Electronic supporting information (ESI)

Non-topotactic Redox Reaction Enabled K₂V₃O₈ as a High Voltage

Cathode Material for Potassium-ion Batteries

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Experiments

Material Synthesis

For the synthesis of $K_2V_3O_8$, all chemicals are analytical grade and used as received without further purification. First, 1 mmol V_2O_5 (99.6%, Alfa Aesar Ltd), 2.5 mmol $K_2C_2O_4$ ·H₂O (99.98%, Aladdin Ltd), and 30 mmol KCl (99.5%, Shanghai Macklin Biochemical Co. , Ltd) were dissolved in 30 mL deionized water and stirred for 30 minutes. Next, the solution was transferred to a sealed PTFE bomb, which was heated to 200 °C (heating rate~5 °C min⁻¹) and held for 24 h. After the bomb naturally cooled to room temperature, the solution was transferred out of the bomb and centrifuged to obtain a dark precipitate. Then, the precipitate was washed with DI water and ethanol for several times, and subsequently dried in a vacuum oven set at 80 °C for 12 hours to obtain the K₂V₃O₈ sample.

Material Characterizations

XRD tests were performed on a SmartLab (9KW) with Cu K α radiation ($\lambda = 1.5416$ Å). TGA test was performed in air from room temperature to 800 °C on NETZSCH STA 449 F3 thermogravimetric/differential thermal analysis (NETZSCH Inc., German) with a heating rate of 10 °C min⁻¹. FT-IR spectra were recorded on a Nicolet IS10 FT-IR Microscope. Field-emission scanning electron microscope (HITACHI, SU8020, 15kV) and transmission electron microscope (JEOL, JEM-1200EX, 120 kV) were used to characterize the morphology and structure of the sample. XPS tests were performed by a Thermo Scientific ESCALAB 250Xi equipment with Al K α (hv = 1486.6 eV) X-ray radiation.

For the *ex situ* XRD tests, the $K_2V_3O_8$ electrode was charged/discharged to the desired states in a coin-type half-cell with a Kapton window on the cathode side under 10 mA g⁻¹. Then, the $K_2V_3O_8$ electrode was directly characterized by the X-ray without disassembling the cell, which avoids contamination of the sample by air and moisture.

To characterize the morphology of the after-cycled $K_2V_3O_8$ sample, the $K_2V_3O_8$ electrode was retrieved from the cycled cells, which was charged-discharged for 50 cycles and dissembled at 2.82 V (*vs.* K⁺/K), which is the open circuit potential of pristine $K_2V_3O_8$ electrode, and then immersed in diethyl carbonate for overnight. Then, the electrode was rinsed with diethyl carbonate and ethanol for several times to remove the electrolyte salt residues, and dried for the SEM characterization. The TEM sample was prepared by ultrasonically dispersing the electrode in ethanol and then dropping the dispersion onto TEM grids for characterizations.

Electrochemical Measurements

For the electrode preparation, 70 wt.% active material (\sim K₂V₃O₈), 20 wt.% acetylene black, and 10 wt.% sodium alginate (Aladdin Ltd) were dissolved in deionized water with continuous stirring to form a slurry. Then, electrodes were prepared by uniformly pasting the formed slurry onto a circular aluminum foil (diameter \sim 1 cm) with active material mass loading around 1 mg cm⁻². After the electrode naturally dried at room temperature, it was further dried in a vacuum oven set at 80 °C for 12 hours. All electrochemical tests were conducted with CR2032 coin-type cells with metallic potassium as both reference and counter electrodes, which were assembled in an Ar-filled glovebox (both O₂ and H₂O below 0.05 ppm). For the half-cell assembly, the K₂V₃O₈ working electrode was separated from metallic potassium by a Whatman glass microfiber filter and 7 M KFSI (potassium bis(fluorosulfonyl) imide, Ark, 99.5%) in ethylene carbonate/diethyl carbonate (EC/DEC, 1:1 by

volume) was used as the electrolyte. For the full-cell assembly, graphite anode was first prepared according to the similar procedure of the $K_2V_3O_8$ cathode. Then, graphite electrode was pre-cycled for 5 cycles in a potassium half-cell prepared as above described. After that, the cycled graphite anode and fresh $K_2V_3O_8$ cathode were assembled into coin cells (mass ratio of graphite: $K_2V_3O_8$ =1:4) with 7 M KFSI in EC/DEC as the electrolyte and Whatman glass microfiber filter as the separator.

Cyclic voltammetry tests in the potential range of 1.5-4.5 V (*vs.* K⁺/K) were conducted on a CHI660E workstation (Shanghai Chenhua Co. Ltd., China) for the potassium half-cells. Galvanostatic charge-discharge tests for the potassium half-cells (1.5-4.5 V *vs.* K⁺/K) and the $K_2V_3O_8||$ graphite full-cell (0.005-4.5 V) were recorded with the Land battery testing system (CT2001A, Wuhan LAND electronics, China). All electrochemical tests were conducted at room temperature. Unless otherwise specified, all the specific capacity and current density were calculated on the basis of the mass of $K_2V_3O_8$ in the working electrode.



Fig. S1 TGA curve of the as-prepared $K_2V_3O_8$ sample tested in air atmosphere from room temperature to 800 °C.



Fig. S2 FT-IR spectrum of the as-prepared $K_2V_3O_8$ sample.



Fig. S3 Estimation of the capacity originated from the electrolyte decomposition during the 1^{st} anodic CV scan from open circuit potential to 4.5 V (*vs.* K⁺/K).



Fig. S4 Discharge voltage profiles under different current densities from 10 mA g^{-1} to 200 mA g^{-1} while charge was conducted at a constant current density of 10 mA g^{-1} .



Fig. S5 (a, b) Schematic illustration of the crystal structure changes between $K_2V_3O_8$ and KV_3O_8 viewed from various angles.



Fig. S6 The XRD patterns of the pristine $K_2V_3O_8$ electrode and the one cycled for 50 times under 10 mA g⁻¹.



1 mol K⁺ transferred : $K_2V_3O_8+8C \xrightarrow{-2.71\%} KV_3O_8+KC_8$

Fig. S7 Schematic illustration of the volume variation of a full-cell consisting of a $K_2V_3O_8$ cathode and a graphite anode.

Calculation of the volume change of a K₂V₃O₈||graphite full-cell during charge

For simplicity, we assume that the capacity ratio between cathode and anode is 1:1. Thus, upon l mol potassium-ion transferring from $K_2V_3O_8$ to graphite, below reaction takes place:

$$K_2V_3O_8 + 8C \xrightarrow{Charge} KV_3O_8 + KC_8$$

The density of $K_2V_3O_8$, KV_3O_8 , graphite, and KC_8 is taken as 2.66, 3.09, 2.25 and 1.95 g cm⁻³, respectively.¹ Thus, the volume reduction from $K_2V_3O_8$ to KV_3O_8 is calculated to be -31.40 cm⁻³. Meanwhile, graphite experiences a volume increase of 26.59 cm⁻³. Thus, the percentage of the full-cell volume change is calculated to be: 2.71%.



Fig. S8 Galvanostatic charge-discharge curves of a $K_2V_3O_8$ cathode||graphite anode full-cell at a current density of 10 mA g⁻¹. Both current density and specific capacity are calculated on the basis of the mass of $K_2V_3O_8$ in the full-cell.



Fig. S9 Comparison of the electrochemical performance between $K_2V_3O_8$ and some reported vanadium-based cathode materials²⁻⁷(data are presented in Table S1) for PIBs. The energy density was calculated on the basis of the product of the specific capacity and average discharge voltage.

Materials	Discharge capacity	Voltage	Energy	Doforonao
	(capacity retention)	range	density	Reference
K2V3O8	84.5 mAh g ⁻¹ after 50 cycles	1.5-4.5 V	~300 Wh kg ⁻¹	This work
	at 10 mA g ⁻¹ (73%)			
K2V3O8/C	60 mAh g ⁻¹ after 200 cycles	1.0-4.2 V	~150 Wh kg ⁻¹	2
	at 20 mA g ⁻¹ (80%)			
K3V2(PO4)3	43 mAh g ⁻¹ after 100 cycles	2.5-4.3 V	~190 Wh kg ⁻¹	3
/C	at 20 mA g ⁻¹ (80%)			
KVPO4F	69 mAh g ⁻¹ after 50 cycles	· 2.0-4.8 V	~281 Wh kg ⁻¹	4
	at 6.65 mA g ⁻¹ (98%)			
KVOPO4	71 mAh g ⁻¹ after 50 cycles		~276 Wh kg ⁻¹	
	at 6.65 mA g ⁻¹ (101%)			
K0.5V2O5	72.2 mAh g ⁻¹ after 80 cycles	1.5-3.8 V	240 Wh kg ⁻¹	5
	at 20 mA g ⁻¹ (90.3%)			
K ₃ V ₂ (PO ₄) ₃	74 mAh g ⁻¹ after 100 cycles	2.0-4.0 V	~288 Wh kg ⁻¹	6
/C	at 25 mA g ⁻¹ (~93%)			
KVP2O7	49 mAh g ⁻¹ after 100 cycles	2.0-5.0 V	253 Wh kg ⁻¹	7
	at 25 mA g ⁻¹ (~82%)			

 Table S1. Electrochemical performance of some reported vanadium-based cathode materials for PIBs.

(The energy density was calculated by multiplying the specific capacity with the average discharge voltage of the corresponding materials.)

Notes and references

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