***In situ* TEM probing of crystallization form-dependent sodiation behavior in ZnO nanowires for sodium-ion batteries**

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Abstract

Development of sodium-ion battery (SIB) electrode materials currently lags behind electrodes in commercial lithium-ion batteries (LIBs). However, in the long term, development of SIB components is a valuable goal. Their similar, but not identical, chemistries require careful identification of the underlying sodiation mechanism in SIBs. Here, we utilize *in situ* transmission electron microscopy to explore quite different sodiation behaviors even in similar electrode materials through real-time visualization of microstructure and phase evolution. Upon electrochemical sodiation, single-crystalline ZnO nanowires (sc-ZNWs) are found to undergo a step-by-step electrochemical displacement reaction, forming crystalline NaZn₁₃ nanograins dispersed in a Na₂O matrix. This process is characterized by a slowly propagating reaction front and the formation of heterogeneous interfaces inside the ZNWs due to non-uniform sodiation amorphization. In contrast, poly-crystalline ZNWs (pc-ZNWs) exhibited an ultrafast sodiation process, which can partly be ascribed to the availability of unobstructed ionic transport pathways among ZnO nanograins. Thus the reaction front and heterogeneous interfaces disappear. The *in situ* TEM results, supported by calculation of the ion diffusion coefficient, provide breakthrough insights into the dependence of ion diffusion kinetics on crystallization form. This points toward a goal of optimizing the microstructure of electrode materials in order to develop high performance SIBs.

Keywords: Sodium-ion batteries; In situ transmission electron microscopy; ZnO nanowires; Electrochemical sodiation; Microstructure control

Introduction

Rechargeable lithium-ion batteries (LIBs) have become a mainstay of the digital age with dominance in portable electronics market. However, for emerging large-scale stationary applications, e.g., electric vehicles, power grid storage, and load leveling, the issue of the limited natural abundance of lithium resource will arise in the immediate future, along with an inevitable cost increase [1]. Therefore, there arises a tremendous interest in alternative metal-ion batteries based on abundant resources. Sodium-ion battery (SIB) has recently attracted significant attention due to the “rocking chair” operating principle similar to the LIB. Moreover, virtually inexhaustible and ubiquitous sodium resources circumvent the geopolitical issue that plague lithium resource [2–5]. Because the chemistries of LIBs and SIBs are similar, the mechanistic insights obtained from the studies of LIBs may be applicable to the SIBs. In this regard, both SIBs and LIBs have shared some of the same cathode materials including layered AMO_2 ($\text{M} = \text{Co}, \text{Ni}, \text{Ti}$), olivine or maricite AMPO_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{Ni}$), and the NASICON family of compounds [6,7].

In contrast to the great progress on SIB cathode materials, adapting LIB anode materials to SIBs has been thus far problematic. For example, a graphite anode with an interlayer distance of 1.86 Å may not accommodate the reversible intercalation of Na^+ ions (diameter of 2.04 Å) [8]. As a result, pure graphite forms only a NaC_{64} phase during sodiation, thus resulting in a lower capacity, $\sim 35 \text{ mAh g}^{-1}$, compared with $\sim 370 \text{ mAh g}^{-1}$ in the Li-intercalated graphite compound of LiC_6 (stage I). Graphene and hard carbon can circumvent the issue of size [9,10], but their modest specific capacities are insufficient for practical SIB applications. Moreover, the well-studied metal oxide materials in LIBs with high theoretical capacities have also been investigated as viable anode materials for SIBs [11–14]. Due to similar, but not identical, chemistries in LIBs and SIBs, however, not all of them possess reliable electrochemical cycleability upon sodiation/desodiation. In this regard, *in situ* transmission electron microscopy (TEM) has been used to probe the failure mechanism of single-crystalline SnO_2 nanowires for SIBs [15], despite its success in LIBs [16,17]. These reactions are difficult or impossible to be understood by *ex situ* measurements. Thus far, the effort directed toward *in situ* TEM research of SIBs is substantially less than that for LIBs, encouraging us to augment our knowledge of the various electrochemical reaction mechanisms stemming from the inherent characteristics of sodium.

In this paper, we employed state-of-the-art *in situ* TEM to visualize the microstructural evolution and phase transformation and to track ion diffusion during electrochemical sodiation of ZnO nanowires (ZNWs). A slow, step-by-step sodiation process was observed for single-crystalline ZNWs (sc-ZNWs). This process was characterized by a slowly propagating reaction front and the formation of heterogeneous interfaces due to non-uniform sodiation amorphization. In contrast, the sodiation process of poly-crystalline ZNWs (pc-ZNWs), composed of tiny ZnO nanograins, was also investigated, revealing an unexpected, fast sodiation process, thus enabling a better rate

performance. Interconnected nanoscale channels among ZnO nanograins in pc-ZNWs are thought to act as unobstructed ionic transport pathways for fast sodium ion diffusion. To the best of our knowledge, this is the first *in situ* work in which otherwise similar electrode materials possibly respond differently during the electrochemical sodiation, depending on their single/poly-crystalline forms. This work provides breakthrough insights into crystallization forms-dependent ion diffusion kinetics and rate performance, which can be used to guide the design of high-performance SIB electrode materials through microstructural control.

Experimental section

In Situ TEM Experiment of Electrochemical Sodiation/Desodiation

The *in situ* electrochemical sodiation experiments were carried out using a Nanofactory TEM-scanning tunneling microscopy (STM) holder in an aberration-corrected JEOL ARM200CF TEM. In a typical experiment, the electrochemical setup consists of individual ZNWs as the working electrode, a layer of Na₂O solid electrolyte, and bulk Na metal as the counter electrode. The ZNWs were glued to the half TEM copper grid with conductive epoxy as the working electrode. A 0.25 mm-thick tungsten (W) wire was cut to produce a fresh tip that was then utilized inside a glove box filled with argon gas to scratch the Na metal surface to fetch fresh Na onto the tip. The layer of Na on the tip of the W wire was served as the counter electrode and sodium source. Both the ZNWs and sodium electrodes were mounted onto a Nanofactory STM-TEM holder inside the glove box. The holder was transferred into the TEM column within several seconds. A native Na₂O layer formed on the surface of Na metal due to the exposure to air. This served as the solid-state electrolyte to allow transport of the Na⁺ ions. The Na₂O/Na electrode was mounted on the mobile STM probe, which could be driven to contact the ZNW electrode inside the TEM. Electrochemical sodiation took place when a negative bias was applied to the ZNWs with respect to the sodium metal. This drove Na⁺ ions transport through the solid-state Na₂O layer. During the sodiation, electron energy loss spectroscopy (EELS) and electron diffraction (ED) were used to monitor chemical composition and phase transformation. Two advanced Gatan CCDs (Model 894 and Model OneView) were used for imaging and capturing the dynamic sodiation/desodiation process. Additional details are described elsewhere [18–20].

Half Cell Measurement

Galvanostatic electrochemical performance of the single- and poly-crystalline ZNW anodes was obtained with a 2025-type coin cell in the voltage window of 0.01–2.0 V versus Na/Na⁺ at room temperature on a Neware battery cycler at various current densities. The working electrode for the SIBs is the slurry mixture of active material (ZnO powder),

acetylene black, and polyvinylidene fluoride (PVDF) (75:15:10 weight ratio) in *N*-methyl pyrrolidine (NMP) which had been stirred for 12 h. The slurry was coated onto the Cu current collector and dried at 240 °C for 4 h under Argon gas. The thickness of the electrode without current collector was 20±0.5 μm. Metal sodium foil was used as the counter electrode and reference electrode. The electrolyte consists of 1.0 mol/L NaPF₄ in an ethylene carbonate (EC)-diethyl carbonate (DEC) mixture solution (1:1 volume ratio). For the galvanostatic intermittent titration technique (GITT) tests, the coin cells were discharged/charged at C/10 with a current pulse duration of 0.5 h and interval time of 1 h.

Results and discussion

The first sodiation process is critical for the battery because this stage could imprint irreversible damage on the electrode materials due to microstructural evolution and phase transformation. To understand the electrochemical behavior of ZnO in SIBs, the sodiation process of individual sc-ZNWs was first observed *in situ*, as shown in Figure 1 and Movie S1. Figure 1a presents a schematic illustration of the *in situ* experiment setup that enables direct observation of the electrochemical sodiation of a nano-SIB. The taper-like sc-ZNWs are attached to the copper TEM grid and used as the working electrode. The Na metal attached to the tungsten wire serves as the counter-electrode and sodium source where the naturally oxidized Na₂O and NaOH layer is used as a solid electrolyte. Figure 1b shows a panoramic TEM image of the constructed nano-SIB inside the TEM. A magnified TEM image of the tip of the pristine ZNW is displayed in the inset of Figure 1b, showing its taper-like morphology with a taper degree of 1:3. The HRTEM image of the ZnO taper tip in Figure 1c shows its single-crystal nature with a well-resolved fringe spacing of 0.26 nm, corresponding to the (0002) planes of ZnO. The corresponding fast Fourier transform (FFT) pattern (inset in Figure 1c) can be indexed as the hexagonal structure of ZnO (JCPDF No. 79-0207).

After contact was established between the two electrodes, the electrochemical sodiation reaction driving the flow of electrons and Na⁺ ions across the circuit was initiated by applying a bias of −1.5 V to the sc-ZNW with respect to the Na electrode. The bias voltage was used for all sodiation experiments in this study unless otherwise stated. Figure 1d–j shows the morphological evolution of the sc-ZNW during the first sodiation. A nanoparticle (marked with a black arrow) on the nanowire is used as object of reference to measure axial elongation of the nanowire. At 0.5 min (Figure 1d), the sharp tip of the sc-ZNW has completely disappeared due to the sodiation-induced volume expansion. The sodiated region showed a lighter contrast with a length of around 290 nm (the reaction front is marked by a yellow arrow), yielding an average sodiation speed of 580 nm/min along the longitudinal direction of the sc-ZNW. After an additional sodiation of 16 min (Figure 1i), the displacement of the reaction front was about 1230 nm and the sc-ZNW was elongated by ~30.7%. Unexpectedly, we find that the average sodiation speed varied during the sodiation process. The

displacement of the reaction front as a function of sodiation time follows the rule of parabolic kinetics, as shown in Figure 2a, indicating a diffusion-limited reaction process [21]. The average longitudinal sodiation speeds are displayed statistically in Figure 2b, revealing an intriguing step-by-step sodiation process (which will be addressed later).

The sodiation transformed the initially straight nanowire into a slightly bent shape with obvious radial expansion. The diameter located at the marked particle (Figure 1j) was expanded by ~37.5% after full sodiation, and the total volume expansion was estimated to be around 150%. Interestingly, the sodiated region shows pseudo-moiré TEM contrast, a feather not observed in the unsodiated region. Further, the magnified TEM image in Figure 1j discloses the true features. Transverse dark stripes are embedded in the fully sodiated NW, which suggests a large local lattice strain. Note that a significant layer of Na₂O formed on the surface of the nanowire (NW), which was partially associated with the fast diffusion of sodium along the NW surface. This phenomenon is due to the energetic nature of the *in situ* experimental probe and the imaging electron beam. Thus, the electron diffraction (ED) pattern of the fully sodiated NW was conducted on areas free of Na₂O layer, as shown in Figure 1k. Diffraction rings in the ED pattern can be indexed as NaZn₁₃ and Na₂O phases. Thus, the electrochemical reaction in the sc-ZNW upon full sodiation can be expressed as equation (1):

This is a typical displacement reaction [22], leading to the formation of NaZn₁₃ nanocrystals dispersed in the Na₂O matrix. This is similar to the result of electrochemical sodiation of SnO₂, another well-studied oxide NW [15]. Figure 11 schematically illustrates the crystal phase transformation of the ZnO anode during electrochemical sodiation process. Based on this electrochemical reaction, a high theoretical specific capacity of ~685 mAh g⁻¹ can be predicted for the fully sodiated ZNW ($x = 13$), which significantly exceeds that of most SIB anodes presently available.

To better understand the stepwise electrochemical sodiation mechanism in sc-ZNWs, more in-depth localized observations were conducted to probe sodium ion transport pathways and microstructural evolution, as shown in Figure 3. After initial ZNW contact with the sodium electrode, the sodium species first diffused along the axial direction of the sc-ZNW. The Na₂O layer formed gradually on the surface and wetted the ZNW, as shown in Figure 3a–c. Moreover, sodium diffusion also took place inside the sc-ZNW synchronously, which resulted in the longitudinal propagation of dense clouds of mobile dislocations, as observed in Movie S2. The dense clouds of mobile dislocations also occur in the reaction front of lithiated SnO₂ nanowires [16]. The ED pattern changes of dislocation areas further verified the inward diffusion of sodium ions (Figure S1). Single-crystalline diffraction spots of the pristine sc-ZNW gradually evolved into

diffraction spots superimposed on amorphous haloes, finally resulting in the formation of poly-crystalline diffraction rings after full sodiation. However, the dense clouds of dislocations were not observed during the lithiation of the ZNWs [23,24], indicating a different electrochemical behavior in the sodiation of the ZNWs. At 507 s (Figure 3c), the morphology of the ZNW still remained unchanged, except for a slight expansion in diameter. Obviously, the morphological evolution of the ZNW lagged behind sodium ion diffusion. Interestingly, the dynamic dislocation clouds gradually disappeared, leaving behind many transverse dark stripes dispersed inside the ZNW (Figure 3d). This could be because the sodium species initially diffusing along the surface of the ZNW had infiltrated inwardly, resulting in the transverse amorphization. When the longitudinal amorphization inside the ZNW was blocked by the transverse amorphization, the two amorphization regions caused heterogeneous interfaces (dark stripes in Figure 3d) due to their discontinuous atomic structures [25]. Electron energy loss spectroscopy (EELS) also corroborates the presence of sodium species prior to the violent electrochemical reaction (inset in Figure 3d). Up to this point, it took a long time for the ZNW to complete the slow wetting and infiltration processes that are considered as an incubation period for subsequent sodiation process.

After the incubation period, an ultrafast sodiation of the ZNW suddenly occurred and was completed only in 10 s, as shown in Figure 3e–h and Movie S3. A diameter expansion of 28% exceeds the expansion of 11% observed during the whole incubation period of ZNW (nearly 10 min). This resulted in discrete transverse cracks due to rapid inward diffusion of sodium along the transverse heterogeneous interfaces, as shown in Figure 3k,l. The stepwise electrochemical sodiation process can repeat itself and ultimately sodiate the entire ZNW (Figure 3i,j). The step-by-step sodiation process, including wetting, infiltration, and sodiation substeps, is schematically illustrated in Figure 4a. After physical aging of the sodiated regions, the heterogeneous interfaces still existed in the form of dark stripes inside the NW matrix (Figure 3k) and were embedded in light-colored areas whose components are a mixture of Na_2O and NaZn_{13} phases (Figure 3l). Moreover, the structural degradation caused by the heterogeneous interfaces could imprint irreversible damage on the electrode materials. Upon desodiation by applying an equivalent positive bias, we find that the extraction of sodium ions seems to be irreversible by observing the structural evolution and crystal phase change. Therefore, circumventing microstructure damage should be an important consideration for the enhancement of battery performance.

Figure 5 shows the microstructural evolution and phase transformation during the electrochemical sodiation process of pc-ZNWs prepared using our solution methods [26,27]. The pc-ZNWs are composed of tiny self-assembled ZnO nanograins, as shown in Figure 5a and Figure S2. The diffraction rings in the ED pattern of the pristine ZnO NW show its poly-crystalline nature (Figure 5g). When contact between the pc-ZNW and Na electrode was made, the entire

pc-ZNW rapidly expanded uniformly within only several seconds, as shown in Figure 5b,c and Movie S4. After that, the ZNW morphology did not change (Figure 5d). The diameter expanded from 83 nm to 112 nm, nearly 35% expansion rate. Judging by the ED pattern in Figure 5h, the fully sodiated products of the pc-ZNW are mixtures of NaZn_{13} and Na_2O phases. Interestingly, the slow reaction front occurring in the sc-ZNW was not observed subsequently. This could be because that large numbers of interconnected channels among the ZnO nanograins provide abundant pathways for ion infiltration, thus alleviating the large mechanical strain along the longitudinal direction of the sodiated ZNW, resulting in an unexpectedly fast sodiation process. Experimental measurement and first-principles calculations have shown that nanograin boundaries have a lower ion diffusion energy barrier and can provide faster ion diffusion pathways [28,29]. Similarly, we suggest that sodium ion diffusion inside the pc-ZNW should benefit in like manner. In order to further probe the ion diffusion pathways among the nanograins, we have used an advanced CCD (Gatan, Model OneView) to capture the fast sodiation process (Movie S5). Abundant dark thin stripes distributed along grain boundaries after the sodiation, showing the ion diffusion pathways among ZnO grains (Figure S3). This kind of thin stripe is different from the transversely distributed thick stripes in the sc-ZNW (Figure 3d). Therefore, this observation of *in situ* sodiation of the pc-ZNW provides an important guide for designing high performance SIBs. The microstructure of the electrode materials should be optimized, such as by nanocrystallization [30].

Besides the vanished reaction front, we note the absence of the transverse dark stripes inside the fully sodiated pc-ZNW (Figure 5f). The dark stripes are the heterogeneous interfaces where the longitudinal sodiation amorphization inside the sc-ZNW is blocked by the transverse sodiation amorphization from rapid inward diffusion of sodium ions from the surface of the sc-ZNW. In contrast, the sodiation speed in the pc-ZNW is uniform due to the ultrafast Na-ion diffusion that benefits from the abundant ion transport pathways among ZnO nanograins with interconnected channels. In addition, we find no cracks on the surface of the sodiated pc-ZNW (Figure 5e), which strongly indicates that there is no dominant inward diffusion of sodium ions from the surface of pc-ZNWs. As a result, the discontinuous atomic structures between the different sodiation amorphization regions are not expected to occur inside the fully sodiated pc-ZNW. Moreover, we have tried to probe the effect of different grain sizes on the ionic diffusion and sodiation process. However, we do not distinguish the noticeable difference from the ZNW with bigger grains (Figure 5e–l, Figure S3 and Movie S5), except for the negligible change in sodiation speed. The ultrafast sodiation process of the pc-ZNWs is schematically illustrated in Figure 4b. All in all, the *in situ* TEM sodiation experiments can help us compare the difference between the sc-ZNWs and pc-ZNWs, especially in sodiation speed and microstructural evolution. The same electrode material responds differently to their single/poly-crystalline forms during the electrochemical sodiation. By the way, the channels among the ZnO nanograins can also partially buffer the

sodiation-induced volume expansion [31,32]. Note that the reversible desodiation reaction is feasible for a sodiated pc-ZNW (Figure S4 and Movie S6), although the desodiation speed is slightly slower compared with the sodiation process, proving the viability of pc-ZNWs used for SIBs.

In principle, faster ion diffusion and sodiation processes result in improved rate performance in batteries. Thus, we further compared the rate capability of the two ZNW electrodes in SIBs. As shown in Figure 6a, at a low rate of $C/10$, the two ZNW electrodes exhibit a negligible difference in specific ion-extraction capacities. Nevertheless, at higher rates equal to and above $C/2$, the capacities of the sc-ZNW/Na cell are far lower than those of the pc-ZNW/Na cell. The sc-ZNW/Na cell displays 430, 370, and 290 mAh g⁻¹ at $C/2$, 1C, and 2C, respectively, while the pc-ZNW/Na cell shows 475, 440, and 405 mAh g⁻¹ at the same rates. Impressively, at 1C and 2C, the pc-ZNW/Na cell retains 87% and 78% of its capacity at 1C and 2C, respectively, while such retention ratios are only 68% and 57% for the sc-ZNW/Na cell (Figure 6b). To understand why the pc-ZNW cell exhibits a higher rate capability compared with the sc-ZNW cell, we employed GITT to measure the Na-ion diffusion coefficient in pc-ZNW and sc-ZNW cells. The ionic diffusion coefficient can be determined by solving Fick's second law with following equation (2) [33–37]:

$$D_{\text{Na}^+} = \frac{4}{\pi} \left(\frac{iV_m}{ZFS} \frac{\left(\frac{dE}{d\delta}\right)}{\left(\frac{dE}{d\sqrt{t}}\right)} \right)^2 \text{ when } t \ll \frac{L^2}{D_{\text{Na}^+}} \quad (2)$$

where L is finite diffusion length, i is applied current, V_m is molar volume of the material, F is Faraday's constant, S is electrode surface area, $dE/d\delta$ is slope of the coulometric titration curve and $dE/d\sqrt{t}$ is the slope of the voltage versus square root of time plot during a constant current pulse. Figure 6c,d shows the evolving diffusion coefficients as a function of potential, where similar trends are observed in the electrodes of pc-ZNWs and sc-ZNWs, indicating their similar sodium storage mechanism in ZnO material. However, higher diffusion coefficients ranging from 9.5×10^{-14} to 0.5×10^{-13} cm² s⁻¹ are obtained for the pc-ZNWs, compared with a range of 4.5×10^{-16} to 0.5×10^{-14} cm² s⁻¹ for the sc-ZNWs. The huge difference in diffusion coefficients is obviously related to the different crystallization forms in the ZNW. Returning to the *in situ* TEM sodiation experiments and focusing on the observed sodiation processes in a single ZNW, the Na-ion diffusivity can be roughly estimated using the Einstein-Smoluchowshi relation, $D_{\text{Na}^+} = L^2/2t$, where L is the displacement of the reaction front and t is the sodiation time. According to the *in situ* TEM observations, the sodiation reaction front of the sc-ZNWs yielded Na-ion diffusivities of $\sim 10^{-16}$ cm² s⁻¹, which are lower than values observed in the *ex situ* GITT measurements, suggesting that more complex processes than simple diffusion are

occurring at the reaction front. Thus, additional kinetic studies, particularly involving multi-phase character calculation and simulation, will be required.

Conclusion

In summary, *in situ* TEM has been used to directly visualize the electrochemical sodiation process of ZNW anodes in nano-SIBs. We have compared the electrochemical sodiation behaviors of sc-ZNWs and pc-ZNWs. Upon sodiation, a reaction front propagates slowly along the sc-ZNWs, and heterogeneous interfaces are formed inside the ZNWs due to non-uniform sodiation amorphization. With Na insertion into ZnO, a displacement reaction occurs, leading to the formation of crystalline NaZn₁₃ nanograins dispersed in Na₂O matrix. A step-by-step electrochemical sodiation behavior for the sc-ZNWs is revealed. Further, the electrochemical sodiation of pc-ZNWs composed of ZnO nanograins was also investigated using the *in situ* TEM, revealing an unexpectedly fast and uniform sodiation process, which is attributed to presence of abundant ion transport pathways among ZnO nanograins with interconnected channels. During the synthesis of the pc-ZNWs, interconnected nanoscale channels among ZnO nanograins were formed throughout the pc-ZNWs. These are expected to act as unobstructed transport pathways for ultrafast sodium ion diffusion. As a result, the reaction front and heterogeneous interfaces vanish. These findings demonstrate that chemically identical electrode materials can respond differently, depending on the single- or poly-crystalline form, during electrochemical sodiation, providing an important technique for designing high-performance SIB electrode materials, through microstructure control.

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Figure 1 (a) Schematic illustration of the experimental setup for *in situ* electrochemical sodiation of nano-SIB. (b) Panoramic TEM image of the nano-SIB constructed with a taper-like ZNW inside a TEM. Inset in (b) shows taper-like morphology of the ZNW tip with a taper degree of 1:3. (c) HRTEM image of the ZNW tip shows its single-crystalline nature. Inset in (c) is the FFT pattern corresponding to the HRTEM image. (d–j) Time-resolved TEM images from video frames show morphology and structure evolution as a function of sodiation time. (k) Electron diffraction (ED) patterns of sodiated products demonstrate the formation of NaZn₁₃ and Na₂O phases. (l) Schematic illustration of the crystal phase transformation of the ZnO anode during electrochemical sodiation process.

Figure 2 (a) Plot of the displacement of reaction front as a function of electrochemical sodiation time. (b) Average sodiation speeds at intervals of one minute. The measurements are along the longitudinal direction of the nanowire.

Figure 3 Time-resolved TEM images from video frames show a time-dependent step-by-step electrochemical sodiation process. (a–c) Slow surface diffusion of sodium species first wetted the ZNW and (d) then infiltrated the ZNW from the surface. Inset shows electron energy loss spectroscopy of Na species. (e–h) After a slow wetting and infiltration process, fast sodiation occurs suddenly and is completed within only 10 s, resulting in a huge diameter expansion. (i,j) Another stage including slow sodium diffusion, slow infiltration, and fast sodiation. (k,l) Discrete cracks due to rapid inward diffusion of sodium ions along the transverse heterogeneous interfaces.

Figure 5 (a–d) Time-resolved TEM images from video frames show morphology and structure evolution of a poly-crystalline ZNW as a function of electrochemical sodiation time. A fast and uniform sodiation process of the entire NW was observed. (e) and (f) show local magnified TEM images. (g) and (h) are electron diffraction patterns before and after sodiation, respectively. (i–l) Time-resolved TEM images from video frames show morphology and structure evolution of another pc-ZNW. The ultrafast and uniform sodiation process also was observed.

Figure 6 (a) Comparison of rate performance and (b) comparison of capacity retention between the sc-ZNWs and pc-ZNWs SIBs. (c, d) Comparison of diffusion coefficients calculated from the GITT potential profiles for the sc-ZNWs and pc-ZNWs SIBs as a function of state of potential.

Ultrafast sodiation of pc-ZNWs benefiting from abundant ion transport pathways among ZnO grain boundaries.