Supplementary information

Ordered WO_{3-x} nanorods: Facile synthesis and their electrochemical

properties for aluminum-ion batteries

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Experimental

Materials preparation

In this work, all materials and chemicals were analytical grade and used without further purification. Briefly, 10 mmol $Na_2WO_4 \cdot 2H_2O$ (99.0 *wt.%*, Aladdin) and 10 mmol Na_2CO_3 (99.0 *wt.%*, Aladdin) were mixed and dissolved into 80 ml of distilled water under 30 min of magnetic stirring to form transparent solution. Then, concentrated HCl was dripped gradually till the pH of the solution became 1. Subsequently, the solution was transferred into a 100 ml Teflon-lined stainless steel autoclave, which was sealed and heated at 180 °C for 24 h, and then cooled to room temperature naturally. The obtained precipitates were collected by centrifugation, and washed several times with distilled water and absolute ethanol and then dried overnight at 80 °C. Finally, WO₃ nanorods could be obtained.

Synthesis of the WO_{3-x} samples: The oxygen vacancies were introduced in the samples through annealing WO₃ nanorods in hydrogen atmosphere in a tube furnace. The WO₃ nanorods annealed in 5%H₂-95%Ar at 500 °C for 2 h and 4 h were denoted as WO_{3-x}-1 and WO_{3-x}-2, respectively.

Fabrication of Al-ion batteries

The working electrodes were prepared by dispersing 60 *wt.*% active materials, 30 *wt.*% acetylene black as conducting agent and 10 *wt.*% poly(vinylidene difluoride) (PVDF) as binder in N-methyl-2-pyrrolidone (NMP) solvent to form a homogeneous slurry, which was uniformly coated onto a tantalum (Ta) current collector. After dried at 80 °C over 12 h, the cathode was cut into squares of 20 × 20 mm. AlCl₃ and 1-ethyl-3-methylimidazalium chloride ([EMIm]Cl) were mixed in a molar ratio of 1.3:1 as the electrolyte. Before assembling, the Al foil (25 mm × 25 mm) and Mo foil (6 mm × 60 mm) were washed in an ultrasonic cleaner for 10 min. Mo foil attached to cathode (35 mm × 40 mm) was used as current collector. Cathode, Al foil anode, glass fiber (GF/A) separator from Whatman, and ionic electrolyte was assembled with soft-package cells in a high purity argon atmosphere glove-box ($[O_2] \le 0.1$ ppm, $[H_2O] \le 0.1$ ppm).

Material characterization

The crystal structures of the samples were determined by an X-ray diffractmeter (XRD, Rigaku, SmartLab). FTIR spectra were obtained using a fourier transform infrared spectrometer (NICOLET, NEXUS-470) in the range of 4000-400 cm⁻¹. The valence changes of the elements were conducted by X-ray photoelectron spectroscopy (XPS, Kratos, AXIS Ultra DLD). The morphologies and microstructures were characterized by field emission scanning electron microscopy (FESEM, JEOL, JSM-6701F), high resolution transmission electron microscopy (HRTEM, JEOL, JSM-2010). The normalized X-ray absorption near-edge spectroscopy (XANES) of Cl K-edge spectra was performed at beamline 4B7A of the Beijing Synchrotron Radiation Facility (BSRF) in fluorescence mode using a fixed-exit Si double crystal monochromator. The raw EXAFS data were background-subtracted, normalized and Fourier transformed by the standard procedures with the IFEFFIT package.

Electrochemical measurements

Galvanostatic charge-discharge tests were performed at various current densities with the cut-off potential window of 0.01 to 2.2 V using Neware BTS-53 tester. The asprepared sample was used as the working electrode, and aluminum foil was used as the reference and counter electrode. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a two-electrode configuration with CHI electrochemical analyser (CHI 660E). CV measurements were carried out in the voltage range of 0.01 to 2.2 V (vs. Al³⁺/Al) at different scan rates of 0.2 mV s⁻¹, 0.5 mV s⁻¹, 1 mV s⁻¹ and 2 mV s⁻¹, respectively. EIS measurements were performed using perturbation amplitude of 5 mV in an open-circuit potential with a frequency range from 100 kHz to 10 mHz.



Fig. S1. SEM images of the as-prepared (a,b) WO₃, (c,d) WO_{3-x}-1 and (e,f) WO_{3-x}-2.

FTIR analysis of the series samples was also carried out to investigate the nature of the W-O bonds. Fig. S2a is the FTIR spectra for the series WO_{3-x} nanorods with increasing reduction time under H_2 /Ar atmosphere. The typical bands for W=O (980 cm⁻¹) and bridging oxygens W-O-W (750 and 833 cm⁻¹) appear in the WO₃ sample.¹⁻³ Compared to the WO₃ sample, the spectrum of the WO_{3-x}-1 sample shows little change. For the WO_{3-x}-2 sample, the spectrum is apparently shifted positively, confirming the effect of oxygen vacancies on the stretching vibrations of W=O and W-O-W bonding.⁴



Fig. S2 (a) FTIR spectra and (b) XPS survey spectra of the as-prepared series WO_{3-x} nanorods samples.

Fig. S3a-c shows the CV curves of the series WO_{3-x} nanorods at different scan rates of 0.2 mV s⁻¹, 0.5 mV s⁻¹, 1 mV s⁻¹ and 2 mV s⁻¹, respectively. It can be seen that the three WO_{3-x} nanorods cathodes exhibit the similar redox behaviors. And, the reduction peaks are found at ca. 1.0 V and 1.4 V. Meanwhile, with the increasing scan rate, the reduction peaks shift negatively. Moreover, with increasing reduction time, the series WO_{3-x} nanorods show higher reduction peaks at a scan rate of 2 mV s⁻¹ as presented in Fig. S3d. The above results indicate that increasing the thermal reduction time is beneficial for higher discharge plateau and the improvement of energy density.



Fig. S3 CV curves of (a) WO₃, (b) WO_{3-x}-1 and (c) WO_{3-x}-2 nanorods at different scan rates. (d) The CV comparison curve at a scan rate of 2 mV s⁻¹ of the series WO_{3-x} nanorods.

To understand the improved electrochemical performance of the series WO3-x nanorods, EIS measurements were carried out before and after cycling, respectively. The Nyquist plots of the series samples were presented in Fig. S4a and b using perturbation amplitude of 5 mV in an open-circuit potential with a frequency range from 100 kHz to 10 mHz. In the high frequency region, the intersection with the real axis is on behalf of ohmic impedance (R_s) of the entire battery system. In the high-medium frequency region, it can be seen that all the series WO3-x electrodes display one depressed semicircle (R_{ct}), which is indicative of the charge transfer resistance of Al-ion intercalation by a faradic process. In the low frequency region, an inclined line is mainly attributed to the semi-infinite diffusion of chloroaluminate anions into the bulk of the series WO_{3-x} electrode, which is called as Warburg resistance (W_o). An equivalent circuit shown in Fig. S4c is used to analyze the measured impedance in Fig. S4a and b. Additionally, the fitting is performed using ZView software and the parameters are presented in Table S1. As seen with the results in this table, the series WO_{3-x} electrodes display less and less R_{ct} with the increasing thermal reduction time whether before or after cycling. Simultaneously, compared to the series WO_{3-x} electrodes without any charge-discharge tests, the cycled cathodes show more R_{ct} apparently, which can probably be because the intercalation and deintercalation of chloroaluminate anions break the nanorods during the charge-discharge process, further making the electrons and anions diffuse into the bulk WO_{3-x} more difficultly.



Fig. S4 Nyquist plots of (a) the fresh and (b) cycled WO_3 , WO_{3-x} -1 and WO_{3-x} -2 nanorods. (c) The equivalent circuit model.

Sample	Fresh-WO ₃	Fresh-WO _{3-x} -	Fresh-WO _{3-x} -	$Cycled-WO_3$	Cycled-WO _{3-x} -1	Cycled-WO _{3-x} -2
		1	2			
<i>R</i> _s (Ω)	1.64	1.01	1.03	1.69	1.73	2.13
<i>R_{ct}</i> (Ω)	1026.0	409.1	207.0	1100.0	639.5	457.8
CPE-T (F)	0.0006	0.0005	0.0018	0.0006	0.001	0.0008
CPE-P	0.55	0.59	0.48	0.85	0.62	0.64
σ (Ω s ^{-1/2})	0.47	0.41	0.45	0.33	0.44	0.44

Table S1 The parameters obtained by fitting the impedance spectra of the fresh and cycled WO_3 , WO_{3-x} -1 and WO_{3-x} -2 nanorods.



Fig. S5 XPS survey spectra of (a) the fully charged and (b) fully discharged series WO_{3-x} nanorods.

We investigated the change of the charged and discharged WO_{3-x} nanorods by TEM and EDS, and the WO_{3-x}-2 nanorods were illustrated as a representative. For the fully charged and fully discharged WO_{3-x}-2 nanorods, the length of nanorods both shows shorter size compared to that of the initial WO_{3-x}-2 nanorods, as shown in Fig. S6a,c. And the rod-like structure of the fully charged and discharged WO_{3-x}-2 sample is not ideal, because the intercalation and deintercalation of chloroaluminate anions break the rods during the charge-discharge process, which exerts an important influence on the change of the morphology. Impressively, when the battery was fully charged, the interlayer space (Fig. S6b) is apparently larger than that of the initial WO3-x-2 nanorods, revealing the intercalation behavior of chloroaluminate anions in the charge process. Simultaneously, the fully discharged $WO_{3-x^-}2$ nanorods (Fig. S6d) show the same interlayer space as the initial WO3-x-2 nanorods, disclosing the deintercalation behavior of chloroaluminate anions in the discharge process. The elemental mapping images using energydispersive spectroscopy (EDS) shown in Fig. S7 reveal that when fully charged, Al and Cl characteristic X-ray signals uniformly distributed over the nanorods confirm chloroaluminate anions intercalation into WO_{3-x}-2. When fully discharged, EDS mapping in Fig. S8 reveals that chloroaluminate anions deintercalate from WO_{3-x} -2 with much lower Al and Cl characteristic Xray signals.



Fig. S6 TEM images of (a,b) fully charged and (c,d) fully discharged WO_{3-x}-2 nanorods.



Fig. S7 The mapping images of the fully charged WO_{3-x} -2 nanorods.



Fig. S8 The mapping images of the fully discharged $\mathsf{WO}_{3\text{-}x\text{-}}2$ nanorods.

To clarify the possible composition of the chloroaluminate anions in the charge-discharge process, the corresponding Cl K-edge X-ray absorption near-edge spectroscopy (XANES) spectra of the charged and discharged WO_{3-x}-2 nanorods were carried out in Fig. S9a. In contrast, the Cl K-edge XANES spectra of WO₃ nanorods were also measured. It is interesting to observe the sharp peak at 2827 eV, signifying the same valence state of Cl in the all samples. And the intensity in the discharged state is decreased compared to that of the charged sample. Further, the extended X-ray absorption fine structure (EXAFS) analysis at the Cl K-edge using both a wavelet transform (WT) and Fourier transform was performed.^{5,6} The k³-weighted $\chi(k)$ signals (Fig. S9b) show quite similar profiles, suggesting no substantial differences in Cl atoms for the charged and discharged samples. In Fig. S9c, the peaks at about 1.0-2.3 Å in the samples are attributed to the coordination bond of Cl-Al, and the coordination numbers of the fully charged and discharged samples are similar. According to the above analyses, it can be concluded that mainly AlCl₄⁻ anions are intercalated and deintercalated into the WO₃ layers for both WO₃ and WO_{3-x}-2 nanorods.



Fig. S9 (a) The Cl K-edge XANES spectra, (b) k^3 -weighted EXAFS spectra in k-space and (c) Fourier transforms of k^3 -weighted spectra in R space of the fully charged and fully discharged WO₃ and WO_{3-x}-2 nanorods.

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