Dual-Ion Stabilized Layered Structure of O–V–O for Zero-Strain Potassium Insertion and Extraction

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Supporting Information

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Experimental Section:
Ethanol, dimethyl carbonate (DMC), potassium (K), sodium (Na) and V$_2$O$_5$ purchased from Aladdin (China chemical company). In a beak, whisk together K and Na until smooth, the best Na-K weight ratio was 1:3 (self-made). The materials (V$_2$O$_5$:Na-K alloy = 0.5g:10mL) were carefully mixed by hand, and stirring in a beaker for 20min. It should be noted that the Na-K alloy shows a high activity with O and then embedded in the layer structure of V$_2$O$_5$.

The generated Na/K oxide was removed by DMC, ethanol and deionized water. After centrifuging and washing by deionized water three times, the obtained NaK(VO$_3$)$_2$-V$_2$O$_5$ powders were dried for characterization. It's worth noting that this method is reported for the first time.

Characterization:
HRTEM (high resolution transmission electron microscopy), XRD (X-Ray Powder Diffraction), SEM (scanning electron microscope) and XPS (X-ray photoelectron spectroscopy) were collector on the JEOL, Rigaku, ZEISS and Thermo Fisher.

Electrochemical Measurements:
To fabricate the anode materials of K-ion battery (KIB), PVDF (Polyvinylidene Fluoride, binder), Super P (conductive agent), and NaK(VO$_3$)$_2$-V$_2$O$_5$ and V$_2$O$_5$ (active materials) were weighed with the ratio of 1:1:8; then the obtained homogeneous slurry was uniformly painted on an aluminum foil and dried for 12 h at 60 °C. The foil was cut into wafers with area of 0.785 cm$^2$, as the electrodes. The active mass loading on the circular pieces was about 1 mg. The electrolyte was 3 M KFSI in DME and 1M/KFF$_6$/EC/DEC (1:1 in volume). Potassium metal was used as counter electrodes and glass microfiber membranes were served as separators. The electrochemical performance was conducted in the potential of 0.01–2.5 V on LanHe battery test system. CV was tested on IVIUM (electrochemistry workstation).

The storage mechanism and electrochemical properties of K-ions:
The maximum specific discharge capacity of 406 mAh g$^{-1}$ at 0.1 A g$^{-1}$ from 0.01 V to 2.5 V. For anode of theoretical specific capacity could be calculated by formula: $^{[3]}$

$$\text{Capacity} = nF/3.6M(\text{mAh g}^{-1})$$

M, F and n represent the relative atomic mass, faraday constant and number of K$^+$ intercalation.

The value of n in K$_x$-NaK(VO$_3$)$_2$-V$_2$O$_5$ is 0.41.

The method for judging pseudocapacitance behavior in electrodes:
In CV test, different peak current values (I, mA) are obtained at different voltage scanning rates (v, mV s\(^{-1}\)). The scanning rate is correlated with the peak current response to distinguish the diffusion behavior or pseudocapacitance behavior in the charging and discharging process.

\[ i = a v^b \]

If the value of \( b \) is 0.5, the electrode material behaves as a capacity of battery. If the value of \( b \) is in the range of 0.5-1, the electrode material shows the properties of capacity of battery and pseudocapacitance. If the value of \( b \) is greater than 1, the electrode material exhibits pure pseudocapacitance properties.

**Calculation of \( K^+ \) diffusion coefficient:**

\[ i = 2.69 \times 10^5 n^{3/2} S D^{1/2} v^{1/2} C \]

where \( n \) is the number of electrons per specific reaction, for \( K^+ \) it is 1; \( S \) is the surface area of the electrode which is 0.785 cm\(^2\) in this work; \( C \) is the concentration of \( K^+ \) in the material, \( i \) is the current intensity peak and \( v \) is the scan rate. And the diffusion coefficients could be calculated using the slop of fitting line \( i \) and \( v^{1/2} \).
Figure S1 SEM image of NaK(VO$_3$)$_2$-$V_2$O$_5$ and V$_2$O$_5$.

Figure S2 XRD pattern of electrode of V$_2$O$_5$ and NaK(VO$_3$)$_2$-$V_2$O$_5$.

Figure S3 SEM images of electrode of cycled NaK(VO$_3$)$_2$-$V_2$O$_5$ and V$_2$O$_5$. 
Figure S4 cycling performance of NaK(VO3)2-V2O5 in electrolyte with 4M/KFSI/DME.

Figure S5 cycling performance of NaK(VO3)2-V2O5 in electrolyte with 1M/KFF6/EC/DEC.
Figure S6 XPS results of NaK(VO3)2-V2O5 of discharge and charge state with different electrolyte.
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