Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Self-assembled $(NH_4)_2V_7O_{16}$ hierarchical structures with improved electrochemical performance for aqueous Li-ion batteries

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Experimental

Synthesis of $(NH_4)_2V_7O_{16}$ hierarchical structures

$(NH_4)_2V_7O_{16}$ hierarchical structures were obtained using a simply modified hydrothermal methodology [1, 2]. In a typical experiment, 1.418 g ammonium metavanadate (NH_4VO_3, Aladdin reagent, AR) was dispersed into 40 ml distilled water at first. Next, 1 ml of lithium borohydride ($LiBH_4$, Aladdin reagent, 2.0 M in tetrahydrofuran) was instilled with continuous stirring and after 10 min a black suspension was obtained. Subsequently, the suspension was transferred into a 100 ml Teflon-lined autoclave and maintained at 180 ºC for 10 h. In the process of reaction, the autoclave was rotating at a low speed (15 rpm). After the hydrothermal reaction, the autoclave was naturally cooled to ambient temperature and the black products were collected by centrifugation, washed several times with distilled water and ethanol and finally dried at 80 ºC in a desiccator.

Material characterization

The crystalline phase of the as-synthesized product and cycled $(NH_4)_2V_7O_{16}$ electrodes was carried out by an X-ray diffractometer (XRD, Bruker D8 Advance). Field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) images of the obtained samples were performed using a HITACHI S-4800 microscope and FEI Talos F200S microscope, respectively.

Electrochemical measurements

Preparation of the working electrodes can refer to our previous work [3]. The mass ratio of the active material, carbon black (Super P) and polytetrafluoroethylene (PTFE) is 7:2:1 for the $(NH_4)_2V_7O_{16}$ hierarchical structures and 8:1:1 for the activated carbon and $LiMn_2O_4$. The activated carbon and $LiMn_2O_4$ were purchased from Hefei Kejing Materials Technology Co., Ltd. and used as received.

The electrochemical performance of the $(NH_4)_2V_7O_{16}$ hierarchical structures was characterized using a three-electrode system, in which the $(NH_4)_2V_7O_{16}$ electrode was used as the working electrode and the electrolyte was 2 M Li_2SO_4 aqueous solution. In the Cyclic voltammetry (CV) test, platinum foil electrode and Ag/AgCl electrode (0.197 V *vs*. NHE) are the counter and reference electrodes, respectively. And during the galvanostatic charge-discharge tests, the activated carbon electrode is used as the counter electrode.

The aqueous lithium-ion full battery comprised of $LiMn_2O_4$ cathode, $(NH_4)_2V_7O_{16}$ anode and 2 M Li_2SO_4 aqueous electrolyte was assembled into CR2032 coin-type cells. Excessive $LiMn_2O_4$, with the cathodic/anodic weight ratio of (1.2-1.5)/1, is intended for accurately evaluating the electrochemical characteristics of $(NH_4)_2V_7O_{16}$. Galvanostatic charge-discharge tests of the $(NH_4)_2V_7O_{16}/LiMn_2O_4$ were implemented on a Neware CT4008T cell testing system. Cyclic voltammetry and electrochemical impedance spectrometry (EIS) were performed with an electrochemical workstation (CHI 760E). The capacity was calculated based on the mass of active anode materials.

References

[1] Heo J. W., Bu H., Hyoung J. and Hong S. T., Ammonium vanadium bronze, $(NH_4)_2V_7O_{16}$, as a new lithium intercalation host material, *Inorg Chem*, 2020, **59**(7).

[2] Ma Y., Zhou H., Zhu J., Ji S., Bao S., Li R. and Jin P., Synthesis of flake-like VO_2 (M) by annealing a novel $(NH_4)_{0.6}V_2O_5$ phase and its thermochromic characterization, *Ceramics International*, 2016, **42**(14).

[3] Ma Y., Wu M., Jin X., Shu R., Hu C., Xu T., Li J., Meng X. and Cao X., $(NH_4)_2V_7O_{16}$ microbricks as a novel anode for aqueous lithium-ion battery with good cyclability, *Chemistry-a European Journal*, 2021, **27**(48).

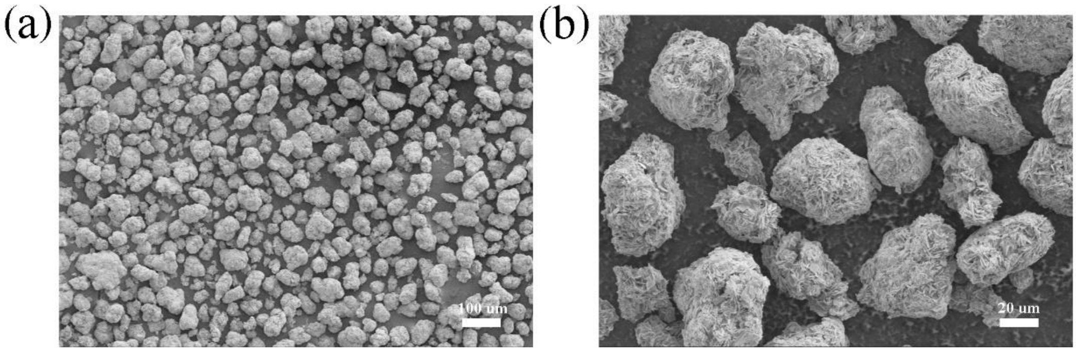

Fig. S1 Low magnification FESEM images of the as-synthesized $(NH_4)_2V_7O_{16}$ by the rotating hydrothermal method.

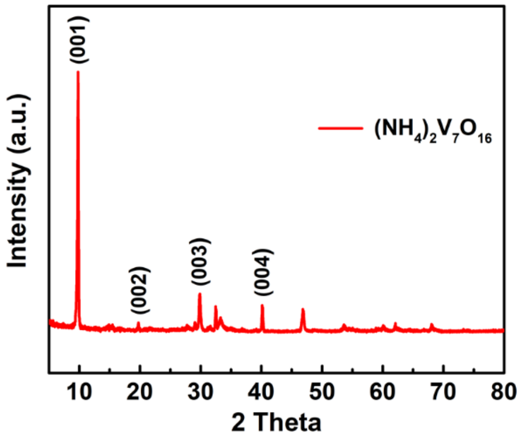

Fig. S2 XRD pattern of the obtained $(NH_4)_2V_7O_{16}$ by hydrothermal treatment without rotating.

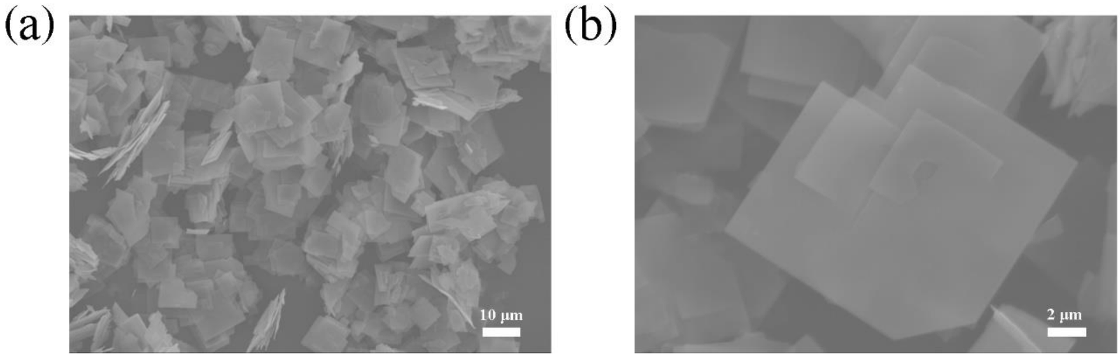

Fig. S3 FESEM images of the obtained $(NH_4)_2V_7O_{16}$ by hydrothermal treatment without rotating.

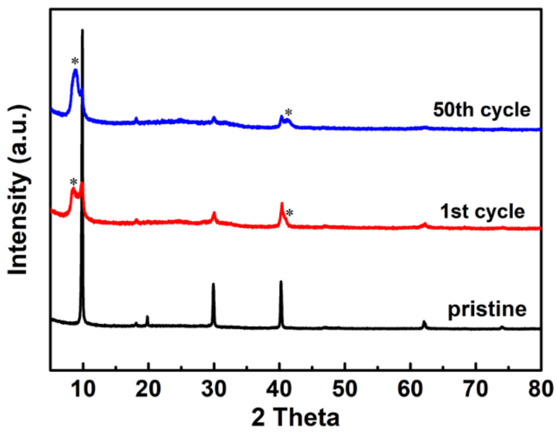

Fig. S4 Ex situ XRD patterns of $(NH_4)_2V_7O_{16}$ electrodes before cycling and after different discharge-charge cycles of the three-electrode cell.

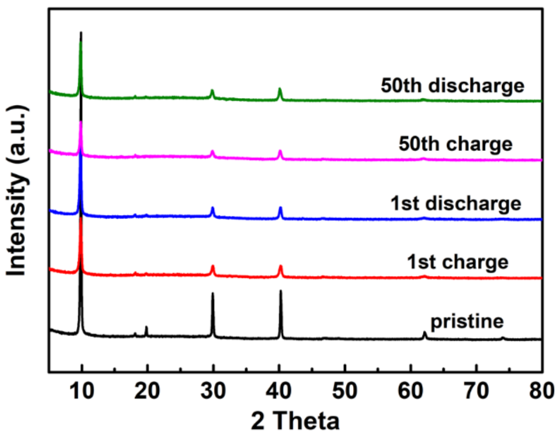

Fig. S5 Ex situ XRD patterns of $(NH_4)_2V_7O_{16}$ electrodes before cycling and at different charged/discharged states of the $(NH_4)_2V_7O_{16}/LiMn_2O_4$ full cell.

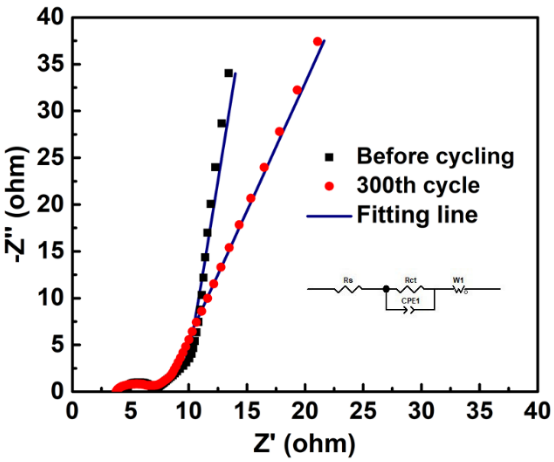

Fig. S6 Nyquist plots of the $(NH_4)_2V_7O_{16}/LiMn_2O_4$ full battery before cycling and after 300th cycle at 100 mA g^{-1}.

Table S1. The EIS primary simulation parameters of the $(NH_4)_2V_7O_{16}/LiMn_2O_4$.

Samples	Rs (Ω)	Rct (Ω)
Before cycling	4.36	2.26
300^{th} cycle	3.66	2.73