Aluminum storage behavior of anatase TiO_2 nanotube arrays in aqueous solution for aluminum ion batteries **

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Preparation and characterization of the TiO_2 nanotube arrays. The metallic Ti foil (1cm^2, 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. % NH_4F and 2 vol. % water in ethylene glycol. After anodization, the sample was calcined at 450°C for 2 h in air. The TiO_2 nanotube array film after polarizing at -1.2 V (vs. SCE) for 3 min in 1 M aqueous $AlCl_3$ solution was separated ultrasonically from the Ti substrate to obtain the net weight of TiO_2. 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 TiO_2 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. ^{27}Al 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 TiO_2 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. $AlCl_3$, $MgCl_2$ and LiCl. The apparent area of the TiO_2 working electrode for CVs is about 0.01 cm^2 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 cm^2 in both sides was charged for 3 min and discharged to -0.4 V (vs. SCE) at a current density of 4 mA/cm^2. All the electrochemical tests were performed at ambient temperature. The Al inserted TiO_2 sample was prepared by polarizing the TiO_2 electrode at -1.1 V (vs. SCE) for 5 min in 1 M aqueous $AlCl_3$, 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 TiO_2 sample.

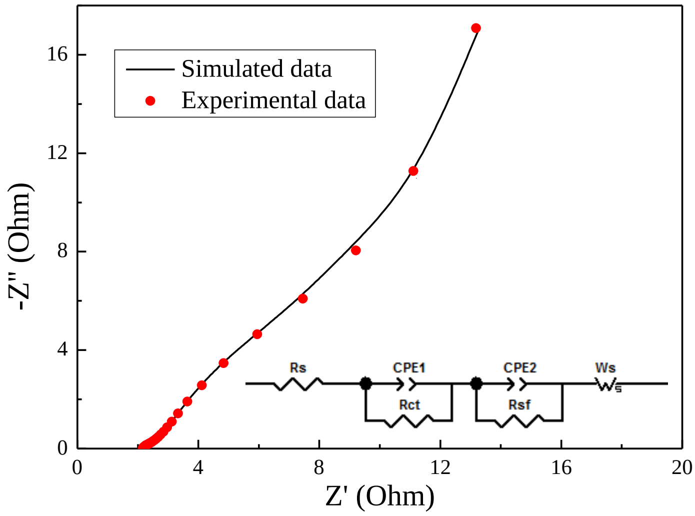

Fig. S1 Electrochemical impedance spectra (EIS) of the TiO_2 electrode in $AlCl_3$ aqueous solution. Inset is the equivalent circuit used to model EIS.

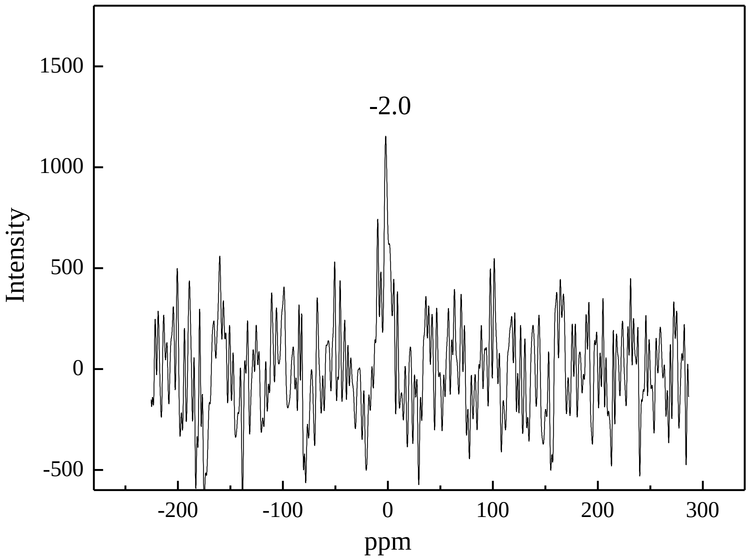

Fig. S2 ^{27}Al MAS NMR spectrum of the Al-inserted TiO_2 nanotube arrays.

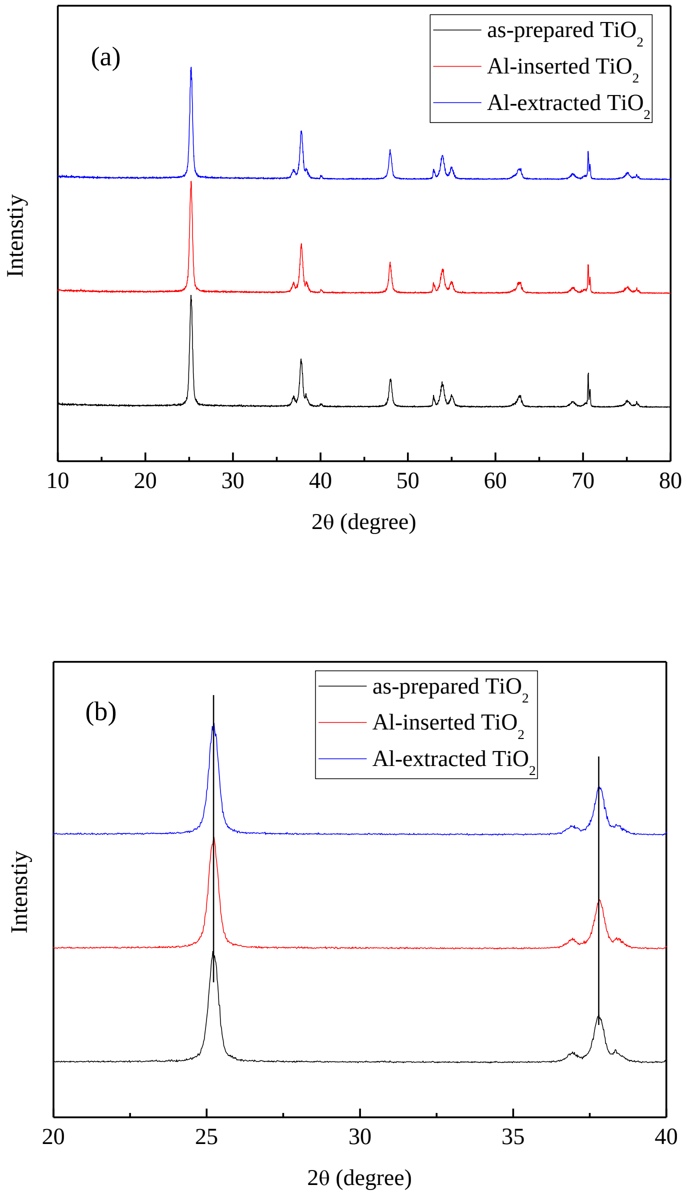

Fig. S3 XRD patterns of the TiO_2 nanotube arrays for all the samples, including the as-prepared, Al-inserted and Al-extracted TiO_2 nanotube array films.