Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use:  S. H. Abdulrahman, M. Ohara, K. Kubota and S. Komaba, J. Mater. Chem. A, 2021, DOI: 10.1039/D0TA10517A.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A phosphite based layered framework as a novel positive electrode material for Na-ion batteries

A. Shahul Hameed, ab Mirai Ohara,a Kei Kubota, ab and Shinichi Komaba*ab

Na-ion batteries (SIBs), perceived as the most promising alternate energy storage technologies, are attractive for large-scale stationary applications due to the cost effectiveness and global abundance of sodium. One of the formidable challenges in the way of its extensive commercialization is the development of suitable low-cost positive electrode materials with high energy density and long cycle life. In this study, a phosphite based layered polyanionic material with the formula, Na2[(VOHPO4)(C6O4)]·2H2O has been investigated as a novel positive electrode for SIBs. The material was synthesized through a room temperature precipitation method and undergoes reversible Na+ insertion at an average discharge voltage of 3.65 V which is higher than the same V4+/V3+ redox couple of NaVOPO4 (3.4 V) in non-aqueous Na cell. The material exhibits a high discharge capacity of ~101 mAh g⁻¹ at C/10 rate in Na half-cells. Capacity fading encountered by the pristine material was overcome with the help of ball-milling with carbon. The layered material facilitates the migration of large Na+ ions, resulting in a superior rate performance (~80 mAh g⁻¹ at 10 C rate). In addition, a long-term cycling stability over 1000 cycles was demonstrated at 2 C rate with 62 % capacity retention. Operando XRD studies reveal that the reversible Na+ insertion in the framework happens via a bi-phasic mechanism. Feasibility of full cells was demonstrated using NaTi3(PO4)3 as the negative electrode and the full cell exhibited a reversible capacity of 71 mAh g⁻¹ at 0.1 C rate and 65 mAh g⁻¹ at 1 C rate with good capacity retention.

Introduction

In recent years, the sales of electric vehicles have soared thanks to the high energy densities offered by Li-ion batteries (LIBs). The electrification of vehicles is also projected to rise exponentially in the next decades. Another large-scale application of LIBs is the stationary electrical energy storage (EES) in smart grids to store renewable energy, such as wind and solar, an important step to alleviate the problems of global warming. Since the size of stationary storage in grids is of several MWh, such large-scale projects using LIBs would rapidly increase the demand for Li. This may disrupt the supply chain of Li, given the low abundance and the associated geopolitical issues in the production of lithium, which in turn may trigger a tremendous escalation of Li cost. Hence, the focus on alternate energy storage technologies using other alkali ions as charge carriers has increased recently. In particular, Na-ion batteries are actively studied owing to the global uniform distribution and high abundance of sodium resources, and an energy storage mechanism similar to that of LIBs has helped in a rapid progress in the field of SIBs.2-4

Exploration and development of suitable positive and negative electrode materials for the reversible Na storage with high energy density and at low-cost is vital for the extensive commercialization of SIBs. Hard carbon, as a promising negative electrode material for Na-ion batteries, delivers high capacity of >300 mAh g⁻¹.5,6 Thus, the energy density of the practical SIBs depends on the performance of positive electrodes. Of the various prospective candidates such as layered transition metal oxides7,8 and polyanionic frameworks9, vanadium containing phosphates and fluorophosphates such as Na2V3(PO4)4·10 NaVPO4F11-14 Na2V3(PO4)F17,18 have attracted huge attention due to satisfactory capacity, high redox potentials and ultra-long cycle life. To understand the structural differences in the frameworks, various polymorphs of NaVOPO4 have been studied and compared by Aparicio et al. They reported that layered α-NaVOPO4 with tunnels in the layer exhibits high ionic conductivity due to their high mobility of Na+ ions and 3D Na diffusion pathways with low activation energy which facilitates better Na-storage properties.12 For the structural similarity, hybrid inorganic-organic open framework materials such as Na2[(VOHPO4)(C6O4)]·2H2O (x = 3, 4) are interesting candidates for SIB positive electrodes since they have a layered structure with tunnels in the layer and suitable interplanar distance to host the large Na+ ions.19-21 These metal organic phosphate/phosphite open frameworks (MOPOFs) were reported earlier as reversible Li-ion and K-ion hosts with excellent electrochemical properties.21-24 For example, K-half cells...
with rGO/K_{3}[\text{VOHPO}_{4}2\text{C}_{2}O_{4}] as composite as a positive electrode delivered a reversible capacity of >100 mAh g\(^{-1}\) at an average voltage of ~3.85 V and a superior rate performance.\textsuperscript{22} In addition, an oxalate sulphate framework material, Na\(_3\)Fe(C\(_2\)O\(_4\))SO\(_4\)H\(_2\)O demonstrated 3 V operation as a positive electrode for LIBs.\textsuperscript{25} With two distinct channels of 5.907 and 4.126 Å, the material demonstrates facile Na migration and delivered a capacity close to its theoretical value of 88 mAh g\(^{-1}\) and good cycle stability over 500 cycles.

Herein, we propose a phosphate based layered open framework, Na\(_2\)\([\text{VOHPO}_{4}2\text{C}_{2}O_{4}]\)_2\(\cdot\)H\(_2\)O (NVpox) as a novel positive electrode material for Na-ion batteries. The material was prepared by a facile room temperature precipitation synthesis and is scalable. Owing to the combined inductive effects of the oxalate\textsuperscript{26-28} and phosphate ligands on vanadium, the material results in an average discharge voltage of 3.65 V which is higher than the 3.4 V of NaVOPO\(_4\) for the same V\(^4+\)/V\(^3+\) redox couple in non-aqueous Na cells. A high discharge capacity of 101 mAh g\(^{-1}\) at C/10 rate and a superior rate performance of 80 mAh g\(^{-1}\) at 10 C was delivered by the material. Long-term cycling stability of the material has been demonstrated for 1000 cycles with 62 % capacity retention at 2C rate.

### Experimental

#### Synthesis

NVpox was prepared in an earlier study by a hydrothermal synthesis at 120 °C for 3 days using \(\text{V}_2\text{O}_5\), oxalic acid, NaOH, and H\(_3\)PO\(_4\).\textsuperscript{21} This study has been prepared at room temperature as reported for another MOPOF material, K\(_3\)\([\text{VOHPO}_{4}2\text{C}_{2}O_{4}]\)_6\(\cdot\)H\(_2\)O.\textsuperscript{23} 10 mmol of \(\text{V}_2\text{O}_5\), 20 mmol of tartaric acid, 20 mmol of NaOH and 100 mmol of H\(_3\)PO\(_4\) were dissolved in deionized water and sonicated for 2 h and thus obtained NVpox is referred from here on as p-NVPox. The pristine material was ball-milled with acetylene black using ZrO\(_2\) balls at 300 rpm for 6 h resulting in a black powder which is referred from here on as bm-NVPox.

### Results and Discussion

#### Characterization

Structure of the prepared samples were analysed by powder X-ray diffraction (PXRD) using Rigaku SmartLab diffractometer with Ni-filtered Cu-K\(\alpha\) radiation. The obtained XRD pattern was fitted by Pawley method using TOPAS software. Morphology of the materials was studied by scanning electron microscope (FE-SEM, JEOL, 45000 FE). Thermal behaviour of as-synthesized NVpox was tested by thermogravimetric analysis using DTG-60, Shimadzu Corporation, Japan. Electronic conductivity of the samples was determined using a Loresta-GX MCP-T700 resistivity meter. In this study, pellets of the material with uniform surface were prepared without any binder. The thickness and diameter of the pellets were ~1.5 mm and 10 mm, respectively. The instrument uses a 4-pin probe which directly measures the electronic conductivity. Particle size of the samples was measured using LA-350 laser diffraction particle size distribution analyser, Horiba, Japan. Samples were dispersed in water by ultrasonication for 2 min and used for the particle size measurement.

Electrochemical measurements were carried out with NVpox working electrodes fabricated from an aqueous slurry containing 7: 2: 1 ratio of active material, acetylene black and sodium polyacrylate (PANa) binder. The amount of conducting carbon in the electrodes of p-NVPox and bm-NVPox was the same. However, acetylene black and active material was ball-milled in the case of bm-NVPox prior to electrode preparation. Coin cells (R 2032) were assembled in an Ar-filled glove box with the prepared electrodes, sodium metal foil as the counter electrode, 1 M NaPF\(_6\) dissolved in EC : PC (1:1 v/v) as electrolyte and glass fiber filter (GB-100R, ADVANTEC) as the separator. Similarly, Li-cells and K-cells were fabricated using lithium and potassium metal foils, respectively, as the counter electrodes. 1 M LiPF\(_6\) and 1 M KPF\(_6\) dissolved in EC : DEC (1:1 v/v) were used as electrolytes for Li- and K-cells, respectively. Na-ion full cells were fabricated as coin cells with bm-NVPox as the positive electrode and carbon coated NaTi\(_2\)(PO\(_4\))\(_3\) (NTP) as the counter electrode with a capacity ratio of 0.8 : 1 (Positive : Negative). Structural changes of NVpox during the charge/discharge tests were examined by an \textit{in situ} XRD technique using two-electrode cell attachment (Rigaku Co., Ltd.). Electrochemical impedance spectroscopy measurement was carried out in a frequency range of 200 kHz to 0.01 Hz using VMP3 potentiosat (Biologic). The Nyquist plots were fitted with an equivalent circuit using ZView software (Scribner).

#### Crystal Structure

The X-ray powder diffraction pattern of p-NVPox is shown in Fig. 1a. The XRD data shows that the structure is similar to that of the hydrothermally obtained Na\(_2\)\([\text{VOHPO}_{4}2\text{C}_{2}O_{4}]\)_2\(\cdot\)H\(_2\)O, reported earlier\textsuperscript{21} and without any impurity phases. Whole powder pattern fitting of the peaks by Pawley method indicates that it can be well-indexed with a triclinic lattice of the P-1 space group. The lattice parameters were calculated as \(a = 6.3257(10)\) Å, \(b = 6.7612(10)\) Å, \(c = 8.0855(16)\) Å, \(\alpha = 104.997(8)\)°, \(\beta = 101.636(16)\)°, and \(\gamma = 98.975(11)\)° which are close to the previously reported values. The material has a layered open-framework structure consisting of two dimensional anionic sheets of [\(\text{VOHPO}_{4}2\text{C}_{2}O_{4}\)]\(_2\), stacked along the b-axis with Na\(^+\) ions and H\(_2\)O in the interlayer space (shown in Fig. 1c). The anionic sheet (shown in Fig. 1d) parallel to the (01-1) plane is composed of the one-dimensional chains of VOHPO\(_4\) along the a-axis, which are interconnected by oxalate ligands to form the 2D open frameworks having a large tunnel in the sheet.
Fig. 1 (a) Whole pattern fitting results (Pawley method) of the XRD pattern of p-NVPox. Red circles represent the experimental values while the calculated pattern is shown as blue lines. The black line represents the difference between the calculated and observed intensities. The vertical bars correspond to the positions of Bragg reflections. (b) The SEM image of p-NVPox. (c, d) Schematic illustrations of crystal structures for Na$_2$[(VOHPO$_3$)$_2$(C$_2$O$_4$)]·2H$_2$O; (c) the layered structure with Na$^+$ ions in the interlayer space (H$_2$O in the interlayers is not shown for clarity) and (d) the intralayer structure of the[(VOHPO$_3$)$_2$(C$_2$O$_4$)] sheet parallel to the (01-1) plane.

VOHPO$_3$ chain, VO$_6$ octahedra are corner-shared with three different (HPO$_3$)$_2$ tetrahedra. The interlayer space was calculated to be 5.8 Å from the peak position of 01-1 reflection in Fig. 1a. Further details on the crystal structure of Na$_2$[(VOHPO$_3$)$_2$(C$_2$O$_4$)]·2H$_2$O can be found in a previous paper. TGA of the material (shown in Fig. S1) infers that the dehydration occurs in two steps with formation of an intermediate monohydrate compound. While the first dehydration occurs at 80-125 °C, the subsequent dehydration happens at 170-220 °C. The TGA also infers that the oxalate group decomposes at temperatures of >360 °C, indicating its good thermal stability. SEM image of p-NVPox (Fig. 1b), demonstrates that the material contains primary particles with plate-like morphology which aggregate to form secondary particles with size of several microns.

**Electrochemical Na extraction/insertion**

The Na extraction/insertion performance of the layered NVPOx was investigated using Na half-cells at a current density of 11 mA g$^{-1}$ (°C/10) in the potential range of 2.0–4.3 V vs. Na. Charge-discharge profiles of p-NVPox for selected cycles are shown in Fig. 2a. The charge processes, during which Na$^+$ ion extraction and the simultaneous oxidation of V$^{4+}$ to V$^{5+}$ should occur, are characterized by three distinct plateaus at 3.58, 3.82 and 3.97 V in Fig. 2a and from the peaks in corresponding $dQ/dV$ plot (Fig. 3a). However, the discharge processes involve the insertion of Na into the framework in two steps at 3.73 V and 3.49 V (Fig. 2b).
2a). The difference in the number of charge and discharge plateaus can be inferred as the difference in the number of intermediate compositions formed during the charge/discharge. A similar phenomenon was reported for NaFePO₄ phase in Na cells, in which an intermediate composition of NaₓFePO₄ was formed during the charge processes while the discharge processes happened without any intermediate composition. The initial discharge capacity of p-NVPox was 101 mAh g⁻¹ which is reasonably close to the theoretical capacity of 115 mAh g⁻¹. However, the initial charge capacity of 177 mAh g⁻¹ is higher than the theoretical capacity. The excess oxidative capacity may be attributed to the side reactions of the material with the electrolyte. As shown in the dQ/dV plots of charge curves (Fig. S2), intensity of the 3.97 V peak decreases from the 1st cycle to the 4th cycle which can be attributed to the side reaction with electrolyte.

To compare the Li- and K-insertion properties of the material, Li//p-NVPox and K//p-NVPox half-cells were cycled at 0.1 C. During the initial charge, Na⁺ ions are removed from the framework while the initial discharge predominantly involves the insertion of Li and K in the Li- and K-cells, respectively. Charge/discharge curves of the material in the three half-cells and the dQ/dV plots of the 10th cycle are compared in Fig. S3 and Figs. 3a-3c, respectively. The dQ/dV plots indicate that the Li insertion/extraction to/from the framework happens at a higher potential than in Na cells. A similar trend was observed in the redox couple of K insertion/extraction. Average discharge voltages of 3.76 V and 3.75 V were exhibited by Li- and K- half cells which is ~0.12 V higher than that of Na- half cells. However, the discharge capacities of Na cells were higher than the Li- and K- cells (Fig. 2a and Fig. S4). From the dQ/dV curves in Figs. 3a-3c, the number of plateaus in the discharge curves increase in the order of Li< Na< K and a similar trend is reported for layered transition metal oxide cathode materials.

During the initial cycles of p-NVPox, high capacities of ~100 mAh g⁻¹ was demonstrated which gradually fades during cycling. At the end of 100 cycles, a discharge capacity of only 53 mAh g⁻¹ was delivered by the p-NVPox electrodes as shown in Fig. 2b. The inferior cycling stability may be linked to the poor electronic conductivity of the material (2 x 10⁻⁷ S cm⁻¹). In earlier reports of MOPOF materials in Li and K cells, improvement in the cycling stability was achieved through enhancement of electronic conduction in the electrode by compositing with reduced graphene oxide (rGO). Since NVPox was prepared in this study by a slow precipitation method, compositing with rGO would result in an inhomogeneous mixture of NVPox and rGO. Therefore, an alternative process was adopted to improve the electronic conductivity of NVPox. The pristine material was ball-milled with acetylene black at 300 rpm for 6 h. The bm-NVPox exhibits high electronic conductivity of 2.05 x 10⁻⁴ S cm⁻¹. This ball-milling process did not induce any phase change as confirmed by the XRD pattern of bm-NVPox (Fig. S5). However, broadening of the peaks infers that the crystallite size was mechanically reduced due to the milling. It is further supported by the SEM micrographs (Fig. S6) and particle size distribution measurement (Fig. S7) indicating a decrease in the size of aggregated particles. As shown in Fig. 2b and Fig. S8, bm-NVPox exhibited better cycling stability. The discharge capacity of bm-NVPox for the initial cycles was ~93 mAh g⁻¹ and after 100 cycles, a discharge capacity of 81 mAh g⁻¹ was retained. In comparison, the p-NVPox electrodes demonstrated a poor capacity retention of only 53 mAh g⁻¹ after 100 cycles at the same current density. The improvement in capacity of bm-NVPox can be attributed to the following two factors. The average particle size of Na₃[(VOHPO₄)₂(C₂O₄)]·2H₂O is smaller in bm-NVPox as observed from the particle size measurement and SEM micrographs. In addition, the ball-milling results in improved contact of NVPox and acetylene black carbon due to smaller particle size of NVPox, enhancing the electronic conductivity.

To further investigate the improved performance of bm-NVPox, EIS measurements of p-NVPox and bm-NVPox were carried out. Nyquist plots (Zₑ vs. Zₘ) of the two electrodes are compared in Fig. 4a. Fitting of these Nyquist plots with an equivalent circuit (show in the inset of Fig. 4a) reveals that the charge transfer resistance (Rₛ) of p-NVPox and bm-NVPox electrodes were 475 and 203 Ω, respectively. The significant decrease in the resistance after the ball-milling shows the improved electronic conductivity of the material. The bm-NVPox electrodes also exhibited lower Rₛ than p-NVPox at the charged state (4.3 V) and the discharged state (2.0 V) as shown
Please do not adjust margins

The Na$^{+}$-ion diffusion coefficient in the material was calculated by determining the Warburg coefficients ($\sigma$) from the low-angular frequencies of the impedance spectra. The slope of a linear plot of $Z_{re}$ versus the reciprocal root-square of the angular frequencies ($\omega^{-1/2}$) gives the Warburg coefficient. Fig. 4b compares the $Z_{re}$ vs. $\omega^{-1/2}$ plots of p-NVPox and bm-NVPox electrodes. Using the calculated slope values, the diffusion coefficient ($D_{Na}$) can be deduced from equation (1).

$$D_{Na} = \frac{R^2T}{2\pi^2A^2n_4F^4C^2\sigma^2}$$

where $R$ is the gas constant, $T$ is the absolute temperature, $F$ is the Faraday's constant, $A$ is the geometrical electrode area, $n$ is the number of electrons per molecule, and $C$ is the molar concentration of Na$^{+}$ ions. The $D_{Na}$ of bm-NVPox ($3.14 \times 10^{-14}$ cm$^2$ s$^{-1}$) was nearly twice that of p-NVPox ($1.7 \times 10^{-14}$ cm$^2$ s$^{-1}$). The downsizing of NVPox particles by ball-milling results in a faster Na$^{+}$-ion diffusivity in the bm-NVPox. Thus, the bm-NVPox electrodes exhibit lower charge transfer resistance and higher diffusion coefficient in the framework.
Rate capability

Rate performance of the bm-NVPox electrodes in Na cells was examined at different current rates ranging from 0.2 C to 10 C (1 C corresponds to 115 mA g\(^{-1}\)) on discharge. The charge current was kept constant at 11 mA g\(^{-1}\) throughout the cycling. Fig. 5a shows the comparison of discharge curves of bm-NVPox electrode at these rates. The ball-milled sample demonstrated a better rate capability than the p-NVPox electrodes (Fig. 5b). The bm-NVPox electrode delivered higher reversible capacities of 91, 88, 86, 84, 82 and 80 mAh g\(^{-1}\) at 0.2, 0.5, 1, 2, 5, and 10 C rates, respectively, compared to 90, 83, 74, 64, 57 and 34 mAh g\(^{-1}\) for the p-NVPox electrode (Fig. S10 and Fig. 5b). When the rate was reduced to 0.2 C, both bm-NVPox and p-NVPox delivered 86 mAh g\(^{-1}\) which corresponds to ~95 % of initial discharge capacity. The excellent capacity retention of the bm-NVPox electrodes, at high current rates of up to 10 C, highlights the facile Na-ion migration in the framework.

Long-term cycling

The long-term cyclability of the material was evaluated at a current rate of 2 C. Both the charge and the discharge processes were carried out at 2 C rate with a constant voltage charging step at 4.3 V for 15 min. As shown in Figure 4c, the capacity of the bm-NVPox electrode for initial cycles was ~80 mAh g\(^{-1}\). The capacity gradually decreases during the cycling and a capacity retention of 62 % was observed after 1000 cycles. Throughout the cycling of bm-NVPox, the average discharge voltage overlap of 86, 84, 82 and 80 mAh g\(^{-1}\) respectively, compared to 90, 83, 74, 64, 57 and 34 mAh g\(^{-1}\) for the p-NVPox electrode (Fig. S10 and Fig. 5b). When the rate was reduced to 0.2 C, both bm-NVPox and p-NVPox delivered 86 mAh g\(^{-1}\) which corresponds to ~95 % of initial discharge capacity. The excellent capacity retention of the bm-NVPox electrodes, at high current rates of up to 10 C, highlights the facile Na-ion migration in the framework.

Structural evolution

Structural evolution of NVPox during the sodiation/de-sodiation was studied by operando XRD using an in-situ XRD cell assembled as Na//p-NVPox cell configuration. Contour maps of the XRD patterns of the first cycle for selected 28 regions is shown in Fig. 6a and the corresponding charge-discharge profile is shown in Fig. 6b. Using differential voltage (dV/dQ) analysis of the first charge curve (Fig. S12), it is estimated that a single-phase domain exists in region I (Fig. 6b). In this region, Na extraction from the framework results in a solid solution and 111, 2-10 and 102 Bragg peaks initially observed at 2\(\theta\) = 28.9\(^{\circ}\), 30.1\(^{\circ}\), and 31.2\(^{\circ}\), respectively, shifts to higher angles. It is followed by a biphasic reaction (region II) and a monophasic reaction (region III) to form intermediate materials, Na\(_{3}\)(V\(_2\)O\(_5\))\(_2\)(C\(_2\)O\(_4\))\(_2\)-2H\(_2\)O. Since the peak positions are closer to the initial phase, it is estimated that the structure of the intermediate phases is similar to the initial phase. Upon further Na extraction, another biphasic reaction proceeds in region IV. The region is characterized by increasing intensities of peaks at 16.9, 17.6, 19.6, 30.4, and 31.6\(^{\circ}\), which can be assigned to the de-sodiated phase, (VOHPO\(_3\))(C\(_2\)O\(_4\))\(_2\)-2H\(_2\)O. The decrease in the interplanar distance upon charging is inferred by the higher-angle shift of 01-1 peak. The side reaction of the material with electrolyte, which results in a large irreversible capacity, overlaps in the region IV. As seen in Fig. S12 and S13, the capacity in the plateau region at 3.97 V is larger during the operando XRD measurement than in coin cells. The fact indicates that the side reactions with electrolyte8 is more pronounced in the in-situ cell configuration compared to coin cells due to the more complicated internal structure of the in-situ cell and very slow in-situ operation at a low current density. During the first discharge, intensity of the peaks at 17.6 and 19.6\(^{\circ}\) assigned to the (VOHPO\(_3\))(C\(_2\)O\(_4\))\(_2\)-2H\(_2\)O phase decrease with the increasing amount of Na. This is indicative of a biphasic reaction as region V, the de-sodiated phase coexists with an intermediate phase Na\(_{3}\)(V\(_2\)O\(_5\))\(_2\)(C\(_2\)O\(_4\))\(_2\)-2H\(_2\)O. Followed by this two-phase domain, there is a monophasic region till the lower cut-off voltage (region VI). At the end of discharge, the peak position of the main diffraction peaks is slightly different to the initial phase. However, an ex-situ XRD pattern at the discharged state (Fig. S14) displays almost the same pattern with that of the pristine electrode. The fact indicates that the structural changes during Na extraction and insertion are completely reversible. The different peak position at the end of first discharge in the operando XRD pattern may be explained by incomplete Na-insertion as only the higher-voltage plateau region was observed in the initial discharge curve during the operando measurement. During the second cycle (Fig. S15), the charged state has the same interplanar distance as the first charge as inferred from the peak position at 17.6\(^{\circ}\) for both cycles. However, due to the significantly low intensities of the peaks and closely related structures of the intermediate phases, it is difficult to understand the complete mechanism of Na storage in the material with the current data. Measurements with synchrotron XRD or neutron diffraction may provide further insight on the mechanism.

Fig. 6 Structural evolution during Na extraction/insertion from/into p-NVPox: a) contour maps of operando XRD during the first cycle for selected 28 regions and b) Charge-discharge profile during the operando XRD measurement.
Conclusions

The vanadium based hybrid inorganic-organic open framework material, Na$_3$[(VOHPO$_4$)$_2$(C$_2$O$_4$)]·2H$_2$O, with a layered structure was investigated as a Na insertion positive electrode for the first time. It was prepared via a room temperature precipitation method which enables scaling-up. A high discharge capacity of 101 mAh g$^{-1}$ was delivered by Na-half cells at an average discharge voltage of 3.65 V which is slightly higher than the working potential of the pure inorganic material NaVOPO$_4$ (~3.4 V) functioning on the same V$^{4+}$/V$^{5+}$ redox couple. Since the pristine material (p-NVPox) suffered from poor electronic conductivity, ball-milling was employed. The bm-NVPox exhibited higher capacities at high current rates up to 10 C (80 mAh g$^{-1}$) while p-NVPox delivered only 32 mAh g$^{-1}$ at 10 C. In particular, the material can be cycled over 1000 cycles with a satisfactory retention rate of 62 % at a high rate of 2 C. The enhanced performance of bm-NVPox electrodes can be credited to the enhanced electronic conductivity and faster Na diffusion due to smaller particles. Feasibility of full cell was also demonstrated using NaTi$_2$(PO$_4$)$_3$ as counter electrode. The NTP/bm-NVPox full cells exhibited discharge capacities of 71 and 65 mAh·g$^{-1}$ at current rates of 2/10 and 1 C, respectively, with good capacity retention for 50 cycles.

Acknowledgments

This study was partly funded by the MEXT program “ESICB” (No. JPMPX0112101003), the Japan Science and Technology Agency (JST) through A-STEP program (No. JPMJTS1611), and JSPS KAKENHI Grant Numbers JP16K14103, JP16H04225, JP18K14327, and JP20K05690.

References

1. C. Vaalma, D. Buchholz, M. Weil and S. Passerini, Nat. Rev. Mater., 2018, 3, 18013.
2. D. Larcher and J. M. Tarascon, Nat. Chem., 2015, 7, 19-29.
3. K. Chayambuka, G. Mulder, D. L. Danilov and P. H. L. Notten, Adv. Energy Mater., 2020, 10, 2001310.
4. K. Kubota, M. Dahbi, T. Hosaka, S. Kumakura and S. Komaba, Chem. Rec., 2018, 18, 459-479.
5. A. Kamiyama, K. Kubota, T. Nakano, S. Fujimura, S. Shiraishi, H. Tsukada and S. Komaba, ACS Appl. Energy Mater., 2020, 3, 135-140.
6. X. Dou, I. Hasa, D. Saurel, C. Vaalma, L. Wu, D. Buchholz, D. Bresser, S. Komaba and S. Passerini, Mater. Today, 2019, 23, 87-104.
7. K. Kubota, S. Kumakura, Y. Yoda, K. Kuroki and S. Komaba, Adv. Energy Mater., 2018, 8, 1703415.
8. C. Delmas, D. Carlier and M. Guignard, Adv. Energy Mater., 2020, 2001201.
9. P. Barpanda, L. Lander, S.-i. Nishimura and A. Yamada, Adv. Energy Mater., 2018, 8, 1703055.
10. W. Duan, Z. Zhu, H. Li, Z. Hu, K. Zhang, F. Cheng and J. Chen, J. Mater. Chem. A, 2014, 2, 8668-8675.
11. Y. Fang, Q. Liu, L. Xiao, Y. Rong, Y. Liu, Z. Chen, X. Ai, Y. Cao, H. Yang, J. Xie, C. Sun, X. Zhang, B. Aoun, X. Xing, X. Xiao and Y. Ren, Chem, 2018, 4, 1167-1180.
12. A. P. Aparicio, J. A. Dawson, M. S. Islam and N. H. de Leeuw, J. Phys. Chem. C, 2018, 122, 25829-25836.
13. G. He, A. Huq, W. H. Kan and A. Manthiram, Chem. Mater., 2016, 28, 1503-1512.
14. J. Song, M. Xu, L. Wang and J. B. Goodenough, Chem. Commun., 2013, 49, 5280-5282.
15. J. Barker, M. Y. Saidi and J. L. Swoyer, Electrochem. Solid-State Lett., 2003, 6, A1-A4.
16. M. Law and P. Balaya, Energy Storage Mater., 2018, 10, 102-113.
17. L. Zhu, H. Wang, D. Sun, Y. Tang and H.-Y. Wang, J. Mater. Chem. A, 2020, 10.1039/d1030ta07872g.
18. C. Zhu, C. Wu, C.-C. Chen, P. Kopold, P. A. van Aken, J. Maier and Y. Yu, Chem. Mater., 2017, 29, 5207-5215.
19. J. F. Colin, T. Bataille, S. E. Ashbrook, N. Audebrand, L. Le Pollès, J. Y. Pivan and E. Le Fur, Inorg. Chem., 2006, 45, 6034-6040.
20. M. Nagarathinam, K. Saravanan, E. J. H. Phua, M. V. Reddy, B. V. R. Chowdari and J. J. Vittal, Angew. Chem. Int. Ed., 2012, 51, 5866-5870.
21. A. S. Hameed, M. V. Reddy, N. Sarkar, B. V. R. Chowdari and J. J. Vittal, RSC Advances, 2015, 5, 60630-60637.
22. A. S. Hameed, A. Katogi, K. Kubota and S. Komaba, Adv. Energy Mater., 2019, 9, 1902528.
23. A. S. Hameed, M. V. Reddy, M. Nagarathinam, T. Runčevski, R. E. Dinnebier, S. Adams, B. V. R. Chowdari and J. J. Vittal, Sci. Rep., 2015, 5, 16270.
24. A. Shahul Hameed, M. Nagarathinam, M. Schreyer, M. V. Reddy, B. V. R. Chowdari and J. J. Vittal, J. Mater. Chem. A, 2013, 1, 5721-5726.
25. T. Song, W. Yao, P. Kiadkhunthod, Y. Zheng, N. Wu, X. Zhou, S. Tunmee, S. Sattayaporn and Y. Tang, Angew. Chem. Int. Ed., 2020, 59, 740-745.
26. W. Yao, A. R. Armstrong, X. Zhou, M.-T. Sougrati, P. Kidkhunthod, S. Tunmee, C. Sun, S. Sattayaporn, P. Lightfoot, B. Ji, C. Jiang, N. Wu, Y. Tang and H.-M. Cheng, Nat. Commun., 2019, 10, 3483.
27. X. Wang, R. Kurono, S.-I. Nishimura, M. Okubo and A. Yamada, Chem. Eur. J., 2015, 21, 1096–1101.
28. W. Yao, M.-T. Sougrati, K. Hoang, J. Hui, P. Lightfoot and A. R. Armstrong, Chem. Mater., 2017, 29, 2167–2172.
29. W. Tang, X. Song, Y. Du, C. Peng, M. Lin, S. Xi, B. Tian, J. Zheng, Y. Wu, F. Pan and K. P. Loh, J. Mater. Chem. A, 2016, 4, 4882–4892.
30. P. Moreau, D. Guyomard, J. Gauboutcher and F. Boucher, Chem. Mater., 2010, 22, 4126–4128.
31. X. Bie, K. Kubota, T. Hosaka, K. Chihara and S. Komaba, J. Mater. Chem. A, 2017, 5, 4325–4330.
32. Y. Hironaka, K. Kubota and S. Komaba, Chem. Commun., 2017, 53, 3693-3696.