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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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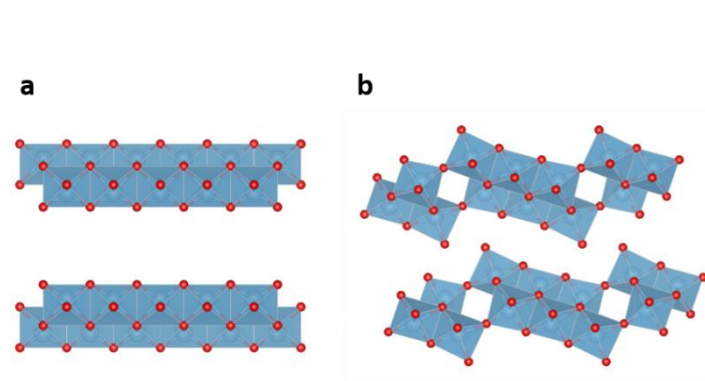


Fig. S1. Structural representation of a) lepidocrocite and b) trititanate structure.

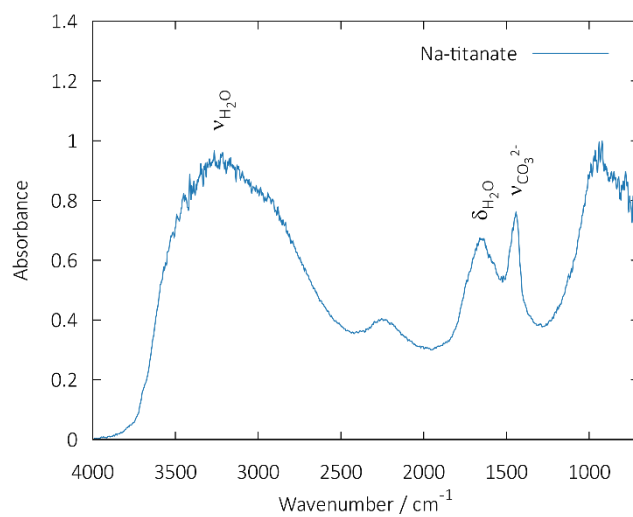


Fig. S2. ATR FT-IR spectrum of Na-titanate.

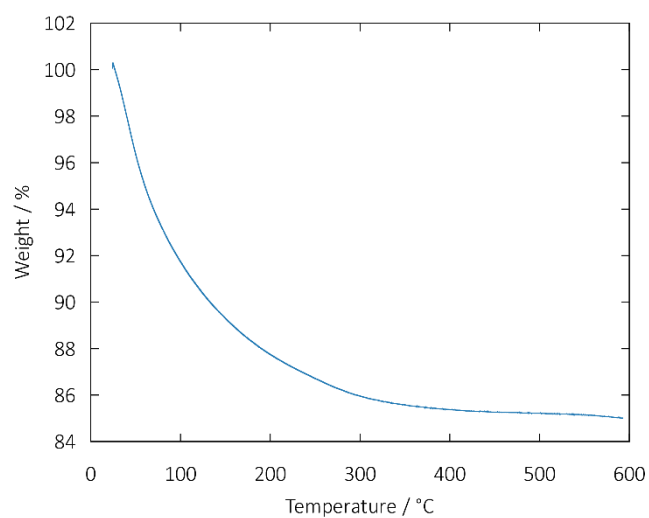


Fig. S3. Thermogravimetric analysis curve of Na-titanate.

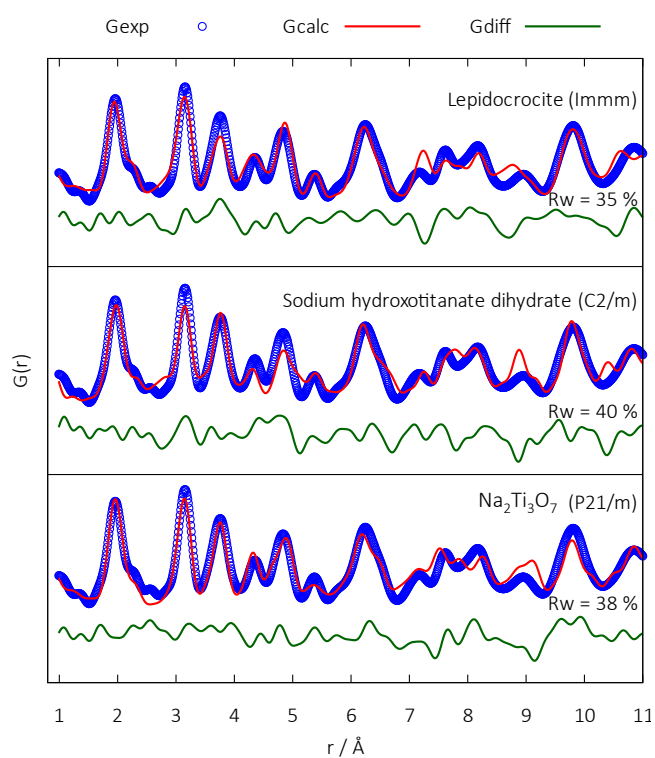


Fig. S4. PDF refinements of Na-titanate using different structural models.

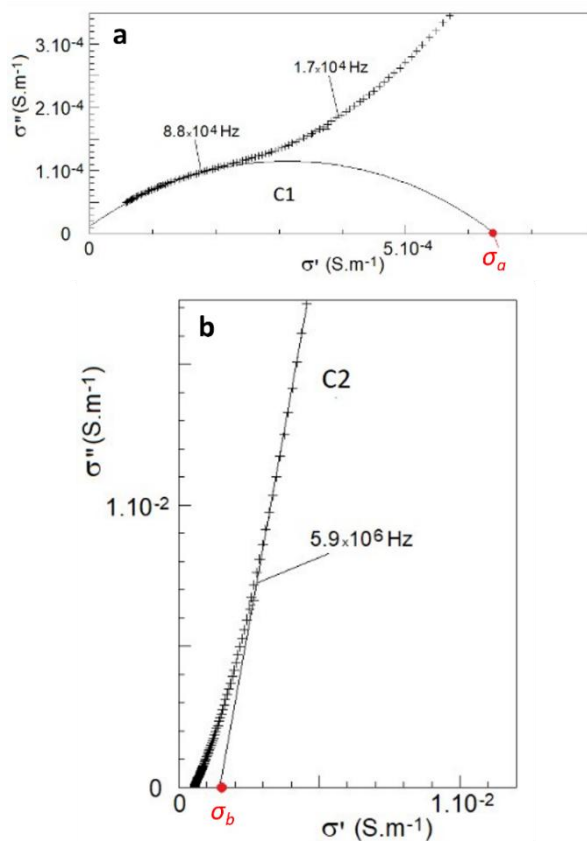


Fig. S5. Nyquist plots of conductivity at RT.

- 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.

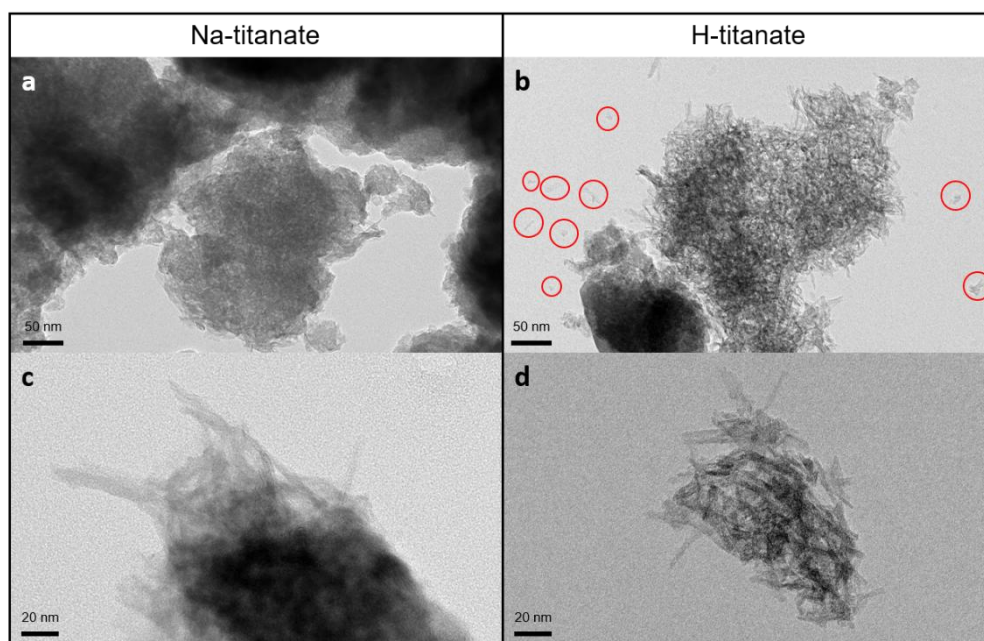


Fig. S6. TEM images of Na-titanate (a, c) and H-titanate (b, d).

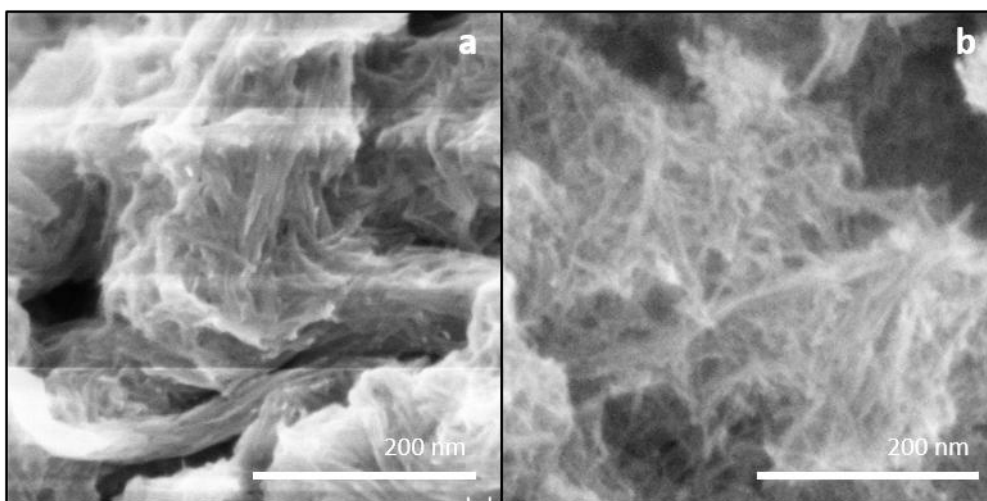


Fig. S7. SEM images of Na-titanate (a) and H-titanate (b)

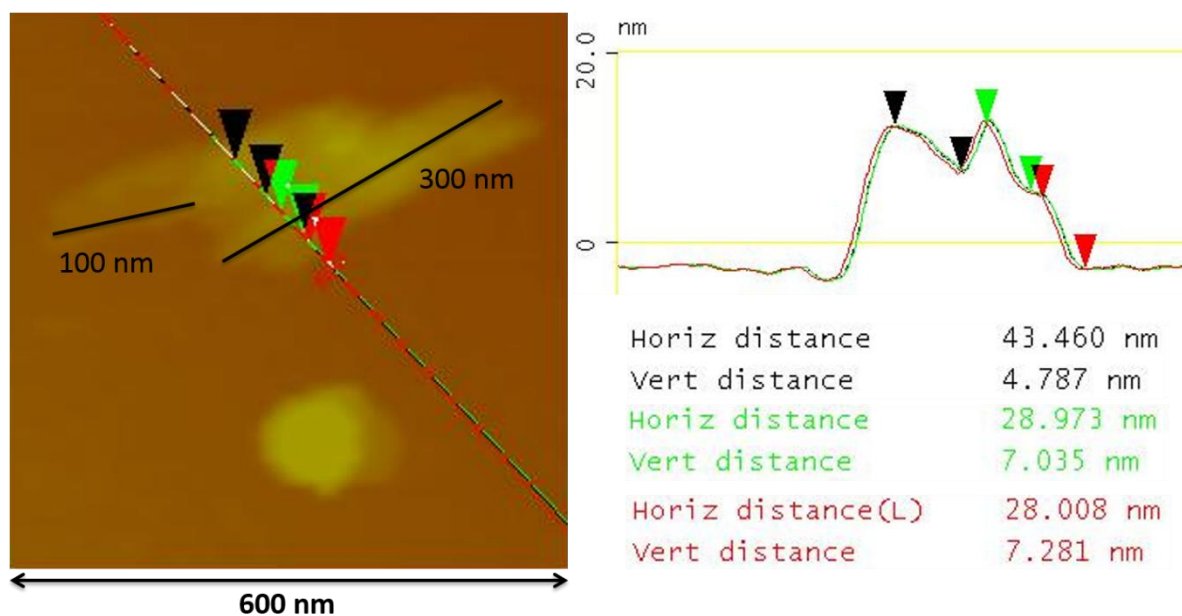


Fig. S8. Atomic force micrograph with a section of an aggregate of elongated particles of H-titanate. Horizontal and vertical distances are between black, green, and red arrows. The longest sizes of two elongated particles are given in the picture.

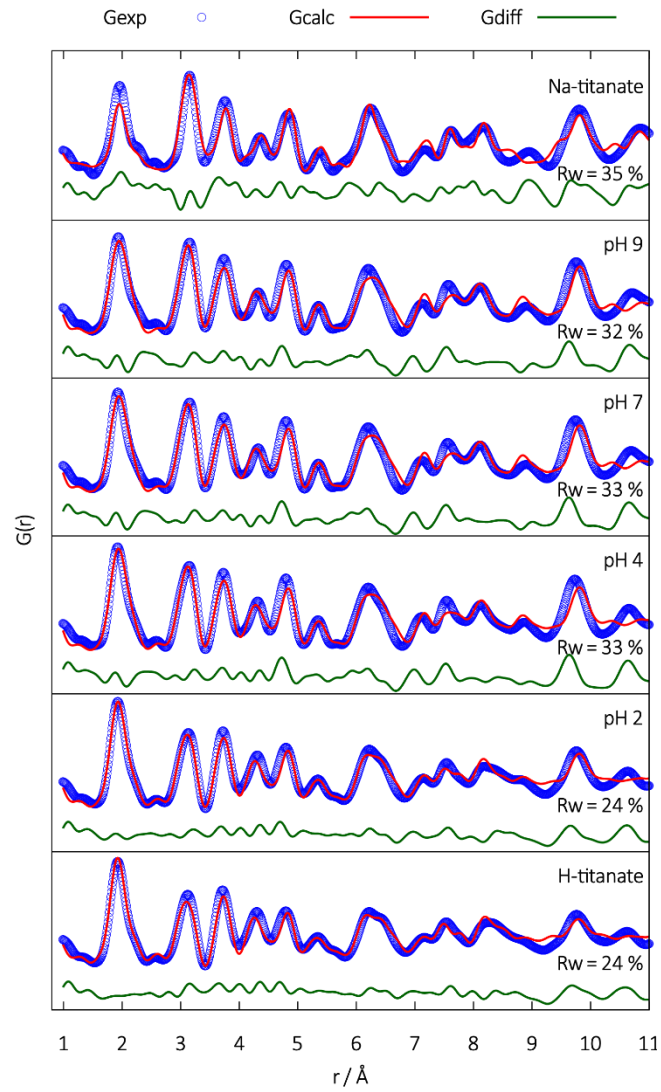


Fig. S9. Real-space refinements of the PDFs of the samples collected at different pH values.

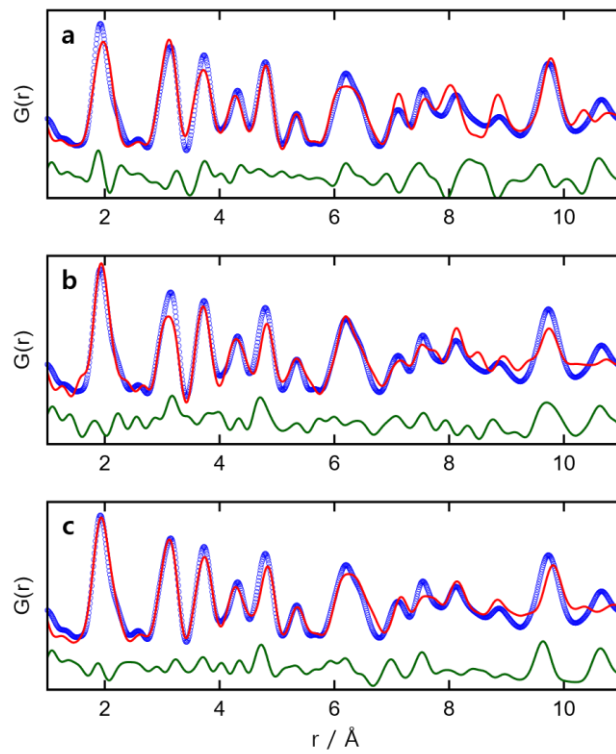


Fig. S10. Real-space refinements of the PDF of the sample collected at pH 4 using lepidocrocite (a), trititanate (b), and both models (c).

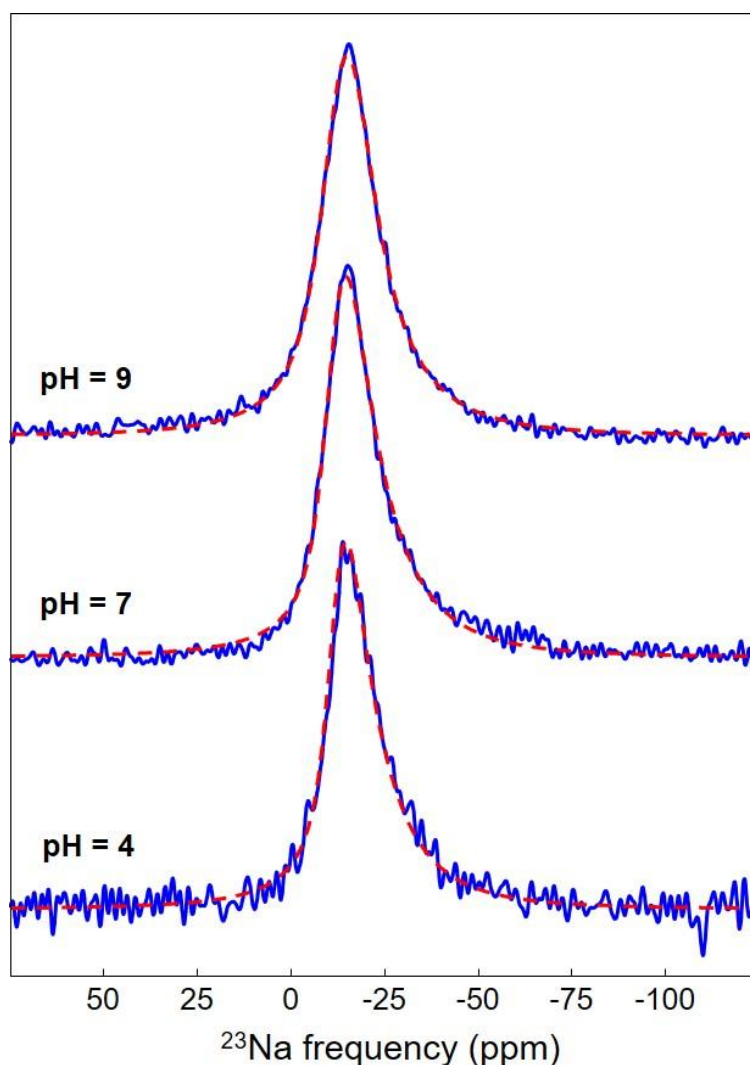


Fig. S11. Experimental (blue) and fitted using the Gaussian Isotropic Model¹ (red dashed line) ²³Na MAS (44 kHz) NMR spectra of three samples collected at different pH values. This model involves a Gaussian distribution of chemical shifts and a distribution of quadrupolar interactions. The parameters 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 (ΔCS /ppm), average quadrupolar frequency ($\langle\nu_{\text{Q}}\rangle$ /kHz) and quadrupolar constant ($\langle C_{\text{Q}}\rangle$ /MHz) used to fit the ²³Na MAS NMR spectra of three samples collected at different pH values (see **Fig. S8**).

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

¹ 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.

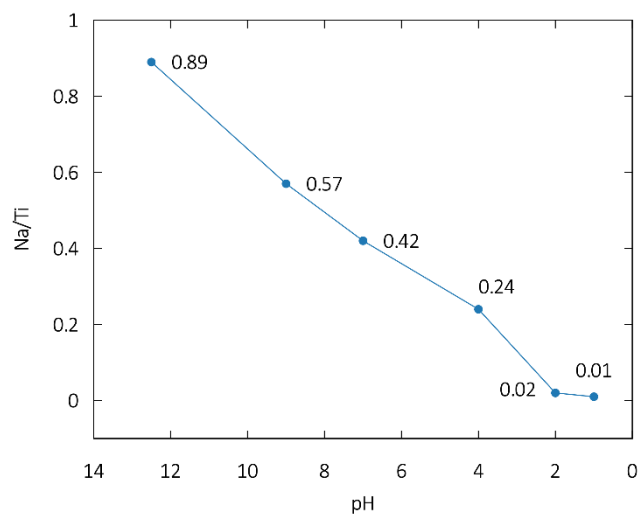


Fig. S12. Na/Ti ratio quantified using energy dispersive X-ray spectroscopy for the samples collected at different pH.

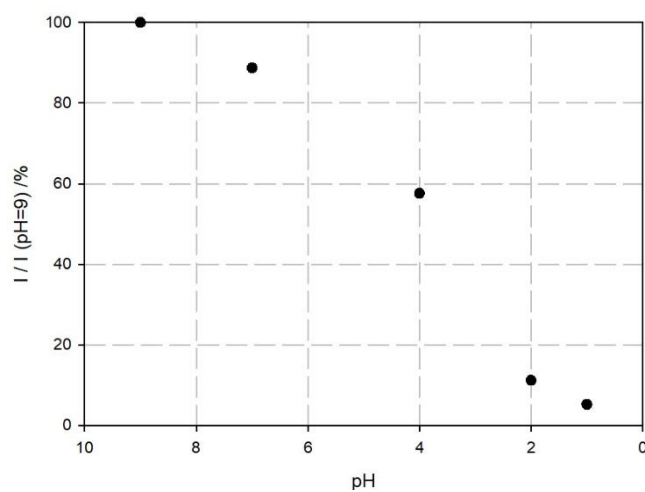


Fig. S13. Intensity / Intensity (pH = 9) ratio of the ^{23}Na non-normalized NMR spectra for the samples collected at different pH. Intensity estimated as the area under the curve of the fit of each non-normalized spectrum. The ^{23}Na non-normalized spectra correspond, for each sample, to the same number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

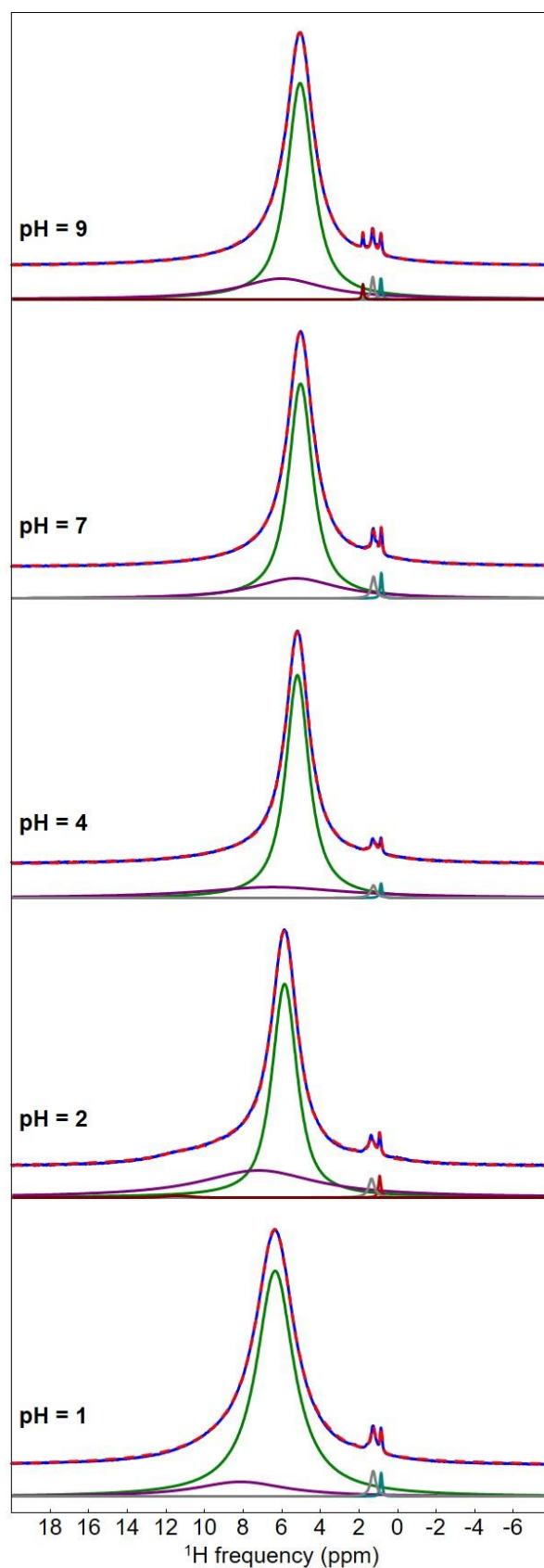


Fig. S14. Experimental (blue) and fitted (red dashed line) ^1H MAS (60 kHz) NMR spectra of the samples collected at different pH. The individual resonances used for these fits are shown below (see **Table S2**).

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

| pH | δ_{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 |

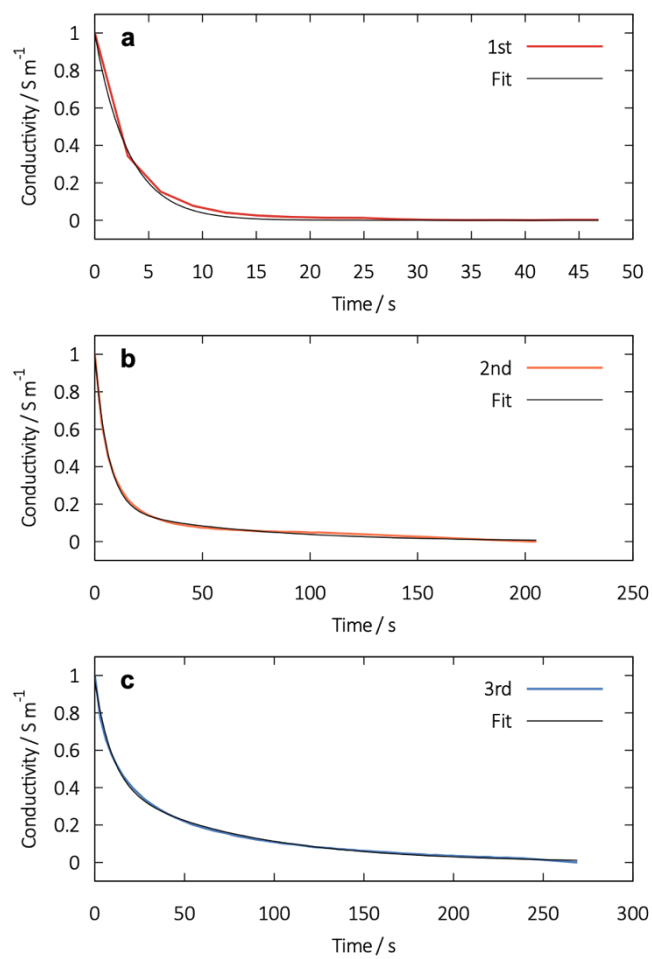


Fig. S15. Results of to fit the decay of the ionic conductivity during the Na⁺-H⁺ ionic exchange.