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Supplementary Information

Hydrophobic nanoporous carbon scaffolds reveal the origin of polarity-dependent electrocapillary imbibition

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Figure S1. Experimental set-up to study the partly submerged hydrophobic NCS-85 material in 1 M KCl solution. (a) Working electrode (WE) design with NCS-85 pressed and sealed on Torray carbon paper, and (b) illustration of electrochemistry experiment, where the reference electrode (RE) is Ag/AgCl in 3 M NaCl, Platinum (Pt) mesh is the counter electrode (CE).

Properties	NCS-85			
Dimensions (Length x Width x Thickness)	(10-21) mm x (5-8) mm x 100 µm			
Dominant pore diameter ^a	$85 \pm 12 \text{ nm}$			
Dominant pore throat diameter ^a	16 ± 3 nm			
Macro-contact angle ^b	> 100°			
Porosity ^c	90 %			

Table S1 Physical characteristics of the NCS-85 membrane material.

^a Dominant pore and pore throat diameters were determined from SEM images and gas sorption measurements.¹

^b Macro-contact angle on NCS-85 was measured under ambient conditions using 1 M KCl solution and the sessile droplet method.²

^c Porosity of NCS-85 was estimated from gas sorption measurements.³



Figure S2 SEM cross-section of 1500 °C heated (hydrophobic) NCS-85 membrane.



Figure S3 Concave meniscus seen at the hydrophobic NCS-85/1 M KCl interface in the potential range where no electro-imbibition occurs. The yellow dashed line is provided as a guide to the eye.



Figure S4 Electro-dewetting phenomena seen at hydrophobic NCS-85 membranes in 1 M KCl at various negative voltages. (a) -1 $V_{Ag/AgCl}$; (b) -1.2 $V_{Ag/AgCl}$, and (c) -2 $V_{Ag/AgCl}$.

Voltage [VAg/AgCl]	Current [mA]	Measured charge [C]	NCS Width [mm]	H [mm]	Wetted NCS area [m²]	Theoretical double layer charge [C]
0.8	0.03	0.03	6.7	9.1	0.49	0.018
1	0.09	0.1	6	13.9	0.67	0.03
1.2	0.50	0.42	6.4	15.6	0.80	0.04
1.6	4.50	2.4	6.2	15.6	0.77	0.05
2	17.2	8.0	5.9	15.7	0.74	0.06

Table S2 Charge passed during time of holding at positive voltage polarization (Figure 4(a)).

*Capacitance was assumed to be 15 μ F cm^{-2 4,5} the NCS-85 surface area is 200 m²/g (ref. 3) and the density was assumed to be 0.2 g/cm³ (based on its known 90% porosity³).



Figure S5. Superimposed cyclic voltammograms of an initially dry, hydrophobic NCS-85 membrane submerged in 1 M KCl, recorded after extension of E+ in 100 mV increments from 0 to 1.45 $V_{Ag/AgCl}$ at 5 mV/s, with Ag/AgCl and carbon paper used as the reference and counter electrodes, respectively. This demonstrates the onset of what is likely the OER at ca. 1.05 $V_{Ag/AgCl}$ (1.6 V_{RHE} , see red dashed line), when electro-imbibition is already well underway. The X axis is given vs. both Ag/AgCl (bottom) and the RHE (top).



Figure S6. Contact angle gradient along electrocapillary imbibition height after polarizationinduced electro-imbibition of the NCS-85 membrane in 1 M KCl after 480 s at (a) +1.6 and (b) +2 $V_{Ag/AgCl}$, as measured by the sessile droplet method.



Figure S7. XPS analysis of hydrophobic, heat-treated NCS-85 before polarization. (a) Deconvoluted C1s spectrum and (b) Deconvoluted O1s spectrum.



Figure S8. Oxygen content measured using XPS analysis at various locations on the electroimbibed NCS-85 surface (with regions of analysis designated as bottom, middle and top in relation to the distance from the solution surface) after polarization for 480 s at +2 $V_{Ag/AgCl}$ in 1 M KCl solution.



Figure S9. Deconvoluted C1s and O1s spectra of NCS-85, polarized at +2 $V_{Ag/AgCl}$ for 480 s, corresponding to the bottom, middle and top regions of the imbibed area in (a), (b) and (c), respectively (see **Figure S8**) and exhibiting various oxygen functionalities introduced at the NCS surface during the imbibition experiments, all at E+.



Figure S10. Deformation observed of the initially dry and hydrophobic NCS-85 membrane when immersed in water.



Figure S11. Schematic illustration of various stages of electrocapillary imbibition into the pores of the dry, hydrophobic NCS-85 membrane at negative voltages, showing the entry of fluid inside an NCS pore as a "finger" as the result of pressure induced by the high rates of gas evolution. (a) At t = 0, no E- is applied and hence no imbibition occurs (H = 0). (b) At time t and a sufficiently negative E- value, liquid (blue) imbibes into the pores. (c) Liquid partially fills the pores, but not entirely, as the pores are hydrophobic, producing pockets of trapped air (grey). (d) Hydrogen evolution in the wetted area causes the further generation of H₂ bubbles (red) with some of the H₂ entering the air pockets and causing a pressure build-up. (e)The pressure build-up either moves fluid up the NCS-85, causing H to increase or it drives fluid out of the NCS-85 to the surface, following the easiest pathway, e.g., through interconnected pores leading to a nearby outer surface.



Figure S12. Superimposed H vs. time and E vs. time plots for imbibition observed at NCS-85 membrane in 1 M KCl, showing start-stop imbibition behavior. E vs time plots were recorded between $E_{Ag/AgCl}$ + = +2.0 and $E_{Ag/AgCl}$ = -2.0 V at 25 mV/s.

Please note that all the videos play at 100 times real time.

Video S1 Electrocapillary imbibition at $-2 V_{Ag/AgCl}$.Video S2 Electrocapillary imbibition at $-1.6 V_{Ag/AgCl}$.Video S3 Electrocapillary imbibition at $-1.2 V_{Ag/AgCl}$.Video S4 Electrocapillary imbibition at $-1 V_{Ag/AgCl}$.Video S5 Electrocapillary imbibition at $-0.9 V_{Ag/AgCl}$.Video S6 Electrocapillary imbibition at $+0.7 V_{Ag/AgCl}$.Video S7 Electrocapillary imbibition at $+0.7 V_{Ag/AgCl}$.Video S8 Electrocapillary imbibition at $+0.8 V_{Ag/AgCl}$.Video S9 Electrocapillary imbibition at $+1 V_{Ag/AgCl}$.Video S9 Electrocapillary imbibition at $+1.2 V_{Ag/AgCl}$.Video S10 Electrocapillary imbibition at $+1.6 V_{Ag/AgCl}$.Video S11 Electrocapillary imbibition at $+2 V_{Ag/AgCl}$.Video S12 Electrocapillary imbibition during cyclic voltammetry between $+2 V_{Ag/AgCl}$ and $-2 V_{Ag/AgCl}$ at 25 mV/s for three cycles.

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