Electronic supplementary information

First Investigation on Charge-discharge Reaction Mechanism of Aqueous Lithium Ion Batteries: A New Anode Material of $Ag_2V_4O_{11}$ Nanobelts

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S1. FT-IR spectrum variation of SVO nanobelts during the first charge process

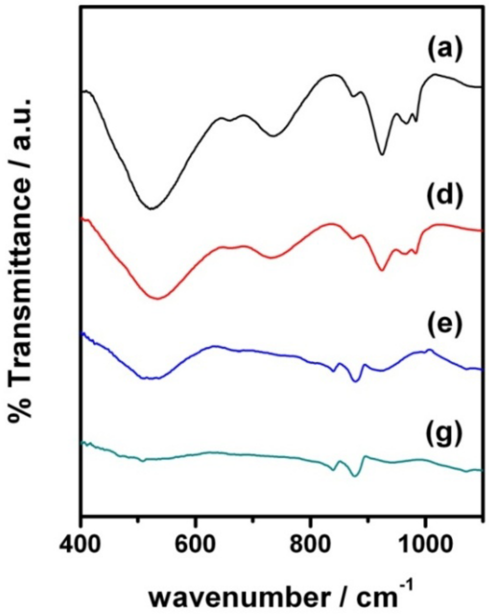

Figure S1. FT-IR spectrum of SVO nanobelts at various cell voltages during the first charge process: (a) before electrochemical measurement, (d) 1.08 V, (e) 1.37 V, and (g) 1.60 V.

Two bands located at 967 and 875 cm^{-1} were reported to correspond to the symmetric and asymmetric stretching modes of V=O bonds.[1] In comparison to V_2O_5, the addition of silver to the vanadium oxide matrix leads to a red shift for the V=O stretching frequencies, which has been explained as the result of a weakening of the V=O bond due to interaction between Ag^+ and the unbridged oxygen atoms of the vanadium oxide lattice.[2] The bands at 924 and 524 cm^{-1} correspond to the V-O-V bending vibration and edge-sharing V-O stretching vibration, respectively.[3] Of note, the relative intensity of the band at 924 cm^{-1} with respect to the band at 524 cm^{-1} decreased significantly. Such a decrease of the band relative intensity could be attribute to introducing of Ag^+ into the V-O framework, which interrupts the V-O-V linkages and produces more edge-sharing V-O bonds.[4] In addition, the band at 735 cm^{-1} could be assigned to V-O-V stretching mode.

Reduction of SVO is accompanied by a change in intensity and position of the infrared bands observed for the starting material. The FT-IR spectrum is hardly changed by the end of the first plateau (d). However, just as the intensity of the V-O-V bands decreasing for VO_2 relative to V_2O_5,[5] the bands at 924, 735 and 524 cm^{-1} decreased gradually in intensity with the reduction of vanadium during the second electrochemical reaction. By the time the voltage was up to 1.6 V (g), the low-frequency bands have almost disappeared. In addition, the V=O bands display a red shift down to 877 cm^{-1}, which is consistent with the reduction of V^{5+} to V^{4+} in this charge process, where V^{4+}=O would be expected to display a lower stretching frequency than V^{5+}=O.

S2. XAFS data of SVO nanobelts during the first charge process

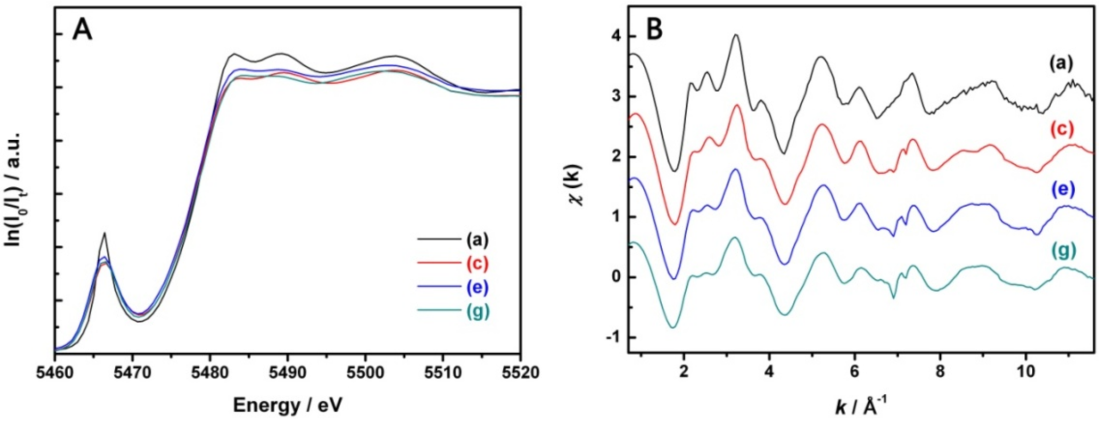

Figure S2. V *K*-edge XAFS (A) and EXAFS $\chi(k)$ spectra (B) for SVO nanobelts at various cell voltages during the first charge process: (a) before electrochemical measurement, (c) 0.95 V, (e) 1.37 V, and (g) 1.60 V.

S3. Demonstration of anode's major influence on cell cyclibility

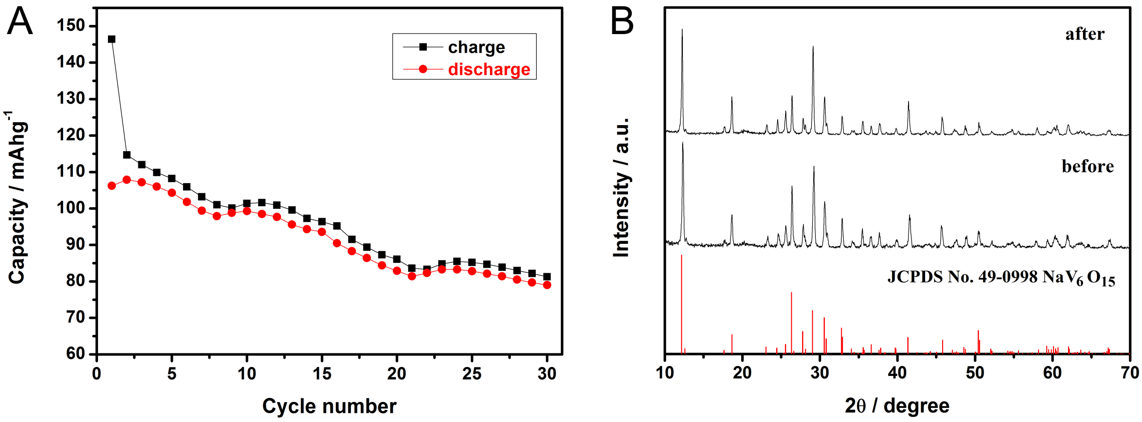

Figure S3. (A) Charge and discharge capacity versus cycle number curves of the $LiMn_2O_4/NaV_6O_{15}$ aqueous cell. The cell was charged and discharged at the current density of 60 mA g^{-1} in aqueous electrolyte. (B) XRD patterns of NaV_6O_{15} electrode before and after 30 charge and discharge cycles.

Although $LiMn_2O_4$ cathode would also have influence on cell cyclibility, we used NaV_6O_{15} one dimensional nanostructures as comparison to demonstrate that anode played more important role on influencing cell cyclibility in our aqueous system. NaV_6O_{15} one dimensional nanostructures were synthesized according to the reported work by Yu's group[6] and was subjected to charge-discharge measurement under the identical conditions (cathode, aqueous electrolyte, current density) in the manuscript. As shown in Figure S3A, the discharge capacity retention after 30 cycles is 74.4%, much better than SVO electrode (27.5% after 30 cycles in Figure S4A). XRD patterns (Figure S3B) of NaV_6O_{15} before and after electrochemical measurement confirm its structural stability without any change or degradation for the diffraction peaks, resulting in strong contrast with SVO (Figure S4B). Therefore, the above comparison clearly gives us the information that, although $LiMn_2O_4$ cathode would have some influence, amorphousness of $Ag_2V_4O_{11}$ took the major responsibility for the rapid capacity decline.

S4. Capacity change and XRD pattern after 30 cycles of SVO nanobelts

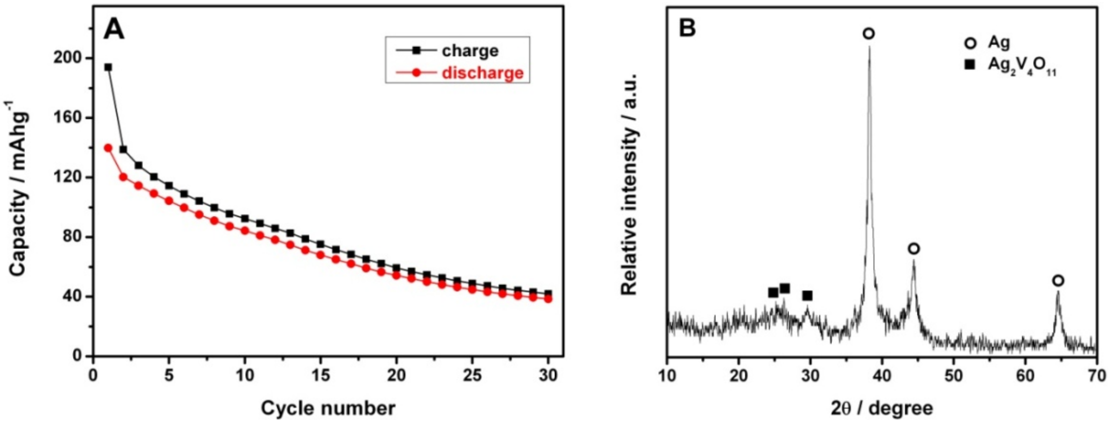

Figure S4. (A) Charge and discharge capacity versus cycle number curves of the $LiMn_2O_4$/SVO aqueous cell. (B) XRD pattern of SVO nanobelts after 30 cycles.

Notes and references

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