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Mechanism of Na⁺ Insertion in Alkali Vanadates and its Influence on Battery Performance.

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Sodium-ion batteries can become an alternative to the widespread lithium-ion technology due to cost and kinetic advantages provided that cyclability is improved. For this purpose, the interplay between electrochemical and structural processes is key and is demonstrated in this

work for $\text{Na}_{2.46}\text{V}_6\text{O}_{16}$ and $\text{Li}_{2.55}\text{V}_6\text{O}_{16}$ employing *operando* synchrotron X-ray diffraction. When NVO is cycled between 4.0 V – 1.6 V, Na-ions reversibly occupy two crystallographic sites, which results in remarkable cyclability. Upon discharge to 1.0 V, however, Na-ions occupy also interstitial sites, inducing irreversible structural change with some loss of crystallinity concomitant with a decrease in capacity. Capacity fading increases with the ionic radius of the alkali ions ($\text{K}^+ > \text{Na}^+ > \text{Li}^+$), suggesting that smaller ions stabilize the structure due to stronger attraction to the vanadate layers. This correlation of structural variation and electrochemical performance suggests a route towards improving cycling stability based on minor Li^+ -retention in an $\text{A}_{2+x}\text{V}_6\text{O}_{16}$ structure. Even though exchange of the majority of Li^+ by the abundant Na^+ occurs, the remaining Li-ions (~10%) are sufficient to stabilize the layered structure, diminishing the irreversible structural damage. These results pave the way for further exploitation of the role of small ions in lattice stabilization that increases cycling performance.

1. Introduction

Sodium-ion batteries (NIBs) have recently become the subject of increasing research efforts, and are considered a viable future electrochemical energy storage technology for a variety of applications such as stationary energy storage. As of now, lithium-ion batteries (LIBs) dominate the market, owing to their excellent performance, which is also the result of decades of research and optimization. Sodium-ion batteries (NIBs), however, could play a similar role in the future, provided that suitable electrode materials are found and fundamental understanding of the respective systems is enhanced.^[1–8] Na-ion-based systems have an advantage in terms of cost, availability, and abundance. Moreover, recent studies^[9–12] relate the larger ionic radius of Na^+ to some benefits emerging from the lower desolvation energy which may facilitate insertion of Na^+ into the active electrode material. Moreover, faster diffusion of Na^+ ions within the active electrode material is also favoured in certain

structures.^[13] In addition, in the search of commercially viable materials the immense structural variety of Na-compounds can be exploited once basic principles are understood.^[2]

In a previous publication^[14], we reported on $\text{Na}_{2+x}\text{V}_6\text{O}_{16}$ (NVO) as a NIB cathode. As in the case of $\text{Li}_{2+x}\text{V}_6\text{O}_{16}$ (LVO), NVO consists of V-O layers, with Na-ions located between these layers (International Crystal Structure Database, ICSD-67844 and -164514). Even though the initial capacity was promising, the cycling stability was low. Therefore, in this paper this material serves as an exemplary system for studies of the origin of strong capacity fading. We note in passing that various studies have investigated similar systems with different foci^[15–25], however, without detailed structural analysis.

In this report, we present in-depth structural characterization of the insertion process of Na^+ into (from) $\text{Na}_{2+x}\text{V}_6\text{O}_{16}$ (NVO) employing electrochemical *operando* synchrotron X-ray diffraction (XRD). Our data indicate that for NVO the structural and electrochemical reversibility of Na^+ -insertion depends on the potential. In a narrow potential region, Na^+ reversibly occupies two distinct lattice sites, while in a wider potential range, *i.e.*, at lower potentials, additional Na-ions insert into interstices. This effect induces irreversible structural changes causing a decrease in discharge capacity. Interestingly, when the isostructural LVO is cycled in a Na-ion half cell, Li^+ is not entirely replaced by Na^+ . Approximately 10% of Li^+ ions are retained and this is the origin of small, although defined structural changes as compared to “native” NVO. Specifically, this small Li^+ -retention is responsible for the improved cycling performance of the capacity.

2. Results and Discussion

2.1. Physical characterization

The crystal structures of the alkali vanadates NVO, LVO, and KVO ($\text{K}_{1.8}\text{V}_6\text{O}_{16}$) were determined using XRD as shown in Figure S1. Their synthesis is described in the Experimental Section. For all three systems, the unit cell was found to be monoclinic with the $P12_1/m1$ space group. VO_x -polyhedra form layers and the respective alkali ion, Na^+ , Li^+ , or K^+ , is located between these layers. The unit cell increases with the radius of the alkali ion as detailed in the Experimental Section. All three materials have a belt-like morphology (Figure S2a-c). The individual belts differ in length (typically several hundred nanometers to a few micrometers) and aspect ratio.

2.2. Electrochemistry

The electrochemistry of NVO, LVO, and KVO depends significantly on the potential range in which the materials are cycled (**Figure 1a,b**).

Potential range 4.0 V – 1.0: NVO shows a rather high capacity of 201 mA h g^{-1} in the first discharge when cycled vs. $\text{Na}|\text{Na}^+$ at a current rate of 20 mA g^{-1} ($\approx C/10$). This initial capacity corresponds to the insertion of 4.7 Na-ions into the lattice of NVO and therefore to a formal unit $\text{Na}_{6.3}\text{V}_6\text{O}_{16}$ at the end of the discharge. The insertion of one Na-ion, based on the initial formula unit for NVO, corresponds to 43 mA h g^{-1} . The most striking feature in Figure 1a is the steep decrease of capacity over the course of 100 cycles. It is this prominent trait that prompted us to study and relate electrochemical information to structural processes (Section 2.3). For LVO the initial discharge capacity at 20 mA g^{-1} is higher (279 mA h g^{-1}) than for NVO and somewhat stable for the first ~ 20 cycles before fading in subsequent cycles (Figure 1a). For KVO the initial discharge capacity is lower (168 mA h g^{-1}) for NVO while its capacity retention resembles the curve for NVO.

Moreover, not only does the capacity of all three materials decrease, but also the shape of the galvanostatic charge/discharge curves change, *i.e.*, they lose structure during cycling (Figure S3). While in the first discharge the shape is quite structured with a plateau at ~ 2.4 V (for KVO at 2.0 V) and a long plateau around 1.3 V, in subsequent cycles these plateaus are washed out. Thus, during cycling the Na-ions appear to occupy lattice sites with a wider range of electrochemical potentials as opposed to the occupation of distinct lattice sites in a well-defined structure. The similar shape of the discharge curves for all three isostructural materials (Figure S3) suggests a similar structural insertion process (for a more detailed description of the discharge curves, see Supporting Information).

Potential range 4.0 V – 1.6 V: When the potential range is limited to 4.0 V – 1.6 V, the second, long plateau is not reached (Figure 1b). All capacities increase ($< 10\%$ for NVO and KVO, 30% for LVO) over the first ten cycles due to ongoing Na^+ insertion into the oxide lattices, so that the discharge capacity in the 10th cycle is 70 mA h g^{-1} for NVO (consistent with a recent report by Dong *et al.*^[25]), 97 mA h g^{-1} for LVO, and 70 mA h g^{-1} for KVO (50 mA g^{-1}).

This difference in stability dependant on the potential range cycled suggests that potential-dependent material characteristics are the origin of the observed capacity fading rather than failing of the Na-electrode as proposed elsewhere.^[21] Such interpretation would be consistent with Na-ions which reversibly occupy specific lattice sites when cycled in the smaller potential range between 4.0 V – 1.6 V, whereas the process causing the extended plateau in the discharge curve starting at 1.5 V involves irreversible capacity fading. In the following section we test whether and how these electrochemical observations are correlated with structural developments.

2.3. Electrochemistry and Structure. *Operando* X-ray diffraction

2.3.1. $\text{Na}_{2.46}\text{V}_6\text{O}_{16}$ in Sodium-Ion Batteries

Narrow potential range 4.0 V – 1.6 V: Upon limiting the potential to this range, the development of the XRD pattern is reversible (**Figure 2**). As these measurements were performed with synchrotron radiation in transmission mode, all the observed processes can be attributed to bulk processes. The Na content, x , in $\text{Na}_x\text{V}_6\text{O}_{16}$ is calculated based on the assumption that the cells at 3.0 V, the typical open-circuit potential (OCP), contain the amount of Na^+ that was determined for the powder by Inductively-Coupled Plasma Optical Emission Spectrometry (ICP-OES) and that all the current goes into Na^+ -insertion or extraction (no side reactions).

For a better understanding of the structural processes which are occurring, individual reflections representing the different planes were analysed. The crystal structure of this material is depicted in **Figure 3**. The a -lattice parameter is perpendicular to the plane of VO_x -polyhedra and thus is the interlayer spacing, while the b - and c -lattice parameters span this plane. In this work, the (100), (020), and (001) reflections are used to calculate the a -, b - and c -lattice parameters, respectively. During discharge, the a -lattice parameter increases up to a Na^+ -content of 2.5 and then stays constant, whereas the b - lattice parameter continuously expands from 4.0 V to 1.6 V (**Figure 4a**). The c -lattice parameter remains constant until a Na content of $x \sim 2.8$ and then increases. At Open Circuit Potential (OCP), Na-ions are located at two different sites in the crystal lattice, α and β , one of which (β) is only partially occupied. During charge, these positions are partially vacated such that the Na^+ -content of the formula unit is decreased by one, and the resulting formula unit is $\approx \text{Na}_{1.6}\text{V}_6\text{O}_{16}$. Upon discharge, *i.e.*, the insertion of Na-ions, these sites are gradually occupied, which leads to an increased number of Na-ions between the VO_x -layers. Complete occupation of the α and β sites would

result in a discharge capacity of 103 mA h g^{-1} , 70% of which is achieved in a coin cell set up tested at 50 mA g^{-1} (see Electrochemistry section). Initial contraction of the unit cell, coming from electrostatic interaction between Na^+ and O^{2-} in the layers, is overcompensated by the electrostatic repulsion between the cations and / or the space requirement of the ‘new’ Na-ions. This results in an increase of the unit cell volume (Figure S4), and an increase of the a -lattice parameter up to a Na^+ -content of $x = 2.5$ (Figure 4a). Interestingly, this corresponds to the Na^+ -content of the pristine material, in which the α -positions are fully occupied. Hence, as the a -lattice parameter stays constant after the α positions are fully occupied, it is suggested that the length of the a -lattice parameter, and thus the interlayer spacing between the VO_x -layers is predominantly influenced by the Na^+ on the α -position. The b -lattice parameter expands continuously with increasing Na^+ -content, which is consistent with a repulsion of the inserted Na-ions. The c -lattice parameters does not increase up to Na^+ -content of $x = 2.8$ while the α positions are occupied. Once the α positions are fully occupied, Na^+ inserts onto the β positions. Initially, this has no effect on the c -lattice parameter. Starting from a Na^+ -content of ~ 2.8 , which corresponds to an occupation of $\sim 40\%$ of the β positions, c expands due to repulsive interaction between the Na-ions. This coincides with a decrease of conductivity in the structure as determined by Galvanostatic Intermittent Titration Technique (GITT, Supporting Information).

The integrated areas of the (100), (001) and (020) reflections change reversibly (Figure 4b), which corresponds well with the reversibility of the electrochemistry. While the area of (100) reflection shows a minor decrease during discharge, which is reversed during the subsequent charge, the area of the (001) reflection shows an increase during discharge and a decrease during charge; the area of the (020) reflection increases slightly during discharge and decreases during charge. Simulations of diffraction patterns using the Mercury software, based on gradually filling up the two lattice sites α and β , were conducted. Qualitative

comparison of the development of the reflection area to the measurement data substantiates the hypothesis that during Na-insertion the α -position is occupied first, followed by the β -position.

Wide potential range 4.0 V – 1.0 V: In the subsequent cycle (after one cycle within the narrow range), when discharging now from 4.0 to 1.0 V, *i.e.*, increasing the Na⁺-content in the crystal structure from 1.5 to 6.2, the a -lattice parameter, again, expands up to a Na⁺-content of 2.5, after which it remains constant (**Figure 5**). The b -lattice parameter increases steadily until the onset of the large plateau in the discharge curve. Then, the driving force to expand along the b -lattice parameter weakens and the gradient of the curve depicting the change of the b -lattice parameter decreases. Moreover, an increase in the c -lattice parameter is observed. Over the course of several cycles in this wide potential range, this lattice expansion/contraction is observed to be irreversible (**Figure 6**). To be more specific, the lattice vectors at both the onset and the end of the 5th discharge to 1.0 V are larger as compared to the respective values for the 2nd discharge in the same potential range. This increase is most pronounced for the a - and c -lattice parameter, while the change for the b -lattice parameter is insignificant. In addition, in the 5th discharge the c -lattice parameter starts increasing at a higher Na⁺ content than in the 2nd discharge to 1.0 V. The increase of the b -lattice parameter in the second discharge at wide potential range, (Figure 5), changes its slope at a Na⁺-content of $x = 3.25$. Together with the slope and subsequent plateau of the a -lattice parameter, this change in the slope indicates that the α - and β -sites are initially filled followed by occupation of the interstices for $x > 3.25$. These Na-ions are located on distorted trigonal bipyramidal interstices (Figure 3b) in the plane of the VO_x polyhedra, which forces the c -planes apart. We speculate that the occupancy of these interstices results in the irreversible deterioration of the structural integrity of NVO during deep cycling to 4.0 V - 1.0 V. This is also substantiated by GITT measurements (Supporting Information) as the Na⁺-diffusion coefficient decreases starting

from a Na^+ -content of $x = 3.25$, which suggests structural changes. This effect is also reflected in the irreversible change of the unit cell volume (Figure S4). At both the onset and the end of the 5th deep discharge, the unit cell volume is larger than at the onset and end of the 2nd deep discharge, which is showing irreversible expansion of the unit cell during cycling. This irreversible expansion is attributed to an increasing amount of Na-ions which, over the course of cycling get increasingly trapped in the structure. A correlation between structural changes and electrochemistry has been reported previously^[26,27], although for a different system (Ge as LIB anode) and different parameters (C-rate).

To confirm the insertion of Na^+ into crystal structure interstices, the diffraction pattern of a hypothetical NVO structure with a Na^+ -content of 6 was simulated in **Figure 7**. The pattern at OCP ($\text{Na}_{2.5}\text{V}_6\text{O}_{16}$) was simulated using the unmodified $P12_1/m1$ unit cell. For the simulation of $\text{Na}_6\text{V}_6\text{O}_{16}$, all α and β positions are fully occupied, and additional Na^+ is inserted into the four interstices (0.5 Na^+ each) of the initial unit cell (Figure 3b). These simulations for $\text{Na}_6\text{V}_6\text{O}_{16}$ and $\text{Na}_{2.5}\text{V}_6\text{O}_{16}$ are qualitatively similar. The simulated pattern of $\text{Na}_6\text{V}_6\text{O}_{16}$ shows an anticipated shift to lower angles as compared to the simulated OCP pattern, as well as some new low intensity reflections (Figure 7). The NVO pattern measured at the end of the 5th discharge shows features from both simulations, including the new reflections (Figure S5). This indicates a coexistence of regions with and regions without Na^+ in the interstices, *i.e.*, a two-phase region, which corresponds well with the long plateau observed for the galvanostatic discharge tests. Thus, four Na-sites ($2x\alpha$, $2x\beta$) in the unit cell can potentially be occupied reversibly without detrimental structural effects, resulting in a high stability for the narrow potential region. For a Na^+ -content > 3.25 , *i.e.*, fully occupied α and partially occupied β positions, it is concluded that interstices are filled and Na-rich regions form (interstices are occupied). This latter process is irreversible. It should be noted that this new structure is different from the one which was shown to form upon Li^+ -insertion into LVO.^[28] Thus,

although isostructural initially, NVO forms a different phase upon Na^+ -insertion than LVO does upon Li^+ -insertion.

Structural irreversibility is confirmed by the development of the integrated areas of the (100), (001) and (020) reflections. Between the beginning of the second deep discharge and the fifth deep discharge (Figure 6a) the areas of several reflections irreversibly decrease by 20 – 30%. One potential reason for this is a distortion of the regular arrangement of the crystal structure upon Na^+ -insertion, leading to a loss of the long-range order, and thus a decrease of reflection intensity. As Na^+ -insertion could be more detrimental to the structure than Li^+ -insertion, due to its larger ionic radius, this effect is potentially amplified compared to Li^+ -insertion. Loss of crystallinity also explains the fading of the capacity accompanied by the lack of distinct plateaus in the discharge curves after several cycles.

Overall, our data show parallel development of structural and electrochemical reversibility. Between 4.0 V – 1.6 V, the lattice parameters show reversible changes as Na^+ is inserted into and extracted from the distinct lattice sites α and β , with a concomitant stable electrochemical behaviour for > 100 charge / discharge cycles. Insertion of higher Na-amounts into interstices results in a higher capacity, but has a detrimental effect on the reversibility of both structural changes and electrochemical behaviour. Irreversible changes of the lattice parameters result in some loss of long range order, and a concomitant irreversible capacity fading.

2.3.2. Advantage of $\text{Li}_{2.55}\text{V}_6\text{O}_{16}$ in a Sodium-Ion Battery

LVO was cycled vs. $\text{Na}|\text{Na}^+$ in order to test whether the Li-ions have an effect on the performance. If *operando* ion exchange resulted in a complete replacement of Li^+ by Na^+ , cycling stability is expected to be similar.

In contrast to the pattern development of NVO, some significant changes become apparent when cycling LVO between 4.0 V – 1.6 V (Figure S7). Particularly, during discharge, the reflection at approximately $2\theta = 8.9^\circ$ appears to broaden, and eventually a new reflection can be resolved at a lower angle ($2\theta \sim 8.2^\circ$), indicating the co-existence of two phases. This (100) reflection is indicative of the interlayer spacing between the VO_x -layers, between which Na^+ inserts during discharge. During cycling, the new low angle reflection becomes more pronounced (Figure S8), while the intensity of the original reflection continuously decreases. The patterns in **Figure 8a** show the gradual change from LVO (lowest pattern) to a Li^+ -modified NVO (3rd pattern). These patterns were measured at 4.0 V in consecutive cycles. As reference, the diffraction pattern of NVO in the 3rd cycle at the same potential is shown at the top. As can be seen in Figure 8a, the initial (100) peak for LVO eventually disappears, and only the reflection at a lower angle remains. The XRD pattern of LVO after several cycles shows a strong resemblance to the NVO pattern at the same potential. In the charged state after three cycles, for both NVO and LVO the (100) reflections occur at $2\theta = 8.13^\circ$. While, during charge, both Li^+ and Na^+ are extracted during discharge, the insertion of Na^+ is favored owing to the large amount of Na^+ in the system.

Thus, based on the similarity of the NVO and LVO patterns after the 3rd charge, our data show that an *operando* ion-exchange occurred, and LVO partially transforms into NVO. One explanation for the difference between NVO and LVO regarding both capacity and cycling performance is that, despite structural conversion, some Li^+ remains in the original sites stabilizing the structure.

This interpretation has been substantiated by electrochemical *operando* laboratory scale XRD measurements.^[29] Figure 8b-e show the development of the *a*-lattice parameter of the original

LVO and the mixed phase in consecutive cycles. As can be seen in Figure 8b, the a -lattice parameter does not increase for LVO during the first discharge in the narrow potential range. The NVO phase already emerges during the first discharge (Figure S8). At the start of the second discharge (until 1.6 V, Figure 8c), the NVO phase is present from the beginning, and both phases coexist, while neither shows a remarkable increase of the a -lattice parameter. In the subsequent discharge steps (to 1.0 V, Figure 8d-e), reflections indicating the LVO phase gradually disappear. Rather broad reflections of LVO after several cycles, as well as not quite full accordance of every reflection with NVO (Figure 8a), suggest that some Li^+ still remains and stabilizes the structure. This is substantiated by the slightly smaller value ($\sim 0.1 \text{ \AA}$) for the a -lattice parameter of the converted structure as compared to the ‘pristine’ NVO phase (Figure 8 b-e). Upon applying Vegard’s law^[30] to this Li^+/Na^+ -vanadate system we find that the contribution from the LVO-phase is of the order of 10%. Thus, it can be concluded that the majority of Li^+ is replaced by Na^+ during cycling. The effect of this Li^+ -remnant is an increase of cycling performance.

3. Conclusions

In parallel to the electrochemical measurements in NIB half cells, we monitor the structure by employing *operando* synchrotron X-ray diffraction for studying “native” NVO ($\text{Na}_{2.46}\text{V}_6\text{O}_{16}$) and “native” LVO ($\text{Li}_{2.55}\text{V}_6\text{O}_{16}$) cathodes. When NVO is cycled between 4.0 V – 1.6 V, Na-ions reversibly occupy two different crystallographic sites, α and β , which results in remarkable cycling stability. Upon discharge to 1.0 V, however, Na-ions additionally occupy interstitial sites in the crystal structure. This occupation of interstices induces irreversible structural change with some loss of crystallinity concomitant with a decrease in capacity. Capacity fading increases with an increase of the ionic radius of the alkali ions ($\text{K}^+ > \text{Na}^+ > \text{Li}^+$), suggesting that smaller ions stabilize the structure due to the formation of stronger bonds with the vanadate layers. This correlation of structural variation and electrochemical

performance also suggests a route towards improvement of cycling stability. Key is a minor Li^+ -retention in an $\text{A}_{2+x}\text{V}_6\text{O}_{16}$ structure, where A in the “native” structure is Li. Even though an *operando* exchange of the majority of Li^+ -ions by the vast abundance of Na-ions takes place, the remaining Li^+ -ions (~10%) are sufficient to stabilize the layered structure, thus diminishing the irreversible structural damage. The nature of this damage has been identified in this paper. These experimental results pave the way for further exploitation of the role of small ions in lattice stabilization that increases cycling performance.

4. Experimental Section

Synthesis and Electrode Preparation: NVO was synthesized as described previously.^[14] 20 mL of a vanadium pentoxide solution (0.01 M, Sigma Aldrich, 98%) in deionized water was mixed with a sodium hydroxide solution (0.01 M, Sigma Aldrich, 98%) and stirred overnight to obtain a brownish-orange solution. It was transferred to a 50 mL Teflon-lined stainless steel autoclave and then heated to 180°C for 48 h. The resulting precipitate was filtered and washed using deionized water, and dried at 80°C for 4 h. The resulting powder was annealed in air at 400°C for 2 h. The chemical composition $\text{Na}_{2.46}\text{V}_6\text{O}_{16}$ was determined by ICP-OES.

To synthesize LVO^[31], a solution of CH_3COOLi in DI water was prepared. Then V_2O_5 was added (molar ratio V:Li = 1:1.2) and dispersed, followed by the stepwise addition of 8.5 mL H_2O_2 (32%). Afterwards, the orange-brownish solution was stirred for 3 h, and subsequently heated at 110°C for 24 h. The resulting powder was heated at 400°C for 2 h. The chemical composition $\text{Li}_{2.55}\text{V}_6\text{O}_{16}$ was determined by ICP-OES. KVO was synthesized using a hydrothermal process.^[32] 2 mmol of K_3VO_4 were dissolved in 30 mL DI water and vigorously stirred. 2 M HCl was added until the pH was 3.0 and the solution turned orange. This step was followed by 5 min of gentle stirring. Then, the solution was heated to 200°C for 24 h in an autoclave. The product was centrifuged, washed with DI water and ethanol, and subsequently dried at 50°C. Unlike for NVO and LVO, a final calcination step was omitted, as it leads to

irreversible phase transformation. The chemical composition $K_{1.8}V_6O_{16}$ was determined by energy dispersive X-ray spectroscopy.

Composite electrodes were prepared by mixing the active material, acetylene black (Alfa Aesar, >99%), and polyvinylidene fluoride (PVDF, Arkema, Kynar HSV 900) at a weight ratio 6:2:2 with *N*-methyl-2-pyrrolidone (NMP) to form a homogeneous slurry. This slurry was then coated onto Al foil using a doctor blade. The dried coating was punched into circular electrodes ($\varnothing = 16$ mm). Crystallographic water was found previously in NVO with 0.6 molecules of water per formula unit at room temperature using thermogravimetric analysis.^[14] In order to maximally reduce the water content, all electrodes studied were exposed to long-term (17 hours) drastic drying at 110°C in vacuum (10^{-6} bar) and then assembled in 2016 type coin cells with sodium metal as the anode (half cell). Glass fibre (Whatman) was used as separator, and the electrolyte for all measurements was a 1 M solution of NaClO₄ in a mixture of propylene carbonate (PC) and ethylene carbonate (EC) (wt % 1:1).

Structure and Morphology: Powder X-ray diffraction of the synthesized materials was performed on a Rigaku SmartLab X-ray diffractometer (200 mA, 45 kV) in reflection mode with Cu-K α radiation, *i.e.*, with a wavelength of 1.54 Å. For NVO, a Rietveld refinement was employed in the PDXL2 software (.cif file: Inorganic Crystal Structure Database 164514). Based on this, the lattice parameters are $a = 7.207(4)$ Å, $b = 3.596(2)$ Å, and $c = 12.124(7)$ Å. The angle β between the a - and c -lattice parameters is $107.80(2)^\circ$ ($R_{WP} = 9.63$, $S = 4.8299$). For LVO, using the same approach, the lattice parameters were found to be $a = 6.648(1)$ Å, $b = 3.592(1)$ Å, and $c = 11.988(1)$ Å, and $\beta = 107.758(2)^\circ$ ($R_{WP} = 11.22$, $S = 5.3687$). For KVO, according to a Pawley fit, the lattice parameters are $a = 16.325$ Å, $b = 3.595$ Å, and $c = 12.171$ Å, with an angle $\beta = 106.63^\circ$. As this fit was performed with the supercell, the a -lattice parameter is $\sim$ twice as large as for LVO and NVO. The crystal structure in Figure 3 was

drawn from the NVO .cif file using the CrystalMaker software (version 8.76). Diffraction patterns (Figure 7) were simulated using the Mercury software (version 3.6). For field emission scanning electron microscopy (FESEM), a Zeiss Supra 55 FESEM was used.

Electrochemical Measurements: Galvanostatic cycling was carried out using a Neware battery tester system. Galvanostatic intermittent titration technique was measured using a Biologic VMP3 potentiostat. The constant current pulse was 50 mA for 200 seconds, with a subsequent OCP relaxation period of 5 h. If the potential relaxation stabilized below a change of $dE/dt = 2 \text{ mV h}^{-1}$ the next current pulse was inserted. The diffusion coefficient was calculated according to the following formula:

$$D = \frac{4}{\pi} \left(\frac{i V_m}{z_A F S} \right)^2 \left[\frac{\left(\frac{dE}{d\delta} \right)}{\left(\frac{dE}{d\sqrt{t}} \right)} \right]^2$$

In this equation, V_m is the molar volume of the unit cell, i is the applied current, z_A is the charge number, F is Faraday's constant, S is the electrode/electrolyte contact area which was assumed to be the geometric surface of the electrode, $\frac{dE}{d\delta}$ is the slope of the Coulometric titration curve, $\frac{dE}{d\sqrt{t}}$ is the slope of the linearized plot of the potential $E(V)$ during the current pulse. The calculation for the diffusion coefficients is based on the volume of the initial unit cell; even though its volume changes slightly, this can be neglected in light of the significant changes of D_{Na} .

Synchrotron in operando diffraction measurements: A small hole (3 mm in diameter) was drilled into commercial 2016 coin cells and subsequently sealed using Kapton film (25 μm) and epoxy resin. The active material was prepared as a pellet by mixing it with acetylene black and teflonized acetylene black (6:2:2) and pressing it onto aluminum foil. Synchrotron X-ray diffraction was performed at the Stanford Synchrotron Radiation Lightsource at

beamline 11-3. The beam energy was 12.7 keV, and a MAR345 area detector was used. The scattering vector range measured was $0.45 - 5.0 \text{ \AA}^{-1}$. The sample-detector distance was 166.9 mm and the GSAS 2 software³² was used to convert the diffraction data from 2D to 1D and concurrently from Q to 2θ for better comparability with previous studies. The sample was rocked by 0.3 mm in one direction to improve the powder averaging.

Laboratory scale in operando X-ray diffraction: Measurements were performed using a set-up without Kapton described previously using a Rigaku SmartLab X-ray diffractometer (200 mA, 45 kV)^[29]. This was done to avoid the Kapton reflections in the pattern. The position of both the original and the newly emerging (100) reflection were determined based on maximum reflection intensity, and employed to monitor the development of the a -lattice parameter of the unit cell.

[Further details of the crystal structure investigation(s) may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-164514 and - 67844]

Supporting Information

Supporting Information is available from the Wiley Online Library.

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References

- [1] D. Kundu, E. Talaie, V. Duffort, L. F. Nazar, *Angew. Chemie Int. Ed.* **2015**, *54*, 3431.
- [2] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, *Chem. Rev.* **2014**, *114*, 11636.
- [3] V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-González, T. Rojo, *Energy Environ. Sci.* **2012**, *5*, 5884.
- [4] V. Palomares, M. Casas-Cabanas, E. Castillo-Martínez, M. H. Han, T. Rojo, *Energy Environ. Sci.* **2013**, *6*, 2312.
- [5] H. Pan, Y.-S. Hu, L. Chen, *Energy Environ. Sci.* **2013**, *6*, 2338.
- [6] B. L. Ellis, L. F. Nazar, *Curr. Opin. Solid State Mater. Sci.* **2012**, *16*, 168.
- [7] M. D. Slater, D. Kim, E. Lee, C. S. Johnson, *Adv. Funct. Mater.* **2013**, *23*, 947.
- [8] S.-W. Kim, D.-H. Seo, X. Ma, G. Ceder, K. Kang, *Adv. Energy Mater.* **2012**, *2*, 710.
- [9] M. Okoshi, Y. Yamada, A. Yamada, H. Nakai, *J. Electrochem. Soc.* **2013**, *160*, A2160.
- [10] Y. Yamada, Y. Iriyama, T. Abe, Z. Ogumi, *Langmuir* **2009**, *25*, 12766.
- [11] Y. Yamada, Y. Koyama, T. Abe, Z. Ogumi, *J. Phys. Chem. C* **2009**, *113*, 8948.
- [12] K. Kuratani, N. Uemura, H. Senoh, H. T. Takeshita, T. Kiyobayashi, *J. Power Sources* **2013**, *223*, 175.

- [13] S. P. Ong, V. L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. Ma, G. Ceder, *Energy Environ. Sci.* **2011**, *4*, 3680.
- [14] S. Hartung, N. Bucher, V. S. Nair, Y. L. Cheah, Y. Wang, H. E. Hoster, M. Srinivasan, *Chemphyschem* **2014**, *15*, 2121.
- [15] S. Tepavcevic, H. Xiong, V. R. Stamenkovic, X. Zuo, M. Balasubramanian, V. B. Prakapenka, C. S. Johnson, T. Rajh, *ACS Nano* **2012**, *6*, 530.
- [16] H. He, G. Jin, H. Wang, X. Huang, Z. Chen, D. Sun, Y. Tang, *J. Mater. Chem. A* **2014**, *2*, 3563.
- [17] H. Liu, H. Zhou, L. Chen, Z. Tang, W. Yang, *J. Power Sources* **2011**, *196*, 814.
- [18] S. Hartung, N. Bucher, H.-Y. Chen, R. Al-Oweini, S. Sreejith, P. Borah, Z. Yanli, U. Kortz, U. Stimming, H. E. Hoster, M. Srinivasan, *J. Power Sources* **2015**, 288, 270.
- [19] G. Wang, G. Pistoia, *J. Electroanal. Chem.* **1991**, *302*, 275.
- [20] K. West, B. Zachau-Christiansen, T. Jacobsen, *Solid State Ionics* **1988**, 28-30, 1128.
- [21] K. West, B. Zachau-Christiansen, T. Jacobsen, S. Skaarup, *J. Power Sources* **1989**, *26*, 341.
- [22] K. West, B. Zachau-Christiansen, T. Jacobsen, S. Skaarup, *Solid State Ionics* **1990**, *40/41*, 585.
- [23] D. Nguyen, J. Gim, V. Mathew, J. Song, S. Kim, D. Ahn, J. Kim, *ECS Electrochem. Lett.* **2014**, *3*, A69.
- [24] H. Kang, Y. Liu, M. Shang, T. Lu, Y. Wang, L. Jiao, *Nanoscale* **2015**, *7*, 9261.
- [25] Y. Dong, S. Li, K. Zhao, C. Han, W. Chen, B. Wang, L. Wang, B. Xu, Q. Wei, L. Zhang, X. Xu, L. Mai, *Energy Environ. Sci.* **2015**, *8*, 1267.
- [26] L. Y. Lim, S. Fan, H. H. Hng, M. F. Toney, *Adv. Energy Mater.* **2015**, *5*, 1500599.
- [27] L. Y. Lim, S. Fan, H. H. Hng, M. F. Toney, *J. Phys. Chem. C* **2015**, *119*, 22772.
- [28] L. A. de Picciotto, K. T. Adendorff, D. C. Liles, M. M. Thackeray, *Solid State Ionics*

1993, 62, 297.

- [29] S. Hartung, N. Bucher, R. Bucher, M. Srinivasan, *Rev. Sci. Instrum.* **2015**, 86, 086102.
- [30] L. Vegard, *Zeitschrift fuer Physik.* **1921**, 5, 17.
- [31] M.-X. Zhang, Y.-X. Zhang, *Chinese J. Inorg. Chem.* **2012**, 28, 2065.
- [32] L. Bai, Y. Xue, J. Zhang, B. Pan, C. Wu, *Eur. J. Inorg. Chem.* **2013**, 2013, 3497.

Figure 1. Cycling performance of LVO, NVO, and KVO in the potential regions a) 4.0 V – 1.0 V and b) 4.0 V – 1.6 V.

Figure 2. NVO, Narrow Range. Development of the X-ray diffraction pattern (synchrotron radiation, $\lambda = 0.974 \text{ \AA}$) during charge/discharge (* denotes aluminium reflections, + denotes teflonized acetylene black).

Figure 3. NVO crystal structure without (left) and with interstices marked (right).

Figure 4. NVO, Narrow Potential Range. a) Changes of the lattice parameters (top/black: c -lattice parameter, middle/red: a -lattice parameter, bottom/blue: b -lattice parameter). Note: y-axis: different spacing for lattice parameters a , b , c (same spacing: Figure S11), b) Changes of the integrated areas of the (001), (020) & (100) reflections in the first cycle, c) galvanostatic charge / discharge profile.

Figure 5. NVO, Potential Range. a) Changes of the lattice parameters in the 1st cycle from 4.0 V – 1.0 V (top/black: c -lattice parameter, middle/red: a -lattice parameter, bottom/blue: b -lattice parameter). Note: y-axis: different spacing for lattice parameters a , b , c (same spacing: Figure S11), b) Changes of the integrated areas of the (001), (020) & (100) reflections in the first cycle (the difference between the endpoint of the discharge and the starting point of the charge is due to cell change after the discharge), c) galvanostatic charge / discharge profile.

Figure 6. NVO, Wide Potential Range. a) Changes of the lattice parameters (top/black: c -lattice parameter, middle/red: a -lattice parameter, bottom/blue: b -lattice parameter) in the 2nd and 5th cycle from 4.0 V – 1.0 V (development 2nd discharge: $a = 7.21 \text{ Å} - 7.28 \text{ Å}$, $b = 3.61 \text{ Å} - 3.67 \text{ Å}$, $c = 12.20 \text{ Å} - 12.51 \text{ Å}$, development 5th discharge: $a = 7.25 \text{ Å} - 7.31 \text{ Å}$, $b = 3.61 \text{ Å} - 3.67 \text{ Å}$, $c = 12.22 \text{ Å} - 12.56 \text{ Å}$.) Note: y-axis: different spacing for lattice parameters a , b , c (same spacing: Figure S11), b) Changes of the integrated areas of the (001), (020) & (100)

reflections for the 2nd and 5th discharge from 4.0 V to 1.0 V, c) galvanostatic charge / discharge profile (the glitches in the 5th discharge were due to problems with the coin cell holder; this did not influence the typically observed characteristics in the 5th discharge for this material); the measurements presented in this figure were conducted with the same cell.

Figure 7. Top/Black: XRD pattern (synchrotron radiation, $\lambda = 0.974 \text{ \AA}$) of NVO at the end of the 5th discharge (+: reflections attributed to teflonized acetylene black used for making the pellets and from the epoxy resin used for sealing the coin cells; *: aluminum reflections); Middle/Grey: Simulated pattern based on the original structure, Bottom/Blue: Simulated pattern of the NVO structure with fully occupied lattice sites and interstices ($\text{Na}_6\text{V}_6\text{O}_{16}$); dotted lines denote significant new reflections.

Figure 8. a): XRD pattern (synchrotron radiation, $\lambda = 0.974$ Å) of LVO at 4.0 V in the 1st, 2nd, and 3rd cycle, and XRD of NVO at 4.0 V in the 3rd cycle, (hkl) of LVO and NVO at OCP (*: aluminum reflections; ⁺: teflonized acetylene black); b) – e): change in the a -lattice parameter for LVO (pristine) and NVO (newly emerging) during cycling (data based on Figure S8).

Na⁺-insertion into Na_{2.46}V₆O₁₆ (NVO) and Li_{2.55}V₆O₁₆ (LVO) were investigated using *in operando* synchrotron X-ray diffraction. Two crystallographic sites (orange, red) are reversibly occupied upon Na⁺-insertion into NVO between 4.0 V – 1.6 V. In contrast, at lower potentials Na⁺ occupies interstices (blue) resulting in irreversible structural changes concomitantly with capacity fading. For LVO, cycling performance is enhanced due to minor Li⁺-retention.

Sodium-ion battery

*Steffen Hartung, Nicolas Bucher, Joseph B. Franklin, Anna M. Wise, Linda Y. Lim, Han-Yi Chen, Johanna Nelson Weker, Maria-E. Michel-Beyerle, Michael F. Toney, Madhavi Srinivasan**

Mechanism of Na⁺ Insertion in Alkali Vanadates and its Influence on Battery Performance.

Supporting Information

Mechanism of Na⁺ Insertion in Alkali Vanadates. and its Influence on Battery Performance.

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The Supporting Information comprises:

Figure S1) Powder XRD data for Li_{2.55}V₆O₁₆ (LVO), Na_{2.46}V₆O₁₆ (NVO), and K_{1.8}V₆O₁₆ (KVO).

Figure S2) FESEM pictures of LVO, NVO, and KVO.

Figure S3) Galvanostatic discharge profile of LVO, NVO, and KVO (20 mA g⁻¹) in the 1st and 5th cycle

Figure S4) Changes in the NVO unit cell volume for all cycles.

Figure S5) Depiction of the new reflections in the NVO pattern at the end of the 5th discharge to 4.0 V.

Figure S6) Synchrotron *operando* measurement of LVO in the first cycle between 4.0 V – 1.6 V.

Figure S7) Development of the (100) reflection of LVO during *operando* cycling using a laboratory X-ray diffraction set-up.

Figure S8) Relaxation behavior of NVO and LVO in the galvanostatic intermittent titration technique (GITT) measurement at various potentials.

Figure S9) Development of the diffusion coefficient of NVO and LVO as measured by GITT during one discharge to 1.0 V

Figure S10) Development of the NVO lattice parameters during cycling with uniform spacing on the y-axis.

Figure S1. XRD patterns ($\text{Cu}_{K\alpha}$ -radiation, $\lambda = 1.54 \text{ \AA}$) of $\text{Li}_{2.55}\text{V}_6\text{O}_{16}$ (LVO), $\text{Na}_{2.46}\text{V}_6\text{O}_{16}$ (NVO) and $\text{K}_{1.8}\text{V}_6\text{O}_{16}$ (KVO).

Figure S2. SEM image of a) $\text{Li}_{2.55}\text{V}_6\text{O}_{16}$ (LVO), b) $\text{Na}_{2.46}\text{V}_6\text{O}_{16}$ (NVO), and c) $\text{K}_{1.8}\text{V}_6\text{O}_{16}$ (KVO).

Figure S3. Galvanostatic discharge profile of LVO, NVO and KVO between 4.0 V – 1.0 V, 1st & 5th discharge (20 mA g⁻¹). The onset of the long plateau is at a deeper potential for LVO as compared to NVO and KVO. The radius of Li⁺ is smaller compared to Na⁺ and Li-O-bonds are typically stronger than Na-O bonds.^[1,2] This difference potentially results in an increased electrostatic attraction of the surrounding VO_x-polyhedra, and thus in a smaller unit cell for LVO than for NVO. Thus, the electrochemical force to insert Na⁺ into the LVO structure needs to be higher, which would explain the plateau at a lower potential as compared to the Na- and K-analogue.

Figure S4. Change of the unit cell volume during a) discharge / charge between 4.0 V – 1.6 V, b) discharge / charge between 4.0 V – 1.0 V, c) 2nd and 5th discharge to 1.0 V.

Figure S5. XRD pattern development (synchrotron radiation, $\lambda = 0.974 \text{ \AA}$) of NVO at the end of the 5th discharge.

Figure S6. Development of the X-ray pattern (synchrotron radiation, $\lambda = 0.974 \text{ \AA}$) of LVO in the narrow potential region between 4.0 V – 1.6 V (*: aluminum reflections; +: teflonized acetylene black).

Figure S7. Development of the $(100)_{\text{LVO}}$ and the $(100)_{\text{NVO}}$ reflection as measured with a laboratory scale diffractometer ($\text{Cu}_{\text{K}\alpha}$ -radiation, $\lambda = 1.54 \text{ \AA}$) in reflection mode.

Figure S8. Time-dependent variation of the GITT curve of NVO and LVO: a) before the 1st plateau, b) during the first plateau, c) during the 2nd plateau.

Relaxation times vary during cycling. For NVO, up to a Na⁺-content of approximately 2.8, *i.e.*, until the end of the first plateau, the system relaxes after one current pulse (a) and b)). At higher Na⁺-contents, in the second plateau, the material is clearly not in equilibrium after 5 hours of relaxation time (c). As relaxation criteria were the same throughout the measurement (5 hours, or a potential change of $< 2 \text{ mV h}^{-1}$), this behavior is attributed to a decrease of electric and/or ionic conductivity. For LVO, relaxation times are comparable to NVO. While the system appears to be in equilibrium after a relaxation time of 5 hours or less until the end of the first plateau, *i.e.*, a Na⁺-content of ~ 3.1 (a), b)), it does not fully relax anymore in the long plateau at 1.3 V. Thus, similar to NVO, electronic and/or ionic conductivity decreases upon insertion of high Na⁺-contents.

Figure S9. Development of the diffusion coefficient for Na^+ during the discharge of a) NVO (dotted lines indicate which site is being filled up in the respective range of Na-occupancy) and b) LVO, as measured by galvanostatic intermittent titration technique (GITT).

Na^+ -diffusion in NVO and (initial) LVO: In section 3.2, we correlated structural and electrochemical reversibility and suggested that different sites in the crystal structure are occupied successively. In this section, we investigate if this is also reflected in the diffusion behaviour of Na^+ within the active electrode material using galvanostatic intermittent titration technique (GITT).^[3,4] Changes in the occupation of lattice sites or phase changes often result

in a change of the diffusion behavior of the respective ions in the crystal structure.^[5] Therefore, GITT was employed to monitor the change of the diffusion properties of NVO and LVO and to relate this to the structural changes described above.

The GITT for NVO is in good qualitative agreement with the galvanostatic discharge curve. In general, the long relaxation times are indicative of rather slow kinetics. The effective diffusion coefficient (Figure S10), for Na⁺ in the NVO structure is relatively constant at the beginning of the discharge up to a Na⁺-content of approximately 2.2. At the same Na⁺-content at which the discharge curve reaches a plateau, Na⁺-diffusion in the structure also decreases, followed by an increase at the end of the electrochemical plateau. At approximately $x = 3.25$, Na⁺-diffusion drops again; this coincides with the onset of the plateau at 1.3 V in the discharge curve. Minor differences regarding Na⁺-content between the galvanostatic measurements described above, and GITT measurements, are attributed to diffusion processes during relaxation times.^[3] For oxide cathodes, a minimum of the diffusion constant in combination with a plateau in the galvanostatic profile is typical for structural changes^[5]. This suggests, as also argued above based on structural data, that until the diffusion minimum Na⁺ occupies the pre-defined lattice sites, the α and β sites, in the given crystal structure. However, the XRD data shows no phase transition for the region around the diffusion coefficient minimum. It can be hypothesized that the minimum corresponds to a rearrangement of the Na-ions between the different sites, but ultimately the reason for the observed minimum remains unknown. The second minimum coincides with the plateau around 1.3 V. In this region, the XRD data shows structural changes, *i.e.*, insertion of Na⁺ into the interstices of the NVO structure. Thus, the GITT measurements support the hypothesis that for the initial insertion of Na-ions, the structure does not change, whereas subsequent structural changes occur based on the insertion of Na⁺ into the interstices (Figure 7, S7).

For LVO (Figure S10), the Na^+ -diffusion coefficient is slightly lower in the beginning than for NVO. This is attributed to the smaller interlayer spacing of LVO, which makes it harder for the Na-ions to move in the structure. This trend of higher ionic conductivity for NVO as compared to LVO was reported for the case of Li^+ -conductivity before.^[6] During discharge, the underlying trend is comparable, albeit the curve is more stretched out. However, the minimum of the diffusion coefficient which coincides with the plateau at 1.3 V starts at a higher Na^+ -content for LVO. Thus, structural changes seem to occur at higher Na^+ -contents as compared to NVO. This is in line with the initial hypothesis that Li^+ has a stabilizing effect on the structure, and can therefore increase cycling stability.

Figure S10. Development of the lattice parameters with uniform spacing on the y-axis during cycling between a) 4.0 V – 1.6 V, b) subsequent cycle between 4.0 V – 1.0 V, c), 2nd and 5th discharge to 1.0 V, respectively.

References

- [1] S. P. Ong, V. L. Chevrier, G. Hautier, A. Jain, C. Moore, S. Kim, X. Ma, G. Ceder, *Energy Environ. Sci.* **2011**, 4, 3680.
- [2] J. Malcolm W. Chase, *NIST-JANAF Thermochemical Tables.*, American Chemical Society ; American Institute Of Physics For The National Institute Of Standards And Technology, Washington, DC : New York, **1998**.
- [3] E. Markevich, M. D. Levi, D. Aurbach, *J. Electroanal. Chem.* **2005**, 580, 231.
- [4] D. W. Dees, S. Kawauchi, D. P. Abraham, J. Prakash, *J. Power Sources* **2009**, 189, 263.
- [5] K. M. Shaju, G. V. Subba Rao, B. V. R. Chowdari, *Electrochim. Acta* **2004**, 49, 1565.
- [6] M. Pasquali, G. Pistoia, *Electrochim. Acta* **1991**, 36, 1549.