Electronic Supplementary Information

Porous V_2O_5 Microspheres: A High-Capacity Cathode Material for Aqueous Zinc-Ion Battery

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Experimental Section

Synthesis

The porous V_2O_5 microspheres were synthesized by a spray drying method followed by annealing in air. 10 mmol V_2O_5 were dissolved in 130 mL distilled water and 20 mL H_2O_2 (30 wt. %). Then, 1.0 g sucrose was added into the above solution. The precursor solution was spray dried using a BUCHI Mini Spray Dryer B-290. After annealing the collected powder at 350 ℃ for 4 h in air, porous V_2O_5 microspheres (designated as V_2O_5) were obtained. For comparison, VO_x/C-350 and VO_y/C-500 were prepared by annealing the intermediate powder at 350 and 500 ℃ for 4 h in Ar. V_2O_5-PVP and V_2O_5-OX were synthesized with the same method by replacing the sucrose with PVP and oxalic acid, respectively.

Characterization

Ex-situ XRD during electrochemical measurements was performed on a D8 Discover X-ray diffractometer with a nonmonochromated Cu Kα X-ray source. Field-emission scanning electron microscopy (FESEM) images were collected using a JSM-7001F microscope at an acceleration voltage of 10 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were recorded with a JSM-2100F STEM/EDS microscope. The XPS spectra were recorded on a Shimadzu Axis Ultra spectrometer with an Mg Kα = 1253.6 eV excitation source. The Brunauer-Emmett-Teller (BET) surface area was calculated from nitrogen adsorption isotherms collected at 77 K using a Tristar-3020 instrument. Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) curves were conducted by using a Netzsch STA 449C simultaneous analyzer.

Electrochemical Measurements

The cathode consisted of 60 wt. % active material, 30 wt. % acetylene black, and 10 wt. % polytetrafluoroethylene (PTFE). Metallic Zn foil (~0.25 mm) was used as the anode, 2 mol L^{-1} zinc trifluoromethanesulfonate ($Zn(CF_3SO_3)_2$) was employed as the electrolyte, and Whatman grade GF/A was used as the membrane. 2016-type coin cells were assembled in air. The cyclic voltammetry (CV) and galvanostatic discharge-charge (GCD) tests were carried out on CHI600E and Land Battery Test System.

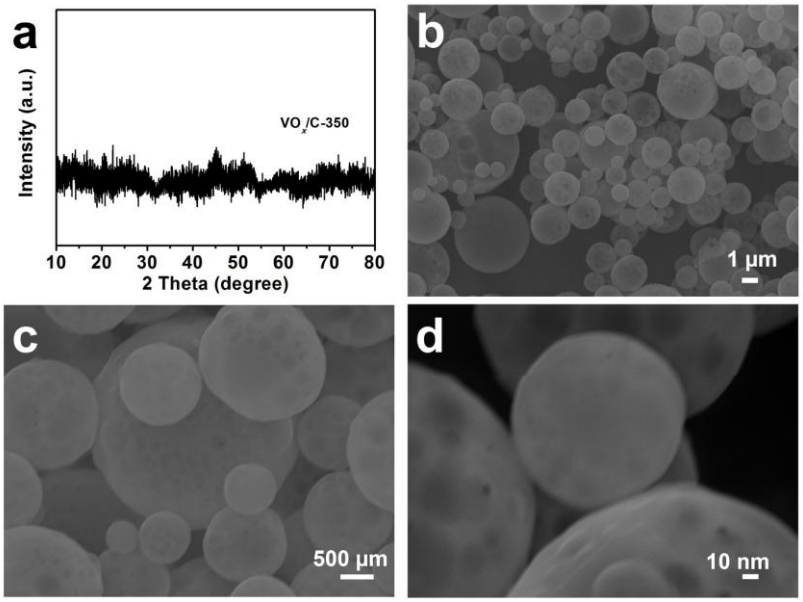

Fig. S1. (a) XRD pattern, (b, c, d) SEM images of VO_x/C-350 porous microspheres.

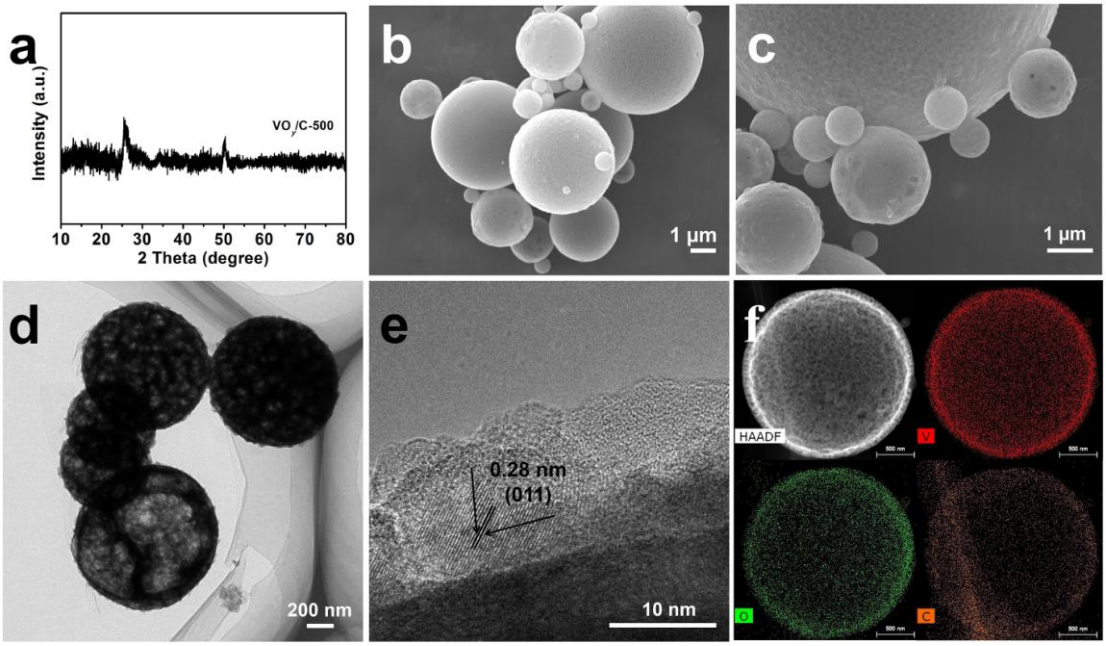

Fig. S2. (a) XRD pattern, (b, c) SEM images, (d) TEM images, (e) HRTEM image, and (f) EDS mapping of VO_y/C-500 porous microspheres.

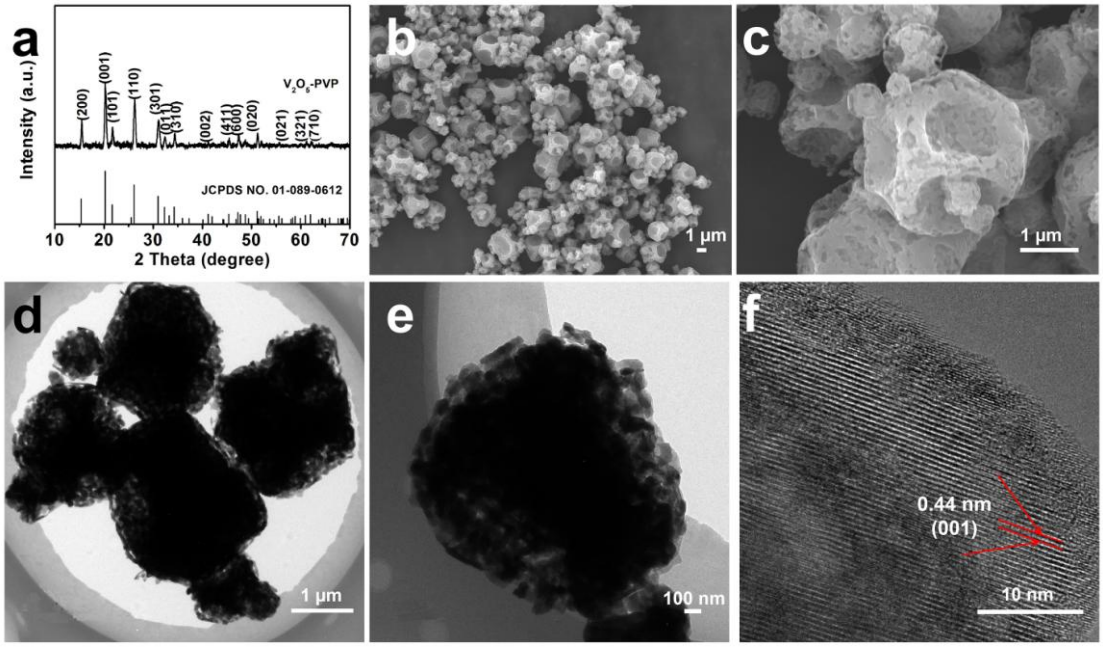

Fig. S3. (a) XRD pattern, (b, c) SEM images, (d, e) TEM images, and (f) HRTEM image of porous V_2O_5-PVP microspheres.

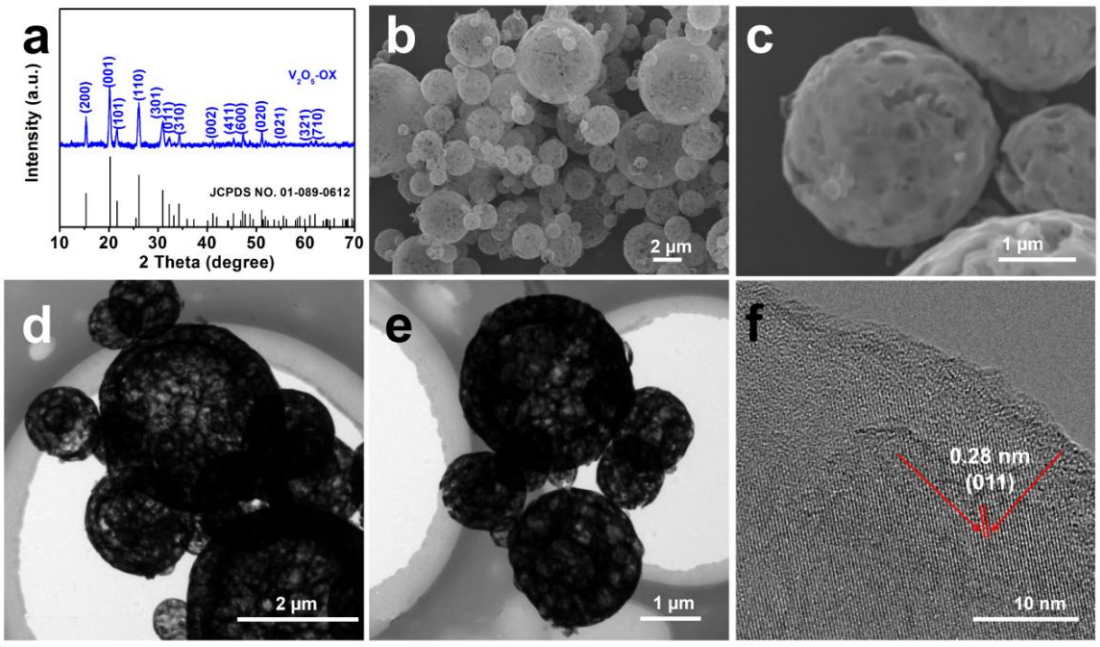

Fig. S4. (a) XRD pattern, (b, c) SEM images, (d, e) TEM images, and (f) HRTEM image of porous V_2O_5-OX microspheres.

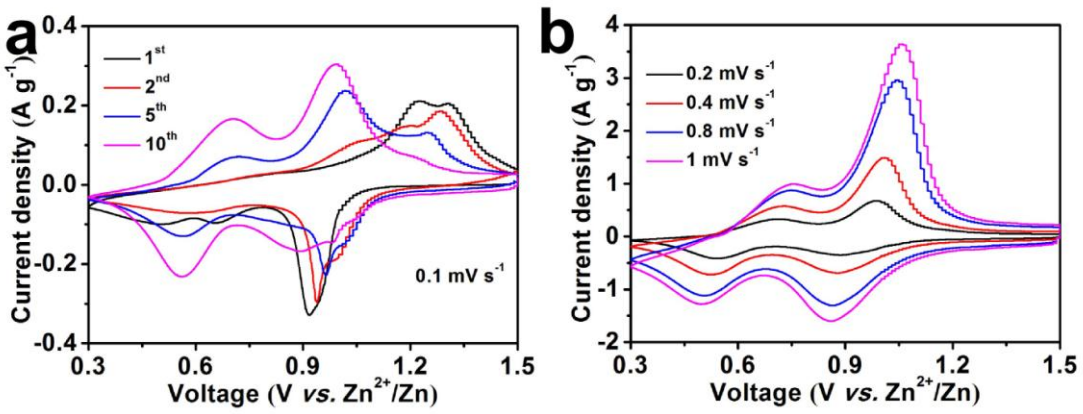

Fig. S5. The CV curves of V_2O_5 for the different cycles at 0.1 mV s^{-1} (a), and for the different scan rates (b).

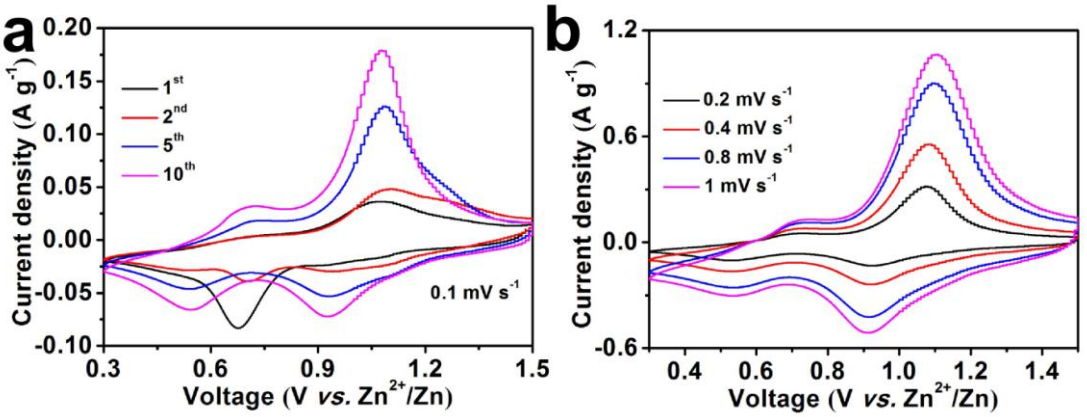

Fig. S6. The CV curves of VO_y/C-500 for the different cycles at 0.1 mV s^{-1} (a), and for the different scan rates (b).

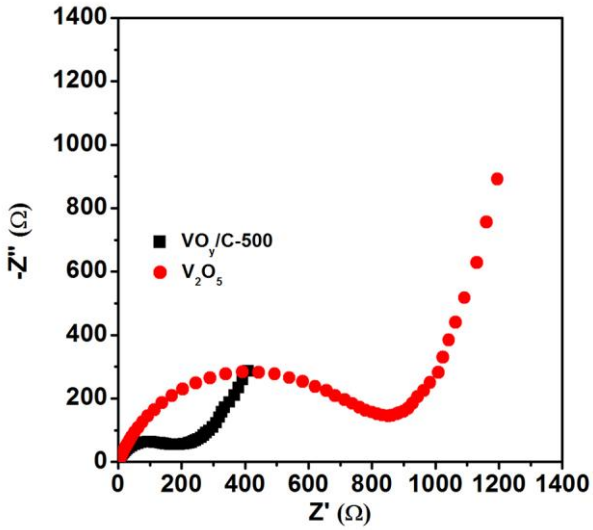

Fig. S7. Nyquist plots of porous V_2O_5 (red) and VO_y/C-500 (black) in 2 M $Zn(CF_3SO_3)_2$.

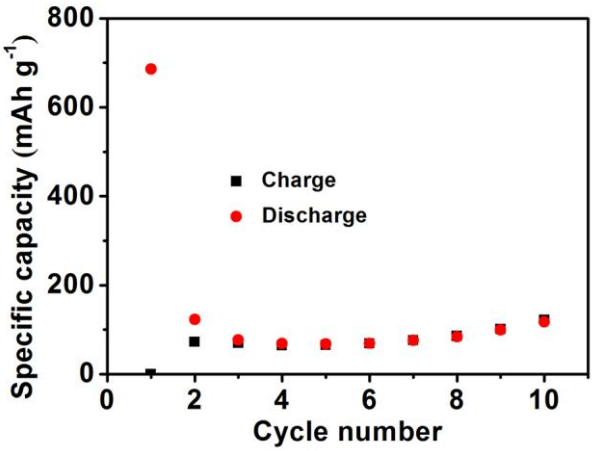

Fig. S8. The cycling performance of VO_x/C-350 at 100 mA g^{-1}.

Table S1. Electrochemical performances of recently reported vanadium-based zinc-ion battery cathode materials

Materials	Electrolyte	Specific capacity at *x* mA g^{-1}	Energy density (Wh Kg^{-1})	Capacity retention after *n* cycles at *y* mA g^{-1}	Ref.
porous V_2O_5 microsphere	$Zn(CF_3SO_3)_2$	401 (*x* = 100)	286	73% (*n* = 1000, *y* = 2000)	Our work
$Zn_{0.25}V_2O_5$ nH_2O	$ZnSO_4$	300 (*x* = 50)	250	80% (*n* = 1000, *y* = 2400)	1
VS_2	$ZnSO_4$	190 (*x* = 50)	123	98% (*n* = 200, *y* = 50)	2
LiV_3O_8	$ZnSO_4$	280 (*x* = 16)	224	75% (*n* = 65, *y* = 133)	3
$Na_3V_2(PO_4)_3$	$Zn(CH_3COO)_2$	97 (*x* = 50)	108	74% (*n* = 100, *y* = 50)	4
V_2O_5	AN-$Zn(TFSI)_2$	218 (*x* = 14.4)	156	95% (*n* = 120, *y* = 50)	5
$Zn_3V_2O_7(OH)_2$ $2H_2O$	$ZnSO_4$	213 (*x* = 50)	150	68% (*n* = 300, *y* = 200)	6
VO_2	$ZnSO_4$	353 (*x* = 1000)	176	75% (*n* = 945, *y* = 3000)	7
V_2O_5 nanopaper	$ZnSO_4$	375 (*x* = 500)	278	77% (*n* = 500, *y* = 10000)	8
porous V_2O_5	$Zn(CF_3SO_3)_2$	319 (*x* = 20)	233	80% (*n* = 500, *y* = 588)	9
V_2O_5 hollow spheres	$ZnSO_4$	280 (*x* = 200)	204	82% (*n* = 6200, *y* = 10000)	10

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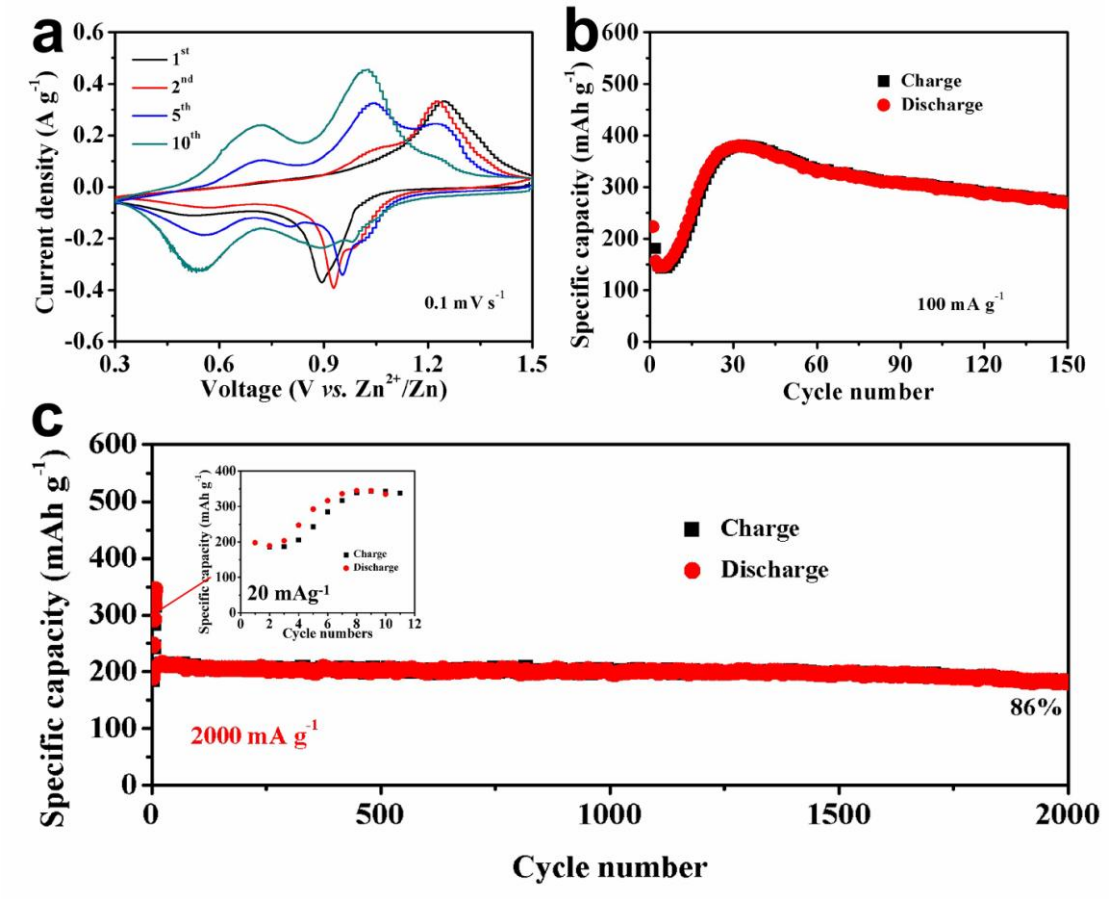

Fig. S9. The electrochemical performances of porous V_2O_5-PVP microspheres. (a) CV curves. (b) Cyclic performance at 100 mA g^{-1}. (c) Long-life cycling performance at 2000 mA g^{-1}.

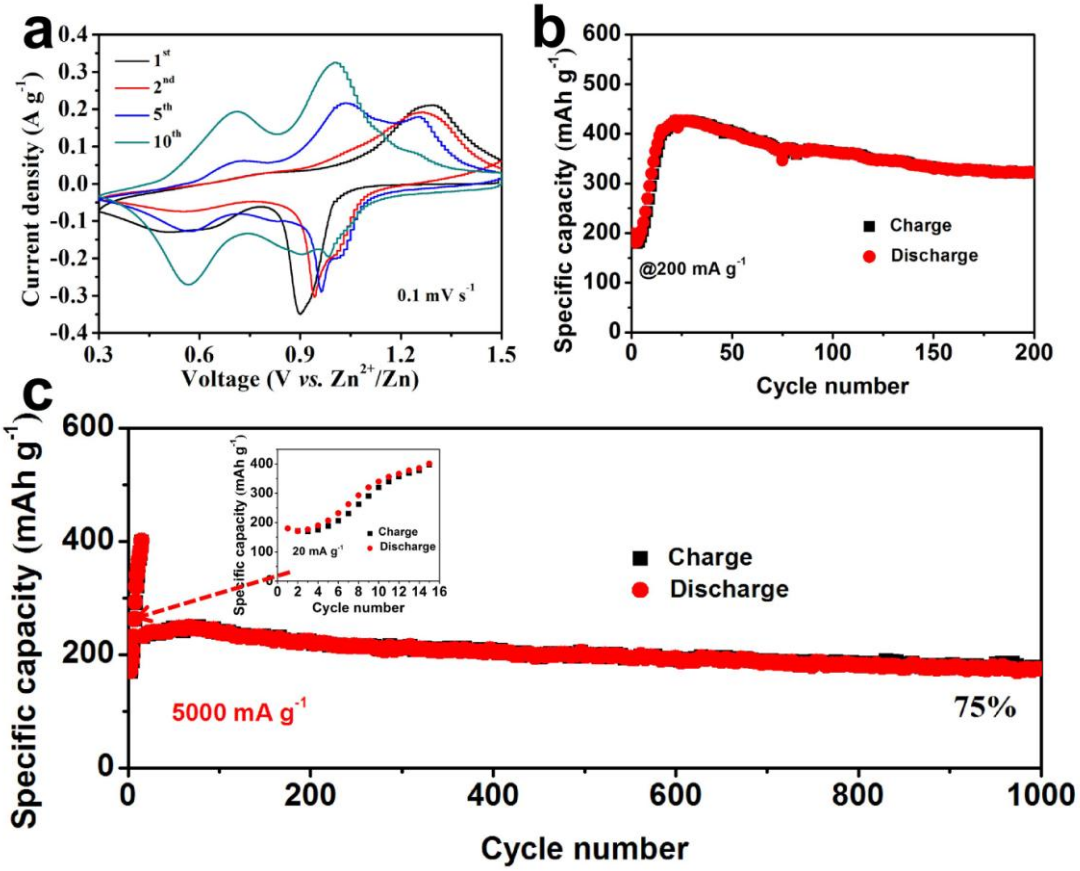

Fig. S10. The electrochemical performances of porous V_2O_5-OX microspheres. (a) CV curves. (b) Cyclic performance at 200 mA g^{-1}. (c) Long-life cycling performance at 5000 mA g^{-1}.

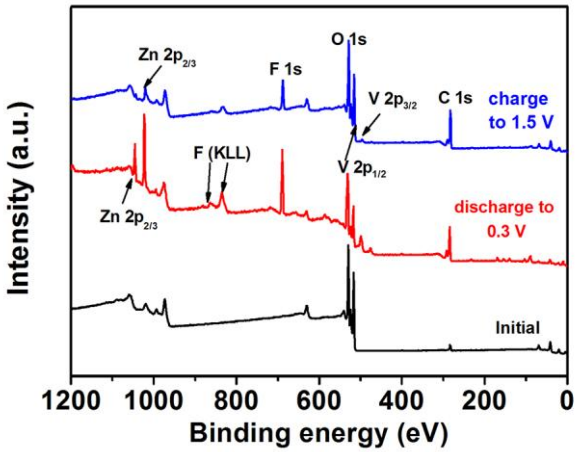

Fig. S11. XPS Survey spectra of the electrodes obtained at different states (original, charged, and discharged states). The fluorine is coming from the PTFE binder.