tetraethylorthosilicate (TEOS)	DMFC	43

Jian-hua	TiO ₂		Ti (OC ₄ H ₉) ₄	PEMFC	44
Jung	SiO ₂		Tetraethylorthosilicate (TEOS)	DMFC	45
Kang	Strontium hydroxide			DMFC	46
Ke	SiO ₂				47
Ke	SiO ₂	Particle size			48
Kim	Fluoroalkylsilane			Fuel cell operations tests	49
Kim	SiO ₂				50
Kim	Alumina			PEMFC	51
Kim	Pd			DMFC	52
Kim	SiO ₂	Proton conductivity and MeOH permeation	Tetraethylorthosilicate (TEOS)		53
Klein	SiO ₂	Review		PEM	54
Klein		Review		PEM/DMFC	
Korin		Review		Fuel Cells	55
Kumar	Au	Anion exchange	HAuCl ₄		56
Kumar	Ag	Poly(perfluorosulfonic) acid membrane			57
Kumar	Pt	Anion exchange membranes	PtCl ₆ ²⁻		58
Laberty-Robert		Review			59
Ladewig	SiO ₂		Methyldimethoxysilane	DMFC	60
Lavorgna	Siloxane	Sulfonated polystyrene			61
Lavorgna	Siloxane		Tetraethoxysilane and a mercaptan functionalized organoalkoxysilane		62
Lee	SiO ₂		3-mercaptopropyltrimethoxysilane precursor		63
Lee	SiO ₂				64

Lee	Pt	Cation exchange, 3 wt%	3-mercaptopropyltrimethoxysilane precursor		65
Li	SiO ₂			DMFC	66
Lin	Amino-SiO ₂			Vanadium redox flow batteries	67
Ludvigsson*** *	Mn ₃ O ₄ , LiCoO ₂				68
Matos	TiO ₂			DEFC	69
Matos	Titanate nanotubes			DEFC	70
Matos	TiO ₂			DEFC	71
Mauritz	SiO ₂ , TiO ₂ , aluminum , zirconium , organoalkoxysilanes	Review			72
Maurtiz	SiO ₂				73
Maurtiz	SiO ₂		Silicon alkoxides		74
Maurtiz	SiO ₂ , TiO ₂ , aluminum , zirconium , organoalkoxysilanes	Review			75
Millet	Pt				76
Mistry	SiOP**			PEM	77
Mohammadi	ZrO ₂ - TiO ₂	75 nm in mean size		PEMFC	78
Nazir	Waterwheel			PEMFC	79

	supramolecules				
Norgaard	SnO ₂	XRD, TGA	SnCl ₂		80
Parasuraman	Carbon nanorice			Fluorescence	81
Park	Ni			Sensor/Actuators	
Patil	Ag	poly (perfluorosulfonic acid)			82
Patil	TiO ₂	Durability testing	Titanium isopropoxide	PEMFC	83
Patil	TiO ₂	Durability Testing	Titanium isopropoxide	PEMFC	84
Patil	TiO ₂	Durability Testing		PEMFC	85
Patil	TiO ₂	Quasi networks			86
Patra	Ag	Studied different sizes and shapes			87
Patra	Ag				88
Patra	Ag	Borohydride reuction of a model dye methylene blue.		Catalyst	89
Raymond	Fe ₂ O ₃				90
Robertson	SiO ₂		Tetraethylorthosilicate	PEMFC	91
Rodgers	SiO ₂			PEMFC	92
Shao	SiO ₂ -TiO ₂				93
So	SiO ₂ -P ₂ O ₅		Tetraethoxysilane (TEOS) and trimethylphosphate (TMP)	PEMFC	94
Song	Zirconium hydrogen phosphate nanoparticles				95
Sun	Ag				96
Suresh	PbS				97
Teng	TiO ₂			Vanadium redox flow	98

				batteries	
Teng	SiO ₂		Tetraethoxysilane (TEOS) and diethoxydimethylsilane (DEDMS)	Vanadium redox flow batteries	⁹⁹
Teng	SiO ₂		Tetraethoxysilane (TEOS)	Vanadium redox flow batteries	¹⁰⁰
Tripathi		SPEEK-MO ₂ -PANI (M = Si, Zr and Ti)		DMFC	¹⁰¹
Wang	ZnO				¹⁰²
Young	SiO ₂		Tetraethoxysilane (TEOS)		¹⁰³
Young	SiO ₂		Tetraethoxysilane (TEOS)		¹⁰⁴
Young	SiO ₂	Mechanical testing	Tetraethylorthosilicate and semiorganic silicon alkoxide monomers		¹⁰⁵
Young	SiO ₂		Tetraethylorthosilicate (TEOS) and semiorganic R'Si-n(OR)(4-n) co-monomers		¹⁰⁶
Yu	SiO ₂	Polytetrafluoroethylene (PTFE)	Tetraethoxysilane (TEOS)	PEMFC	¹⁰⁷
Yu	SiO ₂		Tetraethoxysilane (TEOS)	PEMFC	¹⁰⁸

Table S4: Literature review of works demonstrating the in situ growth of an inorganic phase within Nafion, and to a lesser degree some Nafion related polymers. Search was performed using Web of Knowledge™ utilizing the following search terms: “Nafion ion exchange”, “Nafion ion exchange metal oxide”, “Nafion ion exchange nanoparticle”, “Nafion ion exchange in situ”, “Nafion ion exchange in situ nanoparticle”. “Nafion template”, “Nafion template metal oxide”, “Nafion template nanoparticle”, “Nafion template sol gel”, “Nafion sol gel”, “Nafion sol gel nanoparticle”. Search results yielded 748 candidates (after removing duplicates), of which 102 were deemed relevant. Search was performed on 05/28/2015. Precursors are listed when noted in the abstract.

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