In situ investigation of moisture sorption mechanism in fuel cell catalyst layers

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Supporting information

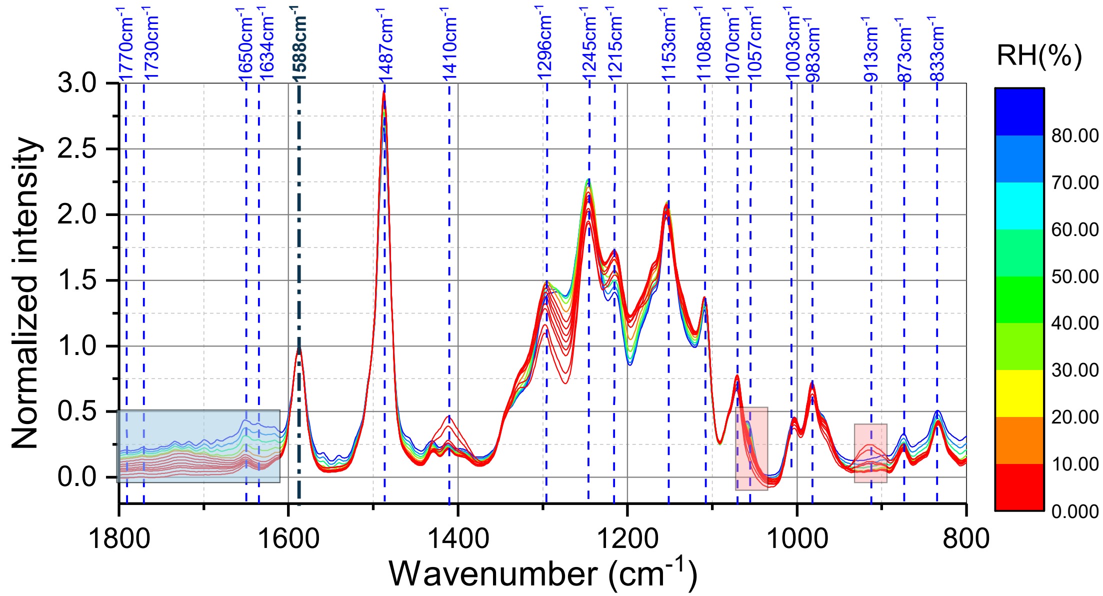

Figure S1: MIR spectra of the IN1515 membrane recorded across the 800-1800 cm^{-1} range while varying relative humidity. The primary spectral bands are highlighted with blue dotted lines, and their assignments are detailed in table S1. The bands associated with water and ionic functionalities are visually distinguished by framing them in blue and red, respectively. (The band at 1588 cm^{-1} indicated in black is the one used for normalizing the spectra)

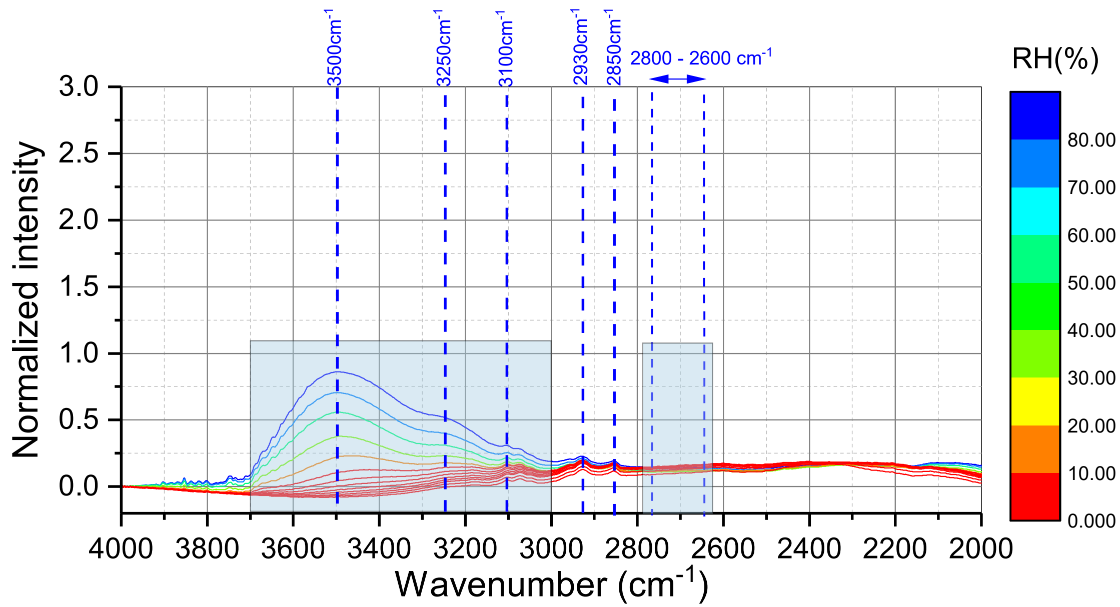

Figure S2: MIR spectra of the IN1515 membrane recorded across the 2000-4000 cm^{-1} range while varying relative humidity. The primary spectral bands are highlighted with blue dotted lines, and their assignments are detailed in table S1. The bands associated with water are visually distinguished by framing them in blue.

	Band (cm^{-1})	Assignments	Backbone	Ionic functions	Water	Ref
1	833	C-H in benzene ring	X			[1]
2	873	C-H in benzene ring	X			[1]
3	913	S-OH sym. Stretching in SO3H		X		[2]
4	983	C-O-C sym. Stretching	X	X		[2]
5	1003	C-H bending in benzene ring	X			[1]
6	1057	S=O stretching in $SO3^-$…$H3O^+/H_2O$		X		[2]
7	1070	C-H bending in benzene ring	X			[1]
8	1108	SO_2 assym. Stretching in backbone	X			[3]
9	1153	CF_2 sym. Stretching + SO_2 sym stretching in backbone. + SO_2 assym stretching in $SO3^-$	X	X		[3,4]
10	1215	CF_2 assym. Stretching + SO_2 sym stretching in $SO3^-$	X	X		[4]
11	1245	C-C stretching in benzene ring	X			[1]
12	1296	C-C stretching + C-O-C in backbone	X			[3]
13	1410	Benzene ring	X			[3]
14	1487	Benzene ring	X			[3]
15	**1588***	**Benzene ring**	**X**			[3]
16	1634	H-O-H bending in H_2O			X	[2,5]
17	1650	H-O-H bending in $H3O^+$, in H^+H_2O			X	[2,5]
18	1730	Zundel ions $H_5O_2^+$			X	[2,5]
19	1770	H_3O^+ ions			X	[2,5]
20	2600-2800	OH stretching in H_3O^+			X	[2]
21	2850	C-H stretching	X			[5]
22	2930	C-H stretching	X			[5]
23	3100	OH stretching in Zundel ions			X	[2,5]
24	3250	OH sym. stretching in H_2O			X	[2,5]
25	3500	OH assym. stretching in H_2O			X	[2,5]

Table S1: Assignments of bands indicated on MIR spectra of IN1515 membrane presented in Figures S1 and S2. The bands have been sorted according to their categories: ionomer skeleton, ionic function, and water. The references used for these assignments are indicated in the last column.

(1) Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*; Holden-Day, 1977.

(2) Dalla Bernardina, S.; Brubach, J.-B.; Berrod, Q.; Guillermo, A.; Judeinstein, P.; Roy, P.; Lyonnard, S. Mechanism of Ionization, Hydration, and Intermolecular H-Bonding in Proton Conducting Nanostructured Ionomers. *J. Phys. Chem. C* **2014**, *118* (44), 25468–25479. https://doi.org/10.1021/jp5074818.

(3) Alenazi, N. A.; Hussein, M. A.; Alamry, K. A.; Asiri, A. M. Nanocomposite-Based Aminated Polyethersulfone and Carboxylate Activated Carbon for Environmental Application. A Real Sample Analysis. *C*. 2018. https://doi.org/10.3390/c4020030.

(4) Moukheiber, E. Understanding of the Structure of Perfluorinated Sulfonic Membranes for Fuel Cell, Université de Grenoble, 2011.

(5) Nguyen, H. D.; Porihel, R.; Brubach, J. B.; Planes, E.; Soudant, P.; Judeinstein, P.; Porcar, L.; Lyonnard, S.; Iojoiu, C. Perfluorosulfonyl Imide versus Perfluorosulfonic Acid Ionomers in Proton-Exchange Membrane Fuel Cells at Low Relative Humidity. *ChemSusChem* **2020**. https://doi.org/10.1002/cssc.201902875.

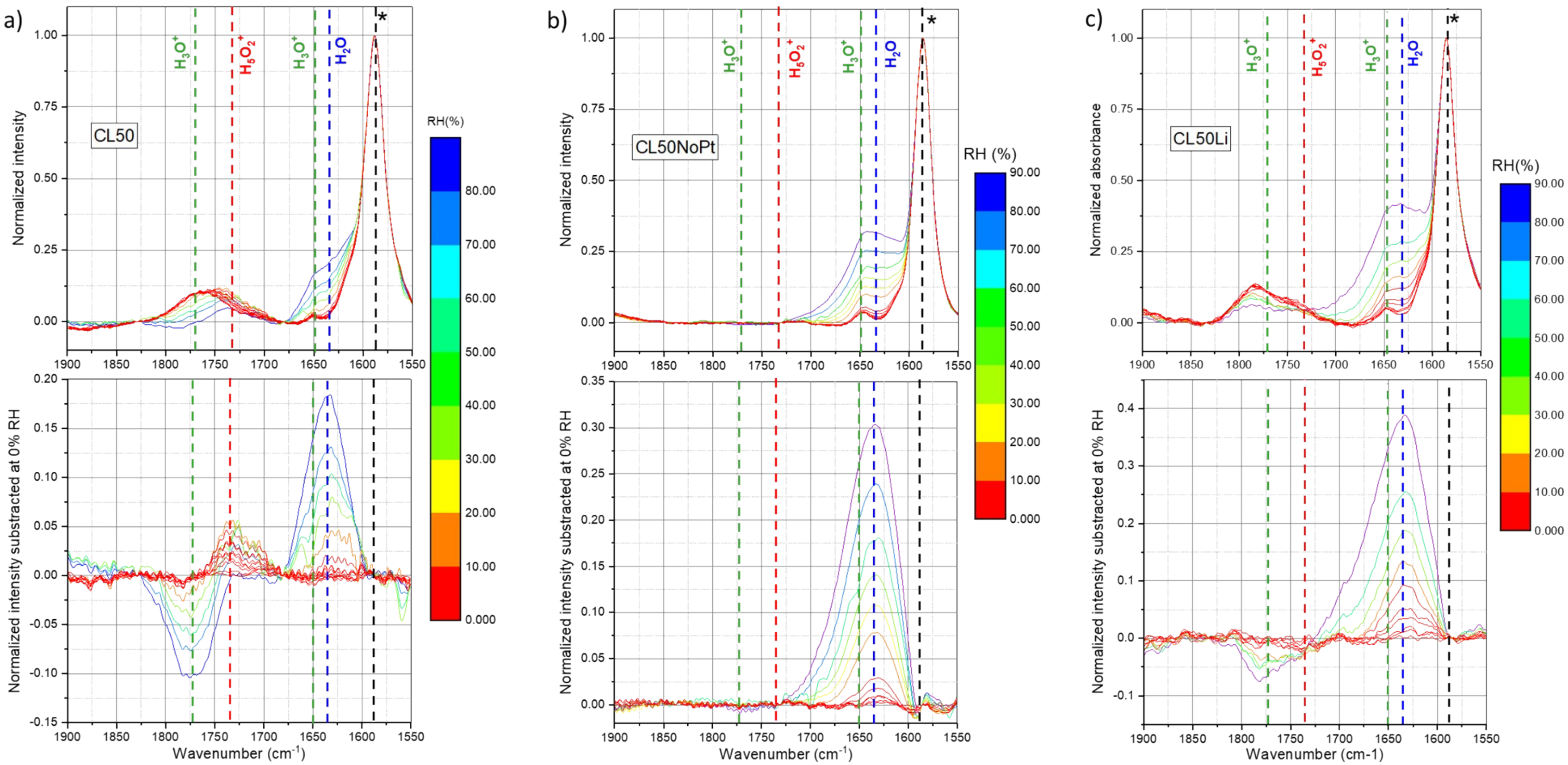

Figure S2: In situ MIR spectra of a) CL50, b) CL50NoPt, c) CL50Li in the range 1500-1900 cm^{-1} (spectra normalized to ionomer backbone band at 1588 cm^{-1}, subtracted spectra from its value at 0%RH): the characteristic bands of specific species (H_2O, H_3O^+, $H_5O_2^+$) relative to the exposition of materials to humidity are indicated by dotted lines.

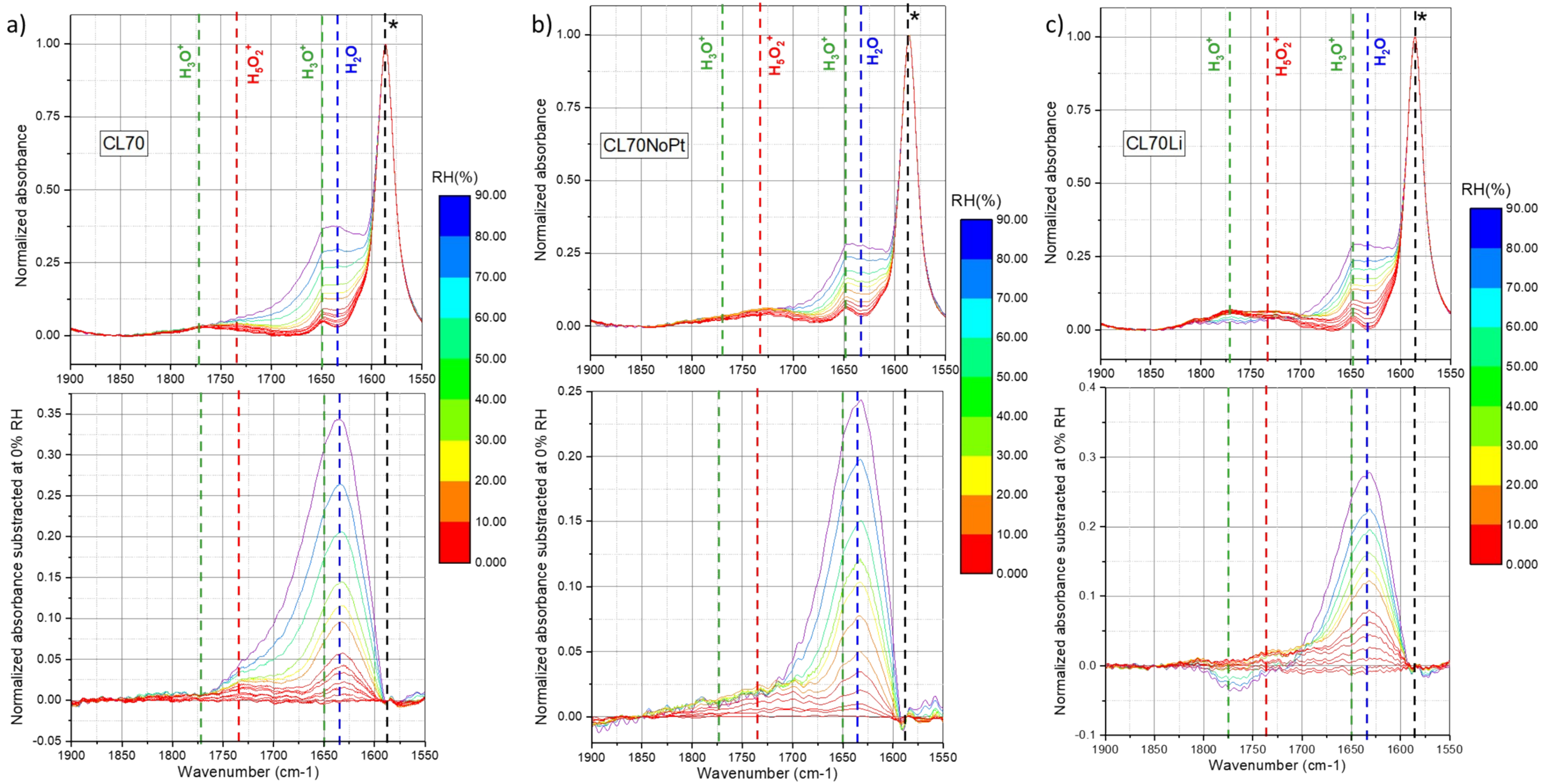

Figure S3: In situ MIR spectra of a) CL70, b) CL70NoPt, c) CL70Li in the range 1500-1900 cm^{-1} (spectra normalized to ionomer backbone band at 1588 cm^{-1}, subtracted spectra from its value at 0%RH): the characteristic bands of specific species (H_2O, H_3O+, $H_5O_2^+$) relative to the exposition of materials to humidity are indicated by dotted lines.