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Improved Electrochemical Performance of NaVOPO$_4$

Positive Electrodes at Elevated Temperature in an Ionic Liquid Electrolyte

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Abstract

Sodium secondary batteries operating in a wide temperature range are attractive as large-scale energy storage devices, and ionic liquid electrolytes are suitable for this purpose. In this study, NaVOPO₄ has been investigated as positive electrode material for Na secondary batteries, and its electrochemical performance has been examined in the Na[FSA]–[C₃C₁pyrr][FSA] ionic liquid (C₃C₁pyrr = N-methyl-N-propylpyrrolidinium and FSA = bis(fluorosulfonyl)amide) at 298 and 363 K. The NaVOPO₄ electrode exhibits a reversible capacity of 60 and 101 mAh g⁻¹ at 298 and 363 K, respectively. Acceptably good rate capability is achieved at 363 K, as 76% of the maximum capacity is maintained at 5 C rate. Cyclability tests prove good reversibility of the material, in which 74% of the initial specific capacity maintains over 300 cycles at 363 K. XRD measurements reveal that the charge–discharge process of NaVOPO₄ involves a single-phase reaction. Galvanostatic intermittent titration technique (GITT) analysis highlights a 3–5-fold increase of the apparent Na chemical diffusion coefficient in NaVOPO₄ upon increasing the temperature from 298 to 363 K, which is reflected in the superior electrochemical performance at 363 K than at 298 K.
1. Introduction

Sodium secondary batteries have attracted considerable attention as alternatives or complements to the prevailing Li-ion batteries, owing to their virtually unlimited supply, low material cost, and large worldwide availability.\textsuperscript{1–3} Research on Na secondary batteries has continued to gain momentum from the systematic extrapolation of the well-established knowledge regarding lithium ion batteries. The larger ionic radii of Na\textsuperscript{+} (1.02 Å) than Li\textsuperscript{+} (0.76 Å)\textsuperscript{3} was formerly deemed to frustrate the reversible insertion and fast transport of sodium within rigid inorganic hosts.\textsuperscript{4}

However, a recent computational study suggested that the diffusion of Na can be faster than that of Li in certain crystal structures.\textsuperscript{5} The milder Lewis acidity of Na\textsuperscript{+} than Li\textsuperscript{+} has also been shown to lead to a commonly smaller desolvation energy in polar solvents.\textsuperscript{6–8} Since the desolvation process of alkali ions highly influences their kinetics of insertion at the electrolyte interface,\textsuperscript{9} the relatively low desolvation energy coupled with the facile bulk diffusion may open up new appealing possibilities for high-power Na secondary batteries.\textsuperscript{5}

One of the main issues for Na secondary battery systems is their inferior energy densities compared to the Li-based ones,\textsuperscript{3,5,10} which is caused by (1) the larger mass (22.99 g mol\textsuperscript{−1} for Na and 6.94 g mol\textsuperscript{−1} for Li) and (2) the higher redox potential (−2.71 V vs. SHE for Na\textsuperscript{+}/Na and −3.04 V vs. SHE for Li\textsuperscript{+}/Li).\textsuperscript{10} In order to
counteract these intrinsic limitations, positive electrode materials that enable the realization of high capacity and high operating voltages are essential for Na secondary batteries. In this respect, vanadium-based phosphates are gaining increasing prominence.\textsuperscript{10–18} Relatively high operating potentials (vs. Na\textsuperscript{+}/Na) were achieved for Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (3.4 V),\textsuperscript{12,13} Na\textsubscript{3}V\textsubscript{2}(PO\textsubscript{4})\textsubscript{2}F\textsubscript{3} (3.9 V),\textsuperscript{10,11} Na\textsubscript{1.5}VPO\textsubscript{4}\textsubscript{8}F\textsubscript{0.7} (3.8 V),\textsuperscript{15} Na\textsubscript{7}V\textsubscript{4}(P\textsubscript{2}O\textsubscript{7})\textsubscript{4}PO\textsubscript{4} (3.88 V),\textsuperscript{16,17} and Na\textsubscript{2}VOP\textsubscript{2}O\textsubscript{7} (3.8 V).\textsuperscript{18} The strong inductive effect of the PO\textsubscript{4}\textsuperscript{3–} polyanion alters the covalent character of V–O (or –F) bonds and moderates the energetics of the vanadium redox couple, resulting in favorable operating potentials for these compounds.\textsuperscript{19–21} However, most of the above electrode materials face limitations in terms of theoretical capacity (ca. 90–120 mAh g\textsuperscript{–1}), because of the heavy polyanion group.\textsuperscript{12,13,16–18}

The vanadium-based phosphate, NaVOPO\textsubscript{4}, characterized by a moderately high operating potential (3.6 V vs. Na\textsuperscript{+}/Na) as well as a relatively large theoretical capacity (145 mAh g\textsuperscript{–1}),\textsuperscript{22} provides one of the highest theoretical energy densities (ca. 530 Wh kg\textsuperscript{–1}) among the positive electrode materials for Na secondary batteries.\textsuperscript{10,11,15} Despite such an attractive energy density, however, NaVOPO\textsubscript{4} has not been significantly explored as positive electrode material as yet. Earlier studies on NaVOPO\textsubscript{4} mostly focused on its synthesis and structural properties.\textsuperscript{23–25} The only electrochemical report to date, by Song et al., revealed that 62% (90 mAh g\textsuperscript{–1}) of the theoretical capacity can
be realized at room temperature in 1 M NaClO₄/propylene carbonate (PC); however, other important electrode characteristics such as rate capability and long-term cyclability, as well as reaction mechanism, remain to be investigated.²²

The energy density has long been considered as the most critical figure of merit for a battery, which is dominated by the performance of positive electrode materials in many Li and Na secondary batteries. On the other hand, the electrolyte also represents a key component that governs many important properties of batteries.²⁶–²⁸ The electrolytes investigated for Na secondary batteries are mainly based on organic solvents, following similar approaches to those developed for lithium ion batteries.³,²⁸ As the interest in Na secondary batteries distributed over a much more diversified and global manner, the electrolytes of choice is not a single one.²⁸ Ionic liquids (ILs), characterized by a suite of unique properties such as nonflammability, nonvolatility, as well as good thermal and electrochemical stability, show considerable potential as advanced electrolytes.²⁹–³⁵ Improved electrochemical performance has been demonstrated for cells adopting IL electrolytes, compared to those involving organic electrolytes.³³–³⁵

In our previous studies, the feasibility of a series of bis(fluorosulfonyl)amide (FSA)-based IL electrolytes for Na batteries has been verified.³⁶–³⁸ The wide liquidus range of the Na[FSA]–[C₃C₅pyrr][FSA] IL (C₃C₅pyrr =
N-methyl-N-propylpyrroldinium) allowed us to investigate the charge–discharge behavior of targeted electrode materials from low (253 K) to elevated temperatures (363 K).\textsuperscript{39–41} The results revealed a considerable enhancement in reversible capacity and rate capability with increasing temperature for Na\textsubscript{2}MnSiO\textsubscript{4},\textsuperscript{39} Na\textsubscript{2}FeP\textsubscript{2}O\textsubscript{7},\textsuperscript{40} and Na\textsubscript{1.56}Fe\textsubscript{1.22}P\textsubscript{2}O\textsubscript{7}.\textsuperscript{41} The performance of batteries with conventional organic electrolyte solvents have been rarely investigated at temperatures greater than 328 K, above which poor storage and inferior cycling behaviors are generally observed.\textsuperscript{42,43} Since a concrete improvement in electrochemical properties was observed in IL electrolytes at elevated temperatures, operation at above room temperature is preferable and also practicable for electric vehicle and stationary storage applications.\textsuperscript{34} In the present work, the electrochemical properties of NaVOPO\textsubscript{4} are investigated in Na[FSAX]–[C\textsubscript{3}C\textsubscript{1}pyrr][FSAX] IL electrolyte at 298 and 363 K. With the aim to understand the characteristics of NaVOPO\textsubscript{4} in higher detail, here we investigate the rate capability, the cyclability, as well as the structural variation of the materials upon electrochemical cycling. Furthermore, the galvanostatic intermittent titration technique (GITT) has been used to elucidate the Na intercalation kinetics within the material.

2. Experimental
Sodium vanadyl phosphate, NaVOPO$_4$, was synthesized by the sol-gel method from Na(CH$_3$COO)$_2$, NH$_4$VO$_3$, (NH$_4$)$_2$HPO$_4$ and citric acid, according to a reported procedure.$^{22}$ Equal amounts of the starting materials were dissolved in ultrapure water with magnetic stirring at 343 K. After a clear blue solution formed, the mixture was further dried at 353 K to transform the solution from sol to gel. The gel was initially heated at 573 K for 4 h and then at 773 K for 4 h in air. The as-prepared NaVOPO$_4$ (denoted as NVP-AP) was thoroughly mixed with acetylene black (AB, 5:1 in weight) via a high-energy planetary ball-milling (Fritsch Pulverisette 7 Premium Line) for 2 h and 8 h at 700 rpm (the corresponding material samples are hereafter denoted as NVP/AB-2h and NVP/AB-8h, respectively).

The crystal structure of NVP-AP was determined by an X-ray diffractometer (Rigaku SmartLab) equipped with a one-dimensional high-speed Si strip detector (Rigaku D/teX Ultra), utilizing Cu K$_\alpha$ radiation (40 kV and 30 mA). The structural refinement was carried out by the Rietveld method in an iterative procedure using the RIETAN-FP program.$^{44}$ The crystal structure was visualized by the VESTA software.$^{45}$ The morphology of the sample was observed using field-emission scanning electron microscopy (FE-SEM, Hitachi SU-8020). The electrochemical properties of NVP-AP, NVP/AB-2h, and NVP/AB-8h were assessed using 2032-type coin cells with a Bio-Logic VSP potentiostat, as described in our previous reports.$^{37,40}$
The positive electrode was prepared by mixing active material, vapor-grown carbon fibers (VGCFs), and polytetrafluoroethylene (PTFE) with agate mortar and pestle. The resultant NaVOPO$_4$/conductive carbon (AB+VGCF)/PTFE weight ratio was 75:20:5. A metallic Na disc pressed onto an aluminum current collector was used as the negative electrode. The Na[FSA]–[C$_3$C$_1$pyrr][FSA] (20:80 molar ratio) IL was used as electrolyte according to our previous report. The mass loading and thickness of the active material were approximately 2.0 mg cm$^{-2}$ and 50 μm. For the GITT, a current of C/20 (7.25 mA g$^{-1}$) was applied for 30 min, followed by a 12 h relaxation, unless the system satisfied the 10 mV h$^{-1}$ stability criterion earlier.

3. Results and Discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern and Rietveld refinement results for NVP-AP. The structure was refined in the monoclinic lattice with $P2_1/c$ space group and lattice parameters $a = 6.51960(9)$ Å, $b = 8.44576(11)$ Å, $c = 7.11499(10)$ Å, $β = 115.2591(4)^o$, $V = 354.314(9)$ Å$^3$, and $Z = 4$, which agrees well with previously reported data for microcrystalline and single crystal samples. The related structural parameters are given in the Supporting Information (Table S1). No impurity was detected, as attested by the good agreement between the experimental and calculated patterns. As shown in Fig. 2a, NaVOPO$_4$ exhibits a structure built from infinite chains of VO$_6$ octahedra interconnected by PO$_4$ tetrahedra, all in a
corner-sharing fashion. The VO$_6$ octahedra are distorted, as the vanadium atom is
152 displaced from the square plane comprising the four equatorial oxygen atoms toward
153 one apical oxygen atom. The V–O$_b$ (O$_b$ = bridging oxygen) bond lengths alternate
154 between longer and shorter bonds, resulting in the trans configuration of the [VO$_5$]$^-$
155 chains (Fig. 2b, c). It was suggested that the distortion of the structural units and
156 the tilted connection between them creates additional space for Na migration.$^{46}$

The XRD patterns of NVP-AP, NVP/AB-2h, and NVP/AB-8h are compared in
158 Fig. 3a. The XRD peaks of the ball-milled samples are remarkably broadened, and the
degree of broadening increases with the ball-milling time, indicative of the reduction
160 in the crystallite size. The Scherrer formula $D = \frac{1.33 \lambda}{\beta \cos \theta}$, where $\lambda$ is the X-ray
161 wavelength, $\beta$ the integral breadth of the diffraction line, and $\theta$ the Bragg angle, was
162 used to estimate the crystallite size from the XRD data.$^{47}$ The crystallite size $D$,
calculated as the average of the values corresponding to 4 discrete diffraction peaks
164 (110 at 18.4°, 111 at 26.7°, $\overline{1}$$\overline{1}$2 at 27.4°, and 200 at 30.3°), was 106(6), 40(4), and
165 32(4) nm for the NVP, NVP/AB-2h, and NVP/AB-8h samples, respectively. FE-SEM
166 images of these samples are illustrated in Fig. 3b–d. The NVP-AP sample (Fig. 3b) is
167 composed of many submicron grains aggregated up to several microns, suggesting a
considerable grain growth even at the relatively low sintering temperature of 773 K
169 and with a short annealing time. A similar phenomenon was observed for NaVOP$_2$O$_7$
synthesized at 673 K. After ball-milling with AB (Fig. 3c and d), there was a significant reduction in particle size, to approximately 100 nm. The trend observed by FE-SEM is consistent with that highlighted by XRD.

Fig. 4a–d show the typical galvanostatic charge–discharge curves of the NVP/AB-2h and NVP/AB-8h electrodes in the three initial cycles at 5 mA g$^{-1}$. For NVP/AB-2h, the galvanostatic profiles exhibit sloping curves without plateau, and the reversible capacities are 40 and 74 mAh g$^{-1}$ at 298 K and 363 K, respectively. In comparison with NVP/AB-2h, NVP/AB-8h shows a higher reversible capacity under the same conditions, delivering 60 and 101 mAh g$^{-1}$ at 298 K and 363 K, respectively, which correspond to 41% and 70% of the theoretical capacity. The average operating potential of 3.6 V $\text{vs.}$ Na$^+$/Na is noticeable, considering that this material does not contain fluorine to facilitate the inductive effect. However, the capacity on the first charge is always larger than that on the first discharge, especially at 363 K, suggesting the occurrence of an anodic parasitic reaction. To account for the abnormally high initial charge capacity, charge–discharge tests were performed on electrodes consisting of only ball-milled AB. Referring to Fig. S1, a large charge capacity was observed in the first cycle, with an apparent decrease in the subsequent cycle. This indicates that a parasitic reaction involving AB occurs, after energetic ball-milling in the composite electrode, which contributes to the observed irreversible
capacity during the first cycle. However, AB does not participate in the Na storage on
the subsequent cycling. In addition, the first-cycle capacity loss could also be ascribed
to Na-consuming reactions, such as the formation of a passivation layer on the
electrode.\textsuperscript{48} For comparison, almost no Na can be extracted from NVP-AP, which is
consistent with the previous report (Fig. S2).\textsuperscript{22} Pure NaVOPO\textsubscript{4} may suffer from low
electronic conductivity as in the case of other phosphate battery electrode materials.\textsuperscript{49}
The enhanced electrochemical properties of NaVOPO\textsubscript{4}/AB electrodes are therefore
attributed to the fine particles in close contact with the conductive carbon matrix, and
to the shortened Na transport path lengths due to the reduction in particle size.

Song et al. reported that the NaVOPO\textsubscript{4}/AB electrode exhibits a capacity of 90
mAh g\textsuperscript{-1} in the voltage range of 2.0–4.4 V in NaClO\textsubscript{4}/PC electrolyte at room
temperature.\textsuperscript{22} Taking into account that the capacity for a positive electrode in the
region above 2.5 V, 60 mAh g\textsuperscript{-1} obtained in the present IL electrolyte is thus similar
to that obtained in NaClO\textsubscript{4}/PC electrolyte at room temperature,\textsuperscript{22} and the capacity of
101 mAh g\textsuperscript{-1} measured at 363 K is quite remarkable. The voltage profiles also exhibit
a substantial difference with respect to the NaClO\textsubscript{4}/PC electrolyte, namely, a more
evident discharge pseudo-plateau is obtained in this study. Most importantly, the
increased capacity is mainly above 3.5 V, which is essential for achieving high energy
density. These results confirm that a moderately elevated operating temperature can
effectively enhance the utilization ratio of the active materials, leading to a higher
capacity. Similar findings were reported by other groups\textsuperscript{33,34,50} and by us.\textsuperscript{39,41}

The structural evolution of NaVOPO\(_4\) upon electrochemical cycling at 363 K
was investigated through an \textit{ex situ} XRD analysis. Comparison of XRD patterns for
the NaVOPO\(_4\)/AB electrode at different charging and discharging states are presented
in Fig. S3. It can be noticed that charging of the electrode up to 4.2 V induces only
slight changes in the diffraction patterns (e.g., the intensity of the 111 peak relative to
that of the \textit{\^{1}12} peak increases upon charging). Since no pronounced new diffraction
peaks are detected, NaVOPO\(_4\) is considered to undergo topotactic Na extraction.
Some structural disorder may also occur for a low Na content as broadening of the
low-angle peaks is observed.\textsuperscript{51} Although the quality of the XRD pattern of the
electrochemically desodiated NaVOPO\(_4\) was unsatisfactory, Rietveld analysis was
performed under highly constrained conditions in order to determine the lattice
parameters (Table S2). The result suggests that desodiation of NaVOPO\(_4\)
(Na\(_{0.4}\)VOPO\(_4\)) leads to a minor (~1.2\%) decrease in volume, which is close to the
value between \(\beta\)-LiVOPO\(_4\) and \(\beta\)-VOPO\(_4\).\textsuperscript{52}

The rate capability of the NVP/AB-2h and NVP/AB-8h electrodes at 363 K is
shown in Fig. 5a and b. The cells were charged to 4.2 V at a constant current density
of C/10 (14.5 mA g\(^{-1}\)), and subsequently discharged to 2.5 V at various rates.
Although the discharge capacity declines with an increase in current density, a sufficiently high rate capability is realized at 363 K. Approximately 76% and 60% of the maximum capacity observed at 5 mA g\(^{-1}\) is maintained at 5 C and 10 C, respectively, for both the NVP/AB-2h and NVP/AB-8h. The discharge capacity is still clearly discernible up to a rate of 40 C (5800 mA g\(^{-1}\)). The long-term cycling performance of the NVP/AB-2h and NVP/AB-8h electrodes at a current density of 1 C is shown in Fig. 6a and b. Fairly stable cycling behavior with limited capacity decay is observed at 298 K for both electrodes; when cycled at 363 K, more than 74% of the initial capacity is retained after 300 cycles. The average coulombic efficiencies over the course of the entire test are higher than 99.7% for all the cells investigated. The good cyclability can be attributed to the minimal volume change experienced by NaVOPO\(_4\) during Na extraction/insertion, as well as to the use of a chemically stable IL electrolyte.

The kinetic behavior of the NVP/AB-8h electrode at 298 K and 363 K was examined using the galvanostatic intermittent titration technique (GITT) (Fig. 7). As shown in Fig. 7a, a relatively small overpotential is observed in the charge curves at 298 K, while a larger overpotential is observed toward the end of discharge. This is attributed to kinetic limitations, due to the high resistance in the particles, that hinder Na\(^+\) access to their centers.\(^{53}\) Other causes, such as the concentration polarization,
may also account for the increased overpotential at the end of these curves.\textsuperscript{54} The
GITT curves at 363 K clearly show that the overpotential is suppressed in the full
range of voltage as compared to that at 298 K, reflecting a lower kinetic barrier for
Na\textsuperscript{+} insertion into this material. For both temperatures, there is no evidence of a
voltage plateau in the GITT data, implying that the electrochemical reaction
undergoes a single-phase rather than a two-phase mechanism.\textsuperscript{55} This assignment is
consistent with the \textit{ex situ} XRD results above. Assuming that Na transport in the
electrode obeys Fick’s second law, the chemical diffusion coefficient can be estimated
from the GITT curves using the following equation:\textsuperscript{56,57}

\[
D_{GITT} = \frac{4}{\pi\tau} \left( \frac{m_B V_m}{M_B S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_c} \right)^2 \left( t \ll L^2/D_{GITT} \right)
\]

where \( \tau \) is the time period of the current pulse, \( m_B \) is the mass of the electroactive
material, \( V_m \) and \( M_B \) are its molar volume and molecular weight, \( S \) is the contact area
between the electrolyte and the electrode, \( \Delta E_s \) is the difference in the open circuit
voltage measured at the end of the relaxation period for two successive steps, \( \Delta E_c \) is
the difference in cell voltage during the single titration current pulse, and \( L \) is the
thickness of the electrode. This equation can be applied if there is a linear correlation
between \( E_c \) and \( \tau^{1/2} \) (Fig. S4). Because the contact area used is the geometric area, the
term apparent chemical diffusion coefficient is used here for \( D_{GITT} \). It must be
mentioned that the actual surface area of the active material in contact with the
electrolyte in composite electrode systems depends on the particle size of the active material and its morphology, and must be larger than the geometric area, due to the penetration of electrolyte.\textsuperscript{58} Care has been taken in the present study to minimize the uncertainty in electrode physical parameters by performing the GITT measurement on the same cell at 298 and 363 K. It has been suggested that this technique gives accurate results especially for small stoichiometric changes.\textsuperscript{56}

Taking these aspects into consideration, the calculated $D_{GITT}$ at the initial stages of charge and discharge is plotted as a function of cell voltage in Fig. 7b. The $D_{GITT}$ values range from $2 \times 10^{-12}$ to $1 \times 10^{-11}$ cm$^2$ s$^{-1}$ at 298 K, and from $1 \times 10^{-11}$ to $3 \times 10^{-11}$ cm$^2$ s$^{-1}$ at 363 K. The diffusivity of Na$^+$ in NaVOPO$_4$ is enhanced by 3–5 times by increasing the temperature from 298 to 363 K, confirming the favorable kinetics at elevated temperatures, and thus leading to improved electrochemical performance.

Furthermore, the obtained $D_{GITT}$ is comparable to that observed for layered oxides, O$_3$-Na$_{0.25}$Fe$_{0.5}$Mn$_{0.25}$O$_2$ and Na$_2$Ti$_3$O$_7$ (ca. $10^{-12}$–$10^{-11}$ cm$^2$ s$^{-1}$),\textsuperscript{59,60} and is considerably higher than that of other positive electrode materials such as Na$_4$Mn$_9$O$_{18}$ (ca. $10^{-16}$–$10^{-15}$ cm$^2$ s$^{-1}$)\textsuperscript{61} and olivine NaFePO$_4$ (ca. $10^{-17}$ cm$^2$ s$^{-1}$),\textsuperscript{62} which were acquired by similar electrochemical methods. These results highlight the potential of NaVOPO$_4$ for high-power applications, although further improvements and optimizations in synthesis and electrode formulation are required.
4. Conclusions

In order to explore the enhanced kinetics at elevated temperatures, the charge–discharge behavior of NaVOPO$_4$ was investigated in Na[FSA]–[C$_3$C$_1$pyrr][FSA] ionic liquid electrolyte at 298 and 363 K. Reversible capacities of 60 and 101 mAh g$^{-1}$ were achieved at 298 and 363 K, respectively, as well as adequate rate capability and cyclability. The apparent Na chemical diffusion coefficient was evaluated by GITT analysis, which indicated that the Na$^+$ diffusivity increases by 3–5 times when the temperature increased from 298 to 363 K. The combined advantages of a moderately high operating voltage (3.6 V) and a large theoretical capacity (145 mAh g$^{-1}$) designate NaVOPO$_4$ as a promising positive electrode material for Na secondary batteries. Cationic substitution of NaM$_x$V$_{1-x}$OPO$_4$ \( (M = \text{Ti}^{3+}, \text{Al}^{3+}, \text{Fe}^{3+}) \) may represent a promising way to boost its performance and decrease the consumption of vanadium.

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References


Figure captions

Figure 1. X-ray diffraction pattern with Rietveld refinement of NaVOPO$_4$ ($R_{wp} = 4.38\%$ and $R_p = 3.13\%$): experimental data (red dots), calculated pattern (black line), Bragg positions (green bars) and difference curve (blue line).

Figure 2. Structure of NaVOPO$_4$. (a) Crystal structure of NaVOPO$_4$, with VO$_6$ and PO$_4$ polyhedra shown in blue and gray, respectively. The Na, Fe and O atoms are colored green, navy, and orange, respectively; (b) distorted VO$_6$ octahedral unit; (c) a [VO$_5$]$\infty$ chain in trans configuration with staggered VO$_6$ octahedra.

Figure 3. (a) X-ray diffraction patterns of as-prepared NaVOPO$_4$ (NVP-AP) and NaVOPO$_4$ ball milled with AB for 2 h and 8 h (NVP/AB-2h and NVP/AB-8h). SEM images of (b) NVP, (c) NVP/AB-2h, and (d) NVP/AB-8h.

Figure 4. Galvanostatic charge–discharge curves for the NVP/AB-2h and NVP/AB-8h electrodes: Na/Na[FSAl–[C$_3$C$_1$pyrr][FSA]/NVP/AB-2h cell at (a) 298 K and (b) 363 K; Na/Na[FSA–[C$_3$C$_1$pyrr][FSA]/NVP/AB-8h cell at (c) 298 K and (d) 363 K. Cut-off voltage: 2.5–4.2 V. Current density: 5 mA g$^{-1}$. Note the different capacity scale in panel (d).
Figure 5. Discharge curves of the (a) NVP/AB-2h and (b) NVP/AB-8h electrodes at various current densities at 363 K. The cells were charged to 4.2 V at a constant rate of C/10 (14.5 mA g$^{-1}$).

Figure 6. Cycling performance and coulombic efficiency (C.E.) of the (a) NVP/AB-2h and (b) NVP/AB-8h electrodes at 298 and 363 K. Cut-off voltage: 2.5–4.2 V. Current density: 1 C (145 mA g$^{-1}$).

Figure 7. (a) GITT evaluation of the NVP/AB-8h electrode at 298 K and 363 K. Conditions: 30 min charging/discharging segments at C/20 (7.25 mA g$^{-1}$) followed by 12 h relaxation. (b) Chemical diffusion coefficient of Na ions in NaVOPO$_4$ ($D_{\text{GITT}}$) calculated from GITT as a function of cell voltage during charge (open symbols) or discharge (solid symbols).
Figure 1

Figure 2

(a)

(b)

(c)
Figure 3

Figure 4
Figure 5
Figure 6
Figure 7