Supporting Information

Stable and Highly Ion Selective Membrane Made from Cellulose Nanocrystal for Aqueous Redox Flow Batteries

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Index for Supplementary Figures and Tables.

Supplementary Figure 11	The appearance of visible pinholes in 45-CNC/PVDF-HFP membrane after cycling.
Supplementary Figure 12	(a-d) SEM images of 45-CNC/PVDF-HFP membrane different magnifications showing pinholes of diameter 21-29 nm.
Supplementary Figure 13	Electrochemical impedance spectra (EIS) of (a) 40-CNC/PVDF-HFP, 45-CNC/PVDF-HFP, 50-CNC/PVDF-HFP, 60-CNC/PVDF-HFP, 45-C-CNC/PVDF-HFP, 60-C-CNC/PVDF-HFP, and Nafion 115 membranes. (b) Zoomed in part of (a).
Supplementary Figure 14	Contact angle measurements of (a) 40-CNC/PVDF-HFP , (b) 45-CNC/PVDF-HFP, (c) 50-CNC/PVDF-HFP, and (d) 45-C-CNC/PVDF-HFP membranes.
Supplementary Figure 15	Picture of crossover testing of (a) Nafion and (b) 45-C-CNC/PVDF-HFP membranes after 24 hours.
Supplementary Figure 16	Full cell cycling of 45-C-CNC/PVDF-HFP membrane using 6 SGL 39 AA carbon paper stack on each side as electrodes and 1 M $VOSO_4$ in 3 M H_2SO_4 as electrolyte at a current density of 40 mA cm^{-2}.
Supplementary Figure 17	Cross-section SEM images of 60-CNC/PVDF-HFP membrane (before calendaring) at magnifications of (a) 250 X, (b) 5 KX, and (c) 30 KX. (d) The surface SEM image of 60-CNC/PVDF-HFP membrane 500 X magnification.
Supplementary Figure 18	Cross-section SEM images of 60-CNC/PVDF-HFP membrane (before calendaring) at magnifications of (a) 250 X, (b) 5 KX, and (c) 30 KX. (d) The surface SEM image of 60-CNC/PVDF-HFP membrane 500 X magnification.
Supplementary Figure 19	Full cell performance of 60-C-CNC/PVDF-HFP (calendared 60 % CNC containing CNC/PVDF-HFP membrane). (a) Voltage profiles, (b) Columbic Efficiency, Voltage Efficiency, and Energy Efficiency and (c) rate performance of 60-C-CNC/PVDF-HFP at different current densities of 40, 60, 80, 100, 150, and 200 mA cm^{-2}.
Supplementary Figure 20	(a) and (b) Picture of two different 60-C-CNC/PVDF-HFP membranes after cycling showing visible cracks.
Supplementary Figure 21	Equivalent circuit used for EIS.

Supplementary Table 1	Material Cost Calculations for 45-C-CNC/PVDF Membrane based on lab scale and corresponding comparison with Nafion 115 membrane.
Supplementary Table 2	Details of the **low temperature (60˚C)** calendaring conditions of 45-C-CNC/PVDF-HFP membranes, where B and C represent two separate batches of 45-C-CNC/PVDF-HFP membranes. MD and TD represent machine direction and transverse direction, respectively, where the machine direction is the direction at which first calendaring was performed. The numeric values (i.e., MDx2) signifies the number of a calendaring pass in each direction.
Supplementary Table 3	Details of the **high temperature** (**90˚C**) calendaring conditions of 45-C-CNC/PVDF- HFP membranes.

Table S 1 Material Cost Calculations for 45-C-CNC/PVDF Membrane based on lab scale and corresponding comparison with Nafion 115 membrane.

Material Cost for Making CNC					
	Company	**Price/Unit**	**Unit**	**Qty.**	**Total Price (USD)**
For making ~ 50 g CNC					
Consumables					
Sulfuric acid (97-98%)	Sigma	65	L	1	65
Microcrystalline Cellulose	Sigma	0.115	g	200	23
Reusables					
Dialysis Membrane (12 -14 K Da MWCO)	Fisher	11.83	meter	5	59.15
Per g cost of CNC					**1.76**
(Did not consider the dialysis membrane as they can be used for multiple batches and for long time.)					
Material Cost of 45-C-CNC/PVDF-HFP Membrane (for 1 m^2 area)					
Area		1	m^2		
Thickness		60	μm		
Volume		60	cm^3		
Density		1.69	g cm^{-3}		
Mass		101.4	g		
(considered an average density of both since the density of the composite is unknown and the density of PVDF and CNC is quite close 1.6 for CNC and 1.78 for PVDF)					
	Company	**Price/Unit**	**Unit**	**Qty.**	**Total Price (USD)**
CNC	Lab made	1.76	g	45.63	80.31
PVDF-HFP	Sigma	0.53	g	55.77	29.56
DMF	Sigma	47.27	L	0.8	37.82
Total Cost					**147.68**
Commercial Price of Nafion 115					
$ 1321 per m^2, according to the price listed in Fuel cell store for 1.525 m^2 Nafion 115					

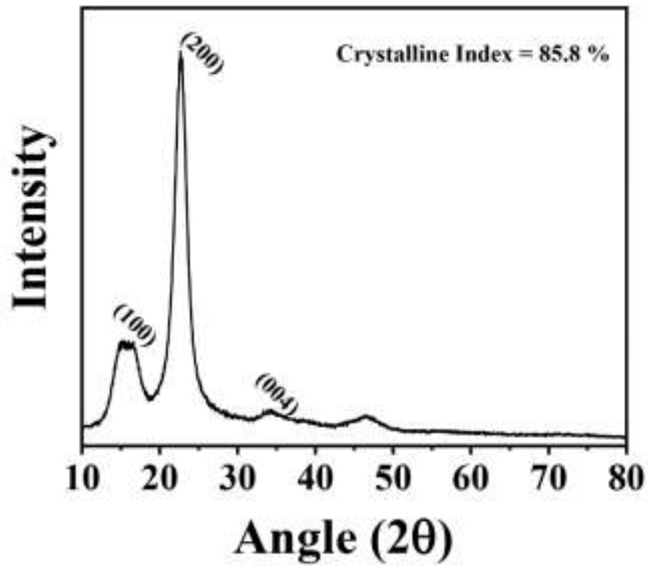


Figure S 1 *X-ray diffraction pattern of pure CNC.*

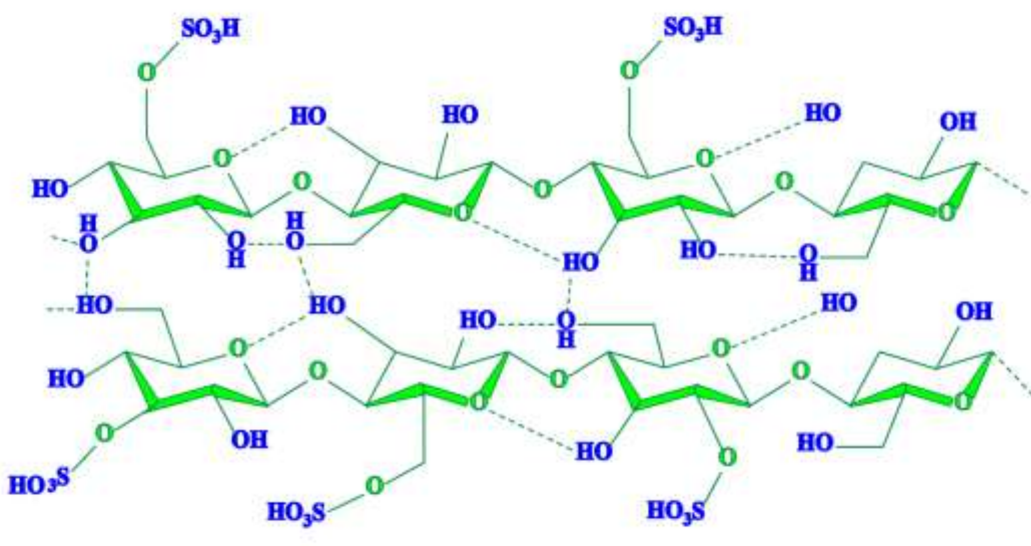


Figure S 2 *Molecular structure of CNC prepared by the acid hydrolysis process using sulfuric acid.*

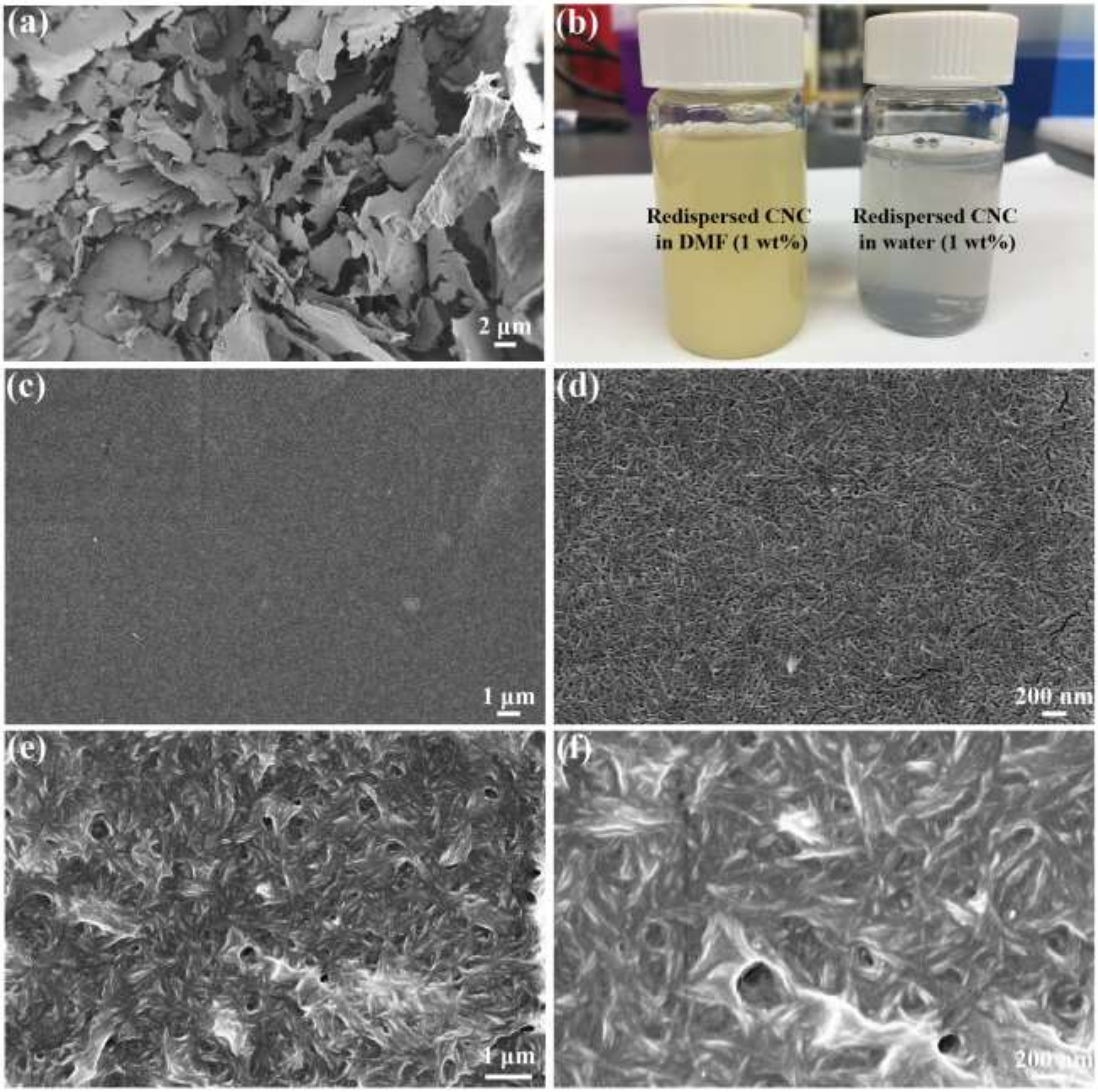


Figure S 3 *(a) SEM morphology of freeze-dried CNC (b) Freeze-dried CNC redispersed in DMF and CNC (1 wt % concentration). SEM images of freeze-dried CNC redispersed in (c and d) water and (e and f) DMF.*

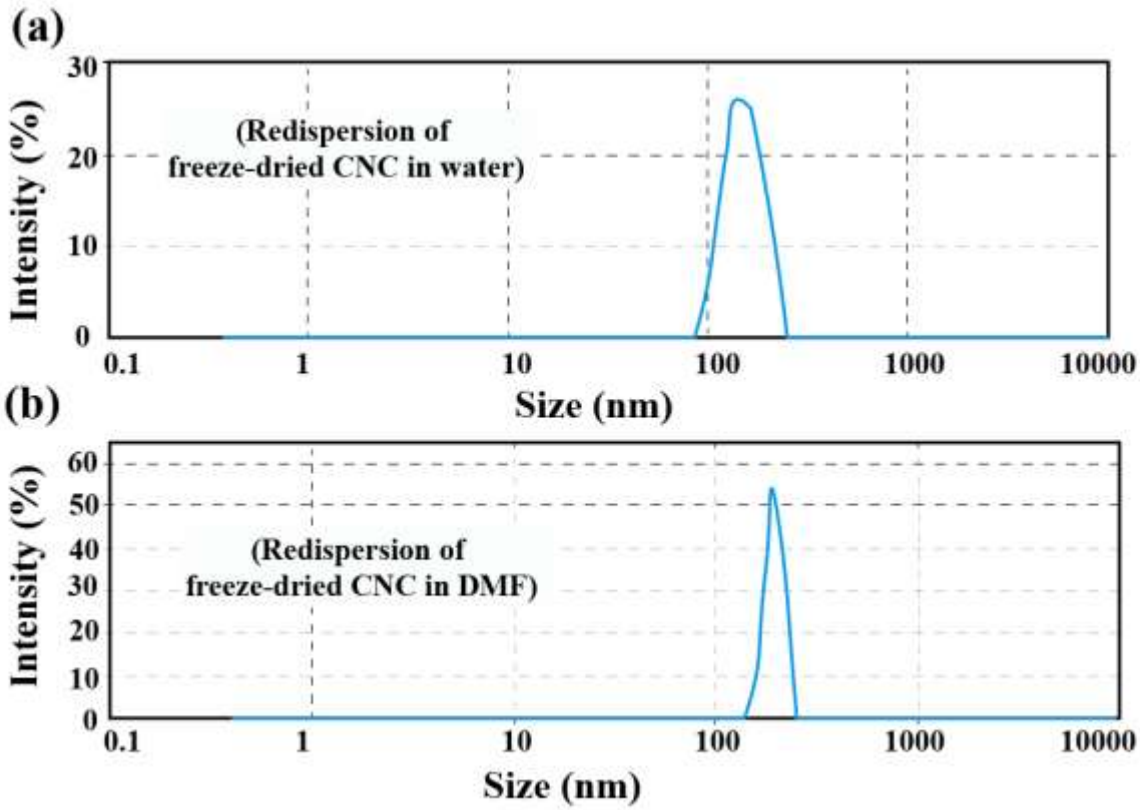


Figure S 4 *Intensity distribution of freeze-dried CNC redispersed in (a) water and (b) DMF using dynamic light scattering (DLS).*

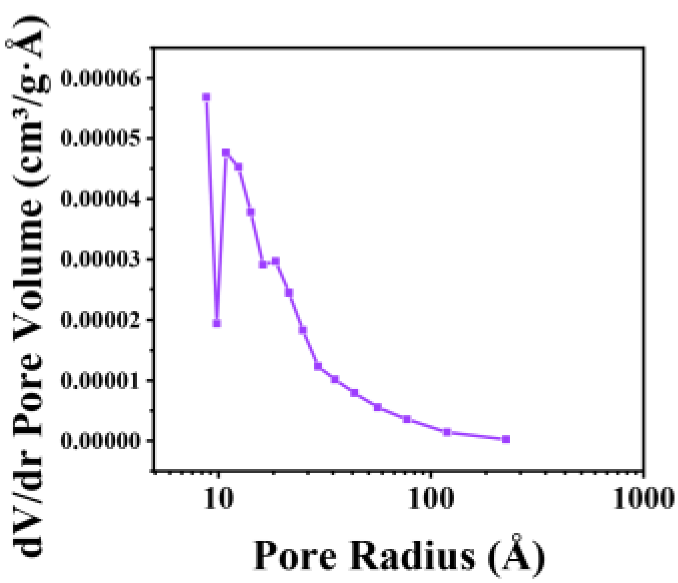


Figure S 5 *Pore distribution of 45-C-CNC/PVDF-HFP membrane.*

Table S 2 *Details of the* **low temperature (60 ̊C)** *calendaring conditions of 45-C-CNC/PVDF-HFP membranes, where B and C represent two separate batches of 45-C-CNC/PVDF-HFP membranes. MD and TD represent machine direction and transverse direction, respectively, where the machine direction is the direction at which first calendaring was performed. The numeric values (i.e., MDx2) signifies the number of a calendaring pass in each direction.*

Sample name	Thickness before calendaring (mm)	Thickness after calendaring (mm)	Calendaring direction
C1	0.137	0.045	MDx2
C2	0.132	0.040	MDx2
C3	0.139	0.045	MDx1, TDx1
B1	0.094	0.042	MDx2
B2	0.090	0.033	MDx2
B3	0.092	0.020	MDx1, TDx1
B4	0.090	0.042	MDx1, TDx1

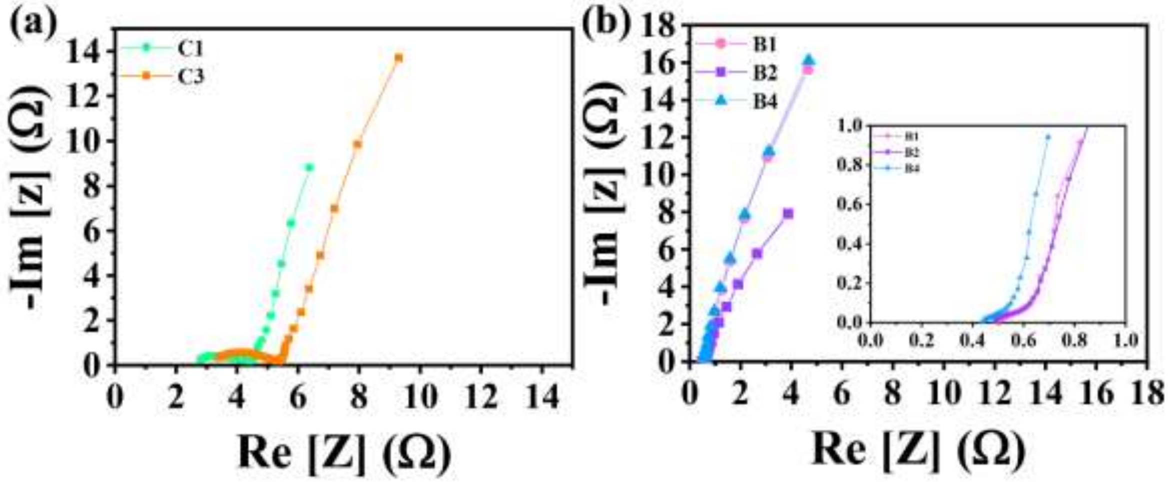


Figure S 6 *EIS curves of 45-C-CNC/PVDF-HFP membranes (after calendering) with different calendaring directions at 60˚C. (a) EIS curves of samples C1 and C3. Sample C2 was fragile and cannot be assembled in the flow cell to measure the EIS. (b) EIS curves of samples B1, B2, and B4. Sample B3 was fragile and cannot be assembled in the flow cell to measure the EIS. The details of the abbreviations are mentioned in supporting* ***Table S 2****.*

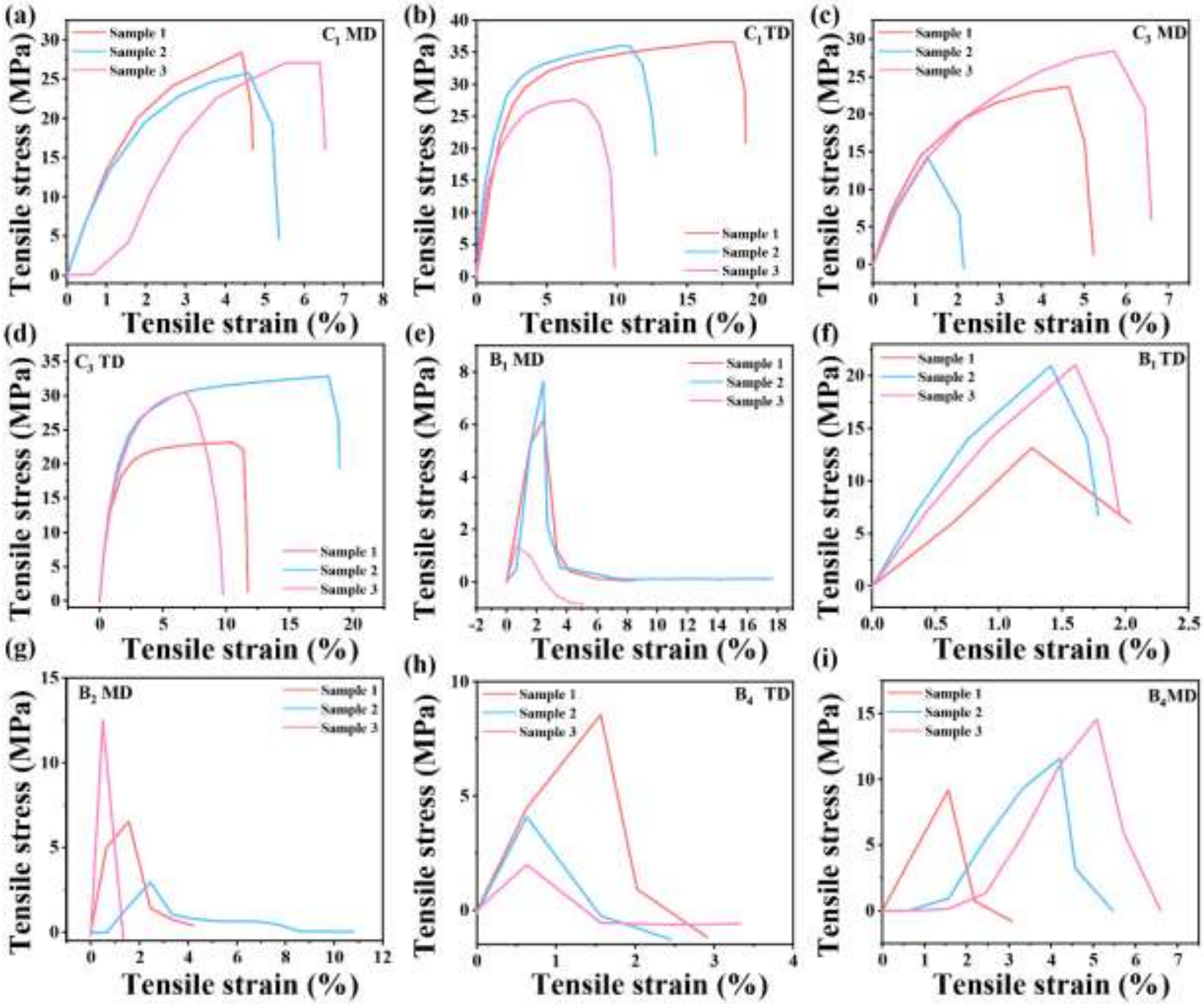


Figure S 7 *Stress-strain curves of 45-C-CNC/PVDF-HFP membranes (after calendaring) with different calendaring directions at 60˚ C. Stress-strain curves of (a) C 1 membranes in machine direction, (b) C 1 membranes in transverse direction, (c) C3 membranes in machine direction, (d) C3 membranes in transverse direction, (e) B1 membranes in machine direction, (f) B1 membranes in transverse direction, (g) B2 membranes in machine directions, (h) B2 membrane in transverse direction, (i) B4 membranes in machine direction. Three samples were tested for each category. The details of the abbreviations are mentioned in supporting* ***Table S 2****.*

Table S 3 *Details of the* ***high temperature (90°C)*** *calendaring conditions of 45-C-CNC/PVDF-HFP membranes.*

Sample name	**Thickness before calendaring (mm)**	**Thickness after calendaring (mm)**	**Number of the calendering pass in MD**
D1	*0.100*	*0.057*	*2*
D2	*0.110*	*0.06*	*1*
D3	*0.090*	*0.049*	*2*
D4	*0.100*	*0.042*	*1*

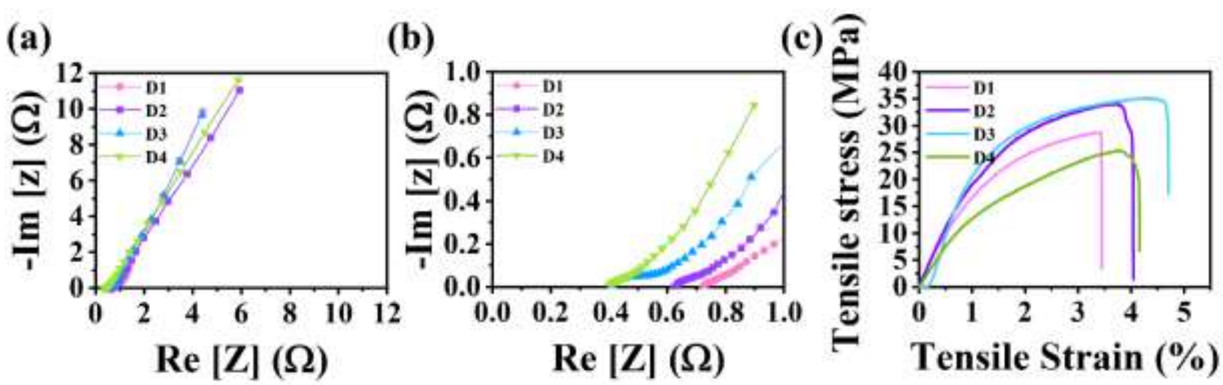


Figure S 8 *EIS curves of 45-C-CNC/PVDF-HFP membranes (after calendering) with different numbers of the calendaring pass in the machine direction at 90˚C. (a) EIS curves of samples D1, D2, D3, and D4. (b) Zoomed in image of (a). (c) Stress-strain curves of D1, D2, D3, and D4. The details of the abbreviations are mentioned in supporting* ***Table S 3****.*

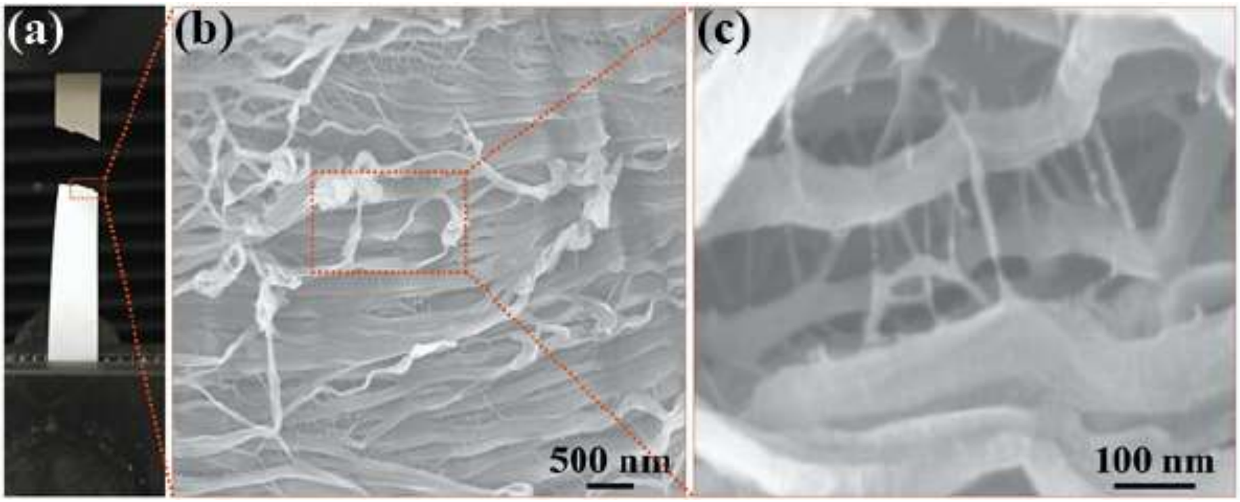


Figure S 9 *(a) Picture of the tensile strength testing of 45-C-CNC/PVDF-HFP membrane. (b) and (c) SEM images of breaking region of 45-C-CNC/PVDF-HFP membrane.*

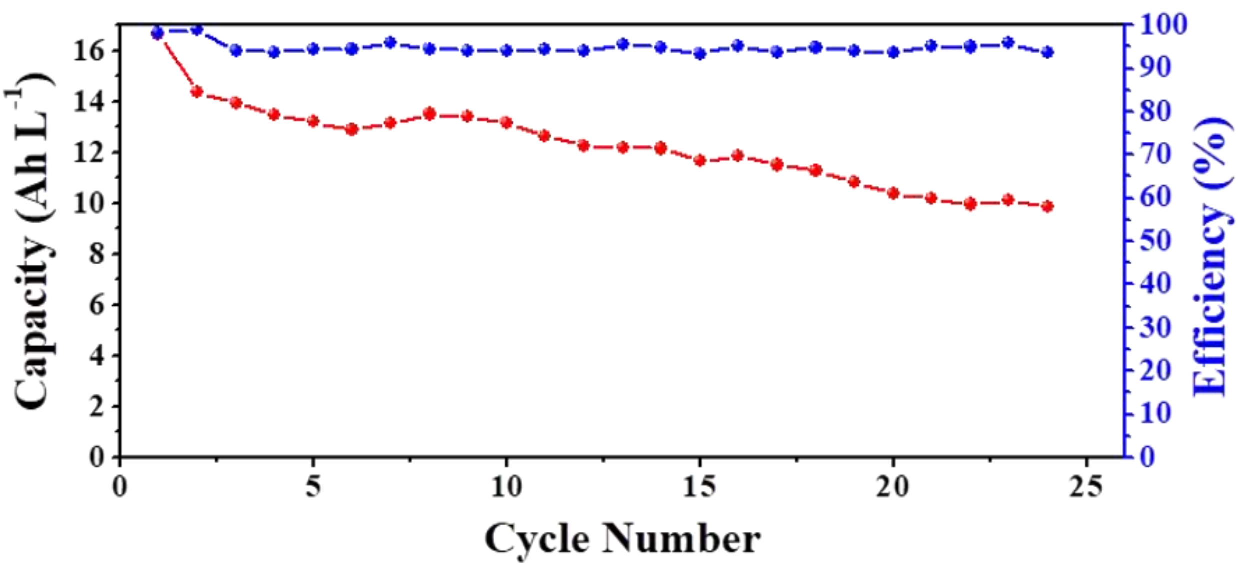


Figure S 10 *VRFB cell cycling of 45-CNC/PVDF-HFP membrane using 1 M $VOSO_4$ in 3 M H_2SO_4 at 40 mA cm^{-2}.*

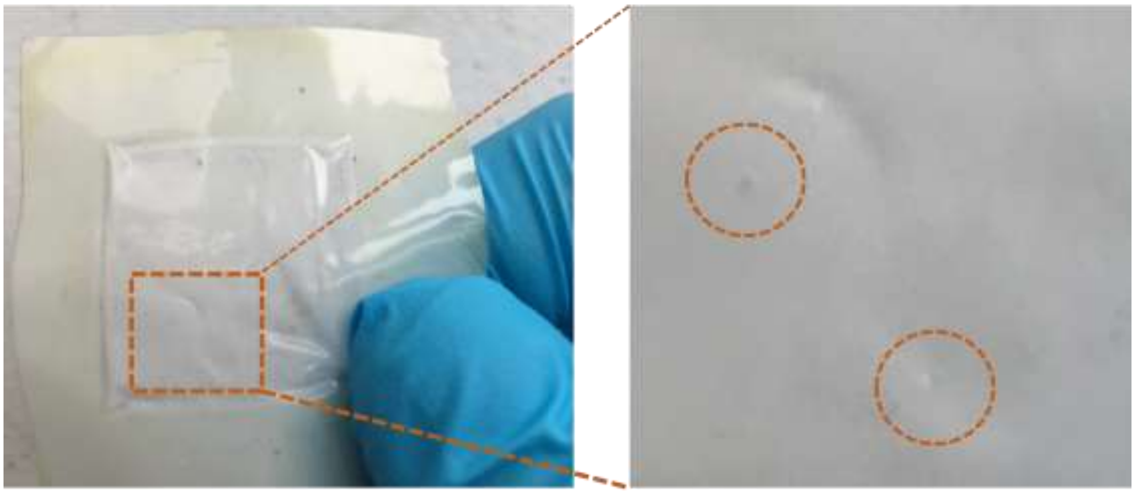


Figure S 11 *The* ***a****ppearance of visible pinholes in 45-CNC/PVDF-HFP membrane after cycling.*

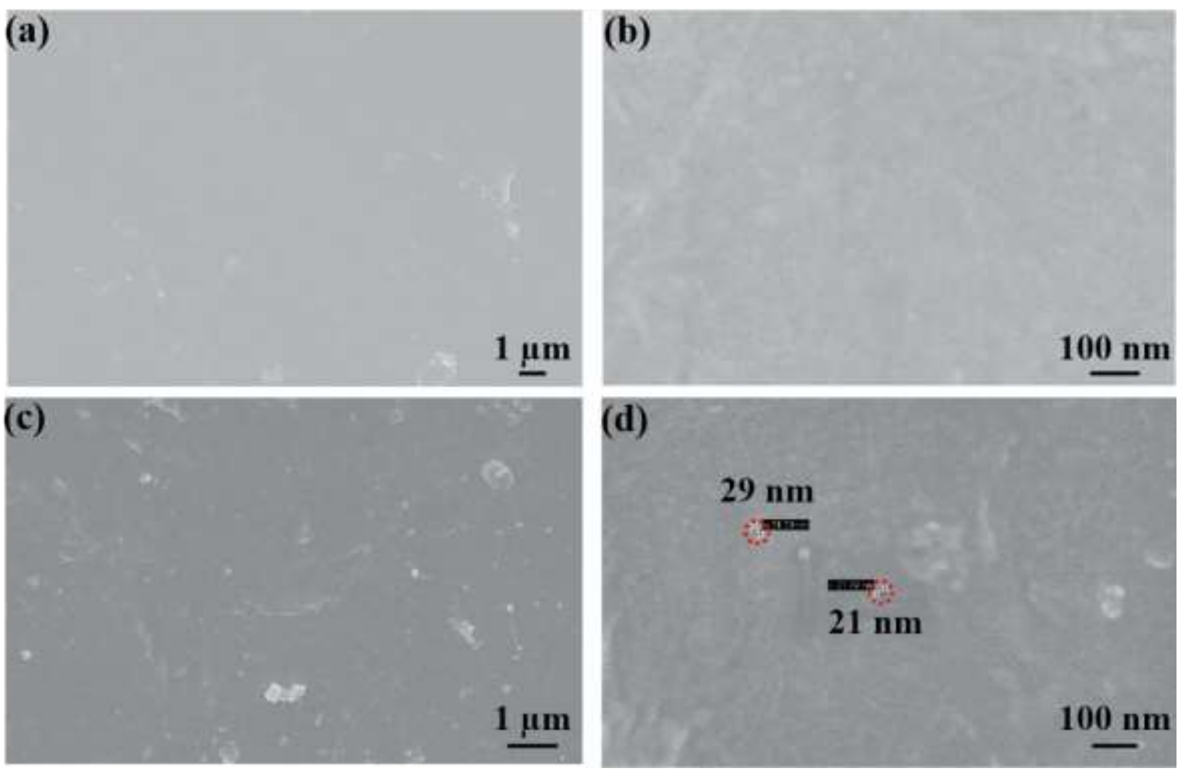
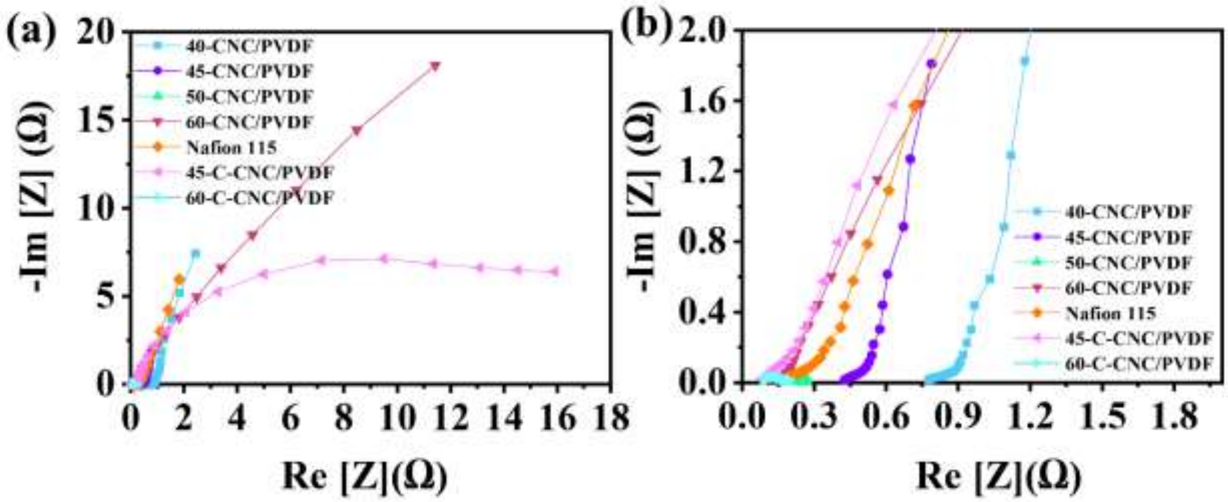


Figure S 12 *a-d SEM images of 45-CNC/PVDF-HFP membrane different magnifications showing pinholes of diameter 21-29 nm.*



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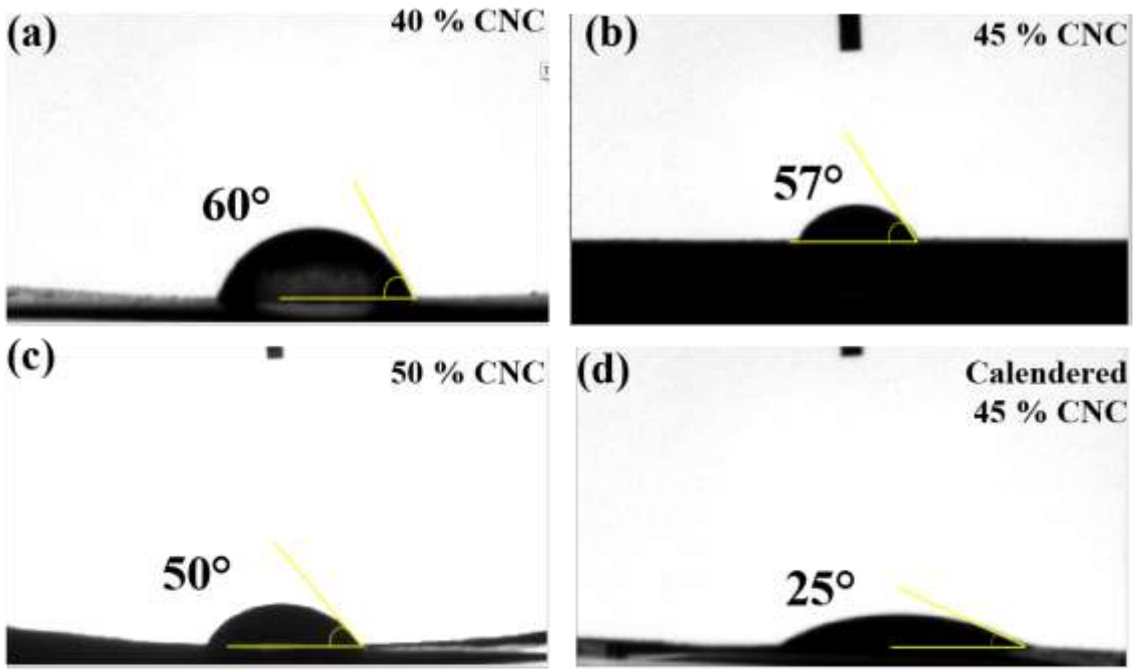
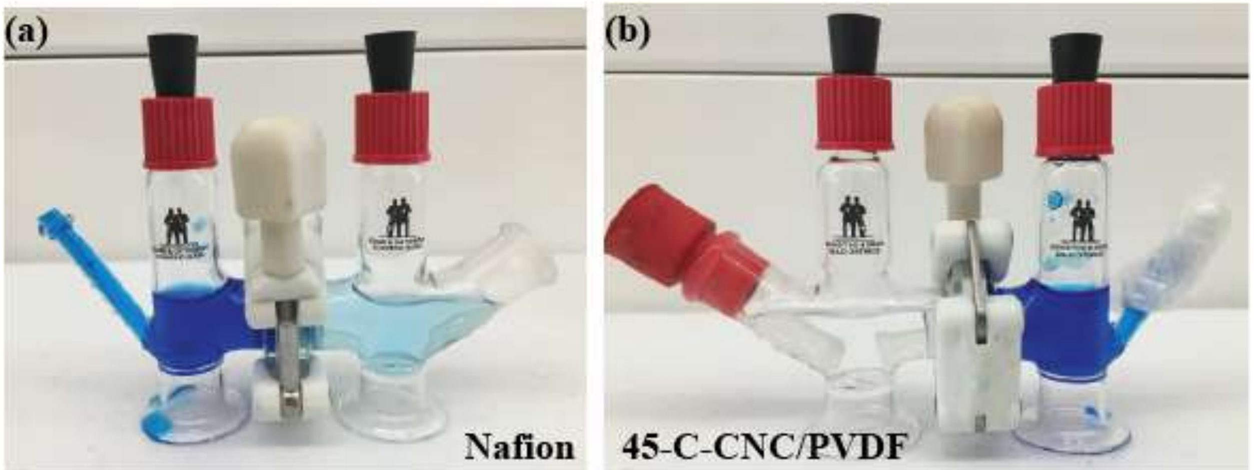


Figure S 14 *Contact angle measurements of (a) 40-CNC/PVDF-HFP , (b) 45-C-CNC/PVDF-HFP, (c) 50 CNC/PVDF-HFP, and (d) 45-C-CNC/PVDF-HFP membranes.*



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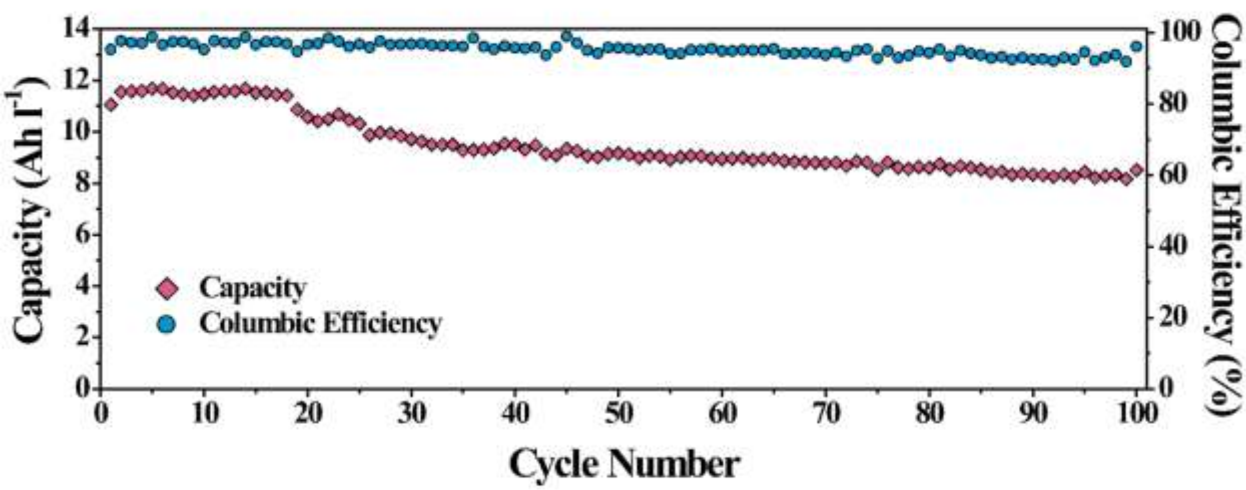

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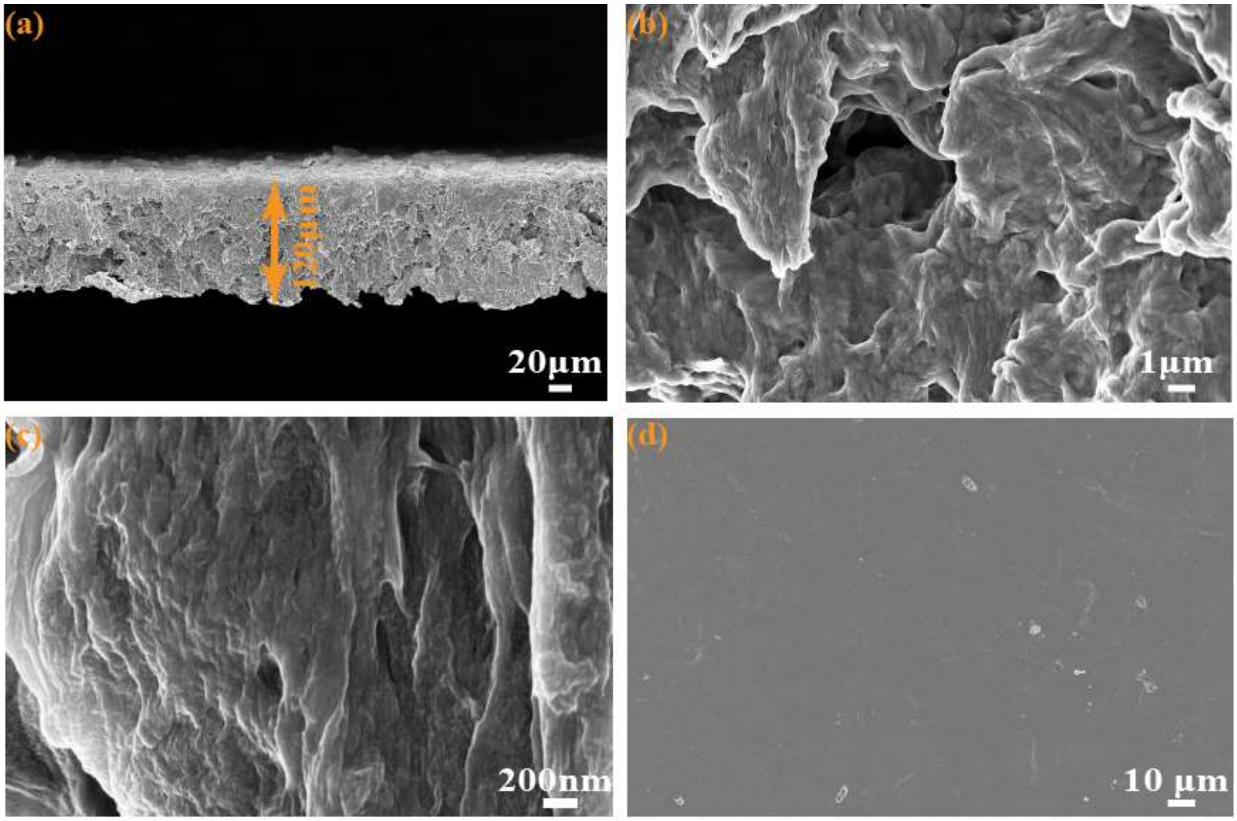
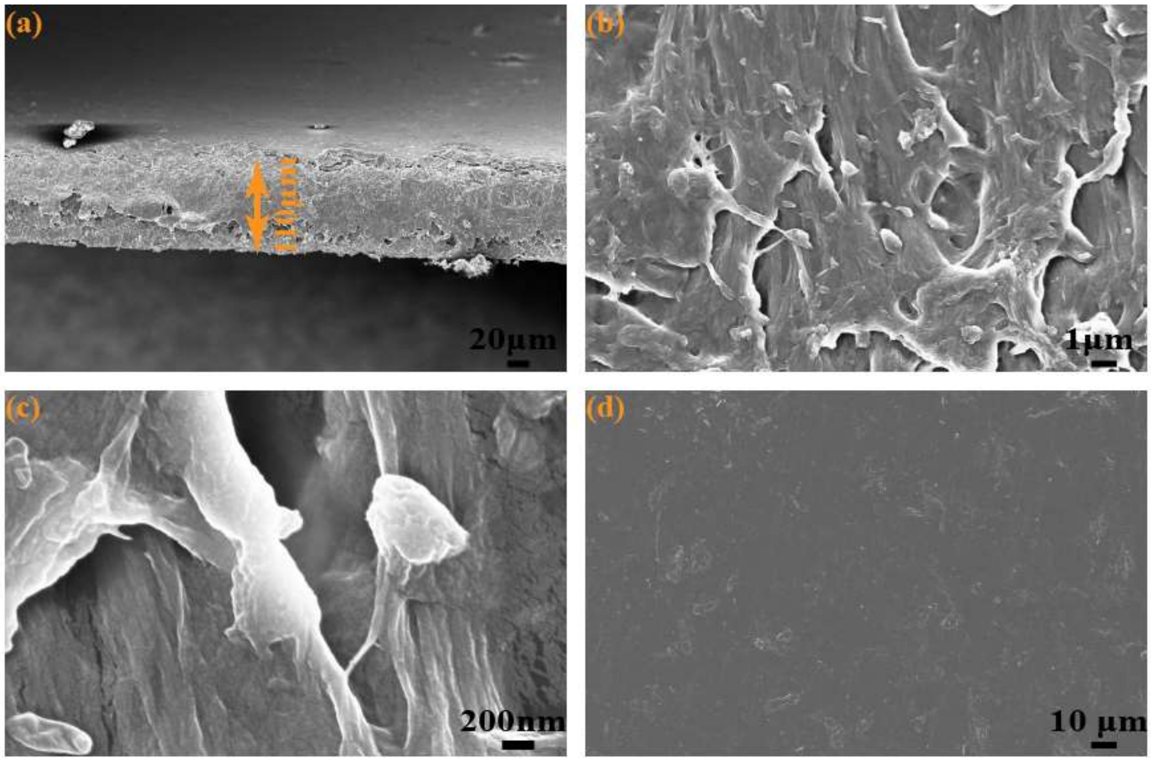


Figure S 17 *Cross-section SEM images of 60-CNC/PVDF-HFP membrane (before calendaring) at magnifications of (a) 250 X, (b) 5 K X, and (c) 30 K X. (d) The surface SEM image of 60-CNC/PVDF-HFP membrane 500 X magnification.*



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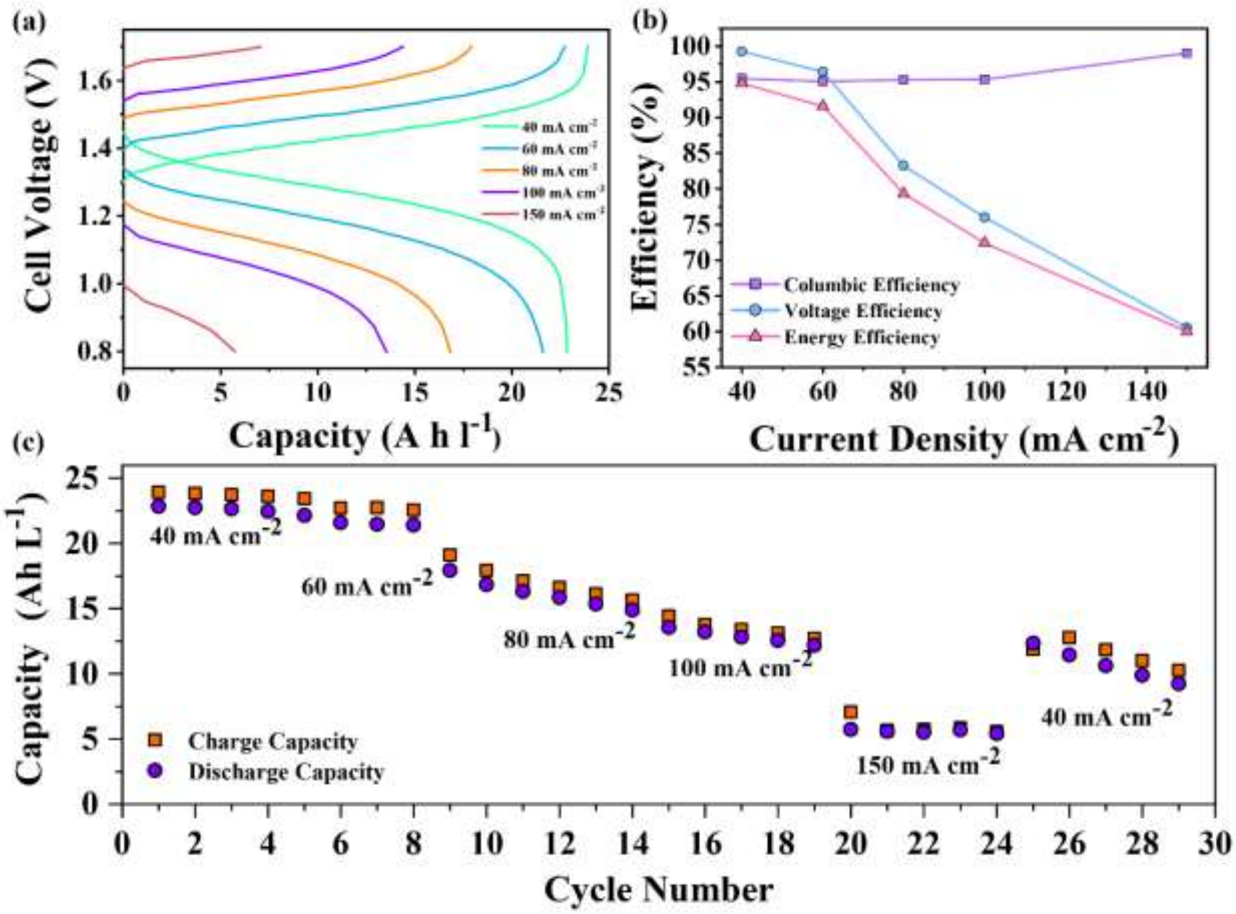

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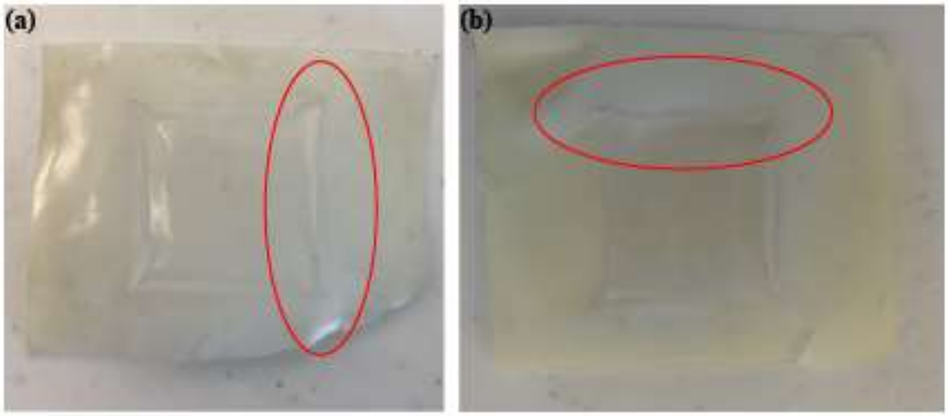

Figure S 20 *(a) and (b) Picture of two different 60-C-CNC/PVDF-HFP membranes after cycling showing visible cracks.*

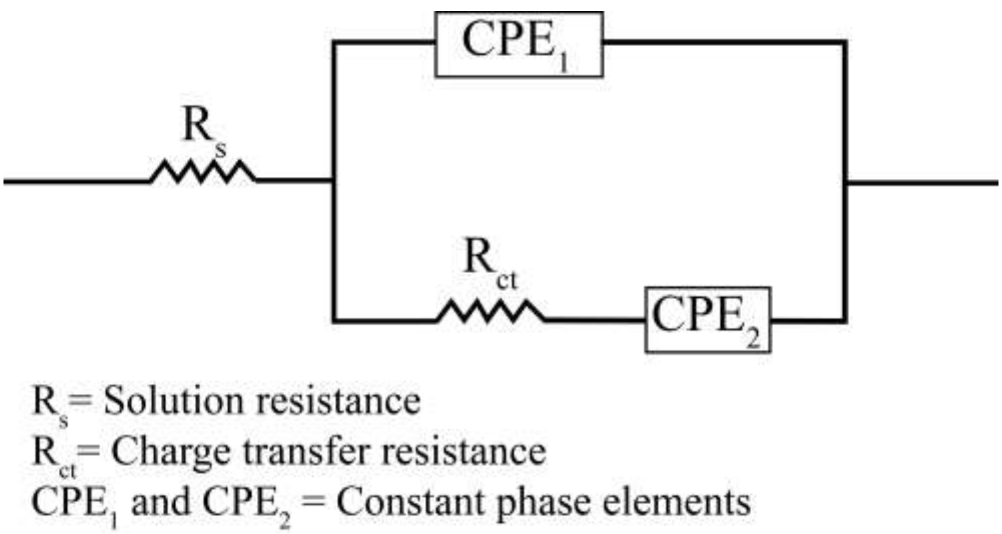

Figure S 21 *Equivalent circuit used for EIS.*