

Supporting Information

Hydronium Ions Stabilized in a Titanate Layered Structure with High Ionic Conductivity: Application to Aqueous Proton Batteries

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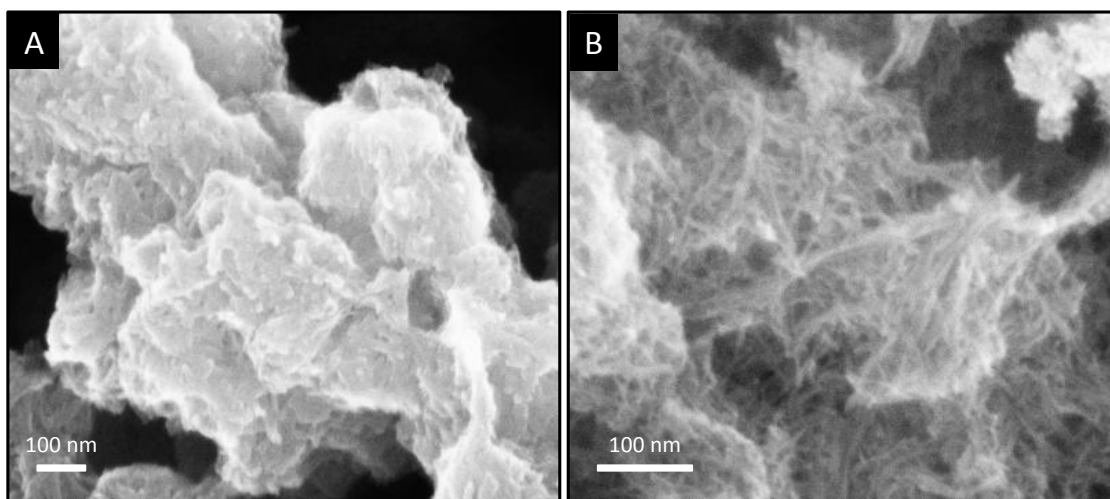


Figure S1. Scanning electron microscopy images of H-titanate.

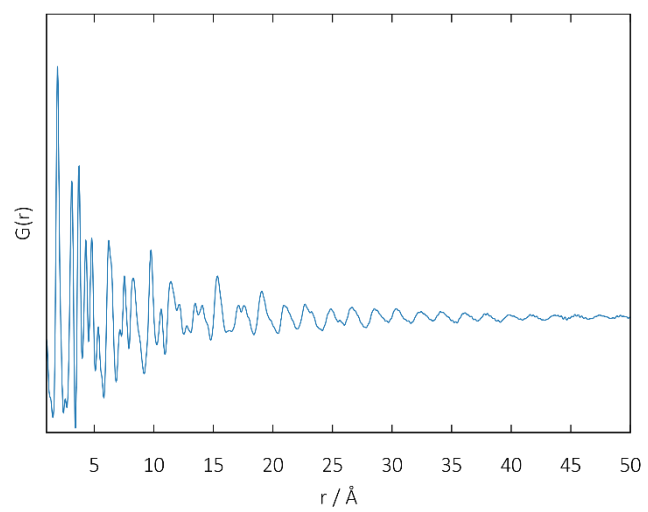


Figure S2. X-ray PDF of H-titanate.

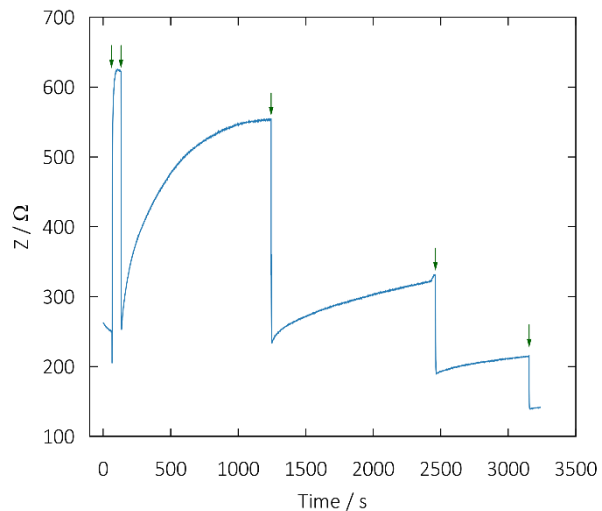


Figure S3. Conductometric titration of H-titanate dispersed in distilled water with 1 M NaOH (Green arrow = addition of 0.1 mL of 1 M NaOH).

H-titanate was first dispersed in distilled water and we titrated the amount of exchangeable H_3O^+ with 1 M NaOH. After the first addition of 0.1 mL of 1 M NaOH, we observed a fast increase of the resistivity related to the neutralization of protons already released in the water. The successive additions show a drop in the resistivity due to the added NaOH and a progressive increase of the resistivity related to the $\text{Na}^+ - \text{H}^+$ exchange. The increase step is attributed to i) the disappearance of the Na^+ via ion exchange and ii) the reaction between released H^+ and OH^- . Graphically, four additions of 0.1 mL of 1 M NaOH, corresponding to $4 \cdot 10^{-4}$ mols of Na^+ were exchanged with H^+ .

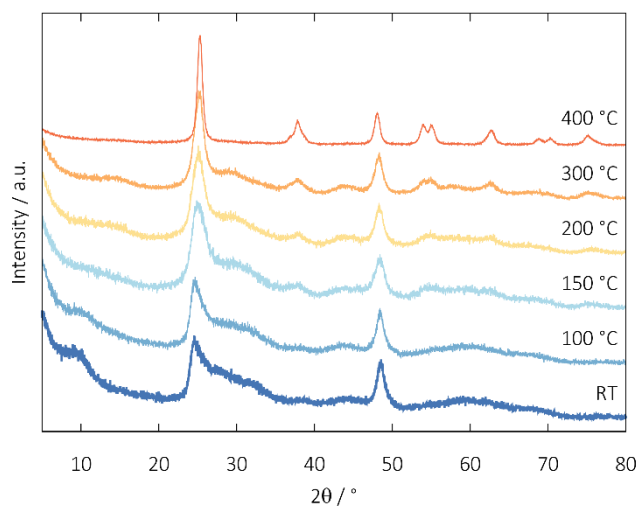


Figure S4. XRD patterns of H-titanates calcined at different temperatures.

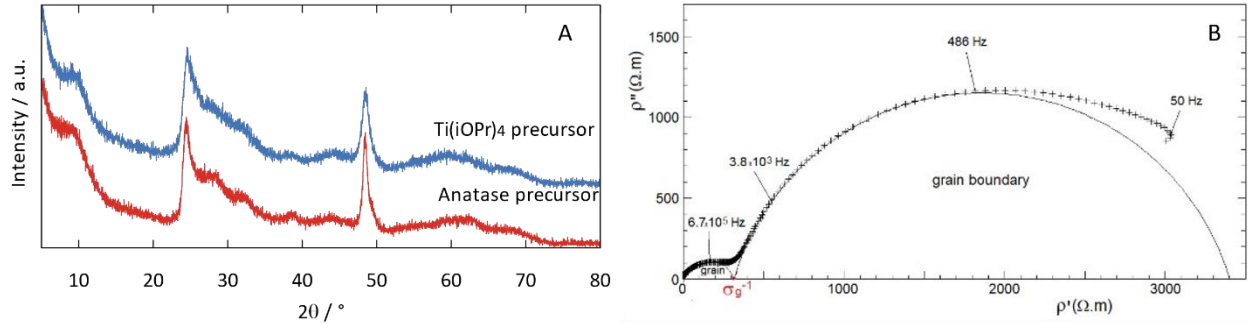


Figure S5. a) X-ray diffraction patterns of H-titanate synthesized with Ti(IV) isopropoxide precursor (= H-titanate) and anatase precursor. b) Nyquist plot of the imaginary part vs. the real part of the complex resistivity.

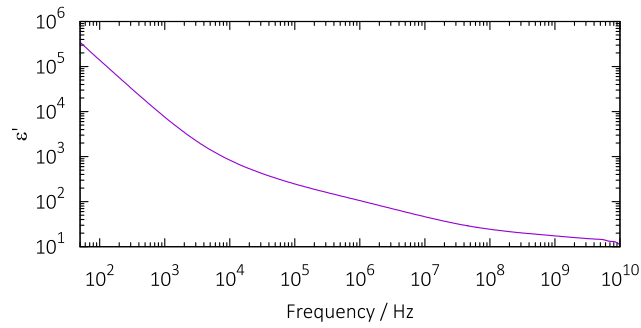


Figure S6. Real part of the complex permittivity recorded from 50 to 10^{10} Hz.

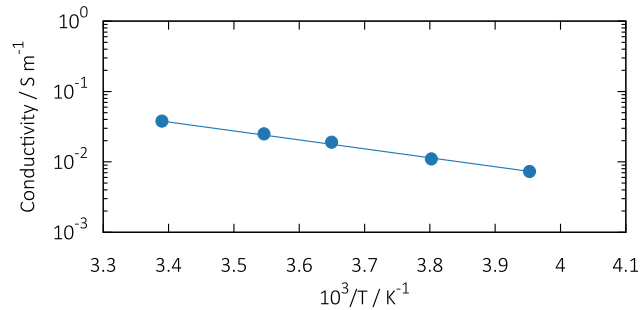


Figure S7. Arrhenius plot of the bulk conductivity. The activation energy deduced from the plot is 0.26 eV.

Table S1. Summary of the conductivities reported in the literature for layered proton titanates synthesized and measured at different conditions.

Conductivity (S/cm)	Measurement conditions	Synthesis	Acid treatment	Refs
$5.5 \cdot 10^{-6}$	25 °C	7.9859 g of rutile TiO ₂ + 20 mL of NaOH (10 M) at 150 °C for 72h	HCl (0.1 M)	1
$5.0 \cdot 10^{-4}$	160 °C 100% RH/6 atm	1 g of TiO ₂ + 200 mL of NaOH (10 M) at 100 °C for 72-120h	Dilute HCl	2
$1.4 \cdot 10^{-6}$	50 °C	0.5 g of anatase TiO ₂ + 100 mL of NaOH (10 M) at 140 °C for 24-72h	200 mL of HNO ₃ (0.2 M)	3
$2.3 \cdot 10^{-6}$	RT	1 g of TiO ₂ + 80 mL of NaOH (10 M) at 130 °C for 24h	HNO ₃ (0.1 M)	4

Table S2. Dielectric relaxation parameters at room temperature of H-titanate.

Dielectric relaxation parameters at RT	Sample polarization (P2)	Grain polarization (P3)	H ⁺ hopping (P4)	H ₂ O rotation (P5)
Frequency ν (Hz)	$9.3 \cdot 10^5$	$1.1 \cdot 10^6$	$1.6 \cdot 10^8$	$2.2 \cdot 10^9$
Activation energy (eV)	0.36	0.28	0.24	undefined
prefactor (Hz)	10^{12}	$6 \cdot 10^{11}$	$2 \cdot 10^{12}$	undefined
Dielectric strength $\Delta\epsilon$	90	29	8.24	4.6
Cole-Cole parameter α	0.18	0.15	0.10	0

References

1. Thorne, A.; Kruth, A.; Tunstall, D.; Irvine, J. T. S.; Zhou, W. Formation, Structure, and Stability of Titanate Nanotubes and Their Proton Conductivity. *J. Phys. Chem. B* **2005**, *109* (12), 5439–5444. <https://doi.org/10.1021/jp047113f>.
2. Yamada, M.; Wei, M.; Honma, I.; Zhou, H. One-Dimensional Proton Conductor under High Vapor Pressure Condition Employing Titanate Nanotube. *Electrochem. Commun.* **2006**, *8* (9), 1549–1552. <https://doi.org/10.1016/j.elecom.2006.07.020>.
3. Gao, T.; Fjeld, H.; Fjellvåg, H.; Norby, T.; Norby, P. In situ studies of structural stability and proton conductivity of titanate nanotubes. *Energy Environ. Sci.*, **2009**, *2*, 517-523. <https://doi.org/10.1039/B821532B>

4. Hu, W.; Li, L.; Li, G.; Meng, J.; Tong, W. Synthesis of Titanate-Based Nanotubes for One-Dimensionally Confined Electrical Properties. *J. Phys. Chem. C* **2009**, *113* (39), 16996–17001. <https://doi.org/10.1021/jp907001n>.