Catalyst Coated Membranes for Fuel Cell and Water Electrolyser Delamination Induced by Organic Solution Soaking and Water Ultrasonication

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Supplementary Information

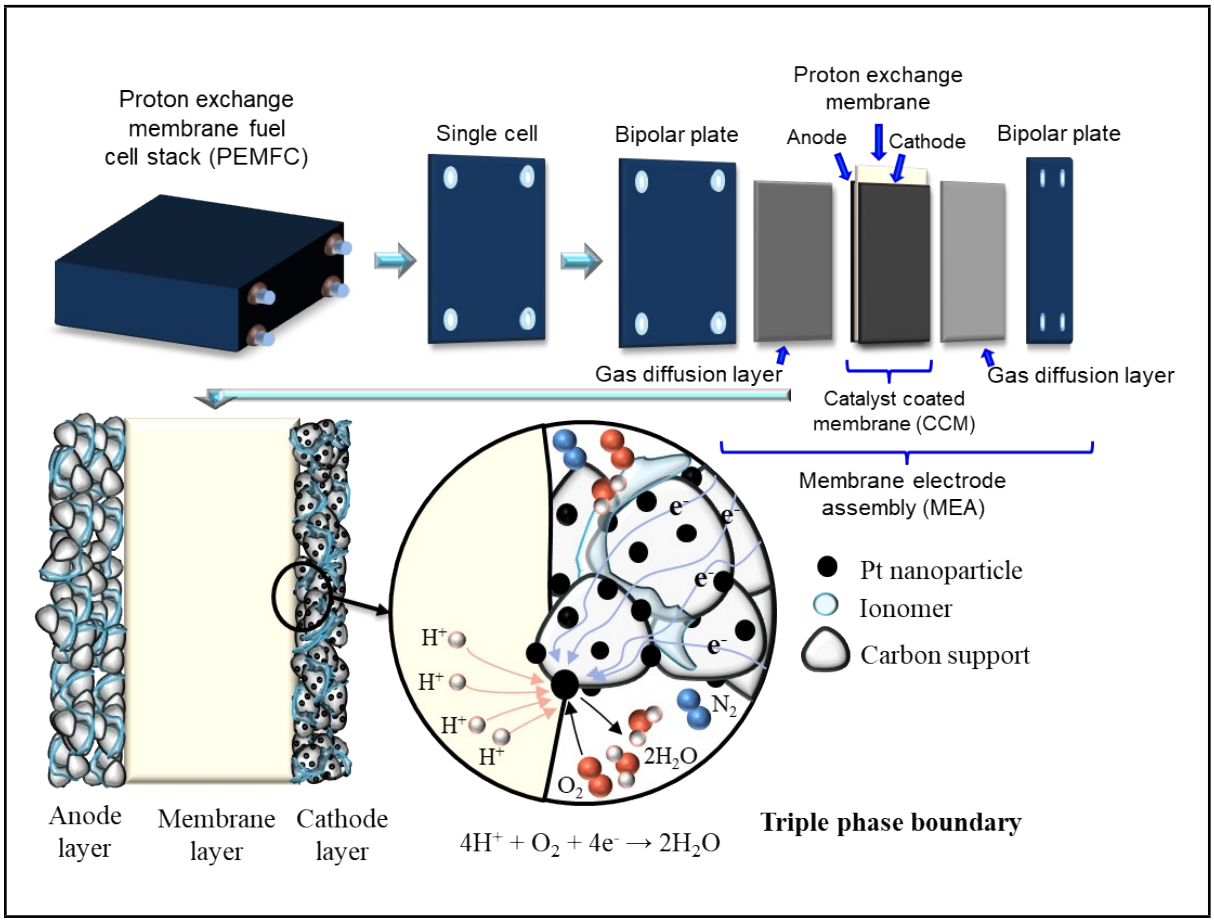

Figure S1 *Membrane electrode assembly of a PEMs (adapted from [1, 2])*

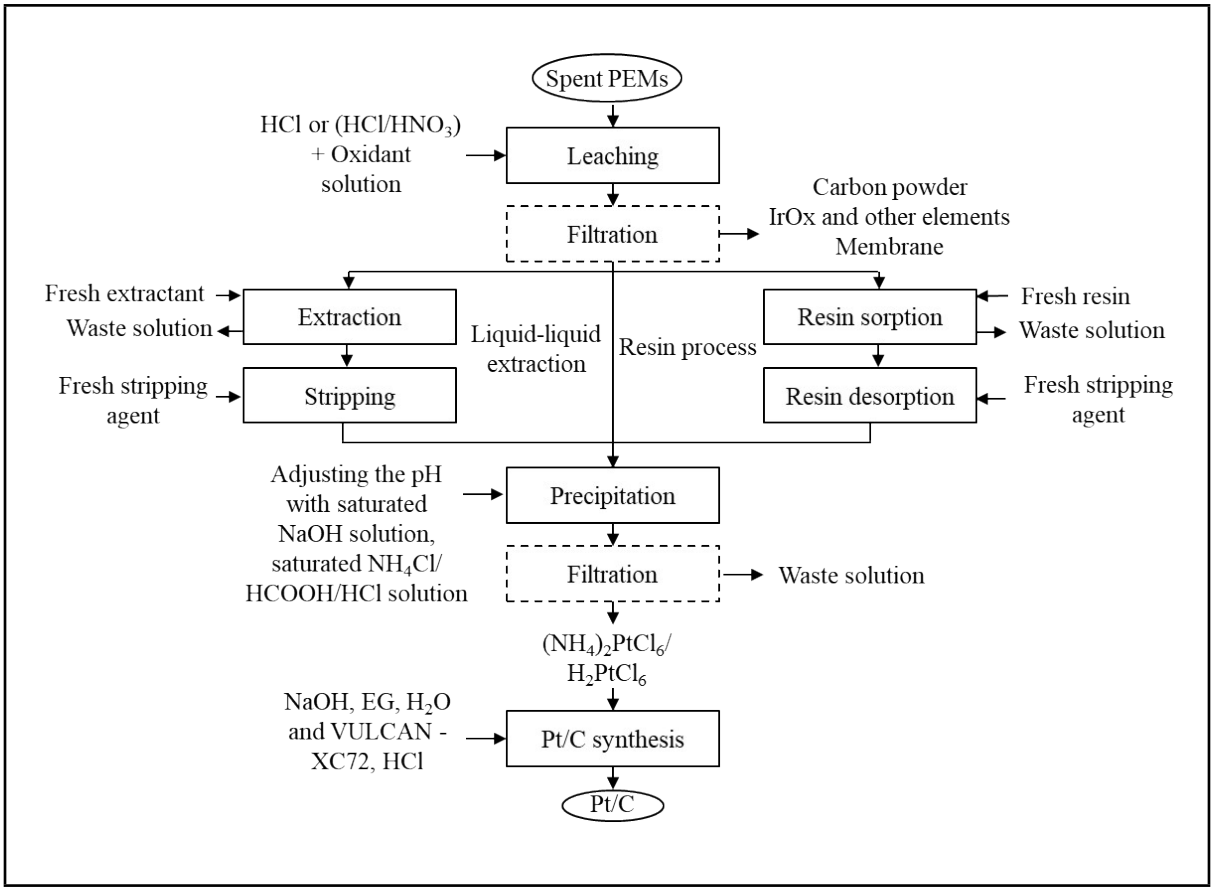

Figure S2 *Hydrometallurgical Pt-recovery process from spent PEMs (concluded from literature in table S1).*

Table S1 Hydrometallurgical PEMs recovery processes.

Initial material	Leaching method	Solvent extraction		Precipitation (% efficiency)	Recovery product	Ref.
		Extraction	Stripping			
Spent catalyst (Pt dust)	Aqua regia for 1.5 h at 109 ºC (S/L = 0.1)	-	-	NH_4Cl to precipitate $(NH_4)_2PtCl_6$	Ignition to get Pt powder 97.9 purity. (98% recovery)	3
		10% trioctylamine (TOA) in kerosine	NH_4OH/ NH_4Cl	-	Ignition to get Pt powder 99.9%purity.	
PEMFC (calcination at 600 ºC for 6 h to eliminate the carbon)	HNO_3 at 65 ºC added HCl and heated at 110 ºC to vaporise fully	-	-	The solid $H_2[PtCl_6]$ is dissolved in water again at a pH value between 3.0 and 4.0 by adding 0.5 mol ml^{-1} NaOH. HCOOH is then added to the solution to reduce the platinum.	$H_2[PtC_{l6}]$ solution	1
CCMs	H_2SO_4 at 150 ºC for 72 h. adjusted to 4–6 with 2 M NaOH solution (filter to separate sediment)	-	-	$Pt(SO_4)_2$ in solution is reduced by adding Cu powder	Pt powder	4
MEA	HCl, H_2O_2 (S/L = 0.00236g/g)	$C_8H_{18}O$, Cyanex 923	NaOH solution	HCl, NH_4Cl, H_2O	$(NH_4)_2PtCl_6$	5
MEA from PEMFC	12.5 M HCl, 3vol% H_2O_2 at 25 °C for 5 h	$[P_{44414}]Cl$	1M HCl precipitation	-	$[P44414]_2[PtCl_6]$, Co in aqueous phase,	6
		$[C_{14}$ pyr$][NTf_2]$	-	-	Pt(IV) in ionic liquid, Co(II) in the aqueous phase	

PEMFC, MEAs	HCl, 3 vol% of H_2O_2 (95.0% of Pt, 99.0% of Co leaching efficiency) for 5h 25 ºC (S/L = 4x4 cm^2/200ml)	15 vol% of Cyanex 923 extractant diluted in octanol solvent (99.4% Pt efficiency)	NaOH solution (90.1% Pt efficiency)	-	Co oxide (84.0% overall efficiency), $PtCl_6^{-2}$(85.0% overall efficiency) in alkaline solution	7
		Lewatit-MP62 resin (R/A = 20 g L^{-1}) (99.0% Pt efficiency)	NaOH solution (82.7% Pt efficiency)	-	Co^{2+} solution (47.0% overall efficiency), $PtCl_6^{2-}$ (78.0% overall efficiency) in alkaline solution	
	1 M HCl, H_2O_2 for 2 h (∼99%)	-	-	2M NH_4Cl (∼98%)	$(NH_4)_2PtCl_6$ (∼97%)	8
MEA	1 M HCl, 3% 1.5 vol % H_2O_2 (50 mL/MEA) for 24 h (98%)	-	-	5 M NaOH (pH=13)	Ru precipitate, Pt solution	9
MEAs	1 M HCl 80 ºC for 48 h	-	-	$C_2H_6O_2$ (5 mg/ml Pt in EG), NaOH (1:10) reflux at 180 ◦C for 3h,	Pt colloid in EG	10
MEA (50% IPA solution and sonication for 30 min at 70 C)	5 M HCl 10% H_2O_2 at 70 ºC for 120 min (90%)	-	-	-	H_2PtCl_6 aqueous solution	11
$PtCl_6^{2-}$ and $IrCl_6^{2-}$ solution	-	[Bmim]PF_6 or 4-(bromomethyl) benzoate and EBTOA]Br, [EBTPEA]Br, or [EBTPA]Brin	0.25 M $NH_2OH{\cdot}HCl$ solution to extract Pt(IV) , then 30%(w/w) H_2O_2 and hydrochlori	-	Pt(IV) and Ir(IV)	12

		a 1:3 M ratio	c acid was added to extract Ir(IV)			
simulated the PEMFC electrodes ((40 wt.% Pt nanoparticles on Vulcan XC72))	H_2O_2/HCl (91% efficiency) and HNO_3/HCl 93% efficiency) for 24 h at 25 °C	Cyanex 923/Octanol	NaOH solution	NH_4Cl, HCl	$(NH_4)_2PtCl_6$	13
		Lewatit-MP-62 resin	NaOH solution	NH_4Cl	$(NH_4)_2PtCl_6$	

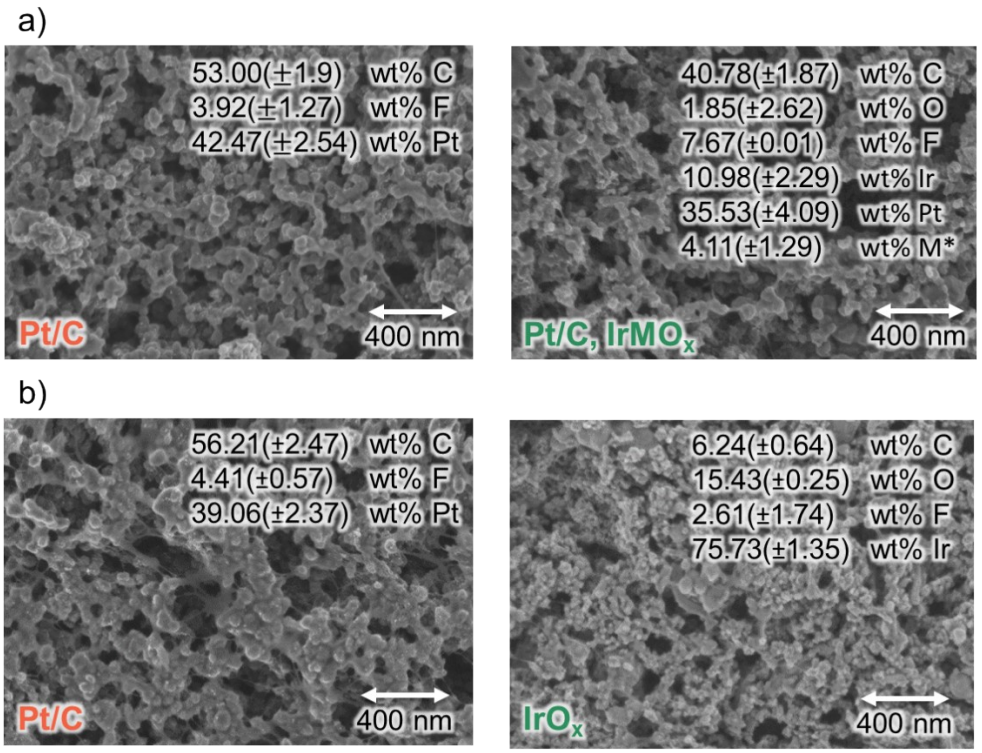

Figure S3 *SEM-EDS images and chemical compositions of the a) fuel cell CCM in each layer and b) water electrolyser CCM in each layer. * The identity of the element 'M' shown has been removed from EDS analysis because the exact composition of this catalyst material is commercially sensitive. The identity of M is unimportant to this work.*

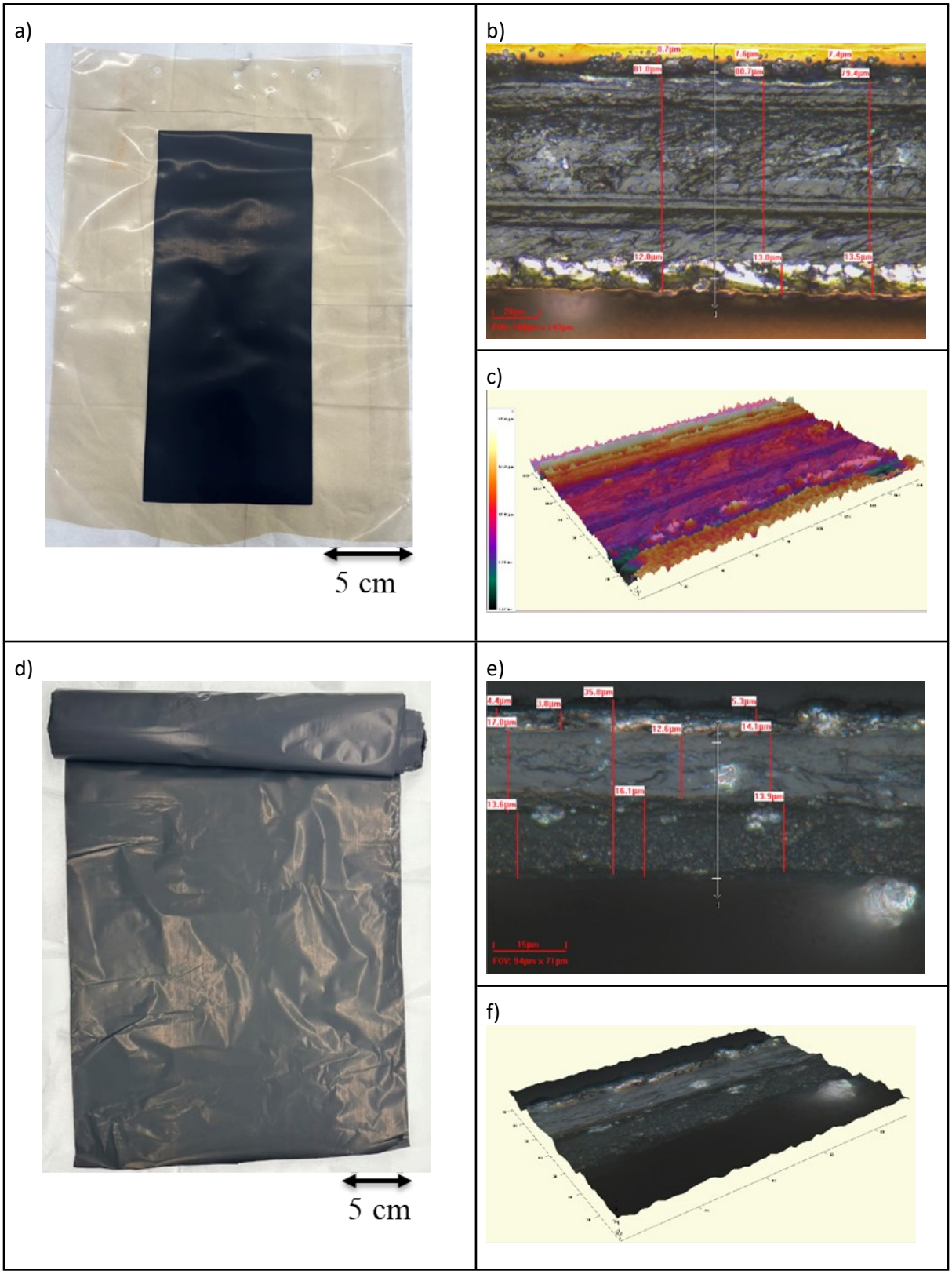

Figure S4 *a) water electrolyser CCM sample, b) and c) thickness and roughness measurement of water electrolyser CCM, d) fuel cell CCM sample, e) and f) are thickness and roughness measurement of fuel cell CCM.*

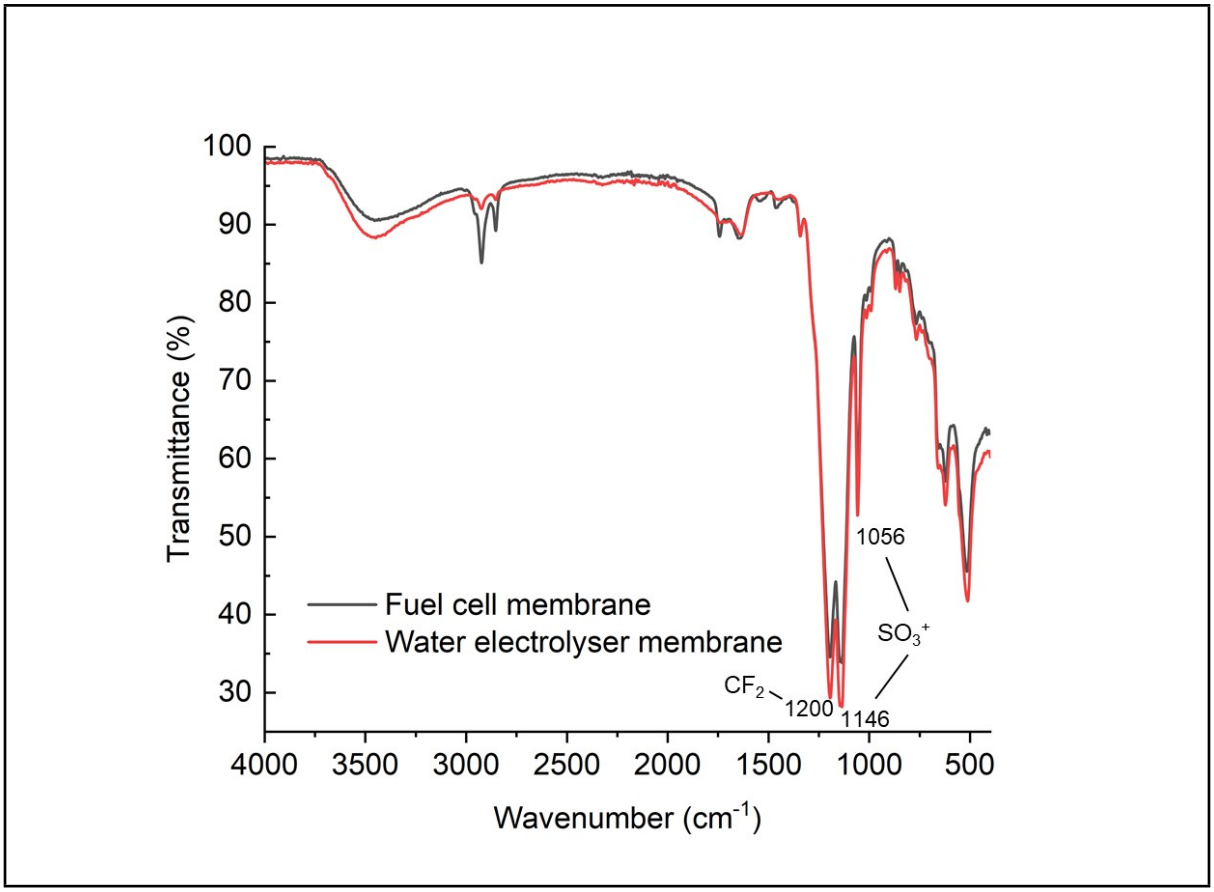

Figure S5 *FTIR spectra of delaminated central membranes of the fuel cell and water electrolyser CCMs.*

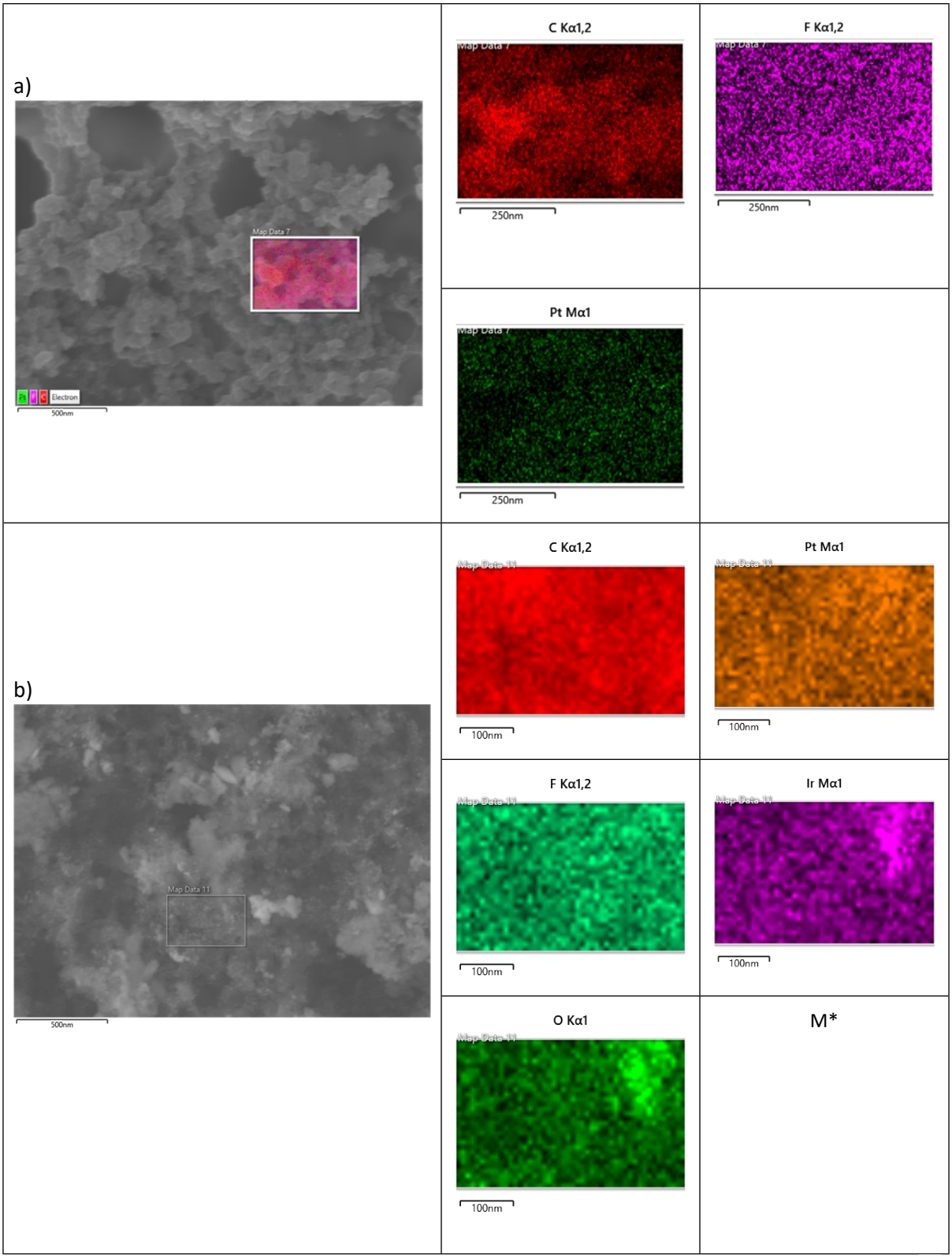

Figure S6 *Photos of EDS-mapping for the fuel cell CCM, a) Pt/C layer, and b) Pt/C, $IrMO_x$ layer. * The element 'M' mapping image has been removed from EDS analysis due to commercial sensitivity. The identity of M is unimportant to this work.*

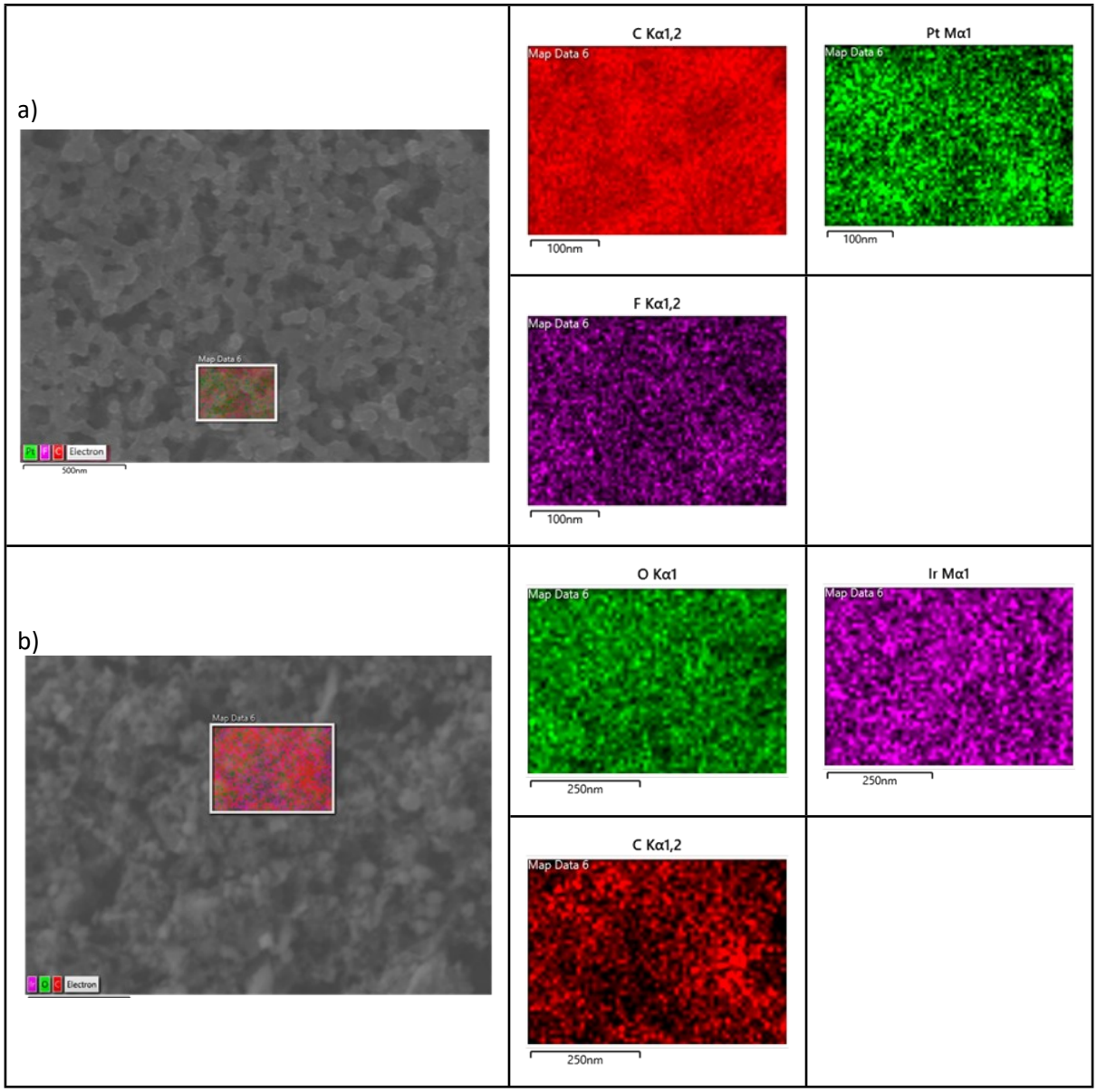

Figure S7 *Photos of EDS-mapping for the water electrolyser CCM, a) Pt/C layer, and b) IrO_x layer.*

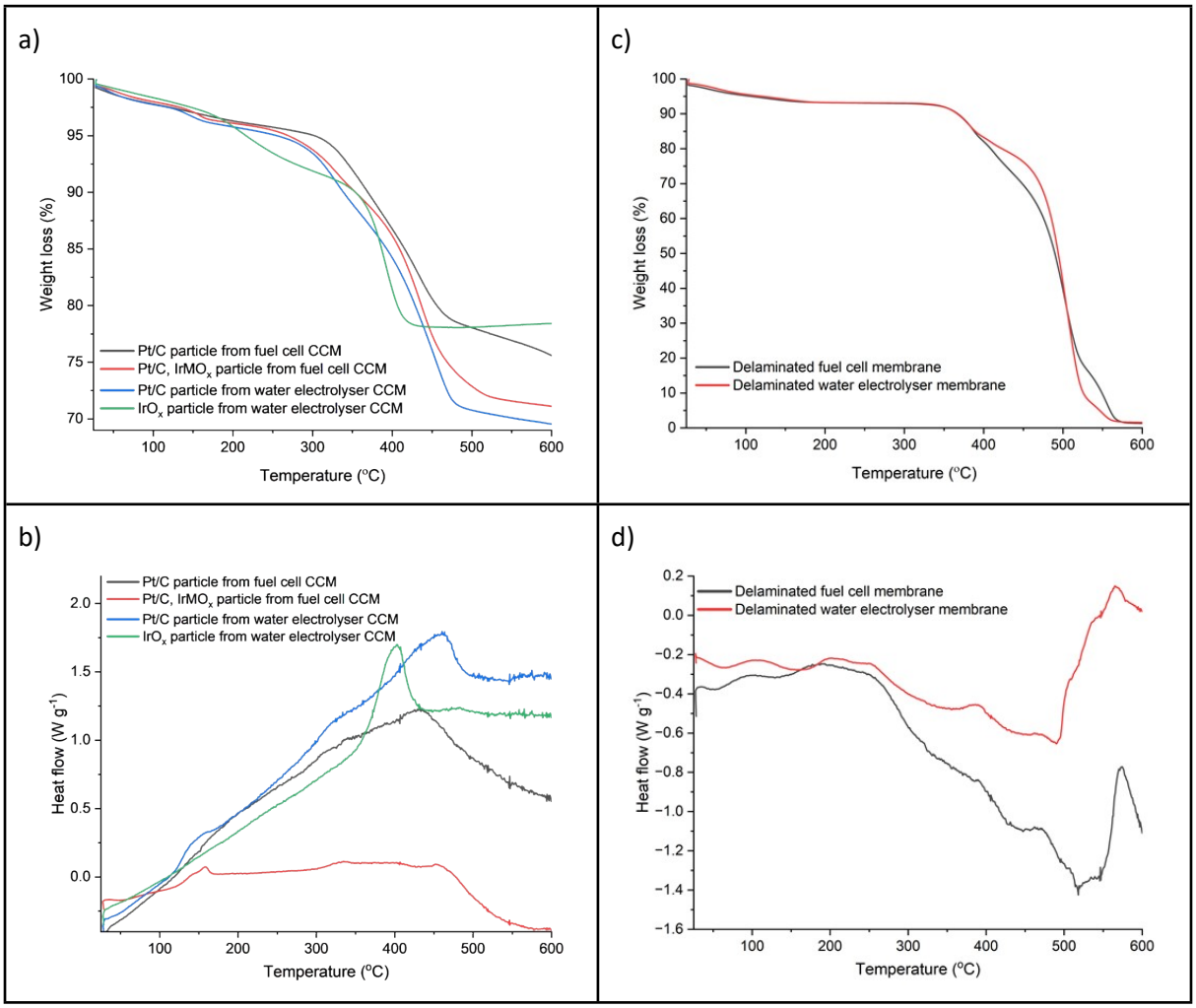

Figure S8 *TGA-DSC results of a) and b) particles from CCMs, c) and d) delaminated central membranes.*

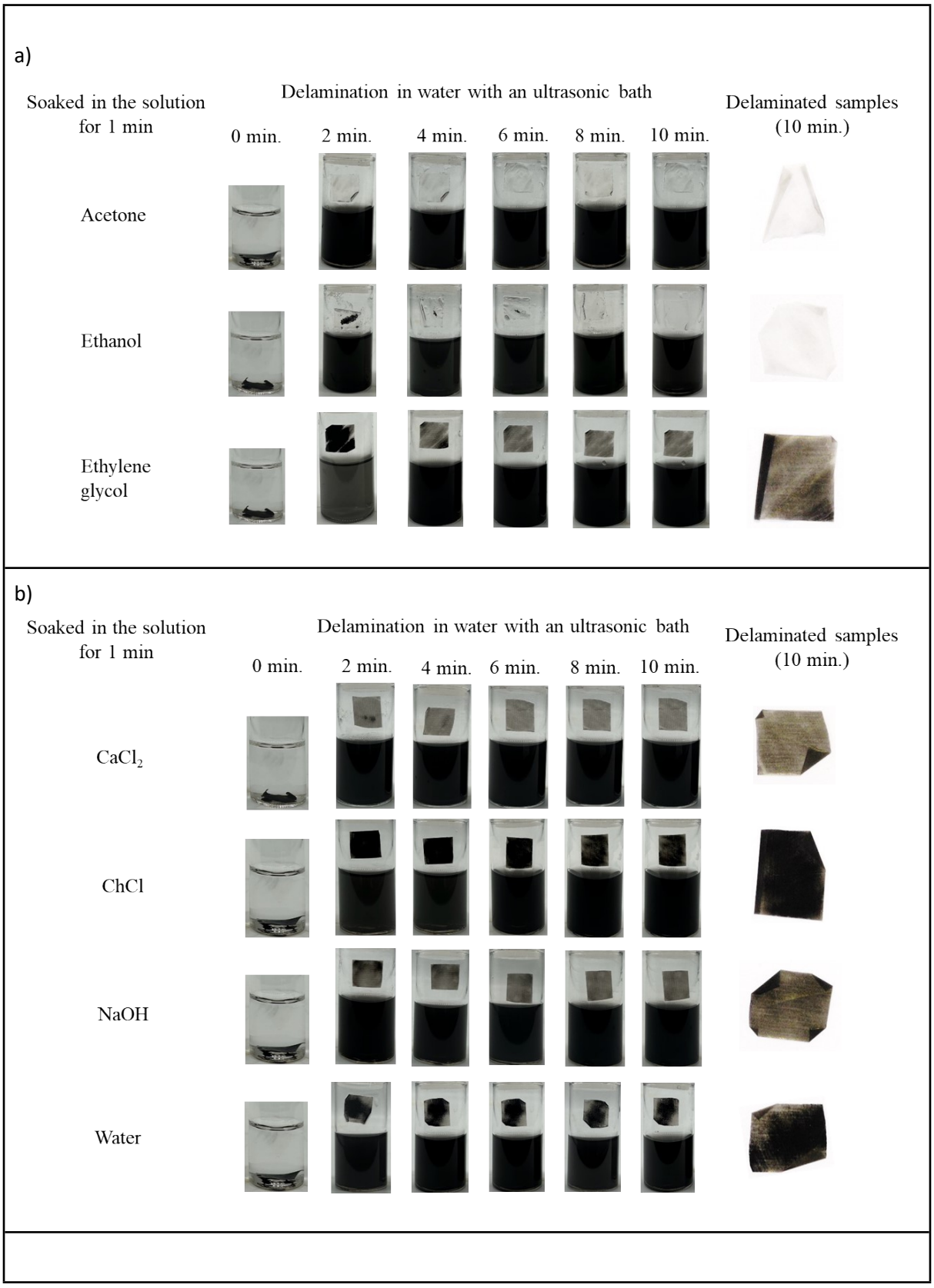

***Figure S9**: Delamination of fuel cell CCM by soaking in different a) organic solutions and b) aqueous solutions for 1 minute, followed by delamination in water with an ultrasonic bath.*

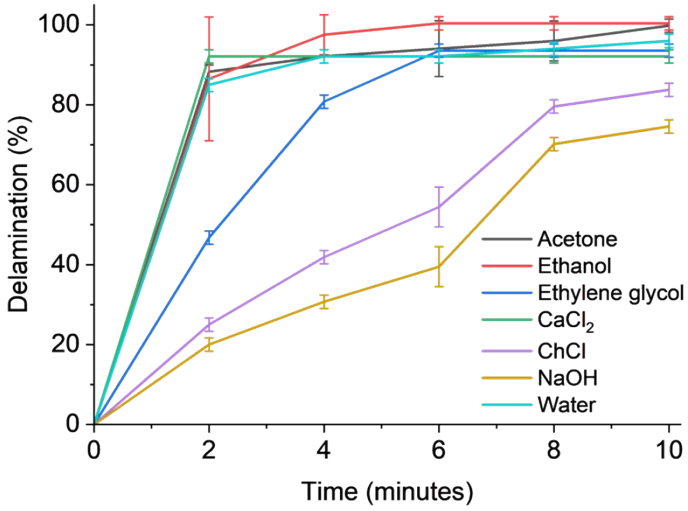

***Figure S10**: Delamination percentage in water with an ultrasonic bath of fuel cell CCM after soaking in different solvents.*

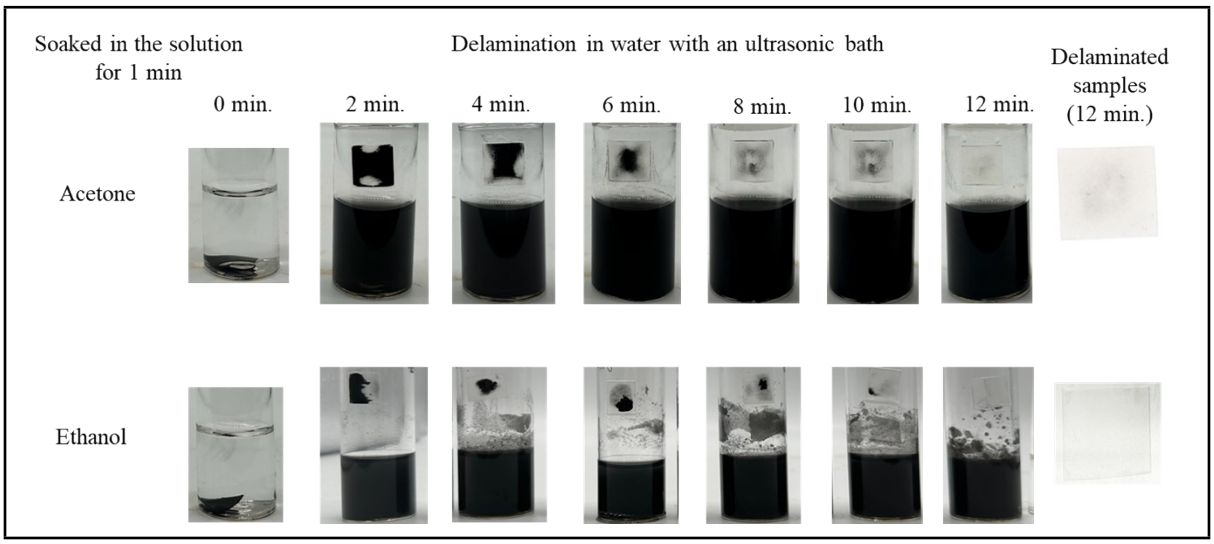

***Figure S11**: Soaked water electrolyser CCM in acetone and ethanol for 1 minute and delaminated it in water with an ultrasonic bath.*

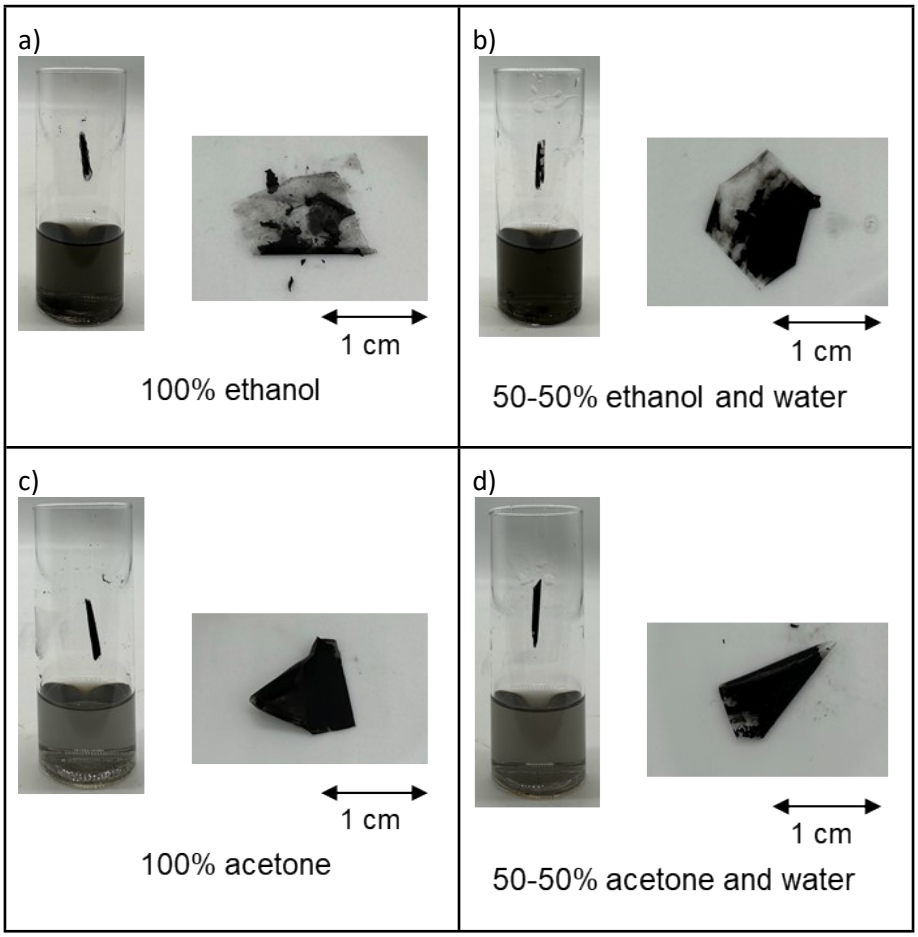

Figure S12: *Ultrasonic delamination with a) 100% ethanol, b) 50-50% ethanol-water, c) 100% acetone, d) 50-50% acetone-water.*

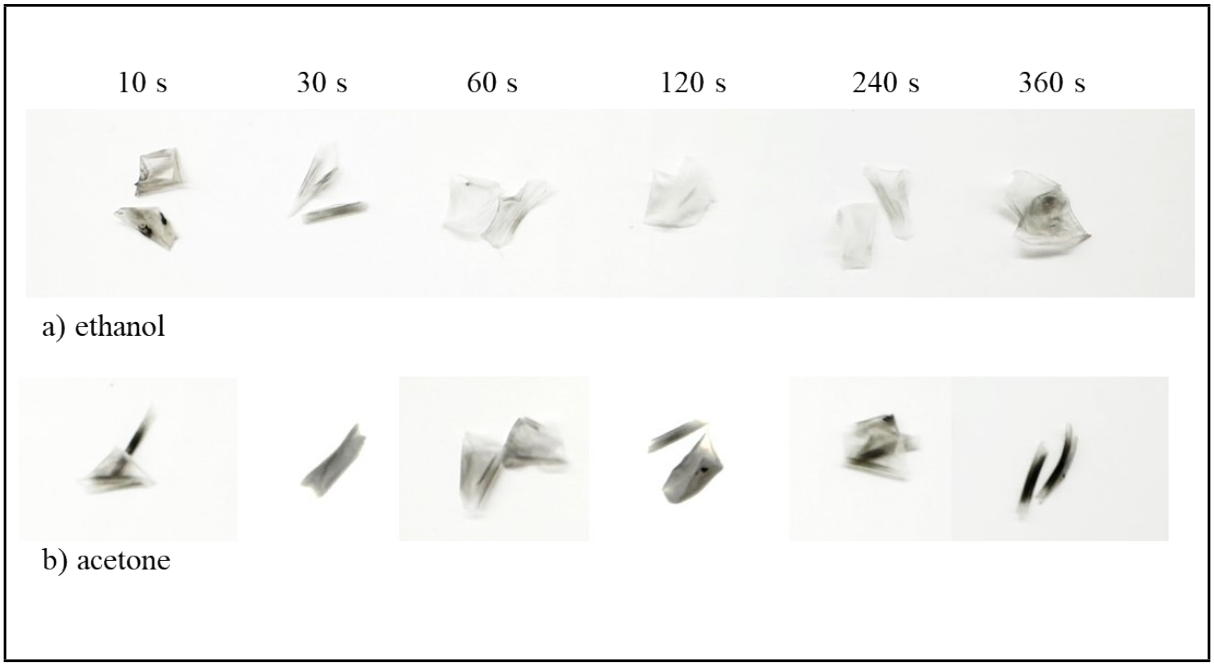

Figure S13*: The fuel cell membrane samples were soaked for 1 minute in (a) acetone and (b) ethanol, followed by delamination in water using an ultrasonic bath for 10 minutes (samples were not subsequently cleaned with fresh water).*

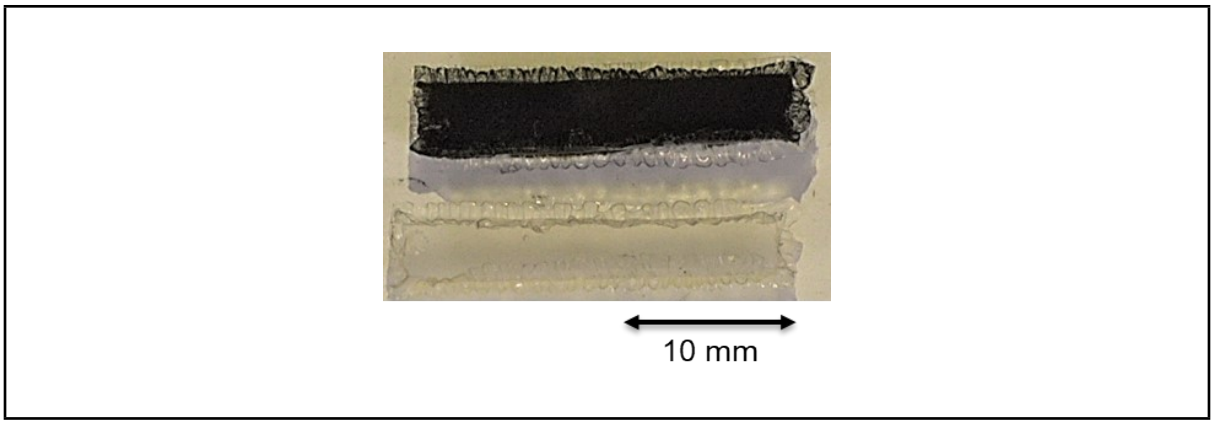

Figure S14 *WECCM (top) and PFAS ionomer membrane (bottom) after immersing in ethanol for 6 minutes.*

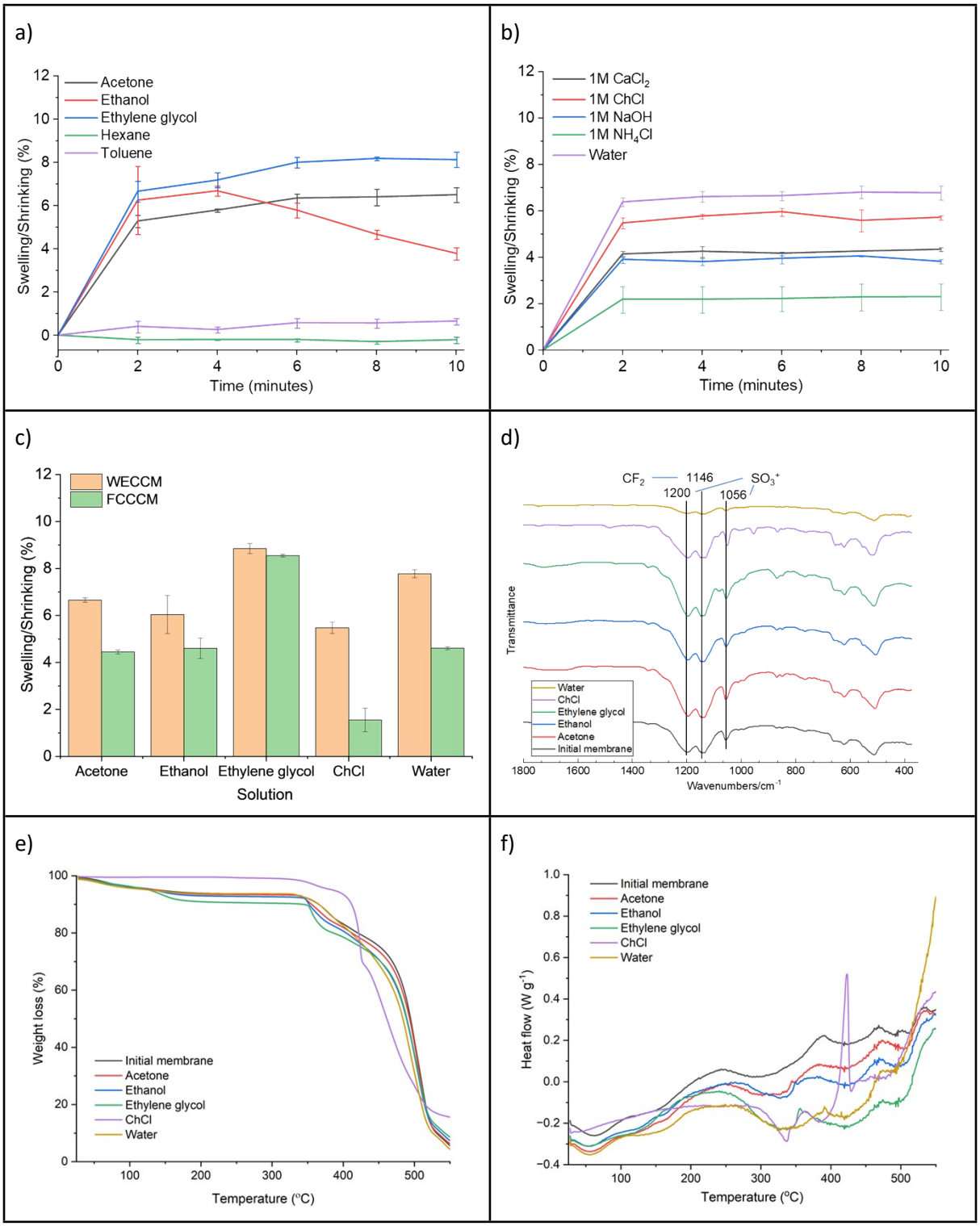

Figure S15: *Swelling percentage of PFAS ionomer membrane in a) organic solvents, b) aqueous solutions, and c) swelling of fell cell and WECCMs in solution at 6 minutes. c) FTIR spectra of post-dry for 24 h in the air of PFAS ionomer membranes after immersing in various solutions for 6 minutes. e) TGA and f) DSC graphs of post-dry for 24 PFAS ionomer membranes in the air after immersing in various solutions for 6 minutes.*

Table S2 *Chemical composition of delaminated membranes in each layer analysed by SEM-EDS*

Fuel cell membrane				
Element	Pt/C side		Pt/C, $IrMO_x$ side	
	wt%	Atomic %	wt%	Atomic %
C	26.98(±0.05)	36.92(±0.09)	27.33(±0.22)	37.33(±0.31)
O	1.87(±0.14)	1.92(±0.15)	1.64(±0.33)	1.66(±0.32)
F	70.04(±0.09)	60.59(±0.04)	70.03(±0.20)	60.49(±0.15)
S	1.13(0.19)	0.53(±0.02)	1.04(±0.29)	0.53(±0.15)
Water electrolyser membrane				
Element	Pt/C side		IrO_x side	
	wt%	Atomic %	wt%	Atomic %
C	28.70(±3.56)	38.86(±4.12)	27.63(±0.04)	37.67(±0.00)
O	2.80(±0.21)	2.85(±0.26)	2.42(±0.19)	2.48(±0.20)
F	67.47(±3.17)	57.81(±3.75)	68.68(±0.61)	59.21(±0.43)
S	1.04(±0.19)	0.53(0.11)	1.30(±0.46)	0.655(±0.23)

Table S3 *Chemical composition of a membrane obtained from the uncoated edge of the water electrolyser CCM analysed by SEM-EDS*

Element	wt%	Atomic %
C	27.91(±2.69)	37.99(±3.37)
O	1.93(±2.72)	1.98(±2.79)
F	69.06(±0.27)	59.47(±0.71)
S	1.12(±0.29)	0.57(±0.14)

References

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