Communication

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Sodiation Kinetics of Metal Oxide Conversion Electrodes: a Comparative Study with Lithiation

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ABSTRACT:

The development of sodium ion batteries (NIBs) can provide an alternative to lithium ion batteries (LIBs) for sustainable, low-cost energy storage. However, due to the larger size and higher m/e ratio of the sodium ion compared to lithium, sodiation reactions of candidate electrodes are expected to differ in significant ways from the corresponding lithium ones. In this work, we investigated the sodiation mechanism of a typical transition metal-oxide, NiO, through a set of correlated techniques, including electrochemical and synchrotron studies, real-time electron microscopy observation, and *ab initio* molecular dynamics (MD) simulations. We found that a crystalline Na₂O reaction layer that was formed at the beginning of sodiation plays an

important role in blocking the further transport of sodium ions. In addition, sodiation in NiO exhibits a “shrinking-core” mode that results from a layer-by-layer reaction, as identified by *ab initio* MD simulations. For lithiation, however, the formation of Li anti-site defects significantly distorts the local NiO lattice that facilitates Li insertion, thus enhancing the overall reaction rate. These observations delineate the mechanistic difference between sodiation and lithiation in metal-oxide conversion materials. More importantly, our findings identify the importance of understanding the role of reaction layers on the functioning of electrodes, and thus provide critical insights into further optimizing NIB materials through surface engineering.

KEYWORDS: Sodiation, kinetics, nickel oxides, reaction pathways, conversion electrodes.

TOC:

Lithium ion batteries (LIBs) have enjoyed great success as power sources for portable electronics and are emerging as energy storage systems of choice for electric vehicles.¹ There have been also increasing interests in developing LIBs for grid storage applications. However, because of the high cost of the electrode materials and limited Li supplies, it is important to explore alternatives, such as a sodium-based battery, which can potentially offer a sustainable, low-cost solution for energy storage.²⁻⁹ Due to the many similarities between sodium and lithium

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3 chemistries, the development of sodium-ion batteries (NIBs), can benefit greatly from the
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5 knowledge developed over the past 25 years on LIBs,⁶⁻⁹ but differences in the lithiation and
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7 sodiation behaviors of electrode materials are evident. In the case of conversion anode materials
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9 for NIBs, only a few compounds have been found to be promising for sodiation reactions, such
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11 as the spinel NiCo_2O_4 .¹⁰ In transition metal oxides MO_x ($M = \text{Fe}, \text{Co}$ and Ni), the sodiation
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13 reactions have much lower capacities and slower kinetics than those commonly observed in
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15 lithiation reactions.^{11,12} The incorporation of cations in conversion electrode materials involves
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17 multiple processes, *i.e.*, Li^+/Na^+ diffusion into the electrode material, an electrochemical reaction
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19 between redox couples, and interfacial reactions between the electrode and electrolyte. Thus
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21 many parameters, such as electronic and ionic transport, the passivation layer formed at the
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23 electrode/electrolyte interface and the intrinsic reaction kinetics can affect the rate of the entire
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25 conversion reaction. To date, the specific rate-limiting steps for Na-ion batteries are not fully
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27 understood, even though the identification of these rate-limiting steps through direct
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29 characterization is critical for developing rechargeable NIBs. To address this question, we herein
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31 utilize multiple characterization techniques to present a comprehensive, correlated study of the
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33 sodiation and lithiation of a model MO_x conversion compound, *viz.*, simple rocksalt structured
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35 NiO that does not involve lithium intercalation or alloying.
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45 It generally is believed that the differences in the ionic size of Na^+ and Li^+ are correlated
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47 with the differences observed in their transport kinetics, which, in turn, leads to their distinctive
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49 electrochemical behaviors.⁶⁻⁹ However, the influence of increasing ionic size is not always
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51 intuitive.¹³⁻¹⁵ It has been reported that layered NaMO_2 compounds ($M = \text{V}, \text{Cr}, \text{Mn}$, and Fe)
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53 exhibit better intercalation kinetics and greater capacity than does LiMO_2 , due to differences in
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55 the stacking of transition-metal oxide layers, and the resulting preferred Li/Na sites and
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occupancy.^{7,8} On the other hand, in materials undergoing conversion reactions, there are not necessarily ionic diffusion channels in the structures and the predominant reaction mechanisms are not based on intercalation. Rather, displacement reactions occur as shown in Eq (1):

where M is a transition metal, and X = O, F, N, or S. The difference in the ionic sizes of Na⁺ and Li⁺ would not be expected to affect the reaction dynamics.^{12,16} Given these observations, we considered it valuable to investigate and compare sodiation and lithiation reactions of a conversion electrode with correlated approaches. In this study, we integrated the insights from a combination of multiple temporally and spatially-scaled characterization techniques, including electrochemical measurements, *in situ* transmission electron microscopy (TEM),¹⁷⁻²⁷ and *ab initio* molecular dynamics (MD) simulations to provide a comprehensive understanding of what governs the rate of sodiation of NiO nanosheets and compared it to the lithiation behavior.

NiO has been investigated as a conversion anode material for LIBs,¹¹ and it is very stable under electron irradiation and suitable for TEM observation.²⁷ The as-prepared NiO nanosheets in this study exhibit a 2D nature with nanoscale perforated holes on the (111) basal planes that may help to improve the reaction kinetics compared to that of micron-sized materials.^{27,28} The electrochemical measurements were performed in half-cells; *i.e.*, sodium or lithium metal was used as negative electrodes, and nickel oxide as the positive one. The charge-discharge profiles show that the sodiation reaction delivers a significantly lower capacity than does the lithiation reaction (Figure 1a and S1) under identical cycling conditions. The first sodiation discharge and charge capacities, respectively, are only 480 mAh g⁻¹ and 93 mAh g⁻¹, which is both much lower than those typically reported in the case of lithiation and far from the theoretical sodiation

capacity (718 mAh g^{-1}). Figure 1b presents the capacity retention and Coulombic efficiency for the sodium half-cell. Overall, the discharge/charge capacities gradually decreased starting from the second cycle (260 mAh g^{-1} and 96 mAh g^{-1}) and then stabilized after 40 cycles at $\sim 110 \text{ mAh g}^{-1}$ and $\sim 60 \text{ mAh g}^{-1}$ respectively. In addition, the Coulombic efficiency as a function of cycle number never exceeded 40-55%; much lower than that found in lithium half-cells.²⁸ This difference likely is due to the irreversible side-reactions associated with the discharge (*i.e.*, sodiation) process. To investigate the sodiation reaction further, we used the surface-sensitive probing capability of synchrotron soft X-ray absorption spectroscopy (XAS) in the total electron yield (TEY) mode to analyze the structural changes of electrodes as a function of their state-of-charge (SOC), as shown in Figure 1c. In the first discharge, we observed that the characteristic O K-edge peak associated with the $\text{Ni}_{3d}\text{-O}_{2p}$ hybridization state in the pristine NiO gradually decayed, while the $\pi^*(\text{C=O})$ peak attributed to carbonate groups formed as the sodiation reaction proceeded. The carbonates may be resulted from the electrolyte decomposition during sodiation at the surface of NiO.²⁸⁻³¹ The absolute intensity of Ni L-edge in the TEY mode decreased as the thickness of carbonate groups built up (Figure 1c, right panel). After a complete cycle the carbonate-enriched layer did not decompose completely: this is similar to the behavior observed in lithium half-cells.²⁸ The probing depth of XAS in the fluorescence yield (FY) mode reaches 50-100 nm, which is far beyond the thickness of the NiO nanosheets studied here, thus XAS/FY is bulk sensitive for NiO nanosheets. The normalized XAS fluorescence yield from the nickel L-edge (Figure S2) exhibits similar L_3/L_2 ratios and similar near-edge features (*i.e.*, no significant change in oxidation state) throughout the entire sodiation process, indicating that the majority of NiO remains unreacted. This is likely due to the fact that the sodiation reaction primarily occurred only at the surface of NiO nanosheets. To justify this hypothesis, representative images

of the morphology of the electrode material after a full discharge are shown in the *ex situ* TEM image (Figure 1d), where only the surface of the NiO was sodiated to a shallow depth. This resulted in the formation of Ni nanoparticles, an observation that is in a good agreement with the Ni L-edge XAS/FY results and the low cycling capacity of sodiation. In contrast, we observed that nickel oxide is fully reduced to metallic nickel when the voltage reached the lower limit of the cycling voltage window in lithium half-cells.^{27,28}

From these observations, we may attribute the inferior sodiation capacity to either the passivation effect of the surface reaction layers and/or the intrinsically slow reaction between Na^+/e^- and NiO. Previous studies have shown that the surface Li_2O may partially react with the organic electrolyte to form a lithium carbonate-containing passivation layer.^{28,29} Based on the similarity between these two systems, we assume that a surface reaction layer (likely sodium carbonates) would be formed from a similar reaction with Na_2O in a sodium cell containing organic carbonate electrolytic solutions, as suggested by the XAS data (formation of $\pi^*(\text{C}=\text{O})$, Figure 1c). However, the entire interfacial layer may be very complicated in the real battery systems, which may comprise a Na_2O layer (as a reaction product), an inorganic surface carbonate-enriched layer, and an organic carbonate layer from the decomposition of electrolyte.³¹ The latter two layers should have similar properties to the interfacial layers in other lithium-ion electrode systems, which should be ionically conducting.³¹ In our case, because of the possibility of extensive damage during exposure to electron beam and air moisture, the organic surface layer cannot be studied directly using TEM. To eliminate the influence of the organic electrolytic solution, we studied sodiation primarily using an *in situ* TEM approach, wherein inorganic Na_2O or Li_2O is used as the solid electrolyte.²⁷

We carried out *in situ* TEM experiments using a dry-cell setup for both sodiation and lithiation, using only a Na₂O or a Li₂O solid electrolyte (Figure 2a), in which Na⁺/Li⁺ ions are transported under a positive bias with respect to the NiO electrode. Figure 2b-d shows the selected area electron diffraction (SAED) patterns for pristine, sodiated, and lithiated samples, respectively, showing the existence of Ni and Na₂O/Li₂O as reaction products, in consistent with what was found from the coin batteries. In addition, radial-intensity profiles as a function of sodiation/lithiation time were derived from the *in situ* SAED videos (Supporting Information Movie 3, and Movie 4 in ref. 27), as shown in Figure 2e,f. Diffraction peaks from pristine NiO and reaction products including Ni, Na₂O, and Li₂O were identified (Figure 2e,f and Figure S3). It is obvious that NiO is gradually converted into Ni and Na₂O or Li₂O as it reacts, respectively, with Na or Li. However, the lithiation process occurs at a much higher rate than the sodiation process (Figure 2g,h), in agreement with our electrochemical measurements. We also note that the Bragg peaks of Na₂O phase have a much smaller full-width-at-half maximum (FWHM) compared to those of the Li₂O and Ni phases (Figure 2i), suggesting that the crystal domain size of Na₂O produced in sodiation is larger than the Li₂O produced in lithiation (Figure 2j).³²

Figure 3a presents still images from a representative sodiation process captured by real-time TEM (Supporting Information Movie 1). These images were taken in a low-dose imaging mode so as to minimize electron beam induced damage and/or the growth of sodium/lithium compounds. At the initial stages of the observation (before recording the movie), a thin surface layer was observed almost immediately upon the delivery of Na⁺ to the electrode *via* fast surface diffusion. This layer was confirmed to be Na₂O from the diffraction pattern. After a short time (240 s), a large number of reduced Ni nanoparticles of ultrafine size (~1 nm) started to become visible on the NiO surfaces, while the Na₂O crystal continued to grow and plate out. Even after

960s, only portions of the NiO nanosheets had reacted and the Ni nanoparticles gradually coarsened and became embedded in the Na₂O layers. The Ni nanoparticles reached an ultimate average size of ~3 nm, and the Na₂O layer thickened to greater than 10 nm. The changes in phase and morphology observed here are consistent with the *ex situ* TEM observation in the coin cell with the organic electrolytic solution (Figure 1d). In contrast, the lithiation reaction went through a different, heterogeneous pathway, as shown in Figure 3b and Movie 2 (Supporting Information): Li⁺ ions first diffused quickly over the surface of the NiO nanosheet, followed by a near-surface to interior transition *via* both “shrinking-core” and “finger” modes, consistent with our prior observations.²⁷ The reaction fingers can expedite the conversion process and lead to a faster reaction in the bulk of the particle than occurs in the shrinking-core mode.²⁷ In contrast, the characteristics of the finger reaction mode are not observed during the sodiation process in the *in situ* experiments, and the shrinking-core mode is also much slower during sodiation than during lithiation: these two observations can explain the low utilization observed in the Na coin-cells, shown in Figure 1.

We then characterized the reduced NiO sheets using aberration-corrected analytical STEM approaches, including annular dark-field scanning transmission electron microscopy (ADF-STEM), and electron energy-loss spectroscopy (EELS). We note that any surface layer (in both *in situ* and *ex situ* TEM specimens) can be damaged by exposure to the strong electron beam.²⁸ STEM-EELS mapping (Ni L-edges, Figure S4d) reveals a direct correlation between nickel reduction and the formation of Ni nanoparticles. Figure 4a presents a cross-sectional, high-resolution STEM image of a NiO slab along the [110] direction. It shows a nearly coherent atomic lattice between the Ni nanoparticles and the NiO nanosheet, as indicated by the fast Fourier transform (FFT). By filtering the FFT, we reconstructed the atomic arrangements of Ni

atom columns for both the NiO and Ni phases (Figure 4b). Given that NiO has a broadly similar crystal structure to Ni (containing additional O atoms at the octahedral sites, as shown in Figure 4c), the phase transformation from NiO to Ni can be thought of as being equivalent to removing all of the O (111) planes, with a consequent lattice shrinkage of ~18.3%: this is in a good agreement with the measured (111) spacing difference of ~14.8% (Figure 4b, inset).

A panoramic three-dimensional (3D) visualization of the sodiation structure was achieved using STEM tomography on a specimen that had been sodiated *in situ*, as shown in Figure 4d and Movie 4 (Supporting Information). The reconstructed 3D tomograms indeed reveal that the reduced metallic Ni nanoparticles (in orange) are only attached on the surface of the incompletely reacted NiO slab (in purple). This finding is in contrast to our prior observations of lithiation, wherein the metallic Ni nanoparticles are embedded in the Li₂O to form a composite.^{27,28} The data shown in Figure 4 and Figure S4 confirm that the reaction proceeds by the shrinking-core mode.

We demonstrated that the thicker Na₂O layer formed during sodiation compared to lithiation will result in slower overall transport of Na⁺, as first-principles calculations predict similar formation energy and migration energy barriers of Li⁺ in Li₂O and Na⁺ in Na₂O, respectively (Figure S6, Supporting Information). The fact that Na₂O forms a thicker reaction layer than Li₂O is partially the result of the large difference in the molar volume of Na₂O compared to that of Li₂O (factor of 2) and in addition to that in lithiation, part of Li₂O is embedded into the composited structure of Li₂O/Ni which left less Li₂O on the surface. Moreover, it is obvious from the diffraction study (Figure 2j) that the Na₂O reaction layer is crystalline with ~4 nm crystal domain size. This is in strong contrast to Li₂O, where the grain

size of Li_2O is approximately 1 nm. Thus, the Na_2O passivation layer has far fewer grain boundaries per unit volume, which can further impede the diffusion of Na^+ .

We undertook *ab initio* MD simulations to clarify the atomistic processes of these reactions. Figure 5a illustrates the decrease in the total number of Ni-O bonds in the MD simulation as a function of time, which is computational proxy for the rate of lithiation and sodiation. The MD simulations indicate that in the initial stage both the lithiation and the sodiation of the NiO proceed in a layer-by-layer fashion, wherein one atomic layer of NiO is reacted at a time. This reaction is initiated by the formation of Li/Na anti-site defects at the Ni site. Simulations show that their formation significantly distorts the local NiO lattice (Figure 5c). This distortion facilitates further insertion of Li, and thus enhances the overall rate of lithiation. In contrast, the formation of Na anti-site defects does not significantly distort the NiO lattice (Figure 5b), slowing down further sodiation reactions.

By combining the findings from MD simulations and TEM experiments, it is possible to describe the complete reaction mechanisms: the MD simulations provide insights into the atomistic scale mechanisms of the conversion reaction during lithiation and sodiation. Additional physical processes, such as the growth of the reaction products Ni and $\text{Li}_2\text{O}/\text{Na}_2\text{O}$, the local phase separation, and the strain balance resulting from the volume expansion are all captured in the TEM experiments at a longer timescale. In the incubation stage of the reactions, the kinetics of the conversion reaction are determined by the physical nature of Na^+ and Li^+ (their ionic radii and electronegativities): the reactions with Na ions occurs in a layer-by-layer fashion impeding further Na^+ insertion and enhancing the thickening of the Na_2O surface layer. In contrast, heterogeneous reaction fronts, such as the finger-like features shown Figure 5d, are formed during lithiation, and are a result of a larger lattice distortion, as observed in the MD simulations.

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3 These finger-like reaction fronts enlarge into reaction fingers that greatly increase the overall rate
4 performance of the conversion reaction (Figure 5d).
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8 As a result of the intrinsically different reaction mechanisms of sodiation and lithiation,
9 the formation of the surface layers are different in each case, as are the associated ionic transport
10 properties. These passivation layers, in turn, play a critical role in determining the overall
11 reaction rate. In particular, a Na_2O passivation layer is formed, which blocks the incorporation
12 of Na ions and electrons. On the other hand, during lithiation there are more the nucleation sites
13 for the further penetration of lithium, and consequently, for the formation of a nano-composites
14 consisting of Li_2O and Ni nanoparticles. Compared to the thick, highly crystalline Na_2O
15 passivation layers observed during sodiation, this nanocomposite phase of Li_2O and Ni
16 nanoparticles includes a high fraction of grain boundaries and interfaces, which supports the
17 enhanced transport of both Li^+ ions and electrons. It is anticipated that a proper doping on the
18 NiO anti-sites can affect the local strain and that a recently developed Li-activation method can
19 help to break the passivation layers.³³ These approaches may help to improve the reaction
20 kinetics of NiO.
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38 In summary, we have investigated the reaction mechanism of a typical transition metal-
39 oxide, NiO, through a correlated set of multi-scale methods, including an electrochemical study
40 and a synchrotron study of a real battery system, the *in situ* TEM observation of a half-cell, and
41 an *ab initio* MD simulation. Dramatic differences were observed between sodiation and
42 lithiation. In particular, only the shrinking-core mode was observed during sodiation using *in situ*
43 TEM. Further sodiation was blocked by a passivation layer of Na_2O that formed at an early
44 stage, and this, in turn, resulted in sluggish kinetics. MD simulation shows that the sodiation
45 pathway that leads to this shrinking-core mode originates from a layer-by-layer reaction that
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occurs during the insertion of Na ions. This study offers mechanistic insights into the processes of sodiation of a model metal-oxide system, and may guide further studies of Na-based electrode materials.

Methods

Sample preparation. The NiO nanosheets were synthesized using a solvothermal method, aided with an alcohol pseudo-supercritical drying technique.³⁴

Electrochemical measurements. Composite electrodes, prepared with 80wt% active material, 10wt% polyvinylidene fluoride (PVDF), and 10wt% acetylene carbon black in N-methyl-2-pyrrolidone (NMP) were cast on to copper current collectors. 2032-type coin cells were assembled in an argon-filled glove box, using the composite electrode as the positive electrode and the Na (or Li) metal as the negative electrode. A Celgard separator 2400 and a 1 M NaPF₆ (or LiPF₆) electrolyte solution in 1:1 w/w ethylene carbonate/dimethyl carbonate were used to fabricate coin cells. Batteries were tested on computer-controlled VMP3 channels (BioLogic). 1C was defined as full discharging NiO in 1 h, which corresponds to a theoretical specific current density of 718 mA g⁻¹.

Synchrotron XAS. XAS measurements were performed on the 31-pole wiggler beamline 10-1 at Stanford Synchrotron Radiation Lightsource (SSRL) using a ring current of 350 mA, and a 1000 1-mm⁻¹ spherical grating monochromator with 20 μm entrance- and exit-slits, providing ~10¹¹ ph·s⁻¹ at 0.2 eV resolution in a 1 mm² beam spot. During the measurements, all samples of battery electrodes were attached to an aluminum sample holder using conductive carbon. Data were acquired under ultrahigh vacuum (10⁻⁹ Torr) in a single load at room temperature, using total electron yield (TEY) and fluorescence yield (FY). The sample drain current was collected

for TEY. A silicon diode (IRD AXUV-100) was used to collect the fluorescence yield (FY) positioned near the sample surface. Contributions from visible light were minimized carefully before the acquisition of data, and all spectra were normalized by the current from freshly evaporated gold on a fine grid positioned upstream of the main chamber.

TEM characterization. The *in situ* TEM electrochemical cell was incorporated into a Nanofactory TEM-STM specimen holder (Figure 2a), in which NiO nanosheets dispersed on a TEM half-grid with amorphous carbon support are analogous to the NiO-C composite electrode, Na (or Li) metal is coated on to a piezo-driven W probe as the counter electrode, with a thin layer of Na₂O (or Li₂O) formed on Na (or Li) metal as the solid electrolyte. The Na (or Li) and NiO were loaded on to the holder in an Ar-filled glove box and then transferred to the TEM column using a sealed Ar bag to avoid exposing them to air. During the *in situ* electrochemical tests, a constant negative DC potential (1-3V) was applied to NiO electrode against the Na (or Li) source during lithiation, and the lithiation processes were captured in real-time in either the TEM- or STEM-mode. Electron tomography of the *in situ* lithiated sample was acquired in the ADF-STEM mode with a tilt series from -70° to 70° and 1° intervals. The *in situ* measurements and tomography were performed on a JEOL 2100F TEM operated at 200 kV. The high-resolution STEM imaging and analytical EELS were conducted on a Hitachi HD2700C STEM operated at 200 kV, and equipped with a probe aberration corrector (spatial resolution < 1 Å, energy resolution 0.35 eV). The 3D tomography was reconstructed using the eTomo software suite written by Robert Hovden *et al.* (Cornell Muller group) and visualized by Avizo 6.3.

First-principles calculations. The *ab initio* Molecular Dynamics simulations were undertaken using the Vienna Ab initio Simulation Package (VASP) within the projector augmented-wave approach with the Perdew–Burke–Ernzerhof generalized-gradient approximation (GGA) to the

density functional theory (DFT). The computer model consisted of a NiO (001) surface-slab (8.4 Å × 8.4 Å × 10.5 Å) of 48 formulae of NiO in contact with an amorphous Li metal slab (8.4 Å × 8.4 Å × 12.8 Å) of 54 Li atoms, or a Na metal slab (8.4 Å × 8.4 Å × 10.5 Å) of 24 Na atoms. The MD simulations of lithiation and sodiation were performed with a time step of 2 fs for 20-60 ps at 600K, using a NPT ensemble.

ASSOCIATED CONTENT

Supporting Information

Additional details of S/TEM, XAS, DFT calculation, and *in situ* movies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

K.H. and F.L. contributed equally to this work. K.H., F.L., Y.M., H.L.X. and D.S. conceived and designed the experiments. K.H. and D.S. performed the *in situ* and *ex situ* S/TEM experiments with the help of J.L.. R.L. and H.L.X. performed electron tomography and EELS acquisition and analysis. F.L. and M.M.D. performed the electrochemical measurements. Y.Z. and Y.M. performed the theoretical modeling. F.L., D.N. and T.-C.W. performed the synchrotron X-ray measurements. F.L. and R.M.R. synthesized the NiO samples. K.H., Y.M. H.L.X., F.L. and D.S. discussed the scope of the manuscript. K.H. prepared the figures with the help from X.Y. and X.-Q.Y.. D.S., K.H., Y.M., H.L.X., and F.L. wrote the manuscript with help from M.M.D. and E.A.S. All authors participated in discussions of the results. D.S. led the project.

Notes

The authors declare no competing financial interests.

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Figure 1. Cell performance and XAS measurements. (a) The first cycle charge-discharge voltage profiles of Na- (red) and Li- (blue) half-cells at rates of 0.1C. (b) Cycling performance and Coulombic efficiency of the Na half-cell. (c) XAS spectra in total electron yield (TEY) mode for NiO electrodes at different SOC (0, 50%, 100% of the first discharge and 50% and 100% of the subsequent charge). The left panel shows the normalized TEY intensities of the oxygen K-edges and the right panel shows the absolute TEY intensities of the nickel L-edges (the pristine profile is scaled to 50% of its absolute intensity). (d) STEM images of the sodiated electrode showing Ni nanoparticles on the surface of a NiO nanosheet.

Figure 2. Phase evolution during *in situ* sodiation and lithiation. (a) Schematic illustration shows the *in situ* setup of a dry electrochemical cell inside a TEM (details referred to in Methods). Electron-diffraction patterns for (a) pristine, (b) sodiated, and (c) lithiated samples. Colored intensity profiles as function of reaction time for (e) sodiation, and (f) lithiation processes. The profiles correspond to the radial integration of electron diffraction at varying time frames, with the Bragg peaks labeled. Intensity profiles of selected Bragg reflections during (g) sodiation, and (h) lithiation, showing phase evolution of NiO, Na_2O , Li_2O and Ni. (i) Selected Bragg peak profiles showing narrower FWHM of Na_2O reflections than Li_2O and Ni, which further correlate to the crystal size shown in (j).

Figure 3. Morphological evolution during *in situ* sodiation and lithiation. TEM imaging series captured in real time show morphological evolution during an *in situ* (a) sodiation, and (b) lithiation, of NiO nanosheet electrodes. The initial low-magnification images in both series display the entire area of observation, and the latter enlarged image series correspond to the boxed regions to reveal representative features in detail. The last image in (a) shows the outline of an Na_2O layer at sequential time. The arrows in (b) indicate the propagation of a finger penetration during lithiation.²⁷

Figure 4. Atomic structures after sodiation. (a) STEM-ADF image showing the atomically resolved crystal structures of the sodiated electrode materials in a cross-sectional view. The bulk material is an unreacted NiO single-crystal with reduced Ni single-crystal nanoparticles on the surface, both on the zone axis of $[110]$ direction. The inset FFT showing two distinct sets of diffraction spots, attributed to NiO and Ni (indicated by arrows) as labeled. (b) Reconstructed atomic structures of (a) after separating the NiO (red) and Ni (green) reflections by imposing inverse-FFT filters. The inset images of crystal unit cells (top-left) indicate that the lattice parameter decreases as NiO (red) transforms into Ni (green), consistent with the decrease of the lattice spacing between (111) planes (top-right). (c) Models of crystal structures for NiO and Ni. (d) Reconstructed 3D tomograms at different viewing angles showing that the reduced Ni nanoparticles (in orange) are attached on the surface of an incompletely reacted NiO slab (in purple). No sodiation occurred at the back side of NiO contacting the carbon film (not shown in reconstruction). See Movie 4 in Supporting Information for full details.

Figure 5. *Ab initio* MD simulations. (a) The change in the total number of Ni-O bonds over time during the MD simulations for the lithiation and sodiation of NiO. The snapshots of (b) sodiated- and (c) lithiated NiO surfaces at 10 ps showing the formation of Li/Na anti-site defects (highlighted in circles) in NiO. (d) Schematic cartoons showing different reaction modes between sodiation and lithiation.

Figure with high resolution
177x165mm (300 x 300 DPI)

Figure with high resolution
177x178mm (300 x 300 DPI)

Figure with high resolution
177x127mm (300 x 300 DPI)

Figure with high resolution
177x147mm (300 x 300 DPI)

Figure with high resolution
177x136mm (300 x 300 DPI)

88x34mm (300 x 300 DPI)