Rational selection of amorphous or crystalline V$_2$O$_5$ cathode for sodium-ion batteries$^\dagger$

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Vanadium oxide (V$_2$O$_5$), as a potential positive electrode for sodium ion batteries (SIBs), has attracted considerable attention from researchers. Herein, amorphous and crystalline V$_2$O$_5$ cathodes on a graphite paper without a binder and conductive additives have been synthesized via facile anodic electrochemical deposition following different heat treatments. Both the amorphous V$_2$O$_5$ (a-V$_2$O$_5$) cathode and crystalline V$_2$O$_5$ (c-V$_2$O$_5$) cathode show good rate cycling performance and long cycling life. After five rate cycles, the reversible capacities of both the cathodes were almost unchanged at different current densities from 40 to 5120 mA g$^{-1}$. Long cycling tests with 10,000 cycles were carried out and the two cathodes exhibit excellent cycling stability. The c-V$_2$O$_5$ cathode retains a high specific capacity of 54 mA h g$^{-1}$ after 10,000 cycles at 2560 mA g$^{-1}$ and can be charged within 80 s. Interestingly, the a-V$_2$O$_5$ cathode possesses higher reversible capacities than the c-V$_2$O$_5$ cathode at low current densities, whereas it is inversely at high current densities. The c-V$_2$O$_5$ cathode shows faster capacity recovery from 5120 to 40 mA g$^{-1}$ than the a-V$_2$O$_5$ cathode. When discharged at 80 mA g$^{-1}$ (long discharge time of 140 min) and charged at 640 mA g$^{-1}$ (short charge time of 17 min), the a-V$_2$O$_5$ cathode shows a higher discharge capacity than its c-V$_2$O$_5$ counterpart. The different electrochemical performance of a-V$_2$O$_5$ and c-V$_2$O$_5$ cathodes during various electrochemical processes can provide a rational selection of amorphous or crystalline V$_2$O$_5$ cathode materials for SIBs in their practical applications to meet the variable requirements.

Introduction

Over the past few decades, lithium ion batteries (LIBs), as a method of electrical energy storage, have been extensively studied and widely applied in portable electronics, large-scale energy storage systems (ESS) and electric vehicles.$^{14}$ However, the large-scale demand for lithium will bring about an increase in its cost due to its low abundance and uneven geographical distribution on earth.$^{5,6}$ Recently, sodium ion batteries (SIBs) have become a suitable alternative to LIBs due to the abundant reserves and low price of sodium. Moreover, it has similar physicochemical properties to lithium.$^{7,8}$ SIBs can also be operated as “rocking-chair” battery like LIBs; therefore, SIBs with an exceptionally high capacity are a very reasonable choice for the development of large-scale and cheap ESS.$^{7-10}$ Moreover, the absence of Na–Al alloy during the electrochemical reaction permits the use of aluminum current collectors, replacing expensive copper as the anode, which further reduces the cost of the final battery.$^{11-13}$ However, the molar mass and radius of Na$^+$ are 23 g mol$^{-1}$ and 0.98 Å, respectively, which are larger than that of Li$^+$ (6.94 g mol$^{-1}$ and 0.69 Å), lead to a lower gravimetric energy and sluggish electrochemical reaction kinetics.$^{6,11}$ Therefore, an electrode with high capacity and a large open framework is required for SIBs.

Recently, vanadium oxide has been extensively researched for its application in LIBs,$^{14-16}$ supercapacitors$^{17}$ and electrochromism$^{18-20}$ and expresses good energy storage performance. V$_2$O$_5$ as a typical layered structure material with high theoretical capacity (236 mA h g$^{-1}$) has also become a potential positive electrode material for SIBs. More recently, Su et al.$^{21}$ and Tepavcevic et al.$^{22}$ demonstrated that bilayered V$_2$O$_5$ electrodes exhibit high capacities due to the large interlayer spacing contributing to the insertion/extraction of Na$^+$ ions. A hydrated V$_2$O$_5$ cathode, reported by Wei et al.$^1$, showed a larger interlayer spacing than that of orthorhombic V$_2$O$_5$ due to the intercalation of water molecules into the layered structure and exhibited a high initial capacity of 338 mA h g$^{-1}$. However, the hydrated vanadium oxide phases are not a realistic solution since the voltage range compatible with the use of hydrated electrodes is extremely limited. Orthorhombic V$_2$O$_5$ materials have also been reported to possess superior electrochemical performance in SIBs.$^{23,24}$

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Currently, crystalline materials are still the primary choice of electroactive species in the rechargeable battery field. However, some researchers have also reported that amorphous materials may have better electrochemical performance than their crystalline counterparts. For instance, Fang et al. reported that the nanostructured amorphous TiO₂ nanotubes show a higher rate capacity than anatase TiO₂ nanotubes due to the higher Li-diffusion coefficient of amorphous TiO₂, whereas the electronic conductivity of amorphous TiO₂ is lower than that of anatase TiO₂.²⁵ Amorphous TiO₂ nanotubes with large diameters (> 80 nm) also demonstrate good electrochemical performance for use in SIBs.²⁶ Jiang et al. reported that hierarchically porous amorphous Fe₂O₃ films exhibit a narrow voltage hysteresis and enhanced capacitive-like lithium storage, resulting in a longer cycling life and a higher rate capacity than a crystalline Fe₂O₃ anode.²⁷ On the contrary, Xu et al. confirmed that mesoporous crystalline Fe₂O₃ spherical particles show better electrochemical performance upon lithiation than an amorphous Fe₂O₃ anode due to the lower overpotential of crystalline Fe₂O₃ during the structural change from amorphous or crystalline structure to nanocrystalline structure.²⁸ This ambivalent results indicate that the same electrode material with different crystallinity may exhibit inverse electrochemical performance under different conditions. For V₂O₅ electrode materials, Uchaker et al. reported that amorphous V₂O₅ deposited on nickel foam demonstrated superior electrochemical properties in SIBs when compared to its crystalline counterpart.¹³ However, our work shows interesting electrochemical results for V₂O₅ materials as cathodes in SIBs, which are absolutely different from the previously reported amorphous/crystalline electrode materials applied for LIBs.

In this study, amorphous and crystalline V₂O₅ electrodes on graphite paper were fabricated via facile anodic electrochemical deposition following vacuum drying or heat treatment. By systematically comparing the electrochemical results in SIBs, the different nanostructured V₂O₅ cathodes exhibit an interesting electrochemical phenomenon in which the amorphous V₂O₅ cathode presents higher reversible specific capacities than the crystalline counterpart at low current densities, whereas it is exactly the inverse at high current densities. These two V₂O₅ cathodes display long cycling life and good rate cycle stability. The amorphous V₂O₅ cathode shows a higher discharge capacity than the crystalline V₂O₅ cathode at a discharge current density of 80 mA g⁻¹ and a charge current density of 640 mA g⁻¹.

Experimental
Preparation of V₂O₅ electrode materials
Anodic electrochemical deposition of V₂O₅ onto graphite paper substrates was performed at a constant voltage of 2.0 V versus Ag/AgCl for 120 s. Typically, 0.25 M VOSO₄ in a 1:1 mixture (volume ratio) of distilled water and ethanol at pH = 2.7 was used as the electrolyte. Ethanol was used to reduce the surface tension between the electrolyte and the graphite paper substrates. The electrochemical deposition was carried out in a three-electrode configuration with the graphite paper substrate as a working electrode, Pt foil as a counter electrode and Ag/AgCl as a reference electrode. The as-grown samples were washed with ethanol and dried at 60 °C in an oven. Then, some of the sample was further dried at 120 °C for 10 h in a vacuum oven to form the amorphous V₂O₅ (a-V₂O₅) cathode and another portion of sample was annealed at 350 °C for 4 h in air to form the crystalline V₂O₅ (c-V₂O₅) cathode. The distinct color change of a-V₂O₅ and c-V₂O₅ can be seen from Fig. S1 (ESI†).

Characterization
The morphology and nanostructures of the samples were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). SEM images of the samples were collected using a SU8000 scanning electron microscope at an accelerating voltage of 15 kV. TEM-HRTEM was carried out on a TEM (JEOL JEM-2010). X-Ray diffraction (XRD) measurements were performed on a Rigaku D/max-rB X-ray diffractometer with Cu Kα (λ = 0.15418 nm) incident radiation. The diffraction patterns were collected at room temperature in the 2θ range of 5°–80°. An X-ray photoelectron spectroscopy (XPS) study was conducted on a PHI 5700 ESCA System using Al Kα radiation (1486.6 eV). Raman spectroscopy was performed with a laser micro-Raman spectrometer (Renishaw invia, Renishaw, 532 nm excitation wavelength).

Electrochemical measurements
The electrochemical properties of the samples were evaluated using CR 2032 coin cells. The coin cells were assembled in a glove box filled with high-purity argon wherein the as-fabricated a-V₂O₅ and c-V₂O₅ cathodes without a binder and conductive additives were used as the working electrode, a metallic sodium foil as the counter/reference electrode, a glass fiber (Whatman) as the separator, and 1 M NaClO₄ in ethylene carbonate (EC)-diethyl carbonate (DEC) (1 : 1 in volume) as the electrolyte. The discharge-charge performance of the batteries was tested using a channels battery analyzer (Neware CT-3008) with a voltage cut-off between 1.0 and 4.0 V vs. Na/Na⁺. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) measurements were performed using a CHI660E electrochemical workstation. EIS was recorded with frequencies ranging from 100 kHz to 10 mHz and a AC signal of 5 mV in amplitude as the perturbation. The voltage range of the CV measurements was 1.0–4.0 V and the scanning rate was 0.5 mV s⁻¹. All the tests were performed at room temperature.

Results and discussion
The morphologies of the a-V₂O₅ and c-V₂O₅ samples are shown in Fig. 1. It can be clearly seen that the a-V₂O₅ sample is a layered structure composed of irregularly shaped nanoparticles (Fig. 1a and b). After annealing, the SEM image of the c-V₂O₅ sample shows that nanorods with rough surfaces are formed (Fig. 1c and d). The nanorods are interlaced with each other, hence forming large amounts of interconnected voids that are beneficial for effective
electrolyte penetration and enhance the contact area between the active materials and electrolyte. Fig. S2 (ESI†) further reveals the homogeneity of the electrodeposited V₂O₅ samples on a graphite paper substrate. During the annealing process, the adjacent nanorods along a line are connected together to prolong the nanorods, whereas the adjacent nanorods in a parallel arrangement would widen the nanorods, as shown in the red labeled zone of Fig. 1c. The nanorod marked as “A” in Fig. 1d clearly shows that there is a boundary along the middle position, indicating that it is composed of two parallel nanorods. The blue labeled zone in Fig. 1d can further confirm this. Tong et al. explained the growth mechanism in detail. 29 The morphological change indicates that a phase transformation as well as crystal growth occurred during the annealing process at 350 °C in air.

The microstructures of the a-V₂O₅ and c-V₂O₅ samples were further characterized using TEM and HRTEM. Fig. 2a and b show the low and high magnification TEM images of the a-V₂O₅ sample. It confirms that the a-V₂O₅ sample is a layered structure and composed of nanoparticles, which is consistent with the results of SEM shown in Fig. 1a and b. The average size of the nanoparticles is about 80 nm. The HRTEM image in Fig. 2c confirms that four layers exist in the sample and the selected area electronic diffraction (SAED) in the inset reveals its amorphous structure. Fig. 2d and e exhibit the low and high magnification TEM images of the c-V₂O₅ sample. The nanorods are interconnected with each other and a large number of voids were formed among them [Fig. S3a, ESI†]. The HRTEM image (Fig. 2f) exhibits the distinct interplanar spacing of 0.34 nm, which corresponds to the (110) plane of orthorhombic V₂O₅, demonstrating the good crystallinity of the c-V₂O₅ samples. A wider interplanar spacing of 0.58 nm, corresponding to the (200) plane, can also be observed from the HRTEM image (Fig. S4, ESI†). The exposed (200) plane will contribute to the insertion/extraction of Na⁺ ions. The SAED shown in the inset of Fig. 2f further demonstrates the crystalline characteristics of the c-V₂O₅ sample. Energy dispersive X-ray spectroscopy (EDX), as shown in Fig. S3b (ESI†), was conducted to determine the composition of the c-V₂O₅ sample, which confirms that the sample is composed of vanadium and oxygen. The peaks of copper derive from the carbon-coated copper grid. The high intensity carbon peak is due to the superimposed effect of the graphite paper substrate and the carbon-coated copper grid.

The phase and crystal structures of the a-V₂O₅ and c-V₂O₅ samples were monitored and characterized by XRD, Raman spectroscopy and XPS. Fig. 3a shows the XRD patterns of a-V₂O₅, c-V₂O₅ and graphite paper. Both a-V₂O₅ and c-V₂O₅ show (002) and (004) reflections attributed to the presence of the graphite paper substrate. The a-V₂O₅ sample only expresses a broad reflection around 8.5° besides the reflections of graphite paper, indicating its amorphous structure. The main diffraction reflections of c-V₂O₅ can be assigned to the orthorhombic V₂O₅ structure (JCPDS No. 41-1426) belonging to the Pmmn space group, with the lattice parameters a = 11.516 Å, b = 3.566 Å and c = 4.373 Å. This crystalline structure has been confirmed to be a two-dimensional (2D) bilayered stack, separated by large interlayer spacing, corresponding to the (001) diffraction reflection at 20.3° with a d-spacing of 4.37 Å, which is an ideal layer structure for the insertion/extraction of Na⁺ ions. 23 Interestingly, extra diffraction reflections at 9.8°, 12.5° and 28.9° were observed (Fig. 3a). They may be assigned to the orthorhombic V₄O₉ structure (JCPDS No. 24-1391) belonging to the Pnma space group with the lattice parameters a = 17.926 Å, b = 3.631 Å and c = 9.396 Å.
This new phase forming can be ascribed to the oxygen vacancy defect, which can enhance the electrochemical performance.\textsuperscript{7} The V\textsubscript{4}O\textsubscript{9} phase with larger interlayer spacing of 9.40 Å will further facilitate the transport of Na\textsuperscript{+} ions.

The Raman spectra of the a-V\textsubscript{2}O\textsubscript{5} and c-V\textsubscript{2}O\textsubscript{5} samples are shown in Fig. 3b. Both samples display the same Raman bands. The predominant low frequency vibration band at 146 cm\textsuperscript{-1} was ascribed to the skeleton bent mode, which is an evidence of the layered-type structure of V\textsubscript{2}O\textsubscript{5}. Moreover, the band at 994 cm\textsuperscript{-1} was related to the vanadyl mode corresponding to the stretching of vanadium atoms connected to oxygen atoms by double bonds (V=O) and is also a significant fingerprint of the perfect layer-type structure of V\textsubscript{2}O\textsubscript{5}.\textsuperscript{21,30,31} The band located at 198 cm\textsuperscript{-1} arises from VO\textsubscript{2}–VO\textsubscript{2} specifically, translational displacements along the z axis with mixed $A\textsubscript{g}$ + $B\textsubscript{2g}$ symmetry.\textsuperscript{32,33} The bands at around 286, 300 and 404 cm\textsuperscript{-1} originate from the bending vibrations of the V–O bond. The stretching vibrations of the V–O bond occur at about 532 and 706 cm\textsuperscript{-1}. The band located at 1580 cm\textsuperscript{-1} was ascribed to the G band of graphene due to the graphite paper substrate. In addition, the spectrum of c-V\textsubscript{2}O\textsubscript{5} is well resolved, indicating its polycrystalline nature, whereas the spectrum of a-V\textsubscript{2}O\textsubscript{5} was found to be broad, indicating its amorphous nature.\textsuperscript{34,35}

To identify the chemical state of the vanadium species present in both V\textsubscript{2}O\textsubscript{5} samples, XPS measurements were carried out. The wide survey XPS spectra of the samples are shown in Fig. S5 (ESI\textsuperscript{†}), which indicate the same predominant signals of V, O and C. Note that the elemental carbon comes from the graphite paper substrate or carbonaceous molecules in air. This wide range XPS results indicate that the a-V\textsubscript{2}O\textsubscript{5} and c-V\textsubscript{2}O\textsubscript{5} samples are rather pure and no impurity elements were detected. Fig. 3c and d show the V 2p\textsubscript{3/2} spectra of a-V\textsubscript{2}O\textsubscript{5} and c-V\textsubscript{2}O\textsubscript{5}. The V 2p\textsubscript{3/2} core peak spectra of both samples can be deconvoluted into two peaks located at 517.41 eV and 516.13 eV for a-V\textsubscript{2}O\textsubscript{5} and 517.34 eV and 516.00 eV for c-V\textsubscript{2}O\textsubscript{5}, respectively. These two binding energy values are associated with the two formal oxidation states, V\textsuperscript{5+} and V\textsuperscript{4+}. The V\textsuperscript{4+}/V\textsuperscript{5+} ratio of a-V\textsubscript{2}O\textsubscript{5} was 18.7%, which was calculated from the area ratio of the fitted spectra of V 2p\textsubscript{3/2} (V\textsuperscript{5+}) and V 2p\textsubscript{1/2} (V\textsuperscript{4+}). The large concentration of V\textsuperscript{4+} species in the a-V\textsubscript{2}O\textsubscript{5} sample will give rise to intervalence charge transitions (IVCT, V\textsuperscript{4+} → V\textsuperscript{5+}) and explains the different color of the c-V\textsubscript{2}O\textsubscript{5} sample, as shown in Fig. S1 (ESI\textsuperscript{†}). The content of V\textsuperscript{4+} in a-V\textsubscript{2}O\textsubscript{5} may be derived from the co-deposition of unreacted VO\textsuperscript{2+} ions in the electrolyte solution and the presence of oxygen vacancies. For c-V\textsubscript{2}O\textsubscript{5}, the V\textsuperscript{4+/V\textsuperscript{5+}} ratio was 14.0%, which indicates that the V\textsuperscript{4+} in VO\textsuperscript{2+} ions have been oxidized into V\textsuperscript{4+} after annealing in air, corresponding to the color change to yellow, and the V\textsuperscript{4+} present was absolutely due to oxygen vacancies. This is in good agreement with the XRD results of c-V\textsubscript{2}O\textsubscript{5}. The detailed parameters, including peak position, area and full width at half maximum (FWHM) of the V 2p\textsubscript{3/2} spectra for both samples are listed in Table S1 (ESI\textsuperscript{†}).

The electrochemical performance of the a-V\textsubscript{2}O\textsubscript{5} and c-V\textsubscript{2}O\textsubscript{5} cathodes in LIBs was systematically investigated. Fig. 4 compares the rate performances of the two different cathodes, in which the current density was up to 5120 mA g\textsuperscript{-1} from 40 mA g\textsuperscript{-1}. Fig. 4a and b show the galvanostatic discharge/charge curves obtained for the a-V\textsubscript{2}O\textsubscript{5} and c-V\textsubscript{2}O\textsubscript{5} cathodes at different current densities between 1.0 and 4.0 V (versus Na/Na\textsuperscript{+}). It can be clearly seen that the discharge capacities of the a-V\textsubscript{2}O\textsubscript{5} and c-V\textsubscript{2}O\textsubscript{5} cathodes in the fifth cycle are 229.4 and 220.1 mA h g\textsuperscript{-1}, respectively, which are close to the theoretical capacity (236 mA h g\textsuperscript{-1}) obtained for the formation of Na\textsubscript{2}V\textsubscript{2}O\textsubscript{5}. Moreover, in the following rate cycles, both cathodes show higher capacities than the theoretical value at 40 mA g\textsuperscript{-1}, which may be ascribed to the structural evolution from amorphous and crystal structures to a nanocrystalline structure.\textsuperscript{28} The nanocrystals with small particle size, high surface area and loosely packed lattices will contribute to improved pseudocapacitance.\textsuperscript{7,24,36} Fig. 4c shows a comparison of five continuous rate performances obtained for the two cathodes. It is interesting that the a-V\textsubscript{2}O\textsubscript{5} cathode exhibits higher specific capacities (217.1 and 186.9 mA h g\textsuperscript{-1} at 80 and 160 mA g\textsuperscript{-1}, respectively) than the c-V\textsubscript{2}O\textsubscript{5} cathode (186.6 and 158.3 mA h g\textsuperscript{-1}) at low current densities. This can be associated with the amorphous structure, which will contribute to the improved pseudocapacitive storage, particularly for layered oxides in which the pseudocapacitance either occurs at the particle surface or within the interlayer spacing of the material.\textsuperscript{13} However, the c-V\textsubscript{2}O\textsubscript{5} cathode possesses higher specific capacities (121.9, 101.5, 75.3 and 41.2 mA h g\textsuperscript{-1} at 640, 1280, 2560 and 5120 mA g\textsuperscript{-1}, respectively) than those of the a-V\textsubscript{2}O\textsubscript{5} cathode (82.6, 40.5, 14.3 and 5.7 mA h g\textsuperscript{-1}) at high current densities. This should be due to the lower charge transfer resistance ($R_{ct}$) of the c-V\textsubscript{2}O\textsubscript{5} cathode when compared to the a-V\textsubscript{2}O\textsubscript{5} cathode, which was confirmed by the EIS measurements, as shown in Fig. S6 (ESI\textsuperscript{†}). The lower $R_{ct}$ value obtained for c-V\textsubscript{2}O\textsubscript{5} compared to a-V\textsubscript{2}O\textsubscript{5} may be ascribed to the following reasons: (1) crystalline V\textsubscript{2}O\textsubscript{5} has a higher electronic conductivity than amorphous V\textsubscript{2}O\textsubscript{5}, as reported previously.\textsuperscript{37} (2) When compared to the a-V\textsubscript{2}O\textsubscript{5} electrode, the c-V\textsubscript{2}O\textsubscript{5} electrode has large amounts of interconnected voids as shown in Fig. 1 that are beneficial for effective electrolyte penetration and enhancing the contact area between active materials and electrolyte, hence...
shortening the \( \text{Na}^+ \) ions diffusion distance at the interface between the active materials and electrolyte, and limits the range over which small polaron hopping needs to be sustained and mitigating the kinetic impediments imposed by stabilization of a polaron.\(^{\text{18}}\) Other crystalline metal oxides have also been previously reported to have higher electronic conductivity than their amorphous counterparts.\(^{\text{25}}\) The current density at 320 mA g\(^{-1}\) was an obvious boundary where the capacities of the a-V\(_2\)O\(_5\) and c-V\(_2\)O\(_5\) cathodes were 134.4 and 141.7 mA h g\(^{-1}\), respectively. Moreover, both cathodes show excellent cycle performance for their rate capability, which is important for batteries in practical applications.

Another interesting electrochemical behavior is that when the current density returns to 40 mA g\(^{-1}\) from 5120 mA g\(^{-1}\), the c-V\(_2\)O\(_5\) cathode exhibits a faster capacity recovery than the a-V\(_2\)O\(_5\) cathode. Moreover, during cycling, the capacity recovery of the c-V\(_2\)O\(_5\) cathode becomes faster and faster, while it becomes slower and slower for the a-V\(_2\)O\(_5\) cathode, as shown by the green dotted line in Fig. 4c. This interesting electrochemical behavior is consistent with the voltage behavior that the c-V\(_2\)O\(_5\) cathode reveals higher voltage recovery than the a-V\(_2\)O\(_5\) cathode in one minute of standing time after discharge/charge at 5120 mA g\(^{-1}\), as shown in Fig. S7c–f (ESI†). The faster voltage and capacity recoveries observed for the c-V\(_2\)O\(_5\) cathode promise a more favorable practical application than the a-V\(_2\)O\(_5\) cathode in SIBs under certain conditions, which need faster capacity recovery from high current output to low current output.

In order to understand the various insertion/extraction processes of the Na\(^+\) ions in these cathodes, the CV profiles at different electrochemical stages were further studied between 1.0 and 4.0 V (versus Na/Na\(^+\)) at a scan rate of 0.5 mV s\(^{-1}\), as shown in Fig. 5. Fig. 5a and b show the CV curves obtained for the a-V\(_2\)O\(_5\) and c-V\(_2\)O\(_5\) cathodes before any electrochemical performance tests. The CV profiles of the a-V\(_2\)O\(_5\) cathode displays rectangular curves without obvious peaks over the CV scan, which is a characteristic of pseudocapacitive storage.\(^{\text{13}}\) The slope discharge profile shown in Fig. S7a (ESI†) further demonstrates the pseudocapacitive storage type of the a-V\(_2\)O\(_5\) cathode. The area of

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**Fig. 4** The galvanostatic discharge/charge curves obtained for the (a) a-V\(_2\)O\(_5\) cathode and (b) c-V\(_2\)O\(_5\) cathode at various current densities between 1.0 to 4.0 V. (c) A comparison of the rate performance observed for both cathodes.

**Fig. 5** The CV curves obtained for the a-V\(_2\)O\(_5\) and c-V\(_2\)O\(_5\) cathodes between 1.0 and 4.0 V (versus Na/Na\(^+\)) at a scan rate of 0.5 mV s\(^{-1}\), (a and b) before any electrochemical performance tests and (c and d) after the rate performance tests. The ex situ XRD patterns obtained for the (e) a-V\(_2\)O\(_5\) cathode and (f) c-V\(_2\)O\(_5\) cathode.
the rectangular curve becomes larger upon increasing the scan time, indicating the increasing of capacity of the a-V2O5 cathode, which is consistent with the discharge capacity (Fig. S7a, ESI†). When compared to the a-V2O5 cathode, the CV profiles of the c-V2O5 cathode display three couples of redox peaks, corresponding to the multi-electron reaction along with the transformation of various vanadium valence states. The three cathodic peaks located around 3.57, 2.68 and 1.56 V correspond to the anodic peaks around 3.62, 2.90 and 1.75 V, respectively. This is in agreement with the CV curves reported for V2O5 cathodes in SIBs.7,12 However, an extra anodic peak situated at 2.32 V was also observed, which was different from the reported results. This unpredictable anodic peak can be ascribed to the presence of a V4O9 phase, which was consistent with the results of the XRD study. The CV tests at a lower scan rate (0.1 mV s⁻¹) have also been carried out to distinguish the redox peaks (Fig. S8, ESI†). Fig. 5c and d show the CV curves obtained for the a-V2O5 and c-V2O5 cathodes after the rate performances. It is interesting that one couple of redox peaks located around 2.60 and 2.90 V can be found for the a-V2O5 cathode after five rate cycles, as shown in Fig. 5c. For the c-V2O5 cathode, only one couple of redox peaks was located around 2.60 and 2.90 V was also detected after five rate cycles, as shown in Fig. 5d. The occurrence of the redox peaks observed for the a-V2O5 cathode and the vanishing of the redox peaks observed for the c-V2O5 cathode both indicate the phase transformation during the insertion/extraction of Na⁺ ions. These structural changes during the discharge/charge processes can also be reflected in the discharge profiles in which the discharge plateaus observed for both cathodes exhibit an obvious change when compared to the first discharge profile, as shown in Fig. S7 (ESI†). The same position of redox peaks after five rate cycles may indicate that both a-V2O5 and c-V2O5 can transform towards the same phase during the electrochemical process.

Ex situ XRD tests of both cathodes were carried out to further investigate the structural changes and reaction mechanism during charging/discharging, as shown in Fig. 5e and f. The vanishing of reflections in the c-V2O5 cathode indicates the decrease in crystallinity. In contrast to the c-V2O5 cathode, the (011) and (310) reflections occurring in the a-V2O5 cathode indicate an increase in crystallinity. The crystallinity changes in both cathodes can further explain the variations of the redox peaks in the CV curves. Moreover, the (001) reflection of the c-V2O5 cathode is visibly shifted towards a lower angle (from 20.2° to 18.0°) when compared to the initial stage. This reflects the increase in the interlayer spacing, which is due to the intercalation of Na⁺ ions that expands the lattice plane. When the voltage returns to 4 V, the (001) reflection is still at a low angle of 18.0°, indicating a preserved larger interlayer spacing after desodiation, which is beneficial for the insertion/extraction of Na ions occurring in the following cycles. This irreversible phase transition corresponds to the change from a crystalline structure to nanocrystalline structure. The structure changes of both cathodes after 500 cycles were characterized using Raman spectroscopy, as shown in Fig. S9 (ESI†). The obvious changes observed in the band intensity and band position both reflect the phase transformation during charging/discharging process.

The cyclic voltammetry data at various scan rates were analyzed to characterize the pseudocapacitive effect according to the power law relationship between current (i) and scan rate (v):

\[ i = av^b. \]

\[ \log(i) = b \log(v) + \log(a) \]

Both a and b are adjustable parameters with b-values determined from the slope of eqn (2). The b value determines the type of Na⁺ insertion/extraction. When b = 0.5, the electrochemical reaction is controlled by semi-infinite linear diffusion and when b = 1, the process mainly relies on surface-controlled diffusion.36,39,40 Fig. S10a and b (ESI†) compare the b-values obtained for both cathodes at low scan rates (from 0.2 to 1.0 mV s⁻¹) and at high scan rates (from 10 to 200 mV s⁻¹). The corresponding CV curves and log(i) versus log(v) plots obtained for both cathodes at low or high scan rates are shown in Fig. S11 and S12 (ESI†), respectively. At low scan rates, the b-values obtained for the a-V2O5 cathode are larger than those for the c-V2O5 cathode at most voltage states, indicating that the a-V2O5 cathode possesses more pseudocapacitative contribution. This is in accordance with the higher specific capacities of the a-V2O5 cathode at low current densities. While at high scan rates, the b-values of the a-V2O5 cathode are smaller than those of the c-V2O5 cathode. The larger decrease in the b-values of the a-V2O5 cathode may indicate a higher limitation to the rate capability.36 This is in agreement with the lower specific capacities observed for the a-V2O5 cathode at high current densities. This decrease in the b-value at high scan rates reflects an increase in the Ohmic contribution (active material resistance, solid–electrolyte interphase resistance) and/or diffusion constraints/limitations.36 Therefore, the larger decrease in the b-values may indicate that the a-V2O5 cathode suffers from a larger increase in the Ohmic contribution and/or larger diffusion constraints/limitations than those found for the c-V2O5 cathode at high current densities.

To further compare the various electrochemical performances of the a-V2O5 and c-V2O5 cathodes, the cycling capabilities of both cathodes were conducted at different current densities of 80, 160, 320, 640, 1280, 2560 mA g⁻¹ for 150, 500, 1000, 1000, 5000, 10 000 cycles, as shown in Fig. 6. To the best of our knowledge, this work studies the cycling life of V2O5 cathodes in SIBs for such long cycle life for the first time. Just like the comparative results obtained for the rate performance, the comparison of cycling performance also shows the same interesting phenomenon in which the a-V2O5 cathode possesses higher specific capacities than the c-V2O5 cathode at low current densities even after 150 or 500 cycles, while it is inverted at high current densities. The current density of 320 mA g⁻¹ was also a boundary in the interesting electrochemical phenomenon. The reversible specific capacities of the a-V2O5 and c-V2O5 cathodes are 110.9 and 112.2 mA h g⁻¹ after 1000 cycles at 320 mA g⁻¹, respectively. These interesting results can guide one to select the a-V2O5 and c-V2O5 cathodes using in SIBs based on their different applications. It can be clearly seen that the reversible specific capacity of the c-V2O5 cathode decreases gradually after the first few dozen of cycles, especially at high
current densities, which can be ascribed to the irreversible and gradual phase transition from a crystal structure to nanocrystalline structure. Different from the c-V$_2$O$_5$ cathode, the a-V$_2$O$_5$ cathode expresses a sharp capacity decrease after the first cycle, distinctly shown at high current densities from 320 to 2560 mA g$^{-1}$. This difference may confirm that the amorphous V$_2$O$_5$ electrode may have a faster phase transition from its amorphous structure to nanocrystalline structure than its crystalline counterpart after the initial discharge/charge processes. This faster phase transition from the amorphous V$_2$O$_5$ electrode may be due to the high-energy unstable state of the amorphous phase. When compared to the c-V$_2$O$_5$ cathode, the a-V$_2$O$_5$ cathode after phase transition exhibits self-improving capacity after the first several or few dozen cycles via self-organization between V$_2$O$_5$ and Na$^+$ ions at low current densities from 80 to 640 mA g$^{-1}$. Both the a-V$_2$O$_5$ cathode and c-V$_2$O$_5$ cathode exhibit stable cycle life after the phase transition processes. Especially for the c-V$_2$O$_5$ cathode, it retains a high specific capacity of 54 mA h g$^{-1}$ after 10 000 cycles at 2560 mA g$^{-1}$ and can be charged within 80 s. The excellent cycling performance of the two cathodes can be ascribed to the following features: (i) the occurrence of the nanocrystalline structure, which facilitates Na$^+$ diffusion and avoids the grievous structural degradation during Na$^+$ insertion/desertion, and (ii) the robust bonding of the directly grown V$_2$O$_5$ to the current collector, which promotes electronic conduction and eliminates the degradation caused by a binder or conductive agents.$^{32-44}$

The detailed reversible specific capacities of both cathodes after different cycle numbers at various current densities are listed in Table S2 (ESI†). In order to determine the graphite paper substrate contribution to the capacity, CV test and cycling performance of graphite paper were carried out, as shown in Fig. S13 (ESI†). It can be clearly seen that the pure graphite paper substrate shows negligible specific capacity when compared to the total specific capacity between 1.0 and 4.0 V (versus Na/Na$^+$). In addition, ex situ XRD (Fig. 5e and f) shows that the reflection of graphite paper has no shift during charging/discharging, indicating few sodium ions insert into graphite paper above 1.0 V (versus Na/Na$^+$).

The structural changes and phase transformation of the a-V$_2$O$_5$ and c-V$_2$O$_5$ cathodes after the different electrochemical processes were investigated using SEM and HRTEM (Fig. 7). Fig. 7a and e show that both cathodes express no pulverization or dissolution after 500 cycles at 160 mA g$^{-1}$. The two cathodes exhibit similar morphology with layered stacking, which is different from that observed before cycling (Fig. 1a and c) and indicates the phase transformation. Even after 10 000 cycles at 2560 mA g$^{-1}$, there was still no severe pulverization or dissolution occurring in both cathodes (Fig. 7b and f), indicating their excellent cycling stability.

The morphological changes in the two cathodes after five rate cycles from 40 to 5120 mA g$^{-1}$ are presented in Fig. 7c and g. The morphologies have no obvious differences when compared with the samples tested at lower current densities (Fig. 7a and e) due to the phase transformation. The phase transformation from amorphous or crystalline structure to nanocrystalline structure after five rate cycles was further confirmed using HRTEM, as shown in Fig. 7d and h. It can be obviously seen that the nanocrystals are formed and surrounded by an amorphous network in both of the V$_2$O$_5$ cathodes. The nanocrystalline structure can also be observed from Fig. S14 (ESI†). The nanocrystalline structure will possess a high electrochemical Na$^+$ storage performance due to the high number of Na$^+$ diffusion pathways and open intercalation sites of the loosely packed lattices.$^{44}$

To further determine how to reasonably select the amorphous or crystalline V$_2$O$_5$ cathode in practical applications, the electrochemical performances of the a-V$_2$O$_5$ and c-V$_2$O$_5$ cathodes discharged at 80 mA g$^{-1}$ and charged at 640 mA g$^{-1}$ were investigated. Fig. 8a and b show the discharge curves at 80 mA g$^{-1}$ and charge curves at 640 mA g$^{-1}$ obtained for both cathodes at different cycles. They show that the a-V$_2$O$_5$ cathode has a more stable cycle life than the c-V$_2$O$_5$ cathode during this special charge and discharge mechanism. The phase transition can also be observed from the
discharge/charge curves shown in Fig. 8a and b based on the change of the discharge plateau. Fig. 8c and d show the corresponding current–time curves obtained for both the cathodes. It can be calculated that the discharge time was about eight times longer than the charge time for both cathodes, corresponding to the multiples of current density. There is an important practical significance to investigate the fast charge/slow discharge performance of batteries. Fig. 8e further exhibits the cycling life of both cathodes during the special charge and discharge mechanism. It is obvious that the a-V_2O_5 cathode shows a higher discharge capacity than the c-V_2O_5 cathode after the first several cycles, which is also reflected by the discharge time in which the a-V_2O_5 cathode has a longer discharge time than the c-V_2O_5 cathode (Fig. 8c and d). After 200 cycles, the reversible specific capacity of the a-V_2O_5 cathode was 179.6 mA h g^{-1}, retaining 81.6% of its second discharge capacity, while they were 121.4 mA h g^{-1} and 54.9% for the c-V_2O_5 cathode, respectively. To demonstrate their applications, we show that a one coin cell based on the a-V_2O_5 or c-V_2O_5 positive electrode, after being cycled 200 times under these charge and discharge conditions, can still easily power 10 blue light emitting diodes (LEDs) in parallel (Fig. 8f and g). The process of lighting can be further vividly seen from the ESI videos. By comparing the voltage values before and after lighting for about 1 min, the a-V_2O_5 cathode shows a smaller voltage drop (from 3.76 to 2.70 V) than the c-V_2O_5 cathode (from 3.78 to 2.55 V). This may be ascribed to the higher capacity of the a-V_2O_5 cathode when compared to the c-V_2O_5 cathode. Higher charging current densities (1280 and 2560 mA g^{-1}), maintaining the same discharging current density of 80 mA g^{-1}, were also conducted to investigate the fast charge/slow discharge performance, as shown in Fig. S15 (ESI†). This shows that both the cathodes exhibit reduced specific capacities when compared to when charged at 640 mA g^{-1}.

Fig. 7  SEM images of (a, b and c) a-V_2O_5 and (e, f and g) c-V_2O_5 taken after 500 cycles at 160 mA g^{-1}, 10 000 cycles at 2560 mA g^{-1} and five rate cycles, respectively. The HRTEM images of (d) a-V_2O_5 and (h) c-V_2O_5 taken after five rate cycles.

Fig. 8  Electrochemical performances of both cathodes discharged at 80 mA g^{-1} and charged at 640 mA g^{-1}. The galvanostatic discharge/charge curves obtained for the (a) a-V_2O_5 cathode and (b) c-V_2O_5 cathode at different cycles. The current–time curves obtained for the (c) a-V_2O_5 cathode and (d) c-V_2O_5 cathode. (e) The cycle performances of both cathodes. Images of 10 blue LEDs powered by a one coin cell composed of (f) a-V_2O_5 or (g) c-V_2O_5.

Conclusions

Amorphous and crystalline V_2O_5 positive electrodes without a binder and conductive additives were fabricated via facile anodic
electrochemical deposition following vacuum drying or heat treatment for SIBs. By comparing the electrochemical performances of the two cathodes under different electrochemical conditions, an interesting phenomenon was observed in which the a-V$_2$O$_5$ cathode expresses higher reversible capacities than the c-V$_2$O$_5$ cathode at low current densities, whereas it is exactly inverted at high current densities. The c-V$_2$O$_5$ cathode exhibits faster capacity recovery when transferred back to a low current density of 80 mA g$^{-1}$, whereas the a-V$_2$O$_5$ cathode shows a higher discharge capacity at a constant discharge current density of 80 mA g$^{-1}$ and charge current density of 640 mA g$^{-1}$. These interesting electrochemical results will guide the reasonable choice between the amorphous or crystalline V$_2$O$_5$ cathode materials when used in the practical application of SIBs.

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References


