Supplementary Information

Highly proton conductive membranes based on carboxylated cellulose nanofibres and their performance in proton exchange membrane fuel cells

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Additional Experimental details.

AFM Characterization. Figure S1 shows the AFM characterization of the cellulose nanofibers (CNF).



Figure S1. (A) AFM image of Na-CNF-1550. (B) Length and height distribution of Na-CNF-

1550 and Na-CNF-600. A lognormal function $y = \frac{A}{\sqrt{2\pi} \cdot w \cdot x} \exp \frac{-\left(\ln\left(\frac{x}{x_c}\right)\right)^2}{2w^2}$ was fitted to the data from which the mean, \bar{x} , and standard deviation, σ , were calculated according to $\bar{x} = e^{\left(x_c + \frac{w^2}{2}\right)}$ and $\sigma = \bar{x} \cdot \left(e^{w^2} - 1\right)^{\frac{1}{2}}$, respectively.

Water uptake of the CNF membrane. Table SI shows the relative water uptake of the CNF films in the carboxylic (H-) and carboxylated (Na-) form exposed at the different relative humidities.

Relative	H-CNF-600	H-CNF-1550	Na-CNF-600	Na-CNF-1550
Humidity (%)				
55	7.5 ± 0.4	9.5 ± 1.1	9.4 ± 1.4	10.6 ± 0.3
65	8.3 ± 0.4	10.4 ± 1.0	10.9 ± 1.5	12.5 ± 0.2
75	10.4 ± 0.2	13.4 ± 0.8	13.0 ± 1.4	15.6 ± 0.6
85	13.5 ± 0.4	16.7 ± 1.0	17.7 ± 2.9	25.7 ± 1.9
95	39.5 ± 2.6	45.9 ± 4.9	197.0 ± 21.5	237.9 ± 45.4

Table S1 relative water uptake of the CNF films in the carboxylic (H-) and carboxylated (Na) forms exposed at different relative humidities.

Number of water molecules per carboxylic group (λ). The water content represented by the number of water molecules per carboxylic groups as a function of relative humidity, $\lambda(RH)$, was calculated from the weight of the samples (*w*) as

 $\lambda(RH) = \frac{W_{RH} - W_{dry}}{W_{dry}} \times \frac{EW}{18}$ eq. S1

For CNF the value of equivalent molecular weight (EW) in g/mol has been calculated using the surface charge density of the CNF. The values are reported in Figure S2.



Figure S2: Number of water molecules per proton conductive site (carboxylic for CNF and sulfonic for Nafion) of the H-CNF-600, H-CNF-1550 and Nafion 212¹

X-ray characterization of the membranes.

SAXS was used to characterise the overall membrane structure. As it is a transmission technique, the information obtained describes the internal configuration as well. The size of the probed volume is $\approx 20 \times 20 \times 20 \ \mu m^3$, which is several orders of magnitude larger than what can be obtained with electron microscopy, thereby reducing the influence of local motifs.

Figure S3 shows the scattering pattern of Na-CNF-1550 and Na-CNF-600.



Figure S3: SAXS patterns of Na-CNF membranes as a function of RH.



Figure S4: SAXS pattern of the membrane before and after testing in the fuel cell assembly (95 % RH).

Figure		Α	п	В	Ξ	С	χ^2
2c	H1550_55	0.00258	2.74812	0.04594	1.19614	0.11438	0.20308
	H1550 65	0.00292	2.87834	0.03995	1.59088	0.11888	0.38851
	H1550_75	0.00418	2.50431	0.04592	1.42996	0.11722	0.20062
	H1550 85	0.00303	2.35175	0.23599	1.60633	0.1084	0.222
	H1550_95	0.00472	2.29083	0.52533	1.75847	0.1031	0.30036
2d	H600_55	0.00334	2.55324	0.02377	1.00197	0.1169	0.2124
	H600 65	0.00473	2.07539	0.05403	1.1473	0.11275	0.18721
	H600_75	0.0027	2.8315	0.01075	1.03054	0.12208	0.26645
	H600 85	0.00499	2.1816	0.16829	1.51146	0.10992	0.28275
	H600 95	0.0056	2.01169	0.30502	1.54109	0.10276	0.28639
S3a	P1550_55	0.00238	2.59134	0.05939	0.61067	0.08719	0.18917
	P1550_65	0.00317	2.56455	0.05441	0.97787	0.10763	0.19513
	P1550 75	0.00522	1.96406	0.18857	1.72795	0.11345	0.2246
	P1550_85	0.01724	1.71728	0.19675	1.61054	0.10692	0.2001
	P1550 95	0.034	1.7245	1.06587	2.06062	0.09382	0.92703
S3b	P600_55	2.94E-03	2.83486	0.03826	1.08785	0.11594	0.32452
	P600 65	3.33E-03	2.52195	0.06239	1.30521	0.11606	0.24687
	P600_75	3.41E-03	2.73781	0.04195	0.85947	0.10933	0.28909
	P600_85	1.31E-02	1.73762	0.18188	1.73714	0.11178	0.24186
	P600 95	0.03543	1.54192	0.46748	1.79011	0.09728	0.53176
S4a,b	AF600_95	0.00806	2.83534	0.31811	1.61207	0.10471	0.83951
	AF1550 95	0.00682	2.34728	0.35013	1.68483	0.10421	0.68042

Table S2: Fitting parameter of the scattering patterns shown in the corresponding figures.



Figure S5: XRD patterns of the membrane before and after testing in the fuel cell assembly (95 % RH).

In Figure S4 both CNF membranes show that the characteristic signature of their network structure is intact after their use as PEM. At low q the H-CNF-600 after, shows that the CNF agglomerates are slightly tighter connected, that can also be attribute to the individual difference within each membrane. At high q the H-CNF-1550 samples show a decrease in intensity due to the slight lower water content in the membrane extracted from the fuel cell which may reduce the number of pores. However, the pore size remains somewhat constant. Figure S5 shows that the peak width of the membrane before and after use remains constant, which indicates that the crystallinity of the cellulose remains unaffected.



Figure S6:

Description of fuel cell measurement set-up



Figure S7: Illustration of a fuel cell setup

In fuel cell measurements the relative humidity is achieved by setting the temperatures of the humidification bottles and cell. The humidification bottles are designed to result in the gas having reached the saturated vapour pressure (P_{sat}) for the set temperature. The gas is then heated to the cell temperature which is often higher, resulting in it no longer

having a specific relative humidity related to the fuel cell temperature. The relative humidity reported in the article was calculated as below:

$$\% RH = \frac{P_{sat}(Humidifier\ temperature)}{P_{sat}(Cell\ temperature)} * 100 \qquad eq.\ S2$$

This is very common in fuel cell measurements, see for instance <u>http://fuelcelltechnologies.com/humidification-systems</u>



Additional electrochemical impedance spectroscopy (EIS) data

Figure S8: Nyquist plots of N_2/N_2 EIS measurements for the H-CNF membranes with surface charge density of 600 (right) and 1550 (left) μ mol g⁻¹.

Figure S8, shows the impedance data used as a base for the study of membrane conductivity of varying thickness and H-CNF membranes with 600 (right) and 1550 (left) μ mol g⁻¹. This data is used to IR-correct the polarization curves in figure 4 and to calculate the ion conductivity using the following equation.

$$\sigma = \frac{\delta}{R*A} \qquad \qquad \text{eq. S3}$$

Where δ is the membrane thickness, R the high frequency resistance and A the geometric are of the fuel cell.



Figure S9: Nyquist plots of N₂/H₂ EIS measurements for the H-CNF-1550 μ mol g⁻¹ at different RH.

Figure S9, shows the impedance data at varying RH. The largest change in the high frequency resistance can be seen between 65 and 55% RH, there are however also a small decrease between fully humidified and 85-75% RH. An additional observation is that the gas crossover increases at lower RH as can be seen in the bent curves for 65 and 55% RH. This is primarily seen in the impedance here as hydrogen gas is used at one of the electrodes.





Figure S10: Polarization curves upon prolonged use in the fuel cell setup.

The durability and the performance over relatively quick change of RH of the CNF-1550 membrane were evaluated over 28 hours of operation in the fuel cell at 30°C and between 95 and 85 % RH (Figure S10). After 15 minutes at 95 % RH the polarization does not show any significant difference of OCV and slightly lower potential and higher current density. The RH was then lower to 85 %, which lead to a net decrease of OCV and cell potential (green curve). This decrease in performance is attributed to the the fact that at high RH

water channels are from in the membrane due to the condensation of water. Once the water content is lowered (at 85%) these channels give additional pathways for the diffusion of gas, meaning that in this time frame the CNF structure does not recovered. The polarization curves show that the performance of the cell are partially recovered after the RH was set back to 95 %. This indicates that the gas permeability is what is lost in the cell and not the conductivity. Indeed, over the successively 28 hours of operation the performance is very stable and reproducible in accordance to the fact that the membrane retains its crystal structure, functionality and microstructure after 28 hours (Figure S4, S5 and S6).