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TOC

Constructing the best symmetric full K-ion battery with the NASICON-type $\text{K}_3\text{V}_2(\text{PO}_4)_3$

The first time to explore the outstanding symmetric potassium ion battery which is assembled with the $\text{K}_3\text{V}_2(\text{PO}_4)_3$ -based electrodes as both anode and cathode using the *in-situ* measurements

Constructing the best symmetric full K-ion battery with the NASICON-type $K_3V_2(PO_4)_3$

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ABSTRACT: Symmetric full-cells, which employ two identical electrodes as both the cathode and anode, attract great research attention, because it has high safety, facial fabrication and lower costs. Unfortunately, the practical utilization of full symmetric energy storage systems, especially the symmetric potassium ion batteries (KIBs), is hindered by the limited choice of the available electrode materials. In this work, a novel NASICON-type $K_3V_2(PO_4)_3$ is prepared and first employed for the symmetric KIBs. Through *in-situ* measurement, a highly lattice reversibility is found during the K^+ insertion/extraction process. $KV_2(PO_4)_3$ and $K_5V_2(PO_4)_3$ was generated after the depotassiation and potassiation process at about 4.0 V and below 1.0 V, respectively. The reversible capacity of the full symmetric KIBs is about 90 mAh g⁻¹ between 0.01–3.0 V at 25 mA g⁻¹, corresponding to an initial coulombic efficiency of 91.7 % which is the highest one among all the previous reported symmetric energy storage systems (including the symmetric lithium/sodium ion batteries). 88.6 % reversible capacity was maintained even after 500 cycling test. More importantly,

a largest working potential at about 2.3 V was obtained in this work, benefiting the output energy of this symmetric energy storage system. The outstanding cycling stability, large working potential and the highest initial coulombic efficiency endow this work with promising advantages for the future development of the novel energy storage system.

Keywords: symmetric battery, potassium ion batteries, full cell, $\text{K}_3\text{V}_2(\text{PO}_4)_3$

1. Introduction

The lithium ion battery (LIB) is the most successful energy storage system due to its high specific capacity, long cycling life and suitable working potential.[1-3] The main challenges for LIBs are the limited global reserves and increasing cost of the Li.[4-6] The sodium ion battery (NIB) also attracted great attention due to the practically unlimited nature of sodium resources.[7,8] Unfortunately, the standard electrode potential of sodium (-2.71 V vs. RHE) is somewhat higher than that of the lithium (-3.04 V), leading to a limited working potential in the full cell for practical application.[9] Also included in the alkali metal family, potassium, exhibits promising potential to realize affordable rechargeable batteries.[10,11] Despite its large ionic radius ($\sim 0.4 \text{ \AA}$ larger than Na^+ and $\sim 0.7 \text{ \AA}$ larger than Li^+), the working potential (-2.93 V) of potassium is very close to that of the LIB.[12,13] Furthermore, the potassium ion battery (KIB) shows excellent reversible intercalation capability with various electroactive composites.[14,15]

Until now, all the previous studies on KIBs are limited by the traditional fabrication methods, using two different electrodes as the anode and cathode.[16] The same research limitation can also be found in LIBs and NIBs. Therefore, the practical utilization of these systems is hindered by the sophisticated production process and high cost. Moreover, because of the large volume expansion/contraction of the electrodes during the charging/discharging, the volume of the whole battery will be changed, leading to a high safety risk.[17] Therefore, novel energy storage systems with advanced designs are necessary not only for KIBs, but also for NIBs and LIBs.

$\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) with unique crystal structures and relatively high theoretical capacity are promising candidates when used as the cathode electrodes in LIBs and NIBs.[18,19] Both LVP and NVP are endowed with the monoclinic structure, which creates 3D diffusion pathways for the efficient insertion/extraction of the active Li^+ and Na^+ .[20,21] In addition, the reversible insertion/extraction of Li^+/Na^+ in LVP/NVP appear at about 4.1 or 1.7 V, corresponding to the redox reactions of $\text{V}^{+4}/\text{V}^{+3}$ and $\text{V}^{+3}/\text{V}^{+2}$, respectively.[22,23] Therefore, the potential distance is 2.4 V due to the unique redox property of LVP/NVP. Such intriguing properties make monoclinic LVP/NVP attractive and promising for both anode and cathode in LIBs/NIBs, resulting in the possibility of fabricating novel symmetric full cells.

Apart from the electrochemical advantages of the LVP/NVP, the level of safety and the practical fabrication process for symmetric full-cells also benefit significantly from this novel symmetric design. For example, the symmetric full-cell can buffer the large volume changes more effectively, because cathode expansion is always accompanied by anode shrinkage (and vice versa), leading to consistency in the total volume in the whole cell.[22] In addition, the fabrication process and manufacturing costs of the symmetric cell will be significantly simplified and decreased from the commercial viewpoint, because only one type of electrode material needs to be produced and coated on the current collector, which makes it more attractive for commercial production. Furthermore, compared with the half-cells that use lithium/sodium foil as the counter electrodes, the use of symmetric electrodes can enable direct fabrication of the full-cells and may eliminate the possibility of side reactions, such as between the electrolyte and the lithium/sodium foil, improving the safety and cyclability of the full-cell.[16]

Herein, in order to fabricate advanced novel KIBs with acceptable capacity, high safety and a simplified manufacturing process, we first introduced this novel symmetric concept of fabricating advanced symmetric KIBs for exploratory study. In this work, a carbon-coated $\text{K}_3\text{V}_2(\text{PO}_4)_3$ (KVP/C)-based symmetric KIB was proposed. Different from the fabrication methods of the traditional LVP and NVP, centrifugal separation together with freeze drying are employed in our

work. The lyophilized KVP particles with a uniform size distribution within 1 μm are obtained. After the full-cell fabrication, the KVP/C-based full symmetric KIBs in the voltage range between 0.01–3.0 V showed excellent cycling stability with a reversible specific capacity about 90 mAh g^{-1} at 25 mA g^{-1} and over 88 % capacity maintained after 500 cycles. Most importantly, a highest initial coulombic efficiency (CE) of 91.7 % and largest working discharge voltage of 2.3 V were also obtained, benefiting the output energy of this symmetric energy storage system.

2. Experimental Section

2.1. Materials synthesis

All the reagents used in this work were purchased from Sigma Aldrich, and all the chemicals were used directly without any further treatment. The KVP active material was prepared by the traditional solid-state reaction. In detail, K_2CO_3 , V_2O_5 , and $\text{NH}_4\text{H}_2\text{PO}_4$ powders in a stoichiometric ratio were mixed and ground for 30 min. Then, the mixture was heated to 400 $^\circ\text{C}$ under an Ar atmosphere for 2 h in a furnace. After the heat treatment, the powder was fully ground and re-heated to 850 $^\circ\text{C}$ for 51 h under Ar atmosphere. After the re-heat treatment, the powders were washed with deionized (DI) water and the resulting above suspension was collected after the centrifugation under 1000 rpm for 5 min. The final lyophilized KVP particles were prepared after the lyophilisation of the collected suspension solution at -50 $^\circ\text{C}$ in a lyophilizer for 30 h. After the initial centrifuge, different sized KVP particles would be separated. Only the small sized KVP particles can be stayed on the top of the solution. Therefore, in order to maintain its pristine structure, the freeze dry treatment was further employed to obtain the size uniform distributed KVP particles. For the KVP/C composite, the prepared around 2 g KVP particles were first dispersed in 3 ml oleic acid, leading to a uniformly distributed mixture. After the slurry was left to stand for 6 h, the KVP particles were separated from the oleic acid and heated in an Ar-filled furnace at 600 $^\circ\text{C}$ for 2 h. After cooling down to room temperature, the black powders were collected and denoted as KVP/C.

2.2. Characterizations

The morphology and microstructure of the products were characterized by field emission scanning electron microscopy (FESEM, JEOL 7500) and transmission electron microscopy (TEM, JEOL ARM-200F) with high-resolution TEM (HRTEM). Thermogravimetric (TG) analysis was carried out with a PerkinElmer Diamond TG/DTA apparatus. The XRD patterns were collected by powder X-ray diffraction (XRD, GBC MMA diffractometer) with high intensity Cu $K\alpha_1$ irradiation ($\lambda = 1.5406 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) experiment was carried out using Al $K\alpha$ radiation and fixed analyser transmission mode. The pass energy was 60 eV for the survey spectra and 20 eV for specific elements. The elemental ratio inside KVP was examined by the inductively coupled plasma (ICP) technique.

2.3. Electrochemical measurements

The electrochemical testing was conducted on coin-type half cells assembled in an argon-filled glove box. Potassium foil was employed for both the reference and the counter electrodes. 1 mol L^{-1} KPF₆ in a mixture of ethylene carbonate (EC) and polypropylene carbonate (PC) (1:1 by volume) was used as the electrolyte, and Whatman® glass fiber was used for the separator. Electrochemical cycling of electrodes was conducted at 25 mA g^{-1} for galvanostatic measurements within the fixed potential windows. Cyclic voltammetry was performed using a Biologic VMP-3 electrochemical workstation at scan rates of 0.1–0.5 mV s^{-1} within fixed potential ranges. Similar procedures were used for the fabrication of symmetrical KIBs, except that the anode and cathode employed the same KVP/C material. In addition, the active material mass of the cathode on Al foil was properly chosen in order to balance the specific capacity of the anode material on Cu foil. The specific capacity of the full cell is calculated based on the mass of the negative electrode. The mass ratio between the KVP/C-anode and KVP/C-cathode is determined based on their reversible capacities. For example, the reversible capacity for KVP/C-anode and KVP/C-cathode is about 230 and 80 mAh g^{-1} , which means the mass ratio of the active electrode materials between anode and cathode should be controlled at about 0.3–0.35. During the full cell fabrication, about 0.5 ml

electrolyte was used and the mass loading for the electrode is about 1.0 mg cm^{-2} . The voltage window of the full cells during the test is selected based on the practical performance of the KVP/C-anode and KVP/C-cathode. The working potential for the KVP/C-anode is 0.01–2.5V, while for the KVP/C-cathode is 2.0–4.0 V. According to the CV results in Fig. 2, three main active reactions for KVP/C-anode are around 0.5, 1.0 and 1.5 V, but the main reaction for KVP/C-cathode is over 3.5 V. As a result, the potential gap between the KVP/C-anode and KVP/C-cathode is 3.0, 2.5 and 2 V, which are the three different voltage ranges (0.01–2, 0.01–2.5 and 0.01–3.0 V) we employed for the full-cell test.

2.4. *In-situ synchrotron XRD measurements*

A customized CR2032 coin-cell for use in in-situ SXRD experiments was prepared and its assembly details can be found elsewhere. The electrode preparation was similar to the above-mentioned half coin-cells for electrochemical performance testing. In order to enhance the intensity of the diffraction peaks, a thicker KVP or KVP/C coating layer ($\sim 6 \text{ mg active material/cm}^2$) was loaded on the Al foil. To collect the signals of the full cell, two holes with a diameter of 4 mm were punched on the negative and positive caps, respectively, allowing the penetration of X-ray beams through the whole cell. The holes were covered by Kapton film (only resulting in slight bumps in XRD measurements), followed by complete sealing with AB glue, to ensure protection of electrodes from air and moisture. Meanwhile, a battery test system (Neware) was connected to the cell to carry out the charge/discharge process. In-situ SXRD experiments were conducted on the Powder Diffraction beamline at the Australian Synchrotron.

3. Results and Discussion

Morphology and structure of KVP and KVP/C electrodes

The scanning electron microscope (SEM) images in Fig. 1a to 1d indicate that both the KVP (a and b) and the carbon coated KVP (KVP/C) (c and d) particles show similar morphology and are endowed with a layered structure. The size distribution of the lyophilized KVP and KVP/C is in the

range of 0.5–1 μm . However, the size distribution of the KVP without lyophilisation treatment is in the range of 0.5–8 μm , which is around 8 times larger than the lyophilized KVP (Fig. S1a to S1d). Fig. 1e to 1h shows high resolution transmission electron microscope (HRTEM) images and electron diffraction (SAED) patterns of lyophilized KVP (e and f) and KVP/C (g and h). A high degree of crystallinity can be found for the KVP and KVP/C. The distance between two adjacent lattice fringes was ~ 0.55 nm, which is in good agreement with the theoretical d-spacing of the (110) planes, and the other neighbouring lattice fringes spacing were found to be ~ 0.34 and ~ 0.29 nm, which corresponds to the (412) and (512) planes, respectively (Fig. 1e). The SAED pattern contains their corresponding electron diffraction spots (see Fig. 1f and 1h). In Fig. 1g, the carbon layer with a thickness of 4.5 nm was uniformly coated on KVP particles. Fig. S2 shows the energy dispersive X-ray spectroscopy (EDS) mapping of each element in KVP. Uniform distributions of K, V, P, and O can be found inside KVP. According to inductively coupled plasma (ICP) analysis, the atomic ratio among K, V, and P is around 3:2:3, closed to the nominated value. Fig. S3 presents the X-ray diffraction (XRD) patterns of KVP and KVP/C, collected with a Cu K α X-ray ($\lambda = 0.1541$ nm) source. In the carbon coating process, a post-heating process (up to 600 $^{\circ}\text{C}$) was applied but no obvious peak position changes can be observed in the XRD of KVP/C, implying the excellent structural stability of KVP. Compared with KVP, however, the peak width and peak intensity of KVP/C were increased, indicating the increase in crystallinity of KVP after post-heating. The thermogravimetry (TG) curves of KVP and KVP/C in air are shown in Fig. S4. The weight gain of KVP and KVP/C in the range of 350–580 $^{\circ}\text{C}$ could be attributed to the oxidation of KVP, similar to the LVP[24] and NVP[25]. According to the percentage weight gain of KVP and KVP/C, we can see the carbon content inside KVP/C was less than 2%.

Potassium ion storage performance of KVP/C electrodes in half KIBs

The electrochemical performance of KVP/C in a half-cell is shown in Fig. 2. Fig. 2a and 2b illustrate the consecutive cyclic voltammetry (CV) data for KVP/C at a scan rate of 0.1 mV s^{-1} in the voltage range of 1.0–2.5 V (as the anode, KVP/C-anode) and 2.0–4.0 V (as the cathode, KVP/C-

cathode), respectively. Obvious reversible cathodic and anodic peaks can be found when KVP/C is employed as anode and cathode, which means that the reversible and active insertion/extraction of K^+ into/from KVP could be obtained. In addition, the main redox reactions took place between 1.5–2.0 V in the KVP/C-anode and 3.5–4.0 V in KVP/C-cathode, leading to a 2.0 V potential gap, which is similar to LVP and NVP in LIBs and NIBs, respectively. Comparing with the CV results of KVP in Fig. S5a and S5b, similar results can be found in the pure KVP anode or cathode under the same testing conditions, indicating the similar electrochemical activity in KVP. However, the enclosed area and degree of overlap for the CV curves in KVP-anode and KVP-cathode were both decreased, demonstrating that the capacity and cycling stability of KVP electrodes were both improved after carbon coating process. The reversible specific capacity of KVP/C-anode and KVP/C-cathode was around 130 and 91 mAh g⁻¹ for the initial cycling test, and maintained at about 130 and 85 mAh g⁻¹ after testing for 150 and 100 cycles, respectively (Fig. 2c and 2d). The capacity retention for KVP/C-anode and KVP/C-cathode is about 100 % and 93.4 %, respectively, demonstrating their outstanding cycling stability. But for KVP-anode and KVP-cathode, the reversible specific capacity of KVP-anode and KVP-cathode was around 116 and 31 mAh g⁻¹ for the initial cycling test, and maintained at about 115 and 40 mAh g⁻¹ after testing for 250 and 100 cycles, respectively (Fig. S5c to 5f). The capacity for KVP/C-cathode was increased after the carbon coating due to the introduced carbon coating layers which improve electron transfer in KVP and contribute extra active K^+ storage sites. The initial CE for KVP/C-anode is over 86% and reached nearly 100% after the first cycling test, leading to a negligible capacity loss even after 150 cycling test. Compared with KVP-cathode, the CE of KVP/C-cathode was enhanced from 56% to 88%, indicating the stable carbon coating on KVP and the formation of the stable solid electrolyte interphase (SEI) layer. The large irreversible capacity in KVP-cathode, corresponding to the hysteresis of the charge/discharge cycle of KVP-cathode.

The *ex-situ* X-ray photoelectron spectroscopy (XPS) spectra in Fig. S6 demonstrate the presence of V^{+3} inside the original KVP/C, and the main redox reactions at 3.5–4.0 V and 1.5–2.0 V

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correspond to V^{+4}/V^{+3} and V^{+3}/V^{+2} , respectively. Fig. S7 shows the CV and kinetics analysis of KVP/C-anode towards K^+ between 1.0 to 2.5 V. Fig. S7a shows the CV profiles at different scan rates from 0.1 to 0.5 $mV s^{-1}$. According to the separation of the capacitive and diffusion currents in KVP/C-anode at a scan rate of 0.2 $mV s^{-1}$ (see Fig. S7b), the electrochemical reactions of KVP/C are composed of both nonfaradaic and faradaic processes. Obviously, the predominant faradaic behaviour, which contributes about 85% capacity, is derived from the redox reactions between V^{3+}/V^{2+} , which enables the KVP symmetric electrodes to be operated at a fixed voltage range. As for the nonfaradaic behaviour of KVP, we believe that it may exist because of the K^+ diffusion inside the carbon coating layers. Compared with KVP/C-anode, the nonfaradaic behaviour contributes about 10 % capacity in the KVP-anode at a scan rate of 0.2 $mV s^{-1}$ (Fig. S7c). Similar results can be found in KVP/C-cathode and KVP-cathode between 2.0 V to 4.0 V (Fig. S8). Therefore, we believe that the nonfaradaic behaviour contributes more capacity in the symmetric electrodes after the carbon coating.

***in-situ* synchrotron X-ray powder diffraction (SXRD) analysis of KVP/C electrode**

Fig. 3a shows the experimental and simulated SXRD patterns ($\lambda = 0.6888 \text{ \AA}$) of the prepared KVP with Rietveld refinement, confirming the active phase is endowed with a R-3c space group in the framework of NASICON structure, named as $K_3V_2(PO_4)_3$. The main reflections at 3.8° , 6.32° , 7.3° , 8.3° , 13.5° , 14.2° , and 14.7° can be assigned to (003), (10-5), (111), (211), (601), (22-1), and (60-7), respectively. For the unit structure of $K_3V_2(PO_4)_3$, each VO_6 octahedron is corner-sharing with three PO_4 tetrahedrons, leading to an open 3D framework structure with large interstitial space that can accommodate K^+ (see the insert image of the unit structure of $K_3V_2(PO_4)_3$ in Fig. 3a). With the aid of *in-situ* SXRD, we studied the mechanistic reactions of the KVP/C upon potassiation/depotassiation within the potential window 1.0–4.0 V (vs. K^+/K). Fig. 3b to 3d shows the *in-situ* SXRD patterns along with the charge-discharge curves of the KVP/C electrode during the first two cycles at 25 $mA g^{-1}$.

On the first charge (depotassiation), the position of KVP reflections are nearly unchanged with

the intensity being slightly increased, indicating that the $R-3c$ space group of KVP was still maintained after K^+ extraction, which is similar to the NVP-cathode during the Na^+ extraction process. Based on the capacity contribution and the peaks during charging, the unit formula for KVP during K^+ extraction can be named as K_xVP ($1 \leq x \leq 3$). The unit structure evolution of KVP during depotassiation process was provided in Fig. 3e. On the first discharge (potassiation), we can see that the reflections move to the small angles, indicating the lattice expansion. The peak shifts of various reflections in a range of $6.32-6.42^\circ$ are presented in Fig. S9. As for other active peak shifts, such as $7.30-7.42^\circ$, $14.14-14.36^\circ$ and $14.76-14.96^\circ$ showed the similar changes (Fig. S10). No new peaks appear and old peaks disappear during this discharging process. However, at a closer look at the peak evolutions, one can find that the evolution of reflections are discrete and can be divided into 3 regions (I, II, and III). Therefore, we elucidate the mechanistic behaviour as follows: For region I ($x = 3$ to 3.3 , x was calculated based on the capacity contribution from KVP), the lattice of K_xVP expands upon K^+ insertion. When the K concentration is higher than 3.3 , the K_xVP turns into K_yVP ($3.3 \leq y \leq 3.7$), which is the region II. Upon further K insertion, the K_yVP transforms into K_zVP ($3.7 \leq z \leq 4$) with larger lattice due to the extra K insertion. K_zVP maintains the similar structure as the KVP and shows the lattice expansion, similar to the intercalation anodes in SIBs when large ions (Na^+) is inserted.[26] Reversed reactions are observed in the following depotassiation process. The unit structural changes of KVP during discharging process are also provided in Fig. 3e. The extra capacity of KVP during discharge process may come from the carbon coating layer which provides more active positions for the K^+ . During the whole depotassiation/potassiation processes, a highly lattice reversibility upon K^+ insertion and extraction in the SXRD was observed. This excellent reversibility of KVP is mainly because the NASICON structure with a PO_4 tetrahedral network strongly supporting the structure stability, demonstrating the outstanding cycling stability of KVP-based electrodes. A comparison of the unit cells between the KVP and NVP can be conducted and discussed to further study the structural and electrochemical abilities of KVP. Compared with NVP, the KVP has an $R-3c$ space group with a , b

and c being of 18.1329 Å, 18.1329 Å and 31.81227 Å, respectively. The dimension of NVP unit is smaller than KVP with a, b and c being of 8.7288 Å, 8.7288 Å and 21.8042 Å. Therefore, compared with NVP, KVP is endowed with an increased unit size, especially along the c-axis. The increased c-axis contributes the fast insertion/extraction of K^+ and improves its overall structural stability during cycling. The skeleton of the KVP can be well maintained during the continuous charging/discharging processes, which enable KVP has an enhanced cycling stability. Moreover, the solid 3D PO_4 networks within the KVP can better support its structural integrity, which further improve its cycling stability.

After two sodium extraction, although the $R-3c$ space group was maintained, the unit cell parameters of NVP were reduced to $a = 8.426$ Å and $c = 21.720$ Å, leading to an ~ 8.2 % volume decrease. However, the volume change for KVP is smaller than that of the NVP after the potassium extraction. The unit dimension for $KV_2(PO_4)_3$ was changed to $a = 17.7883$ Å and $c = 31.8015$ Å, resulting in an ~ 3.8 % volume shrink. As a result, KVP is endowed with the reduced structural changes during both of the charging and discharging processes.

Furthermore, by exploring the difference of the internal diffusion ways between NVP and KVP, we found that both of the K^+ or Na^+ at the K(2) or Na(2) sites (as shown in Fig. S11) can be extracted more easily than those at K(1) or Na(1) sites due to the smaller bond populations of K(2) or Na(2) sites. However, due to the large interstitial space, the diffusion of K(2) is much easier than Na(2) without damaging the PO_4 constructed skeleton. In addition, during the potassiation process, K^+ also can be easier inserted into the site of K(3) than that of the Na(3), further contributing the structural stability of KVP.

In order to explore the application potential of this novel electrode, we further extended the testing voltage range from 1.0–2.5 V to 0–2.5 V for KVP/C-anode. Fig. S12a shows its CV results at a scan rate of 0.1 mV s^{-1} in the voltage range of 0–2.5 V. For KVP/C-anode, reversible cathodic and anodic peaks located below 1.0 V can also be found, which means that extra and increased reversible insertion/extraction of K^+ in KVP/C can both be obtained between 0–1.0 V. According

to the capacity contribution within this new voltage range, it can be seen that one more V^{3+} was reduced to V^{2+} during the further discharging process below 1.0 V, leading to the generation of the new $K_5V_2(PO_4)_3$. Based on the first-principles calculations, the unit structure of $K_5V_2(PO_4)_3$ was provided as insert in Fig. S12a. Therefore, the potential distance between the KVP/C-anode and KVP/C-cathode was extended from 2.0 V to 2.7 V, which is one of the largest potential distances among all the previous reported symmetric electrodes. Moreover, the excellent cycling stability of KVP/C-anode was still well maintained under this testing condition, this is evidenced by the charge/discharge profiles for KVP/C-anode in Fig. S12b. But for the KVP/C-cathode, the overlap degree of the CV curves between 2.0–4.1 (Fig. S12c) and 2.0–4.2 V (Fig. S12d) is decreased when compared with the voltage range between 2.0–4.0 V, which means the KVP/C-cathode showed poor cycling stability during these broader voltage ranges.

According to the above relevant analysis, KVP/C as a novel electrode shows outstanding cyclability and acceptable capacity in KIBs, leading to a very large potential distance of about 2.7 V between the symmetric electrodes. All of this excellent electrochemical performance of KVP/C allowed us to further fabricate symmetrical full KIBs.

Potassium ion storage performance of KVP/C electrodes in the full symmetric KIBs

Fig. 4 shows the electrochemical data of KVP/C-based full cell, in which the KVP/C was used as both the cathode and anode. The open-circuit voltages (OCV) of full cells were near zero (Fig. S13), because the same initial electrodes were used on both sides. Three different voltage ranges, 0.01–2.0 V (Fig. 4a), 0.01–2.5 V (Fig. 4b) and 0.01–3.0 V (Fig. 4c), were employed in the following CV test. Fig. S14a presents their CV curves. The enclosed area in the CV data was increased along with the increase of testing voltage (Fig. S14b). Moreover, the average working discharge voltage of the full-cells within 0.01–3.0 V was around 2.3 V, which is much higher than most previously reported symmetric systems. For example, the discharge voltage for a $Na_3V_2(PO_4)_3$ -based symmetric NIBs was 1.6–1.8 V,[19,21] and 1.7–1.9 V for the $Li_3V_2(PO_4)_3$ -based symmetric LIBs.[18,20] This very large 2.3 V working potential approximately corresponds

to the potential gap between the KVP/C-cathode (predominant redox peaks located around 3.7 V) and KVP/C-anode (predominant redox peaks located around 1.4 V). In this regard, KVP/C is promising for the construction of symmetric full KIBs. Fig. 4d shows the charge/discharge data of KVP/C-based full cell at a current density of 25 mA g^{-1} between 0.01–3.0 V. The charging and discharging capacity during the first cycling test is 88 and 80.9 mA g^{-1} , corresponding to an initial CE of 91.7 %. 88.6 % reversible capacity was maintained after 500 cycling test (Fig. 4e), indicating the stable and reversible active reactions inside the KVP/C during the K^+ insertion/extraction process. The cycling ability of the KVP/C can be explained by the unique NASICON structure which provides rigid framework for this material with fast ion diffusion pathways. The Nyquist plots of KVP and KVP/C-based symmetric full cell were further collected to check the electrical conductivity. (Fig. 4f, inset: equivalent circuit of KVP/C). The charge transfer resistance (R_{ct}) for the KVP/C symmetric electrode was less than KVP, indicating faster transportation of ions and electrons, due to the intimate contact between the KVP particles and carbon coating.[27-29]

4. Conclusion

In conclusion, we designed a NASICON-type KVP/C composite and tested its feasibility being used as both the anode and cathode for KIBs. A symmetric full KIB showed acceptable reversible capacity and outstanding cycling stability. A largest working potential of 2.3 V and highest CE of 91.7 % were also obtained, which are of benefit for future energy storage system with high energy density and large power. More importantly, this is also the first time that symmetric electrodes have been explored in KIBs, which endows the novel KIBs with improved safety and a facile practical fabrication process. Therefore, considering the novel design of this advanced energy storage system, highest initial coulombic efficiency, outstanding cycling stability and largest working potential, this work will attract widespread interest in the readers and provide important experience for the future development of the potassium ion batteries.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at

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Fig. 1. Morphology and structure of the lyophilized KVP and KVP/C samples. SEM images of KVP (a and b) and KVP/C (c and d), HRTEM images of KVP (e) and KVP/C (g), and the SAED patterns of KVP (f) and KVP/C (h).

Fig. 2. Electrochemical performance of the KVP/C electrodes and their structure information.

CV curves of KVP/C as anode in the voltage range of 1.0–2.5 V at a scan rate of 0.1 mV s⁻¹ (a) and CV curves of KVP/C as cathode in the voltage range of 2.0–4.0 V at a scan rate of 0.1 mV s⁻¹ (b), the discharge-charge profiles for selected cycles of KVP/C-anode (c) and KVP/C-cathode (d).

Fig. 3. *In-situ* SXR analysis of the electrochemical behavior towards K^+ for the KVP electrode. (a) Rietveld refinement of the SXR for the KVP structure, in blue is the experimental points, in green is the calculated patterns and in light blue is the differences between the experimental and calculated patterns (insert is the unit structure of KVP), *In-situ* SXR patterns of the three different ranges 6.2–6.6° (b), 13.8–14.5° (c) and 14.5–15.0° (d) along with the charge-discharge curves of the KVP electrode during the first two cycles in the half cell, and (e) the unit structure evolution of KVP along with the CV profile between 1.0 and 4.0 V.

Fig. 4. Electrochemical performance of KVP/C-based symmetric full cell. CV curves of KVP/C-based symmetric full KIBs at a scan rate of 0.1 mV s⁻¹ in the voltage ranges of 0.01–2.0 V (a), 0.01–2.5 V (b), and 0.01–3.0 V (c); the discharge-charge profiles (d) and the cycling performance (e) of KVP/C-based symmetric full KIBs at between 0.01–3.0 V, and the EIS plots (f) of KVP and KVP/C-based symmetric full KIBs (inset: equivalent circuit; W is the Warburg impedance and CPE (constant phase element) represents a double layer capacitor).

Vitaes

Lei Zhang received his master degree in 2012 from Qingdao University of Science and Technology, China, and PhD degree from the Institute for Superconducting and Electronic Materials at the University of Wollongong Australia under the supervision of Prof. Hua Kun Liu and Prof. Shi Xue Dou. He is currently a Research Fellow in the Centre for Clean Environment and Energy at Griffith University. His work focuses on the development of anode materials for lithium-ion batteries.

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Highlights

- The symmetric K-ion battery with the best performance was prepared.
- The $\text{K}_3\text{V}_2(\text{PO}_4)_3$ symmetric electrodes were used as both the anode and cathode.
- High working potential, facial fabrication process and high safety of the full cell.