Aluminum storage behavior of anatase TiO₂ nanotube arrays in aqueous solution for aluminum ion batteries **

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Preparation and characterization of the TiO₂ nanotube arrays. The metallic Ti foil (1cm², 0.20 mm thick, 99.7% purity, Sigma-Aldrich) coupled with a graphite counter electrode was subjected to the potentiostatic anodization under the voltage of 60 V for 30 min at room temperature. The electrolyte is 0.3 wt. % NH₄F and 2 vol. % water in ethylene glycol. After anodization, the sample was calcined at 450°C for 2 h in air. The TiO₂ nanotube array film after polarizing at -1.2 V (vs. SCE) for 3 min in 1 M aqueous AlCl₃ solution was separated ultrasonically from the Ti substrate to obtain the net weight of TiO₂. The structure and morphology of the as-prepared sample were detected using X-ray powder diffraction (XRD, Rigaku D/MAX-2500v/pc) operated at 40kV/200mA and scanning electron microscopy (SEM, Hitachi S-4800) with an accelerated voltage of 3.0kV. To avoid the experimental errors arising from the TiO₂ film deformation, the film was tightly fixed on the specimen holder with 502 adhesive glue. X-ray photoelectron spectroscopy (XPS) was conducted in PHI5000 VersaProbe with Mg Ka radiation of 1253.6eV. ²⁷Al magic-angle spinning nuclear magnetic resonance (MAS NMR, 7.0T) spectroscopy experiment was carried out in a Varian Infinity-plus 300WB installed at Tianjin University.

Electrochemical performance measurement. The three electrodes were employed in cyclic voltammetry, electrochemical impedance spectra (IM6ex electrochemical workstation, Zahner) and galvanostatic electrochemical charge-discharge curves (Land, Wuhan). The self-standing TiO₂ nanotube arrays film was used as the work electrode, and the graphite electrode and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The electrolyte was 1 M aqueous chloride, i.e. AlCl₃, MgCl₂ and LiCl. The apparent area of the TiO₂ working electrode for CVs is about 0.01 cm² after coating epoxy resin on the edge and back of the metallic titanium foil. In the charge-discharge curves, the electrode with total area of 2 cm² in both sides was charged for 3 min and discharged to -0.4 V (vs. SCE) at a current density of 4 mA/cm². All the electrochemical tests were performed at ambient temperature. The Al inserted TiO₂ sample was prepared by polarizing the TiO₂ electrode at -1.1 V (vs. SCE) for 5 min in 1 M aqueous AlCl₃, followed by washing with deionized water and drying in vacuum at ambient temperature. XRD, NMR and XPS tests were also performed for the Al-inserted TiO₂ sample.
Fig. S1 Electrochemical impedance spectra (EIS) of the TiO$_2$ electrode in AlCl$_3$ aqueous solution. Inset is the equivalent circuit used to model EIS.

Fig. S2 $^{27}$Al MAS NMR spectrum of the Al-inserted TiO$_2$ nanotube arrays.
Fig. S3 XRD patterns of the TiO\textsubscript{2} nanotube arrays for all the samples, including the as-prepared, Al-inserted and Al-extracted TiO\textsubscript{2} nanotube array films.