Elucidating the Role of Defects for Electrochemical Intercalation in Sodium Vanadium Oxide

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Supporting Information

ABSTRACT: Na_{1.25+x}V_{2}O_{8} (with x < 0, = 0, and > 0) was synthesized via a wet chemical route involving the reduction of V_{2}O_{5} in oxalic acid and NaNO_{3} followed by calcination. It was possible to control the sodium composition in the final product by adjusting the amount of sodium precursor added during synthesis. It was revealed that deficient and excessive sodium contents, with respect to the ideal stoichiometry, are accommodated or compensated by the respective generation of oxygen vacancies and partial transition metal reduction, or cation disordering. When examined as NIB electrode material, the superior performance of the cation disordered material with excessive sodium was clearly demonstrated, with more than 50% higher storage capacity and superior rate capacity and cyclic stability. The formation of oxygen vacancies initially seemed promising but was coupled with stability issues and capacity fading upon further cycling. The disparity in electrochemical performance was attributed to variations in the electronic distribution as promoted through Na–ion interactions and the direct influence of such on the oxygen framework (sublattice); these factors were determined to have significant impact on the migration energy and diffusion barriers.

INTRODUCTION

The proliferation of electrical energy demand has driven the rapid progression of improved technologies related to energy distribution and storage. However, energy storage materials and devices have come to be viewed as a crux impeding advanced device development. Lithium-ion (Li-ion) batteries are a mature and robust technology because of their high energy density and portability. Despite their success in such application, Li-ion batteries (LIBs) are a poorly suited choice for large-scale energy storage applications given their high cost, density and portability. Despite their success in such application, Li-ion batteries (LIBs) are a poorly suited choice for large-scale energy storage applications given their high cost, density and portability. Despite their success in such application, Li-ion batteries (LIBs) are a poorly suited choice for large-scale energy storage applications given their high cost, density and portability. Despite their success in such application, Li-ion batteries (LIBs) are a poorly suited choice for large-scale energy storage applications given their high cost, density and portability. Despite their success in such application, Li-ion batteries (LIBs) are a poorly suited choice for large-scale energy storage applications given their high cost, density and portability. Despite their success in such application, Li-ion batteries (LIBs) are a poorly suited choice for large-scale energy storage applications given their high cost, density and portability. Despite their success in such application, Li-ion batteries (LIBs) are a poorly suited choice for large-scale energy storage applications given their high cost, density and portability.

Na-ion batteries (NIB) are attractive because sodium resources are seemingly inexhaustible as well as ubiquitous and, therefore, cost considerably less (by a factor of roughly 30–40 times) than lithium; additionally, sodium does not undergo an alloying reaction with aluminum at low voltage, as is the case with lithium, meaning that aluminum can replace copper as the anodic current collector, which equates to an overall cell cost savings of ∼2%. The lower operating voltage of Na-ion cells results in enhanced stability of the nonaqueous electrolyte but also manifests itself in lower energy density. The majority of the proposed electrode materials for Na-ion battery show similar or slightly lower specific capacity and redox potential than when used in Li-ion cells. Moreover, the accommodation of sodium in traditional host materials is difficult because the ionic radius and reduction potential of sodium are strikingly larger than that of lithium. Therefore, the de/sodiation process induces large distortions in the host lattice that ultimately lead to pulverization of the electrode and the impending failure of the cell. The majority of investigations to date examining Na-ion battery cathodes have focused on intercalation based materials, particularly layered transition metal oxides. The overall process of electrochemical intercalation can be broken down into three simultaneous and sequential processes: (i) redox reactions at the electrode–electrolyte interface, (ii) nucleation and growth of the new interfacial phase, and (iii) charge and mass transfer. Within the layered transition metal oxide paradigm, vanadium oxide is an attractive multifunctional material used for widespread application in various fields such as catalysis and energy storage. Of the many stoichiometries and polymorphs, sodium trivanadate, Na_{x}V_{3}O_{8}, is a propitious positive electrode material for alkali-ion insertion because of its low cost, easy synthesis, and solid electrochemical performance. This oxide has a layered structure, with the anionic V_{3}O_{8} layers held together by alkali ions, typically Li⁺ or Na⁺, which have respective theoretical capacities of 372 and 352 mA h g⁻¹ when cycled against their constituent metal. Simple defect modification is a powerful means toward improving material intercalation capabilities that has been receiving considerable interest lately as it can directly alter both...
chemical and structural characteristics; techniques of note include cationic disordering, amorphization, doping, partial cation reduction, and manipulation of intrinsic defects (e.g., oxygen vacancies, denoted V0 in the Kröger–Vink notation).4–12 Surface defects can directly impact alkali-ion intercalation by shifting the thermodynamics and improving kinetics.13 The presence of surface defects increases the surface energy and can potentially serve as nucleation sites that facilitate the electrochemical phase transition. Surface-reaction-limited dynamics predict the phase boundary extends from surface to surface along planes of fast ionic diffusion where defects or facet edges can act as nucleation sites.14 Such results have been verified experimentally, where defects have been reported to promote the phase transition of TiO2 by providing low energy mass transport routes during the phase transition process.15,16 Defects may also reduce the stress and the electrostatic repulsion between adjacent oxygen layers, which can directly alter the migration energy and diffusion barriers the alkali ion must overcome during intercalation.17

Disordering has been shown to increase the solid solution behavior, reduce the two-phase transformation domains, lower the alkali-ion extraction energy, and modify the diffusion/transport properties during the de/intercalation processes;18–25 the use of amorphous structures is proposed to work in a similar manner while providing a more open framework for ion migration.24–27 Cation disorder involves the intermixing between the alkali ion and the transition metal sublattice and is more likely to exist in systems where there are different redox sites, be it in the form of several transition metal elements or a single multivalent element. Doping is often used as a technique to achieve partial cation reduction, although the later can be successfully done without such means, to introduce mixed valence states in the transition metal and, thus, tune the electronic transport properties of the material.28 Mixed conductivity, both electronic and ionic, is necessary at the atomic scale for charge neutrality preservation during alkali-ion transport where the chemical diffusion coefficient is ultimately rate-limited by the slower of the two processes. The introduction of oxygen vacancies is well known for increasing conductivity in oxide materials.29,30 Supervalent metal doping in LiFePO4 was shown to increase the electronic conductivity of by a factor of ~104, effectively overcoming the low intrinsic limitations of the material.31

Several studies have been devoted to examining the effects of lithium nonstoichiometry in LIB electrodes, particularly for LiCoO2 where such effects are accommodated by oxygen vacancies that can also be accompanied by either cation mixing or perturbation of the oxygen stacking layers. Accordingly, the local environment of some cobalt ions can be modified by the presence of the oxygen vacancies. The structure of these lithium overstoichiometric compounds makes them more stable against the de/lithiation process and is a beneficial approach toward preventing structural distortion and, thus, demonstrate potential for LIB electrode development.32,33 Notwithstanding, the recent rejuvenation in NIB research activity has revealed, if nothing else, that analogous materials can behave substantially different than expected based off their prior LIB performance.34 There have been minimal reports concerning the role of defects on NIB electrode materials and the potential impact they may have on the overall electrochemical performance.35,36 Toward these ends, we propose synthesizing Na3V2O7 with oxygen vacancies and partial cation reduction by adjusting the sodium stoichiometry to induce the formation of such defects. Structural as well as chemical analyses were conducted to verify the presence of these defects, and the electrochemical performance of the corresponding materials was evaluated as positive electrode material for NIB application.

### EXPERIMENTAL PROCEDURE

**Material Synthesis.** All chemicals were analytical grade and used as received without further processing. Approximately 0.90 g of V2O5 (99.8%, Alfa Aesar) and 1.33 g of oxalic acid (Sigma–Aldrich) were incorporated into 40 mL of deionized water and stirred at room temperature until the formation of a clear blue solution was noted, indicating the formation of vanadium oxalate. The reaction can be expressed as follows:

\[
\text{V}_2\text{O}_5 + 3\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{VOC}_2\text{O}_4 + 2\text{CO}_2 + 3\text{H}_2\text{O} \quad (1)
\]

Subsequently, various amounts of NaN3O3 (99.995%, Aldrich) were added to the VOCCO4 solution under stirring for 1 h in order to control the sodium content. Three stoichiometric quantities of NaN3O3 corresponding to sodium contents of 0.75, 1.0, and 1.25, where 1.0 is the ideal stoichiometry of Na1.25V2O7 were then added. The solution was dried at 80 °C before calcination at 400 °C under ambient for 3 h. The obtained materials were designated as deficient (Na8.25V7.5O18, x < 1), stoichiometric (Na12.5V2O7, x = 1), and excessive (Na12.5V7.5O18, x > 1) as based on their stoichiometric sodium concentration.

**Characterization.** Microscopy investigations were carried out using a FEI Sirion scanning electron microscope (SEM). Nitrogen sorption was performed using a Quantachrome NOVA 4200e. The specific surface area, micro pore, and mesopore volumes were determined using multipoint Brunauer– Emmett–Teller (BET), t-method, and Barrett–Joyner–Halenda (BJH) desorption analyses, respectively. Thermogravimetric analysis (TGA) was conducted from room temperature to 600 °C (PerkinElmer TGA 7) under nitrogen flow at a heating rate of 5 °C min⁻¹. The phase of the calcined sodium vanadium oxides was studied using X-ray diffraction (XRD, D8 Bruker X-ray diffractometer) with Cu Kα radiation over the range of 10° to 70° (2θ), a step size of 0.02°, and an exposure time of 10 s. The accelerating voltage and current were 40 kV and 40 mA, respectively. The corresponding Rietveld refinement for each pattern was carried out using the GSAS package.37 The intensities of all the spectra were normalized to the highest intensity peak. Infrared absorption spectra were recorded using a PerkinElmer 1640 Fourier Transform Infrared (FTIR) Spectrophotometer with ATR. X-ray photoelectron spectroscopy (XPS) was completed using a Surface Science Instruments S-probe spectrometer. The X-ray spot size was 800 × 800 μm and the takeoff angle was 55°, corresponding to a sampling depth of approximately 50–70 Å. XPS data analysis was carried out using the Service Physics ESCA 2000-A analysis program (Service Physics, Bend, OR).

**Electrochemical Analysis.** An electrode slurry was prepared by mixing the synthesized Na3V2O7 powders, carbon black (Cabot Vulcan XC72R), and poly(vinylidene fluoride) (PVDF, MTI) binder dispersed in an N-methyl-2-pyrrolidone (NMP, Alfa Aesar) solution at a respective weight ratio of 70:12:8. The slurry was spread onto aluminum foil (99.3%, MTI) and dried in a vacuum oven at 80 °C overnight prior to coin-cell assembly. For electrochemical analysis, 2032 half-cells (Hoshen) were assembled in a glovebox (M Braun) coin-cell assembly. For electrochemical analysis, 2032 half-cells were charged and discharged using a LAND 2000 (LAND) electrochemical test system in the voltage range of 2.0 to 4.0 V with rates of C/10 (1 C = 1 h, for a 2032 cell). The charge/discharge experiments were carried out at different discharge rates (C/5, C/10, C, 2C). The charge/discharge experiments were carried out at different discharge rates (C/5, C/10, C, 2C).
propylene carbonate (anhydrous 99.7%, Sigma-Aldrich) (1:1 vol.), and Whatman GF/A glass microfiber filter were used as the counter/reference electrode, electrolyte, and separator, respectively. Cyclic voltammetry (CV) was completed using an electrochemical analyzer (CH Instruments, Model 605C) in the potential range of 4.0−1.5 V (vs Na/Na+). The current density and cycle stability performance of the electrodes were evaluated using a BT-2000 Arbin Battery Tester operating at room temperature. The half-cells were tested within the potential range of 4.0−1.5 V vs Na/Na+. The implementation of a high temperature thermal treatment from 0.01 to 10.0 mV s⁻¹ for enhanced electrochemical performance.

### RESULTS AND DISCUSSION

The chemical synthesis procedure utilized in this investigation allowed for the direct control, within certain constraints, of the sodium content. Thus, by adjusting the amount of NaNO₃ precursor added to the VOC₂O₄ solution it was possible to attain NaₓV₃O₈ products with deficient, ideal, and excess sodium stoichiometry. A moderately low calcination temperature (400 °C) was employed in order to preserve the purity and structural integrity of the material. When calcined at temperatures higher than 525 °C a NaₓV₆O₁₅ secondary phase would form, as determined through Rietveld refinement, that exhibits markedly lower kinetics toward sodium ions. Sodium plays a significant role in stabilizing the interlayer structure, and the implementation of a high temperature thermal treatment profile to affect the hydration level can result in collapse of the interlayer structure.

TGA was performed to verify that sodium content deficiency was not compensated by hydration or hydrogenation, as was the case for NaₓV₃O₈·nH₂O, where the water content was found to be inversely proportional to the sodium level. The deficient, stoichiometric, and excess Na samples were revealed to have considerably low water contents of 0.70, 0.48, and 0.26%, substantiating that sodium level manipulation was not compensated through a secondary mechanism (shown numerically in Table 1 and graphically in Figure S1 in Supporting Information (SI)).

<table>
<thead>
<tr>
<th>sample</th>
<th>water (wt %)</th>
<th>BET surface area (m² g⁻¹)</th>
<th>BJH pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>deficient</td>
<td>0.26</td>
<td>13.42</td>
<td>3.20</td>
</tr>
<tr>
<td>stoichiometric</td>
<td>0.48</td>
<td>11.41</td>
<td>3.18</td>
</tr>
<tr>
<td>excess</td>
<td>0.70</td>
<td>8.93</td>
<td>3.18</td>
</tr>
</tbody>
</table>

The morphology of the NaₓV₃O₈ compounds following calcination was observed by SEM, the micrographs of which are shown in Figure 1a−c. Comparison of the different samples demonstrates the profound effects that Na-content can have on morphology, homogeneity, and particle size distribution. The resulting particle morphology seems to shift from elongated nanoparticles with approximate width and thickness of 800 and 300 nm, respectively, to 900 nm long and 60 nm wide nanowires with increasing Na-content; correspondingly, the average particle size also decreases. It should be noted that the stoichiometric and excess sodium samples have a wider dispersion of particle morphology, where the elongated nanoparticle morphology is primarily maintained. The Na-deficient material (Figure 1a) has noticeable striations running along the edges that are apparent in the higher magnification images and are somewhat present in the images corresponding to the materials with higher Na-content, perhaps providing insight into the nanowire formation mechanism.

Quantitative elemental analysis was carried out using energy-dispersive X-ray spectroscopy (EDS), the results of which are tabulated and compared with their ideal values in Table 1. The experimentally determined sodium contents match incredibly well with the expected values based off of precursor quantities used during synthesis. These sodium compositions are accommodated by the formation of oxygen vacancies and partial transition metal reduction, and can be expressed as Naₓ₁₂₅₋ₓV₃O₈−ₓ₋₁ (x < 1) and Naₓ₁₂₅₋ₓV₃₋ₓO₈ (x > 1) for the deficient and excess sodium compositions, respectively; the vanadium valence will be verified by XPS. These suppositions are substantiated by previous studies involving overstoichiometric LiₓCoO₂ samples, where it was deduced that the charge
imbalance resulting from excess lithium is compensated by oxygen vacancies;\textsuperscript{40} however, structural and electrostatic considerations should not be as overly influential in this system considering the $d$-electron configurations, affecting the formal valence state and covalent bonding interactions with the nearest-neighbor anions, of the cobalt and vanadium redox couples are disparate. Furthermore, Rietveld refinement was successively completed to ensure that the detected elemental sodium originates from Na$_x$V$_3$O$_8$ and not some vanadia derivative or sodium oxide impurity.

Following calcination, the crystal structure of the samples was analyzed and could be indexed to Na$_{1.25}$V$_3$O$_8$ phase (space group: $P_{2_1}/m$ (11), JCPDS card 24-1156) via XRD, Figure 1d. Sodium trivanadate, Na$_{1+x}$V$_3$O$_8$, is a propitious positive electrode material for alkali-ion insertion because of its low cost, easy synthesis, and good electrochemical performance. This oxide has a layered structure, with the anionic V$_3$O$_8$ layers held together by alkali-ions, typically Li$^+$ or Na$^+$, distributed continuously puckered sheet of VO$_6$ octahedra that comprise ff are linked by corner-shared oxygen that e

The structure can be likened to an analogue of the barnesite or metahewettite groups.\textsuperscript{44} FTIR was conducted to distinguish the chemical nature and comparatively analyze the structural characteristics of the specimens with different Na-content, as shown in Figure 2a; the absorption band values have been compiled in Table S1 in SI. The absorption bands stemming from the symmetric stretching mode of the vanadyl V=$\equiv$O bond is observed at approximately 991 and 944 cm$^{-1}$ for all of the samples; the small inflections in the stoichiometric and excess Na content correspond to this mode as well. The 3-fold-coordinated oxygen asymmetric and symmetric stretching vibrations modes of V$\equiv$O$\equiv$V are represented by the bands localized at 745 and 527 cm$^{-1}$, respectively. The lack of sodium, or presence of oxygen vacancies, in the Na-deficient products with excess, ideal, and deficient sodium stoichiometry.

Table 2. Rietveld Refinement of Na$_x$V$_3$O$_8$ Products with Deficient, Stoichiometric, and Excess Sodium Stoichiometry

<table>
<thead>
<tr>
<th>sample</th>
<th>Na$_{1+x}$V$_3$O$_8$ phase (%)</th>
<th>lattice parameters</th>
<th>fit parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>JCPDS 24-1156</td>
<td>100</td>
<td>$a$ (Å): 7.32</td>
<td>$\chi^2$: 2.02</td>
</tr>
<tr>
<td>excess</td>
<td>94.4</td>
<td>$b$ (Å): 3.61</td>
<td>$wR_p$: 0.09</td>
</tr>
<tr>
<td>stoichiometric</td>
<td>98.6</td>
<td>$c$ (Å): 12.14</td>
<td>$R_p$: 0.06</td>
</tr>
<tr>
<td>deficient</td>
<td>98.3</td>
<td>$\beta$ (deg): 106.73</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. (a) FTIR, (b) V 2p/O 1s XPS, and (c) Na 1s XPS spectra of the Na$_x$V$_3$O$_8$ products with excess, ideal, and deficient sodium stoichiometry.
its largest impact on this mode (Table S1 in SI). The 840 cm$^{-1}$ band for the Na-decient sample can be attributed to the coupled vibration between the V=O and V—O—V bonds but may be an artifact resulting from oxygen vacancies.49,50

XPS was carried out on the samples prior to electrochemical testing in order to obtain more information on the chemical state of the vanadium species present. High-resolution scans, emphasizing the V 2p and O 1s peaks, were collected and are shown in Figure 2b, whereas Figure 2c showcases the Na 1s results. The raw fitted scans are displayed in Figure S3 in SI.

The trends between peak position, peak spacing, and their literature comparisons reveal that both the V 2p3/2 and O 1s orbital peak positions incrementally rose with sodium content. The V 2p3/2 /O 1s peak positions for the deicient, stoichiometric, and excess Na samples were 530.8/517.9, 531.1/518.3, and 531.2/518.4 eV, respectively. The valence of the vanadium phase was confrmed to be predominately pentavalent as determined by the difference in binding energy between the V 2p3/2 and O 1s orbital peak positions incrementally rose with sodium content. The V 2p3/2/O 1s peak positions for the deicient, stoichiometric, and excess Na samples were 530.8/517.9, 531.1/518.3, and 531.2/518.4 eV, respectively. The valence of the vanadium phase was confirmed to be predominately pentavalent as determined by the difference in binding energy between the V 2p3/2 and O 1s orbitals, which was approximately 12.8 eV for all of the analyzed specimens. The difference in binding energy AE between the O 1s and V 2p3/2 level is commonly used to determine the oxidation state of vanadium oxides.51−55 This was further corroborated by the V 2p3/2 and V 2p1/2 spin−orbit splitting of approximately 7.5 eV for all samples. These findings are consistent with literature reports.54,55

A noticeable shoulder on the low binding energy side of the V 2p3/2 peak for the stoichiometric and excess Na-content samples is indicative of a secondary vanadium species, namely V$^{4+}$. Previous studies have indicated that even in stoichiometric specimens, there is a slight preferential occupation of V$^{4+}$ at preferential vanadium sites.56 This is also expected as the ideal stoichiometry, Na$_{1.25}$V$_3$O$_8$, can only be achieved with the presence of some tetravalent vanadium species, but the comparison between the two is still valid because of their concentration differences. An additional feature of interest is the broad peak extending beyond the main O 1s peak in the 532.5 to 535 eV range for the Na-deicient sample that may be attributed to C—O(H).51 The Na 1s peak for all samples is approximately 1074 eV, which is somewhat higher than typical literature values, and there is a clear shift toward higher BE concurrent with the sodium content.54,57 The combination of EDX and XPS results tabulates the sodium contents ($x$ in Na$_x$V$_3$O$_8$) for the deicient, stoichiometric, and excess specimens at 0.92 ± 0.01 (Na$_{0.92}$V$_3$O$_8$), 1.18 ± 0.05 (Na$_{1.18}$V$_3$O$_8$), and 1.42 ± 0.04 (Na$_{1.42}$V$_3$O$_8$), respectively.

Cyclic voltammograms of the Na$^x$V$_3$O$_8$ specimens with varying Na-content collected from sweep rates ranging from 0.1 to 10 mV s$^{-1}$ are shown in Figure 3a−c, whereas a direct
comparison of the scans collected at a potential sweep rate of 1 mV s$^{-1}$ are shown in Figure 3d. The peak magnitude and area of the redox peaks noticeably increase with the potential sweep rate, whereas the oxidation peaks and corresponding reduction peaks shifted to higher and lower potentials, respectively, due to polarization at the higher sweep rates. These features confirm the favorable charge transfer kinetics even at high potential sweep rates. The raw peaks and their locations show similarities that have previously been correlated with annealing temperature; specifically, the sodium content would appear to be inversely related to crystallinity. However, this is known to not be the case as determined on the basis of Rietveld refinement.

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A linear dependency between the anodic and cathodic peak currents and the square root of the potential sweep rate; specifically, the sodium content would appear to be inversely related to crystallinity. However, this is known to not be the case as determined on the basis of Rietveld refinement.
experimental studies showing that the presence of oxygen vacancies can lead to the loss of domain order and capacity fading due to structural collapse, and a similar mechanism may play a role in the performance seen here.64

Electronic localization has been directly observed in other layered transition metal oxides—directly affirming that the exhibited electronic properties are strongly correlated to the Na-ion distribution in the interlayer space.65 Thus, the cationic distribution of the individual samples could differ significantly since the sodium content levels are unequal. On a more global level, the cationic distribution is comprised of: electrostatic repulsions between the individual Na-ions along the interlayer c axis, Na⁺−V⁵⁺ repulsion occurring through the common face of the VO₆ polyhedra, as well as the intraelectron interactions within the vanadium layers. For any given system, the cationic distribution will seek to reach a minimum. Thus, the cationic distribution is highly sensitive to the sodium content as it can have serious impact on the constituent influences. A slight change in sodium composition may even be enough to induce the formation of an entirely new cationic distribution.66

Electron transport has been demonstrated to be affected strongly by solid-solution formation and, correspondingly, other means of introduced atomic-level disorder.67 Consequently, the structure of excess sodium-containing Na₅₋₁V₃O₈ lends itself to both favorable mass and electronic charge transport. The excess sodium bolsters the mechanical integrity of the layered structure itself, whereas the Na⁺ in the original lattice gives way to additional metal–oxygen bonds other than V—O. This ultimately reduces the number of sp³ orbitals of oxygen available for bonding with the incoming sodium-ions, and the interaction between tetrahedrally coordinated Na⁺ and O²⁻ is weak enough to grant fast movement of sodium from site to site.68,69 Based purely on electrostatic considerations, it would be expected that Na₅₋₁V₃O₈ with excess sodium would suffer from low-migration energy given that the sodium sites generate strong electrostatic repulsion on one another. The activation of such forces would induce high migration energy barriers. Moreover, Na-ion ordering or structuring would also be anticipated to negatively impact sodium diffusion in a substantial manner provided the considerable effect of Na—Na interactions on the local Na migration energy. However, cationic mixing poses a route of overcoming these deficiencies by potentially perturbing the ordering of the transition metal sublattice, which would consequently result in a weaker Na ordering and thereby improve sodium diffusion. The defected (disordered) materials consistently delivered higher capacities than the more ordered (pristine) counterpart, clearly demonstrating the critical role of structural ordering on kinetics.

**CONCLUSIONS**

In the present work, we successfully synthesized defective Na₅₋₁V₃O₈ where it was possible to control the dominant defect type through sodium stoichiometry manipulation. Thus, Na-deficiency leads to the formation of oxygen vacancies and Na-excess leads to partial cation reduction, or the formation of a cation disordered structure. When examined as NIB electrode material, the superior performance of the Na-excess, cation disordered, materials was clearly revealed, especially at higher current discharge densities. The formation of oxygen vacancies initially seemed promising, but was coupled with stability issues and capacity fading with further cycling. The disparity in electrochemical performance was attributed to variations in the electronic distribution as promoted through Na-ion interactions and the direct influence of such on the oxygen framework (sublattice); these factors were determined to have significant impact on the migration energy and diffusion barriers. This study provides insight on defect and stoichiometry considerations for cathode materials and provides a potential mechanism toward significantly improving the performance of rechargeable alkali-ion batteries.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b02935.

Additional TGA, N₂ sorption analyses, Rietveld refinement, FTIR, XPS, and electrochemical data. (PDF)

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**Notes**

The authors declare no competing financial interest.

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