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# Intercalation–exfoliation processes during ionic exchange reactions from sodium lepidocrocite-type titanate toward a proton-based trititanate structure

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# Electronic Supporting Information

## Intercalation-exfoliation processes during ionic exchange reaction from the sodium lepidocrocite-type titanate toward the proton-based trititanate structure

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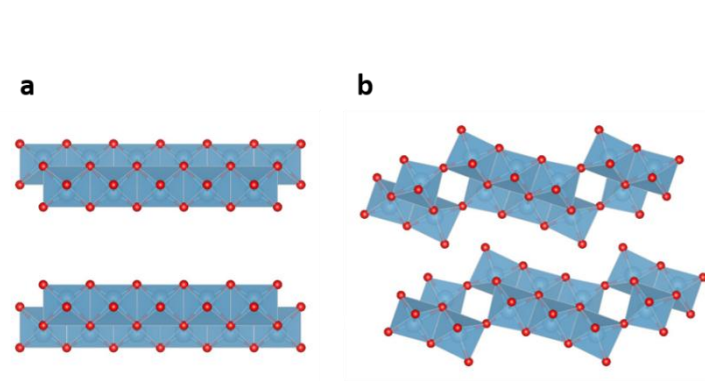
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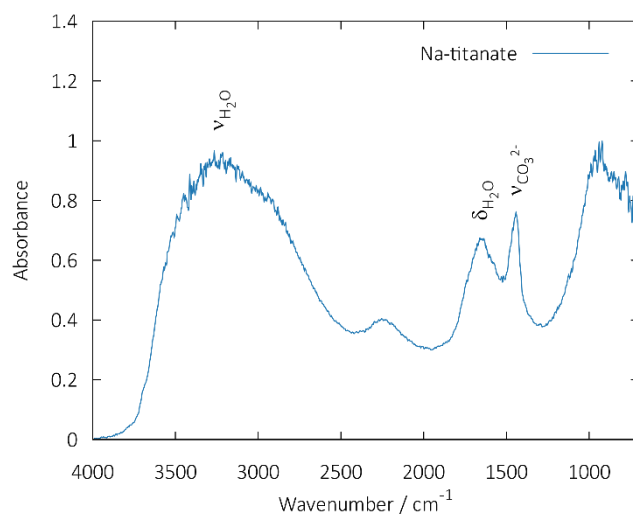
<sup>d</sup> Institut des Molécules et Matériaux du Mans (IMMM) - UMR 6283 CNRS, Le Mans Université, Avenue Olivier Messiaen, 72805 Le Mans Cedex 9, France

<sup>e</sup> X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States

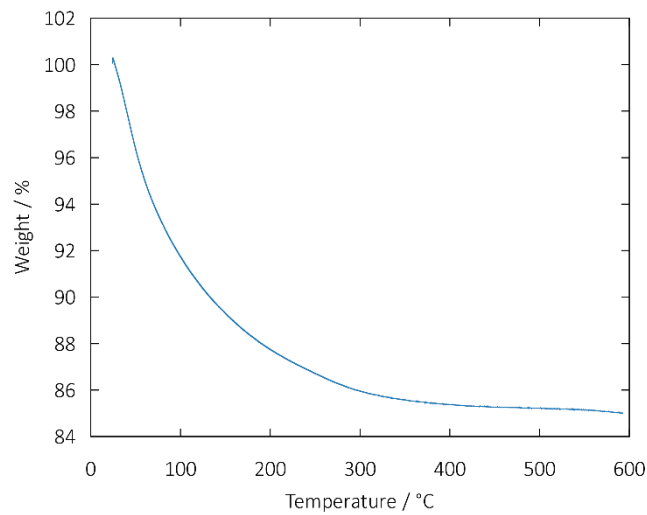
<sup>f</sup> GeePs Group of Electrical Engineering – Paris, UMR CNRS 8507, CentraleSupélec, Sorbonne Université, Univ Paris-Sud, Université Paris-Saclay, 11 rue Joliot-Curie, 91192 Gif-sur Yvette, France



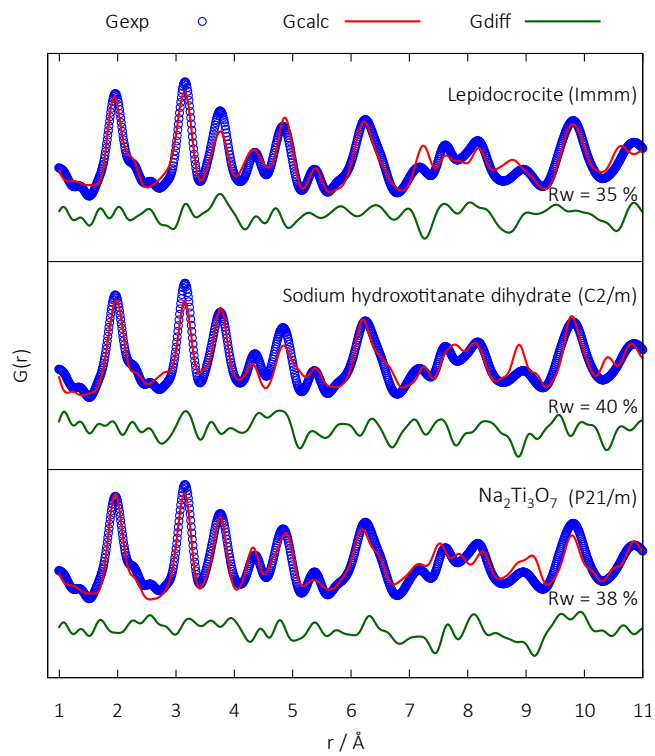
**Fig. S1.** Structural representation of a) lepidocrocite and b) trititanate structure.



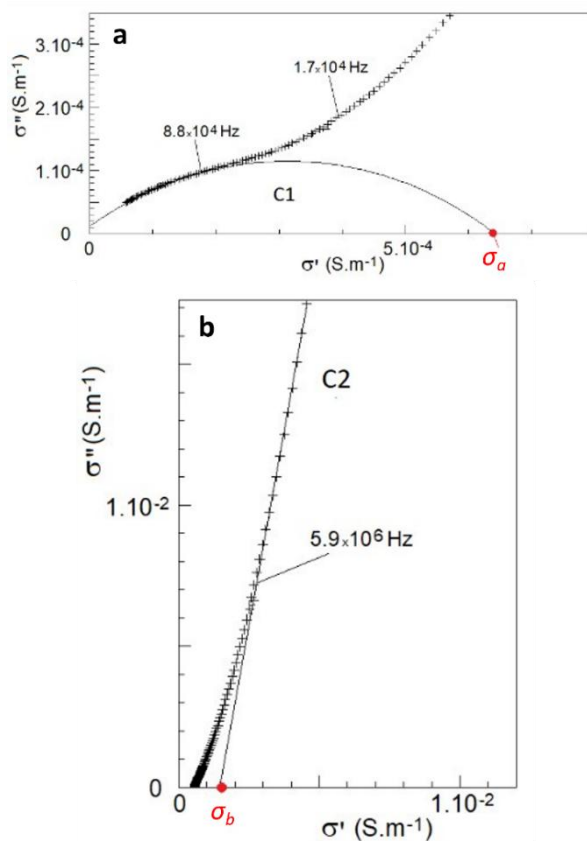
**Fig. S2.** ATR FT-IR spectrum of Na-titanate.



**Fig. S3.** Thermogravimetric analysis curve of Na-titanate.

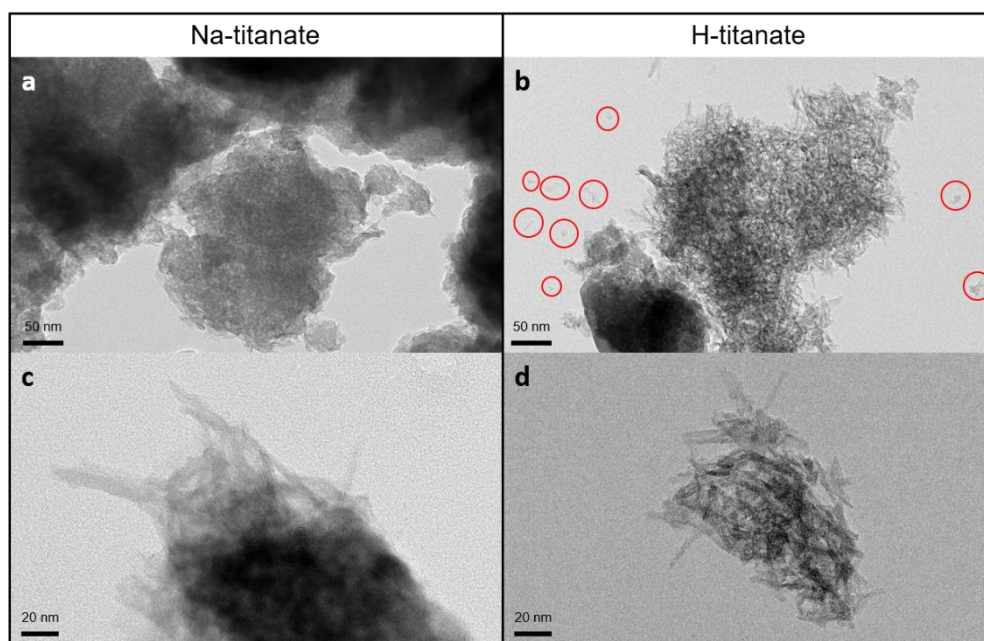


**Fig. S4.** PDF refinements of Na-titanate using different structural models.

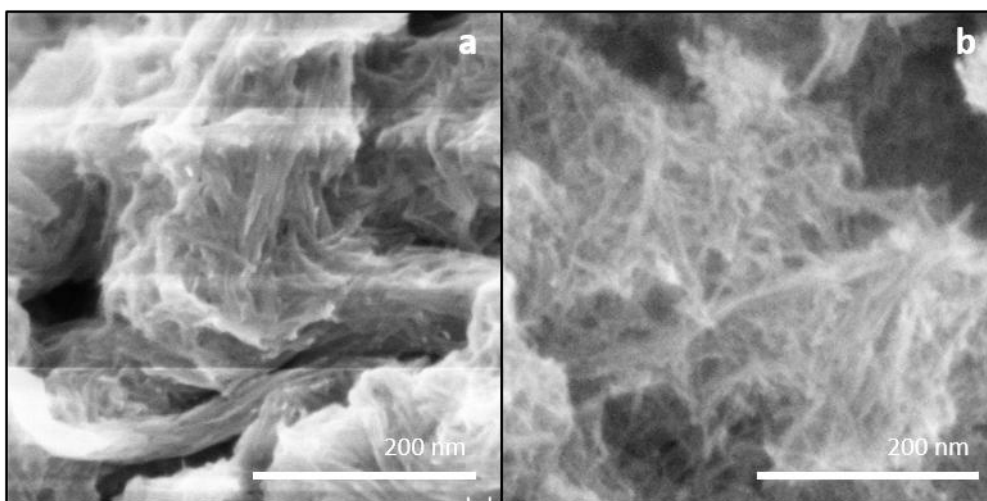


**Fig. S5.** Nyquist plots of conductivity at RT.

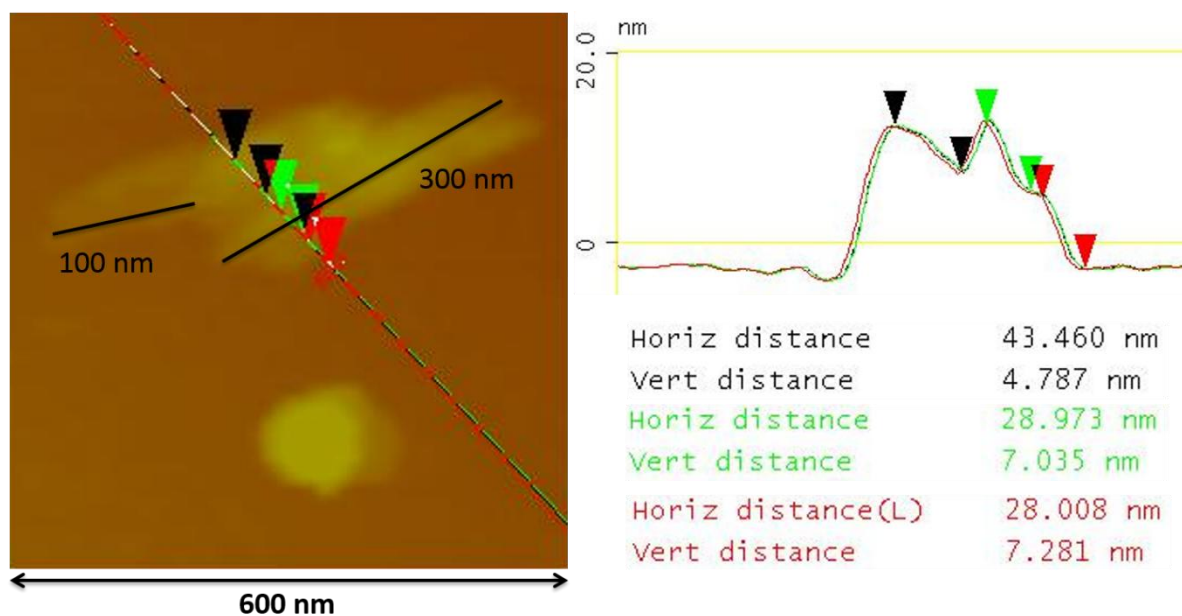
- a)** Low-frequency contribution (double layer capacitance) C1 fitted with a circular arc.  
**b)** Grain bulk contribution fitted with a straight line obtained after the subtraction of C1.  
 $\sigma_a = 6.4 \cdot 10^{-4} \text{ S/m}$  and  $\sigma_b = 1.5 \cdot 10^{-3} \text{ S/m}$  are sample and grain conductivities, respectively.



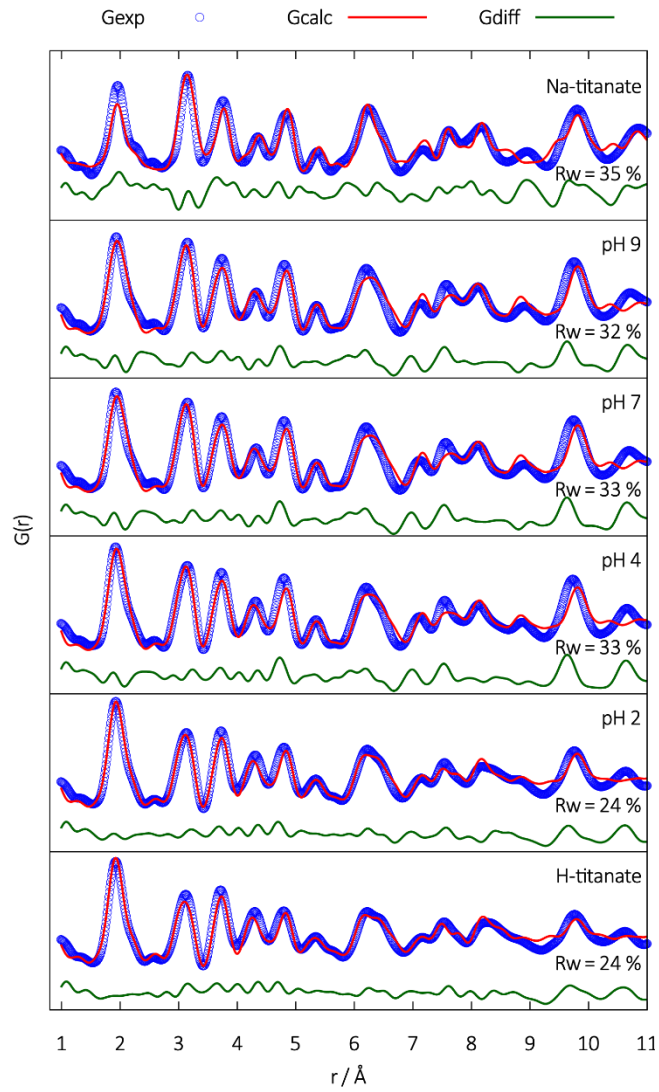
**Fig. S6.** TEM images of Na-titanate (a, c) and H-titanate (b, d).



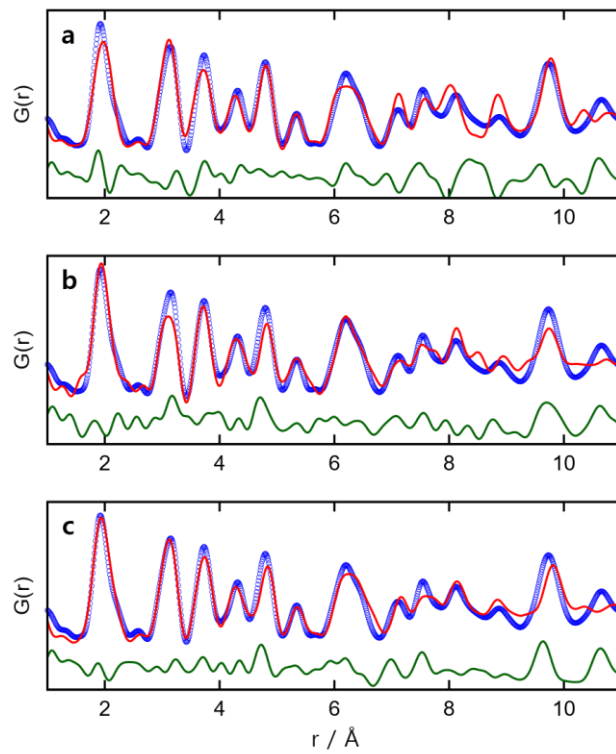
**Fig. S7.** SEM images of Na-titanate (a) and H-titanate (b)



**Fig. S8.** Atomic force micrograph with a section of an aggregate of elongated particles of H-titanate. Horizontal and vertical distances are between black, green, and red arrows. The longest sizes of two elongated particles are given in the picture.

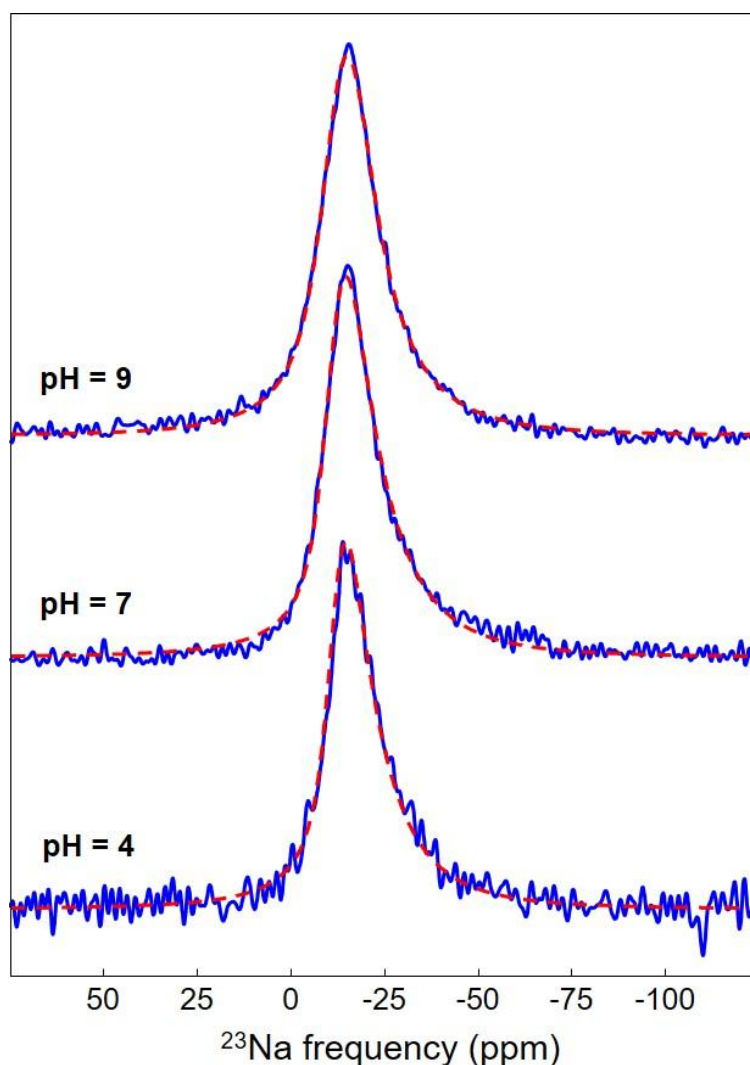


**Fig. S9.** Real-space refinements of the PDFs of the samples collected at different pH values.



**Fig. S10.** Real-space refinements of the PDF of the sample collected at pH 4 using lepidocrocite (a), trititanate (b), and both models (c).



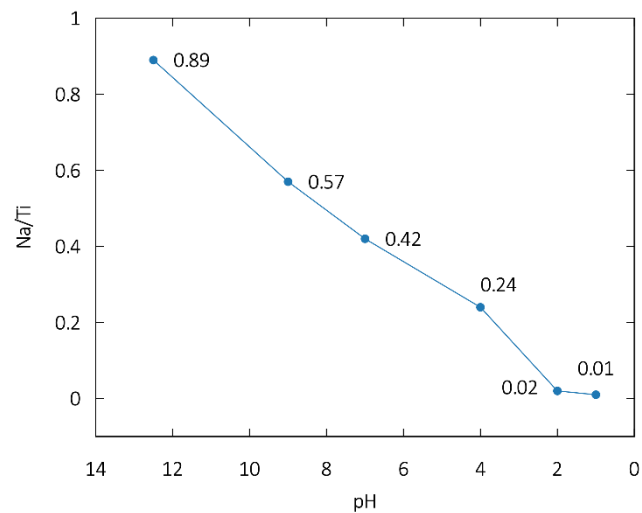


**Fig. S11.** Experimental (blue) and fitted using the Gaussian Isotropic Model<sup>1</sup> (red dashed line) <sup>23</sup>Na MAS (44 kHz) NMR spectra of three samples collected at different pH values. This model involves a Gaussian distribution of chemical shifts and a distribution of quadrupolar interactions. The parameters used for these fits are reported in **Table S1**.

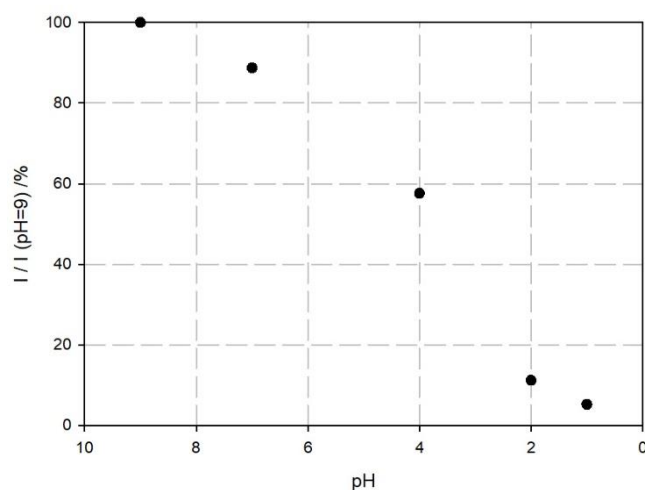
**Table S1.** Average isotropic chemical shift ( $\langle\delta_{\text{iso}}\rangle$ /ppm), full width at half maximum (FWHM) of the isotropic chemical shift Gaussian distribution ( $\Delta\text{CS}$ /ppm), average quadrupolar frequency ( $\langle\nu_{\text{Q}}\rangle$ /kHz) and quadrupolar constant ( $\langle C_{\text{Q}}\rangle$ /MHz) used to fit the <sup>23</sup>Na MAS NMR spectra of three samples collected at different pH values (see **Fig. S8**).

pH	$\langle\delta_{\text{iso}}\rangle$	$\Delta\text{CS}$	$\langle\nu_{\text{Q}}\rangle$	$\langle C_{\text{Q}}\rangle$
9	-12.6	9.1	515	1.03
7	-11.3	7.0	668	1.34
4	-11.7	5.8	631	1.26

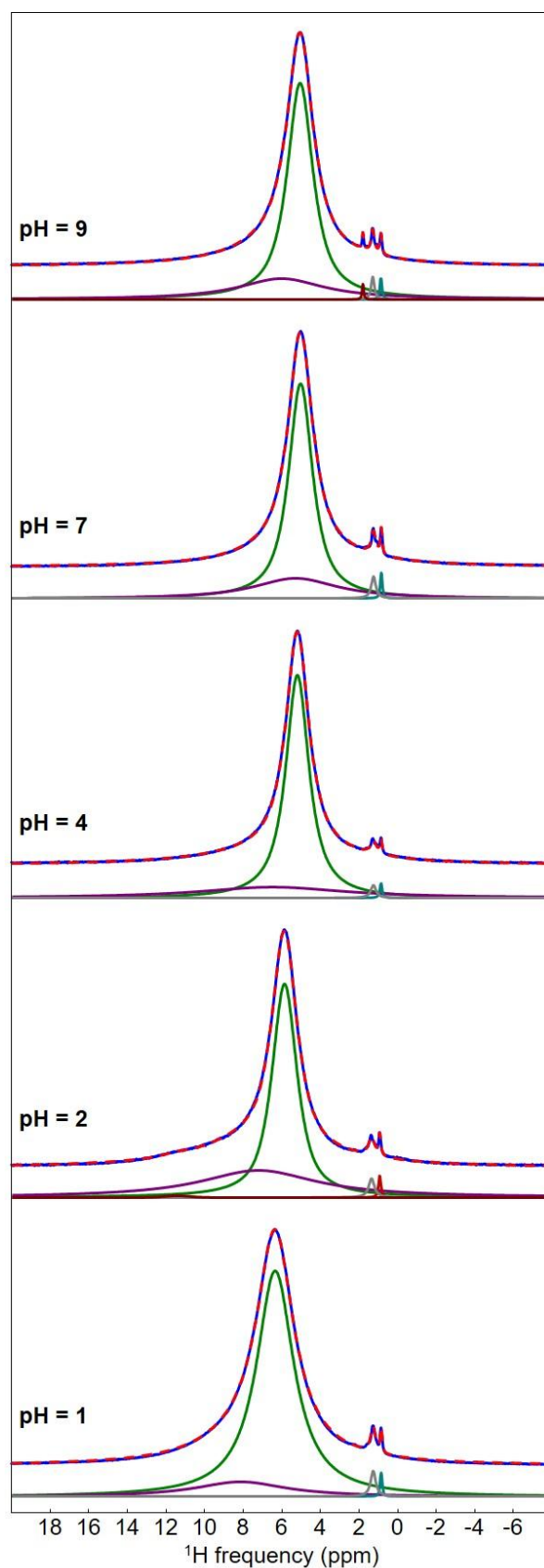
<sup>1</sup> D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J.-O. Durand, B. Bujoli, Z. Gan and G. Hoatson, Modelling one- and two-dimensional solid-state NMR spectra: Modelling 1D and 2D solid-state NMR spectra, *Magn. Reson. Chem.*, 2002, **40**, 70–76.



**Fig. S12.** Na/Ti ratio quantified using energy dispersive X-ray spectroscopy for the samples collected at different pH.



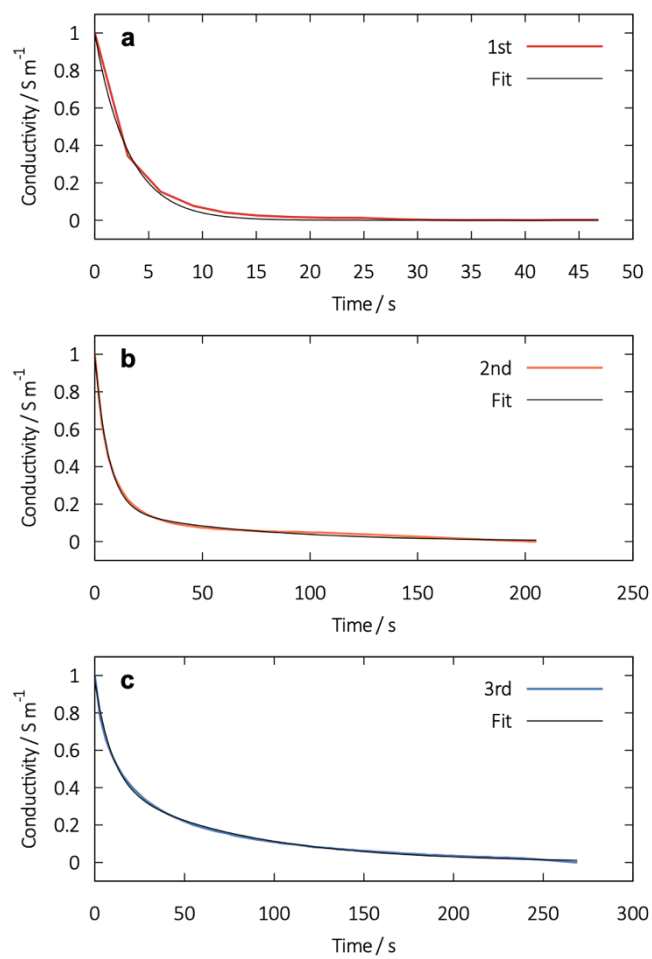
**Fig. S13.** Intensity / Intensity (pH = 9) ratio of the  $^{23}\text{Na}$  non-normalized NMR spectra for the samples collected at different pH. Intensity estimated as the area under the curve of the fit of each non-normalized spectrum. The  $^{23}\text{Na}$  non-normalized spectra correspond, for each sample, to the same number of scans and the same sample mass in the rotor.



**Fig. S14.** Experimental (blue) and fitted (red dashed line)  $^1\text{H}$  MAS (60 kHz) NMR spectra of the samples collected at different pH. The individual resonances used for these fits are shown below (see **Table S2**).

**Table S2.** Isotropic chemical shifts ( $\delta_{\text{iso}}$ /ppm), line widths (LW/ppm), relative intensities (I/%), of the NMR resonances used for the fit of the  $^1\text{H}$  MAS (64 kHz) NMR spectra of the samples collected at different pH (see **Fig. S11**).

pH	$\delta_{\text{iso}}$	LW	I
1	0.85	0.13	0.4
	1.26	0.31	1.3
	6.3	2.3	84.9
	8.1	5.7	13.4
2	0.92	0.14	0.6
	1.35	0.36	1.3
	5.9	1.6	60.3
	7.2	7.3	37.5
	11.4	1.5	0.3
4	0.85	0.14	0.5
	1.25	0.34	1.0
	5.2	1.5	74.6
	6.5	9.1	23.9
7	0.84	0.12	0.7
	1.24	0.28	1.4
	5.0	1.5	73.5
	5.3	5.3	24.4
9	0.86	0.13	0.6
	1.28	0.20	1.0
	1.8	0.09	0.3
	5.1	1.6	74.5
	6.0	5.4	23.6



**Fig. S15.** Results of to fit the decay of the ionic conductivity during the Na<sup>+</sup>-H<sup>+</sup> ionic exchange.