

Electrolyte Stability Determines Scaling Limits for Solid-State 3D Li Ion Batteries

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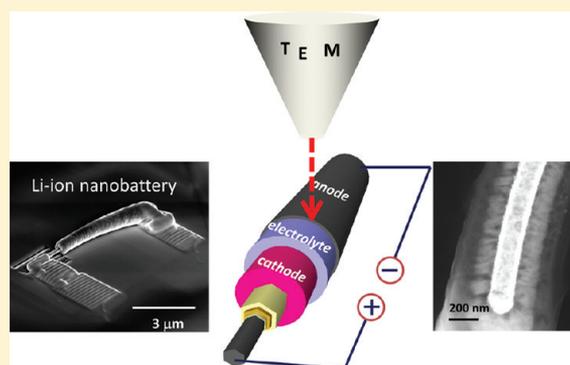
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S Supporting Information

ABSTRACT: Rechargeable, all-solid-state Li ion batteries (LIBs) with high specific capacity and small footprint are highly desirable to power an emerging class of miniature, autonomous microsystems that operate without a hardware for power or communications. A variety of three-dimensional (3D) LIB architectures that maximize areal energy density has been proposed to address this need. The success of all of these designs depends on an ultrathin, conformal electrolyte layer to electrically isolate the anode and cathode while allowing Li ions to pass through. However, we find that a substantial reduction in the electrolyte thickness, into the nanometer regime, can lead to rapid self-discharge of the battery even when the electrolyte layer is conformal and pinhole free. We demonstrate this by fabricating individual, solid-state nanowire core–multishell LIBs (NWLIBs) and cycling these inside a transmission electron microscope. For nanobatteries with the thinnest electrolyte, ≈ 110 nm, we observe rapid self-discharge, along with void formation at the electrode/electrolyte interface, indicating electrical and chemical breakdown. With electrolyte thickness increased to 180 nm, the self-discharge rate is reduced substantially, and the NWLIBs maintain a potential above 2 V for over 2 h. Analysis of the nanobatteries' electrical characteristics reveals space-charge limited electronic conduction, which effectively shorts the anode and cathode electrodes directly through the electrolyte. Our study illustrates that, at these nanoscale dimensions, the increased electric field can lead to large electronic current in the electrolyte, effectively shorting the battery. The scaling of this phenomenon provides useful guidelines for the future design of 3D LIBs.

KEYWORDS: Lithium ion battery, nanowire, nanobattery, in situ transmission electron microscopy, electrolyte, breakdown, space-charge limited conduction



Rechargeable batteries have become ubiquitous in modern society, powering a host of seemingly indispensable portable electronics and communications devices.¹ Combined with energy scavenging mechanisms, rechargeable batteries are also desirable for energizing autonomous microelectromechanical systems (A-MEMS) that operate remotely without a hardware for either power or communications,² and which are increasingly used in biology,³ medicine,⁴ environmental monitoring,⁵ agriculture,⁶ and intelligence gathering. Due to their high-energy density, Li ion batteries (LIBs) are attractive for these applications, and all-solid-state LIBs add many further benefits, including compatibility with MEMS manufacturing, relatively long lifetimes, generally negligible self-discharge rates, and enhanced safety owing to the lack of flammable and/or toxic liquid-phase electrolytes. However, the low areal energy densities of commercial thin film LIBs (TFLIBs) combined

with typical energy demands limits the miniaturization of most prototype A-MEMS to the millimeter range. In fact, the size of the battery often exceeds the dimensions of the rest of the device by several orders of magnitude.⁷ TFLIBs as small as $50 \times 50 \mu\text{m}$ have been demonstrated⁸ using the approach pioneered by Bates et al.,⁹ using physical vapor deposition of three active layers: a LiCoO_2 cathode, a nitrogen-doped Li_3PO_4 solid electrolyte (LiPON), and Li anode. These TFLIBs retain over 90% of their initial energy capacity after 40 000 cycles and are now commercially available.¹⁰ However, with typical energy capacity per unit area of 0.01 to $0.03 \text{ J}/\text{mm}^2$, these batteries store insufficient energy for most potential applications

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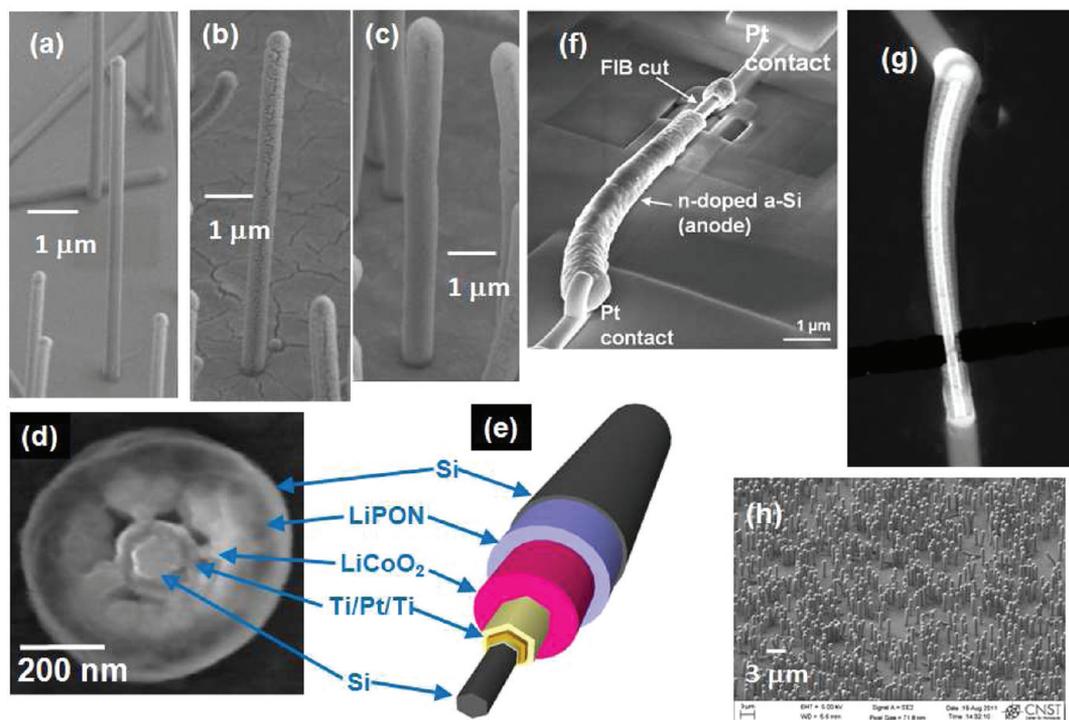


Figure 1. FESEM images of NWLIBs following deposition of (a) Ti/Pt/Ti, (b) LiCoO₂, and (c) LiPON/Si; (d) a FIB cut cross section FESEM image and (e) a NWLIB schematic; (f) a NWLIB contacted with Pt electrodes on a Si/SiO₂ substrate, (g) HAADF STEM of a NWLIB on SiN_x membrane with Pt contacts showing its internal structural arrangement, and (h) a panoramic FESEM of the NWLIBs on the wafer.

envisioned for A-MEMS, even when combined with a photovoltaic or vibrational energy harvesting device.² Increasing the thickness of the battery electrodes to store more energy reduces power capability, because ions must diffuse longer distances. Ultimately, the fracture toughness of the active layers places an upper limit on the electrode thickness, because the stress induced by Li intercalation scales with the electrode thickness. For LiCoO₂, one of the most widely employed cathode materials, this limit is a mere 4 μm,¹ limiting the capacity far below the targets for many emerging applications.

The answer to the energy challenge is to amplify the areal energy density while maintaining fast kinetics. A number of three-dimensional (3D) LIB designs based on trenches, inverse opals, vertical rods, and periodic ‘sponges’ have been proposed,^{11,12} but a complete, fully-3D LIB has yet to be experimentally demonstrated. Regardless of the specific 3D geometry, reducing electrode feature dimensions and the interelectrode separation improves power performance by minimizing electron and ion diffusion times and by limiting Ohmic losses. Reductions in feature sizes also increase the interface area, lowering the local current density and the associated charge transfer overpotentials. Unfortunately, the increased interface area also requires more solid electrolyte, which functions as the electrode separator but does not itself carry any energy storage capacity. In commercial TFLIBs, the LiPON electrolyte is typically 1 to 2 μm thick,¹⁰ and using similar LiPON thickness in a 3D architecture would require electrode features of about 10 μm to maintain the electrolyte volume fraction at 10% or less. Such dimensions would again raise concerns about fracture and sluggish charge-transport kinetics. Substantially reducing the solid electrolyte thickness to below 1 μm is therefore essential for further increasing the power and energy density of 3D LIBs. At first glance, this would simply entail the successful deposition of a uniform,

pinhole-free electrolyte layer over a potentially complex surface incorporating high-aspect-ratio structures. However, as we show in this Letter, at thickness substantially smaller than 1 μm, the ability of the electrolyte to prevent electronic current flow between the anode and cathode and its chemical stability may be drastically compromised due to the onset of space-charge limited conduction (SCLC).

To understand how LIBs behave at reduced dimensions, we fabricate complete nanobatteries using Si nanowires as a template onto which the various battery components are sequentially deposited using physical vapor deposition, resulting in a core–multishell geometry (see Figure 1 and the Methods Section for details). Each nanowire LIB (NWLIB) consists, from center to exterior, of a Si nanowire metalized with Ti/Pt/Ti and coated with LiCoO₂ (cathode), followed by LiPON solid electrolyte, and an n-doped amorphous Si anode. The layers are deposited subsequently, with a 700 °C annealing in oxygen step following the LiCoO₂ deposition. At 0.5–1 μm in diameter and up to 7 μm in length, the NWLIBs are the smallest, complete secondary batteries realized to date.

We use three distinct approaches to characterize individual NWLIBs. The first two approaches use focused ion beam (FIB) milling and electron beam induced deposition (EBID) to locate, prepare, and contact individual NWLIBs, as shown in Figure 1f. The first approach utilized a highly insulating support of a 600 nm thermal SiO₂ layer atop a Si substrate, and the second approach used a free-standing 50 nm thick SiN_x support, allowing for simultaneous in situ transmission electron microscopy observations. In the third approach, we use a tungsten tip controlled by a nanomanipulator to contact individual NWLIBs directly on the fabrication substrate inside of a transmission electron microscope (TEM). In the first two approaches, we deposited the NWLIB onto the support from isopropanol suspension and then used FIB milling to expose

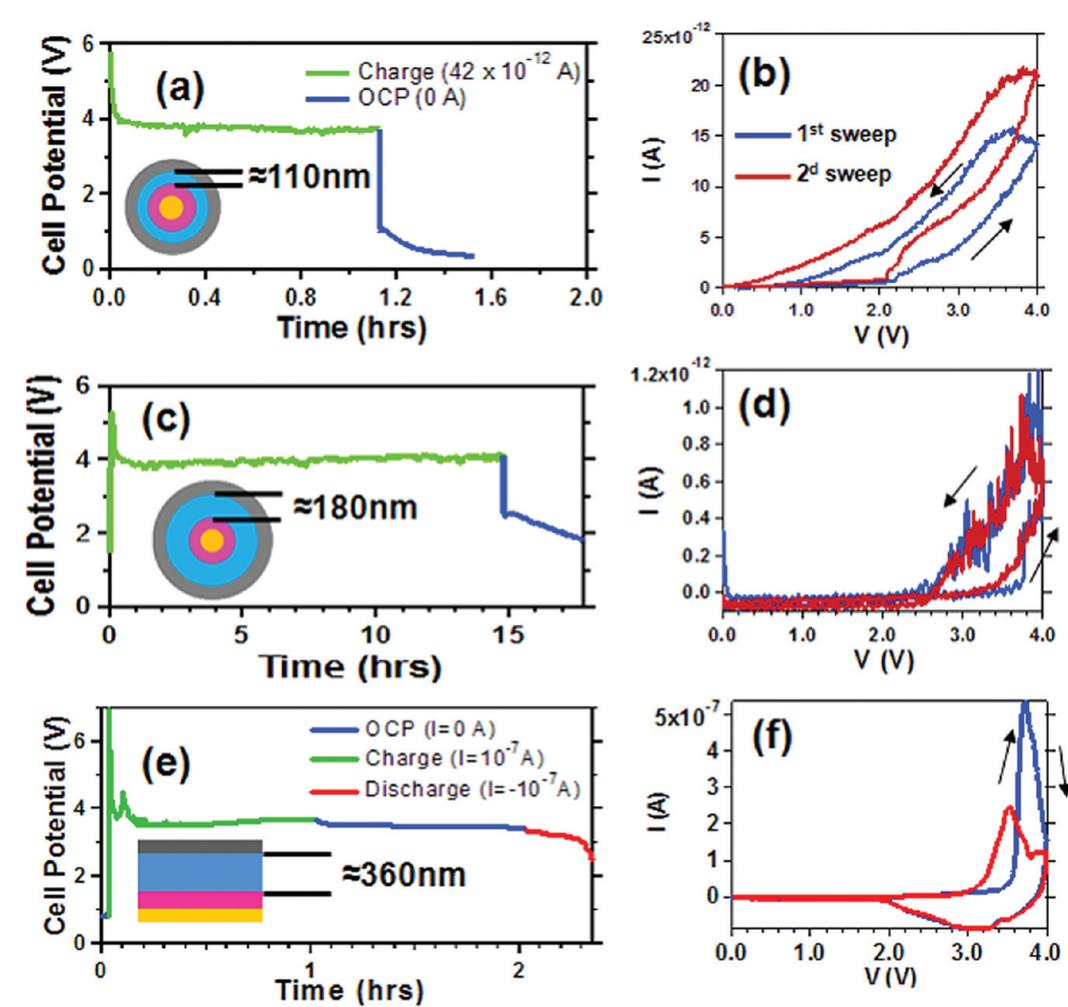


Figure 2. CCC-OCP and (a) slow scan I - V characteristics (b) NWLIB with 110 nm thick LiPON; (c,d) NWLIB with 180 nm thick LiPON; and (e,f) a thin film LIB with 360 nm thick LiPON (discharge shown in red). The voltage scan rate for I - V curves is 0.16 mV/s.

the Ti/Pt/Ti cathode current collector near the narrow end of the NWLIB. This is followed by EBID of Pt to connect the anode and cathode to nearby lithographically defined metal pads. For each NWLIB, near the cathode contact, a 'ring' of the amorphous Si anode is removed by FIB to electrically isolate the anode and cathode. In addition to NWLIBs, thin film LIBs (TFLIBs) are fabricated as experimental control specimens using the same procedure starting with flat Si/SiO₂ substrates. A bright-field TEM cross sectional image for an uncycled TFLIB is shown in Figure S1b, Supporting Information.

By focusing on individual nanobatteries, we eliminate the effects of collective behavior characteristic of large arrays, which simplifies interpretation of results and reduces the probability that a fabrication defect leads to catastrophic failure. Most importantly, the small dimensions allow us to image the entire NWLIB in a TEM, or scanning TEM (STEM), and observe changes in the microstructure during electrochemical cycling. Previously, nanoscale LIBs have been assembled inside TEMs for the purpose of in situ structural characterization during cycling.¹³ However, those one-of-a-kind nanobatteries could not be integrated into a microsystem nor were their current-voltage-time characteristics reported. Alternatively, thin cross sections of all-solid-state thin film batteries have been imaged in the TEM.^{14,15} While extremely informative, thin film cross

sections are difficult to handle, are much more sensitive to FIB damage, and do not capture the radial geometry characteristic of most proposed 3D LIB designs. Our NWLIBs constitute a flexible integrated platform for in situ electrochemical experiments compatible with TEM, STEM, and FESEM aimed at imaging and analyses of the microstructural changes that accompany charge transfer and correlating these with the observed electrical characteristics. Our scheme results in the fabrication of a large number, $\approx 10^6/\text{cm}^2$, of nearly identical specimens. Furthermore, each NWLIB is stable in air prior to charging, facilitating transport and measurement using different instruments and techniques.

Constant current charging-open circuit potential (CCC-OCP) curves for a NWLIB with a ≈ 110 nm thick LiPON and supported by highly insulating SiO₂ are shown in Figure 2a. Two slow scan linear voltammetry (I - V) sweeps collected just prior to CCC-OCP measurement are shown in Figure 2b. CCC-OCP and I - V sweeps for a NWLIB with 180 nm thick LiPON are shown in Figure 2c,d, respectively. During charging, the voltage for both NWLIBs initially rises to > 5 V, then decreases before stabilizing at ≈ 4 V. Once the charging current is turned off, the OCP for the thinner LiPON NWLIB drops rapidly to < 0.5 V. For the NWLIB with 180 nm LiPON, the OCP initially drops to ≈ 2.3 V and remains above 2 V for over 2 h.

Several other NWLIBs with the thinner LiPON and one other NWLIB with the thicker LiPON were also tested and showed similar behavior. For comparison, CCC-OCP constant current discharge and I - V sweeps collected for a TFLIB (LiPON thickness ≈ 320 nm) are shown in Figure 2e,f, respectively. As with NWLIBs, during charging the potential initially rises sharply (≈ 7 V), then decreases before rising again. The exact origin of this peak is presently unknown, but a similar peak was observed by Baggetto et al. during initial charging of a Si electrode coated with LiPON and immersed in an organic electrolyte with a Li metal counter electrode. The authors attributed the effect to an interfacial layer forming at the Si/LiPON interface during deposition.¹⁶ We observed no such interfacial layer, suggesting that the voltage spike may be inherent to Li transport across the Si/LiPON interface. Unlike the NWLIBs, the TFLIB does not rapidly self-discharge and can instead be intentionally discharged at constant current with a stable capacity of $\approx 16 \mu\text{A}\cdot\text{h}/\text{cm}^2$ for more than 10 cycles, as shown in Figure S2, Supporting Information. TFLIBs with LiPON layer thickness ≈ 100 nm were also fabricated but appeared electrically shorted, possibly due to pinholes, a hazard of the TFLIB geometry. No such pinhole shorting is observed for the NWLIBs chosen for electrical characterization. A short like this would likely cause Ohmic I - V characteristics, which is contrary to our observation that both NWLIBs display resistance $> 2 \text{ T}\Omega$ at 1 V.

TEM images of the NWLIBs show a high-quality dense LiPON layer with no readily observed defects, but despite this, both thicknesses of LiPON fabricated show significant self-discharging. The NWLIBs with the thinnest LiPON rapidly and completely self-discharge, and those with thicker LiPON maintain OCP > 2 V for only ≈ 2 h, indicating that electronic transport is still taking place across the thin LiPON electrolyte. To better understand the origin of the electronic current, we next examine in detail the NWLIB I - V characteristics. I - V sweeps for the NWLIBs exhibit the following three distinctive features: (1) the current increases sharply at a threshold voltage that depends on LiPON thickness; (2) there is hysteresis, such that the effective resistance is higher on the upward voltage sweep than on the downward voltage sweep; and (3) the current scales as a power law with voltage, $I \propto V^n$, with $n \approx 1$ at low V during the upward sweep, and $n \approx 2$ at higher V and during the downward voltage sweep, as shown in Figure 3,

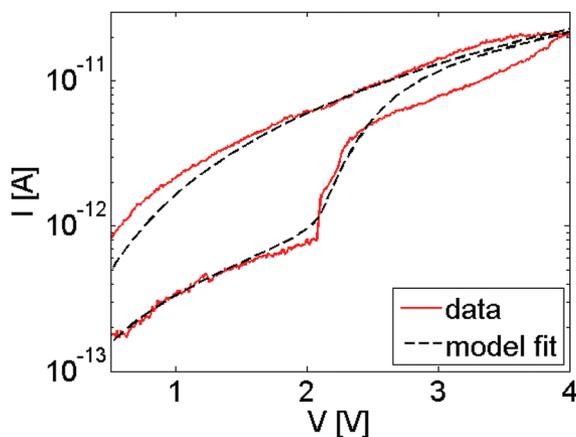


Figure 3. Measured and calculated I - V characteristics for the NWLIB with LiPON ≈ 110 nm (same data as in Figure 2b). Model parameters are: $N_t = 2 \times 10^{19} \text{ cm}^{-3}$, $n_0 = 3.5 \times 10^{16} \text{ cm}^{-3}$, $\mu = 4.5 \times 10^{-9} \text{ cm}^2/\text{V}\cdot\text{s}$, $N_c = 10^{18} \text{ cm}^{-3}$, $\delta = 32$, $l = 10$.

where $\log I$ vs V is plotted for the NWLIB with 110 nm thick LiPON. Similar characteristics have been observed in other devices, namely thin insulating films of various transition-metal oxides and perovskites, sandwiched between two conductor electrodes.¹⁷ As discussed in previous works and as we show here, the theory of trap-controlled SCLC can explain these features.¹⁸

Transport characteristics are governed by SCLC when the injected charge density exceeds the equilibrium thermal charge density n_0 .¹⁸ At low-charge injection, electron transport is Ohmic: $J = e\mu nV/d$, where e , μ , and n are the electron charge, mobility, and density, respectively, V is the applied voltage, and d is the insulator thickness. The current-voltage relation in the SCLC regime is given by $J = 9/8\epsilon\mu(V^2/d^3)$, where ϵ is the dielectric constant of the insulator. In the trap-free case, the transition from Ohmic to SCLC occurs at a cross over voltage $V^* = 8/9(en/\epsilon)d^2$. The dependence of V^* on the insulator thickness squared has important implications for nanobatteries, as we discuss below. The effect of traps, or localized energy levels found in most insulators, is to change the crossover from Ohmic to SCLC regimes in a manner that depends on the details of the traps' energy distribution. We assume a distribution of trap energies given as $D(E) = (N_t/kT_c) \exp[(E - E_c)/kT_c]$, where T_c parametrizes the trap distribution in energy and N_t is the trap density. Finally, we suppose that the escape rate of trapped charge is small compared to the voltage scan rate, so that the occupation of a trap state persists throughout an I - V scan.

Following the analysis of Lampert and Mark,¹⁸ we obtain three distinct regimes in the I - V characteristics. At low voltage, and therefore low charge injection, the transport is approximately Ohmic, $J \propto V$. There is a transition at the voltage (see also Supporting Information) $V_1^* = V_0(\Gamma(l+1)^2/l(2l+1))$, where $V_0 = en_0L^2/e$, $\Gamma = (N_t/n_0)(n_0/N_c)^{1/l}$, $l = T/T_c$, and N_c is the effective density of states for charge carriers. For voltages above V_1^* , progressively more traps are filled so that an increasing fraction of injected charge contributes to transport. Just above V_1^* , $J \propto V^{(l+1)}$ and the current increases rapidly. The second transition occurs at $V_2^* = 4/3V_0(\Gamma(l+1)^2/l(2l+1))^{1/l-1}$. Above this voltage, the traps are filled so that all injected charges participate in transport, and here the trap-free, ideal SCLC behavior is recovered, with $J \propto V^2$. For the downward voltage scan, we assume all the traps are filled, and we take the current to be the sum of thermal and SCLC contributions. Figure 3 shows excellent agreement between experimental and calculated I - V characteristics for the NWLIB with the thin ($d = 110$ nm) LiPON electrolyte.

Trap-controlled SCLC can discharge a battery either via electron detrapping or from direct electron transport from anode to cathode and concomitant Li transport in the same direction. To determine the relative importance of these processes, we first consider electron detrapping. Based on the model fit to the experimental data, the trap density is estimated to be $N_t \approx 10^{18} \text{ cm}^{-3}$, which, given the NWLIB dimensions, yields a total charge of $\approx 10^{-13}$ C. However, charge-discharge curves indicate that appreciable discharge requires $\approx 10^{-9}$ C. Moreover since the total number of traps scales with layer thickness, batteries with thicker LiPON would be more susceptible to discharge, contrary to observations. It is therefore more likely that direct electron transport is responsible for the observed I - V characteristics and also for the battery self-discharge. In this case, the electrolyte thickness is crucial, since the onset of large currents (V_1^*) scales as d^2 .¹⁸ The insulator

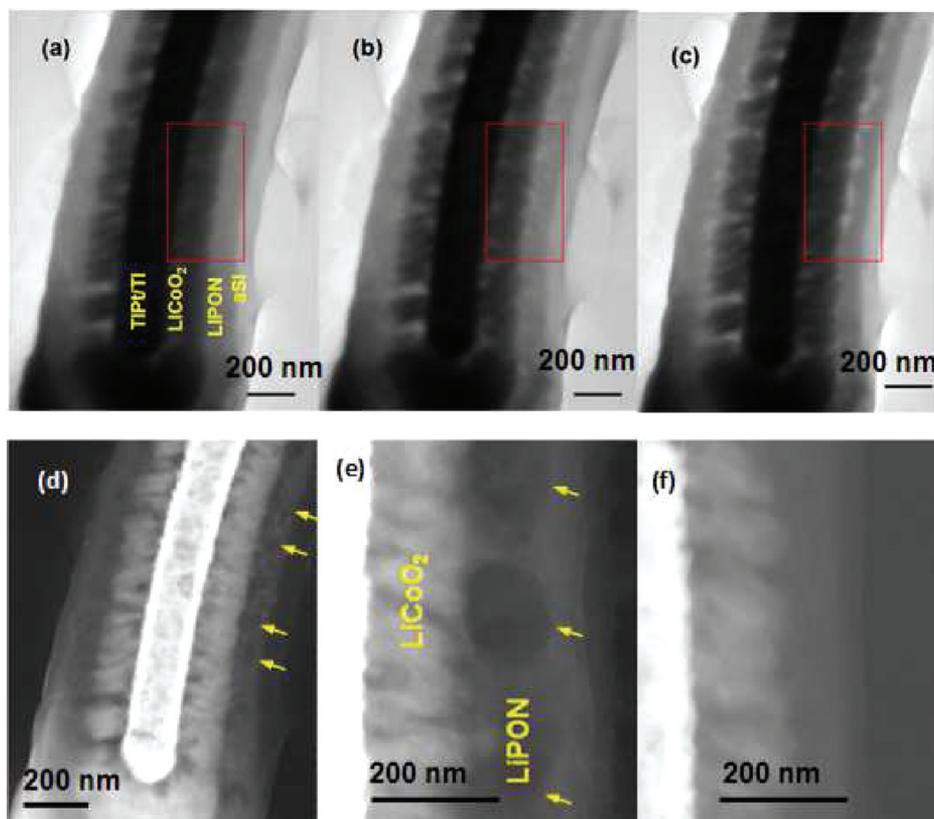


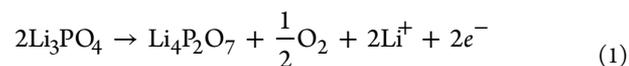
Figure 4. In situ TEM testing of a NWLIB (LiPON \approx 110 nm). (a) Before charging (red box includes LiCoO₂/LiPON interface). (b) After first discharge, LiPON in the box has a striped texture. (c) After seven charge–discharge cycles voids appear at LiPON/LiCoO₂ interface. (d,e) Ex situ HAADF STEM of the same NWLIB after cycling, 50–100 nm voids appear at or near the LiPON/LiCoO₂ interface, as indicated by the yellow arrows. (f) An enlarged area of an uncycled NWLIB from the same batch included for comparison with image (e).

thickness also appears in the SCLC prefactor, $J \propto d^{-3}$, which indicates a steep dependence of the leakage current on thickness. The thicker electrolyte layer ($d \approx 180$ nm) exhibits a larger V_1^* (3.8 V), although this increase is smaller than that predicted by a pure d^2 dependence of V_1^* . The combination of nonuniformity in the LiPON layer thickness and the roughness in the LiCoO₂ could lead to regions of thinner electrolyte that would dominate the I – V characteristics and could explain this discrepancy.

SCLC theory neglects the role of the contact-insulator interface. For aqueous electrolytes, this interface is all-important, due in part to the extremely short Debye length of the electrolyte (which implies that the potential drop is localized at the interface). However in solid-state electrolytes, the potential drop has been observed to extend far into the electrolyte layer,¹⁵ so that the picture of bulk-limited SCLC is applicable.

SCLC is fundamentally a bulk-limited transport mechanism, implying facile injection of charge at the contacts (LiCoO₂ and Si, in the present case). Indeed, Yu et al. reported large electronic current for a 1.5 μm thick LiPON layer sandwiched between Pt electrodes (a Li ion blocking metal) at a potential of ≈ 5.5 V, together with the formation of bubbles at the positive electrode.¹⁹ They also reported a pronounced change in the impedance characteristics suggesting formation of an interfacial layer with large capacitance. To explain the bubble formation and the apparent breakdown of LiPON, these workers proposed the following chemical reaction involving the breaking of P–O bonds, formation of P–O–P chains, and

releasing free oxygen:



To determine whether breakdown of LiPON was occurring in our case, we performed electrochemical cycling of a NWLIB mounted on a Si chip with a 50 nm thick SiN_x membrane window and patterned Au electrodes inside a TEM. A series of TEM images is collected prior to charging to ensure that the microstructure is stable and that the electron beam is not appreciably damaging the LiPON layer. The NWLIB is then biased from 0 to 4.2 V in 0.01 V increments over 20 min period, at which point another series of TEM images is collected (the electron beam is blanked off during the charging). The NWLIB is then cycled 7 times between 2.5 and 4.2 V (discharged and charged states, respectively) over a period of 9 h, and the final images is collected. The net current flowing through the battery cannot be determined precisely because the Si chips with nitride membranes and large-area contacts exhibit current leakage with a voltage dependent resistance similar to that of the NWLIBs, as shown in Figure S3, Supporting Information. Images collected initially, after first charge, and after repeated cycling are shown in Figure 4a–c, respectively. As seen in the TEM images, after the NWLIB is biased to 4.2 V, a striped pattern appears in LiPON, and a brighter contrast can be observed along the LiCoO₂/LiPON boundary (Figure 4b). The bright areas can be interpreted as voids and expanded substantially following seven charge–discharge cycles (Figure 4c). Following the in situ TEM

characterization, the NWLIB is examined *ex situ* in a field-emission STEM (and TEM) operating at 300 kV, which allows higher resolution and contrast images to be collected. High-angle annular dark field (HAADF) STEM examination of the same NWLIB confirmed the appearance of voids, as indicated by yellow arrows in Figure 4d,e. For comparison, another NWLIB that was not cycled and was lying nearby on the SiN_x grid is also imaged and does not show presence of voids (Figure 4f), under similar imaging conditions. Using lowest intensities and blanking of electron beams to minimize radiation damage, we do not observe formation of the voids in both cycled and pristine NWLIBs after several hours of examination under the chosen conditions.

To further explore the nanostructural changes in the batteries upon cycling and to confirm that the observed bubble formation in the LiPON electrolyte is due to cycling and not due to electron damage in the TEM, a NWLIB was electrically tested directly on the fabrication substrate through our third characterization method in a TEM holder equipped with a piezomanipulator that has been described previously.^{13,20} Figure 5a shows a pristine NWLIB directly grown on the substrate after contact with a tungsten tip. The substrate and the tungsten tip served as current collectors in the electrochemical cycling. During charging or discharging, a positive or negative potential was applied to the substrate with respect to the tungsten tip, respectively. During the first charging, the voltage applied to the substrate was gradually increased up to 50 V, and a current in the order of several nA was detected. This large voltage is characteristic of the highly insulating tungsten oxide contact, which helps to limit the current in these tests. During the first charging, a void was formed at the $\text{LiCoO}_2/\text{LiPON}$ interface, as pointed out by the yellow arrow in Figure 5b. Interestingly, the void healed after discharge at a bias of -40 V (Figure 5c). During the second charging/discharging cycle, the void at the $\text{LiCoO}_2/\text{LiPON}$ interface appeared/disappeared again, as shown in Figure 5d,e. Figure 5f,g is a higher magnification view of the areas marked by blue and red dotted rectangles in Figure 5d and 5e, respectively, showing clearly a void was formed at the $\text{LiCoO}_2/\text{LiPON}$ interface after charging and disappeared after discharging.

We have explored the possibility that the reaction described by eq 1 induces discharge via release and subsequent extraction of charge carriers (either Li^+ ions or electrons). This possibility is ruled out by noting that the number of charges collected during a single I - V scan exceeds the total number of atoms in the electrolyte. Moreover, the number of charges collected exceeds the Li capacity of the electrodes, so that the only scenario physically consistent with the data is electron injection and collection.

In summary, substantial reduction in the electrolyte thickness below 100 nm can lead to rapid self-discharge of the battery even when the electrolyte layer is conformal and pinhole-free as demonstrated by *in situ* cycling of individual, solid-state heterostructure NWLIBs. This problem may be addressed by using a different electrode/electrolyte combination or by inserting a thin Li ion transparent layer between the electrode(s) and LiPON to prevent electron/hole injection. Illustrating the importance of electric fields in the electrolyte, this work provides useful guidelines for optimal design of long-cycling life miniaturized 3D LIBs.

Methods. *Fabrication of NWLIBs and TFLIBs.* Fabrication of NWLIBs starts with Si nanowires (≈ 170 nm in diameter) grown by Au-catalyzed VLS on Si (111) substrates

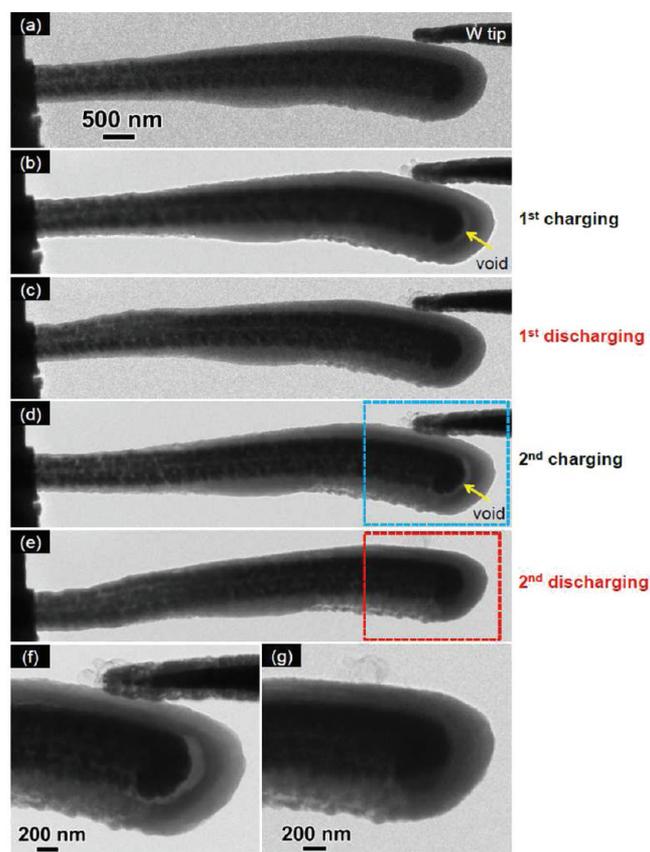


Figure 5. Microstructure evolution of a NWLIB during cycling inside a TEM. (a) A pristine NWLIB directly grown on a Si substrate was contacted by a tungsten tip. During cycling, the potential is applied to the substrate with respect to the tungsten tip, and the substrate as well as tungsten tip served as current collectors. (b) After the first charging, a void is formed at the $\text{LiCoO}_2/\text{LiPON}$ interface, as indicated by the yellow arrow. (c) The void is healed after discharge. (d,e) The second charge–discharge cycle showing the formation and disappearance of the void at the $\text{LiCoO}_2/\text{LiPON}$ interface. Note that the tungsten tip was extracted away after the second discharge. (f) Higher magnification view of the area marked by blue dotted rectangle in (d), showing a void is formed at the $\text{LiCoO}_2/\text{LiPON}$ interface. (g) Higher magnification view of the area marked by red dotted rectangle in (e), showing the void is healed again after discharge.

according to a previously reported recipe.²¹ After removal of the Au catalyst nanoparticles using a Au etch solution, the nanowires are coated with ≈ 10 nm Ti, followed by ≈ 30 nm Pt, ≈ 40 nm Ti, and ≈ 180 nm of LiCoO_2 , all using sputter deposition in the same chamber and without exposure to air (see Supporting Information for more details). We estimate the uncertainty in the thickness of individual layers to be $\approx 15\%$ based on comparison of measurement made with cross section SEM and TEM and mechanical profilometry (used only for TFLIBs). The coated nanowires are then annealed in ambient oxygen at 700 °C for 2 h. Following the heat treatment, the samples are sputter coated with ≈ 110 nm of LiPON or ≈ 180 nm of LiPON and finally ≈ 35 nm of phosphorus-doped amorphous Si. FESEM images of NWLIBs collected at different stages of fabrication are shown in Figure 1a–d, along with a fractured cross section (Figure 1d) and a 3D schematic of a NWLIB (Figure 1e), respectively. Our fabrication scheme results in simultaneous production of a large number ($>10^6/\text{cm}^2$) of NWLIBs (Figure 1h). TFLIBs are

fabricated alongside the NWLIBs starting with Si wafers coated with 100 nm of thermal oxide. The LiCoO₂, LiPON, a-Si layer thicknesses for the TFLIBs are ≈400, ≈360, and ≈80 nm, respectively, with the difference in thickness due to the different substrate geometry. X-ray diffraction (XRD) and electron backscatter diffraction (EBSD) patterns collected after fabrication confirm that the LiCoO₂ crystallizes in the hexagonal phase (*R3m* space group) with a preferred (00.3) orientation nearly perpendicular to the Si nanowire [111] axis (see Figures S4 and S5, Supporting Information). Pt dots with diameters of 940 μm are defined on the top TFLIB a-Si layer and served as the anode current collectors.

Following deposition, NWLIBs are suspended in isopropanol using sonication and then drop-cast onto Si wafers with 600 nm of thermal oxide and Pt contact pads deposited evaporation through a shadow mask. A dual beam FIB is used to expose the inner Ti/Pt/Ti cathode current collector and electrically isolate the anode from the cathode by removing a 'ring' of Si. Electron beam induced deposition is then used to connect the anode and cathode electrodes to the Pt contact pads. Integrated NWLIB on a 600 nm thick SiO₂/Si and on a 50 nm SiN_x membrane is shown in Figure 1f,g, respectively.

In situ and *Ex situ* Electrical Testing/Electron Microscopy and Characterization. Slow scan linear sweep voltammetry (*I*-*V*), CCC-OCP constant current discharge (*I*-*t*) characteristics for the NWLIBs and the TFLIBs are collected using a computer controlled current/voltage source/measure unit with an input impedance of >10¹⁴ Ω and 10 fA resolution, according to the manufacturer, as well as a commercial potentiostat (used only for the thin film batteries). The NWLIB electrochemical measurements are performed in either a FESEM retrofitted with two electrical nanomanipulators or a LaB₆ JEOL TEM 2100 and in a FEI Tecnai F 30 TEMs with custom specimen stages designed for *in situ* electrical measurements. The TFLIBs are electrically characterized in an Ar-filled glovebox. As-fabricated NWLIBs also are analyzed using a FESEM equipped with an EBSD detector. Medium- and high-resolution S/TEM imaging of pristine and cycled NWLIBs and TFLIBs are performed in a field-emission FEI Titan 80-300 analytical S/TEMs operating at 300 kV accelerating voltage. XRD scans are collected on a scanning microdiffractometer equipped with a general area detector diffraction system using Cu Kα radiation.

Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the products identified are necessarily the best available for the purpose.

■ ASSOCIATED CONTENT

📄 Supporting Information

Microstructure and electrical characteristics for TFLIBs; additional NWLIB microstructure and electrical test data; details of the model for space charge-limited conduction with traps. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Supplementary Information

Electrolyte stability determines scaling limits for solid-state 3D Li-ion batteries

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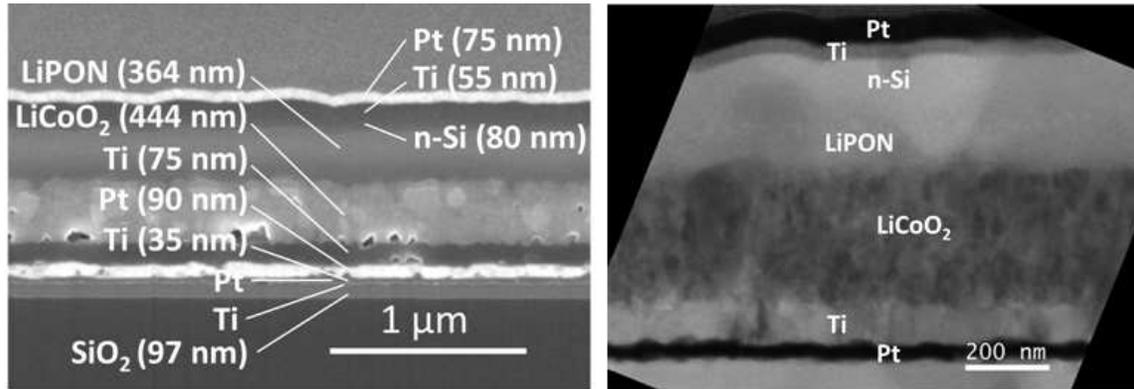


Fig. S1(a) FESEM and (b) TEM of a TFLIB cross section

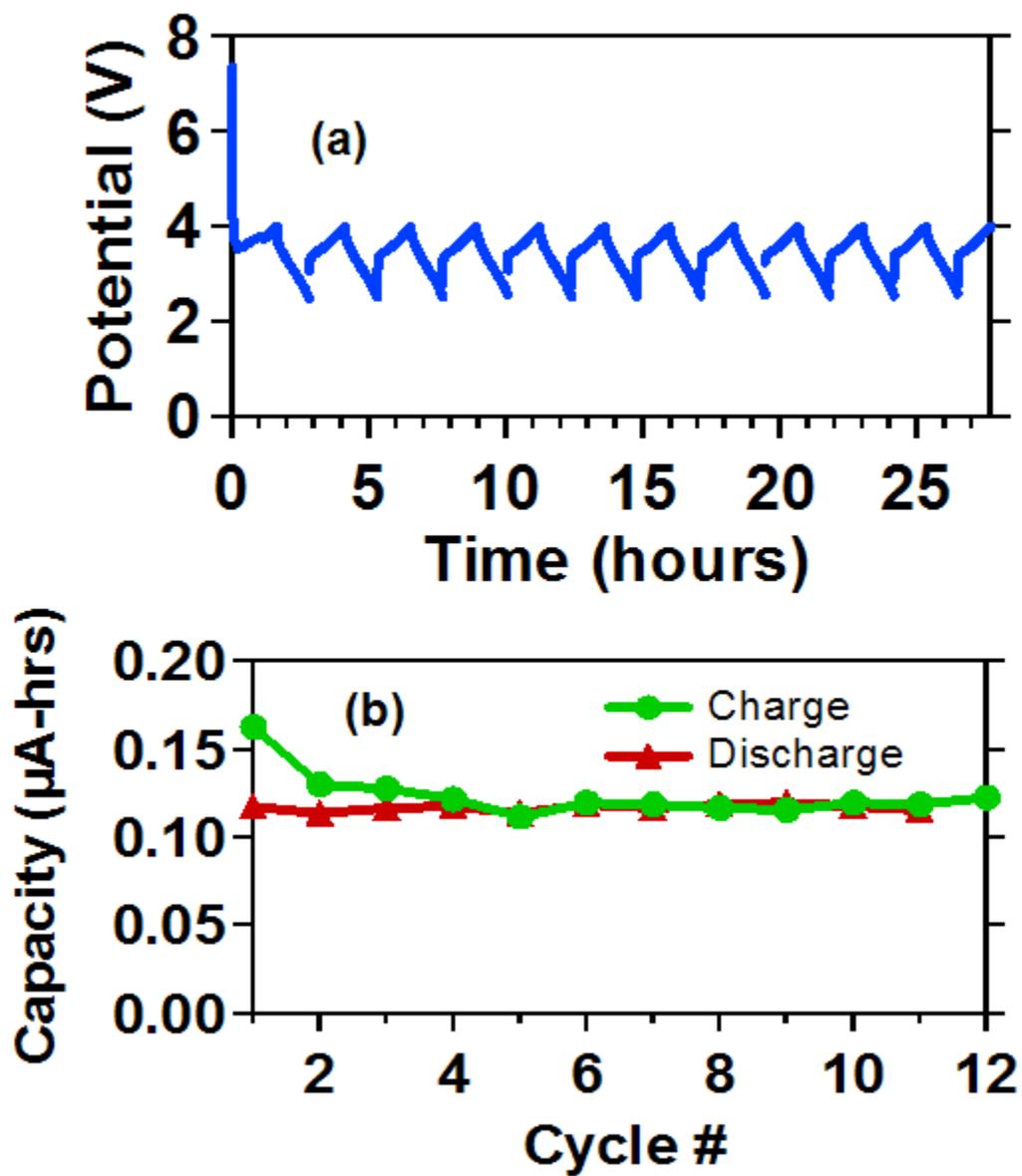


Figure S2 (a) Charge-discharge curves at 10^{-7} A and (b) calculated capacity for a thin film LIB with 0.007 cm^2 active area.

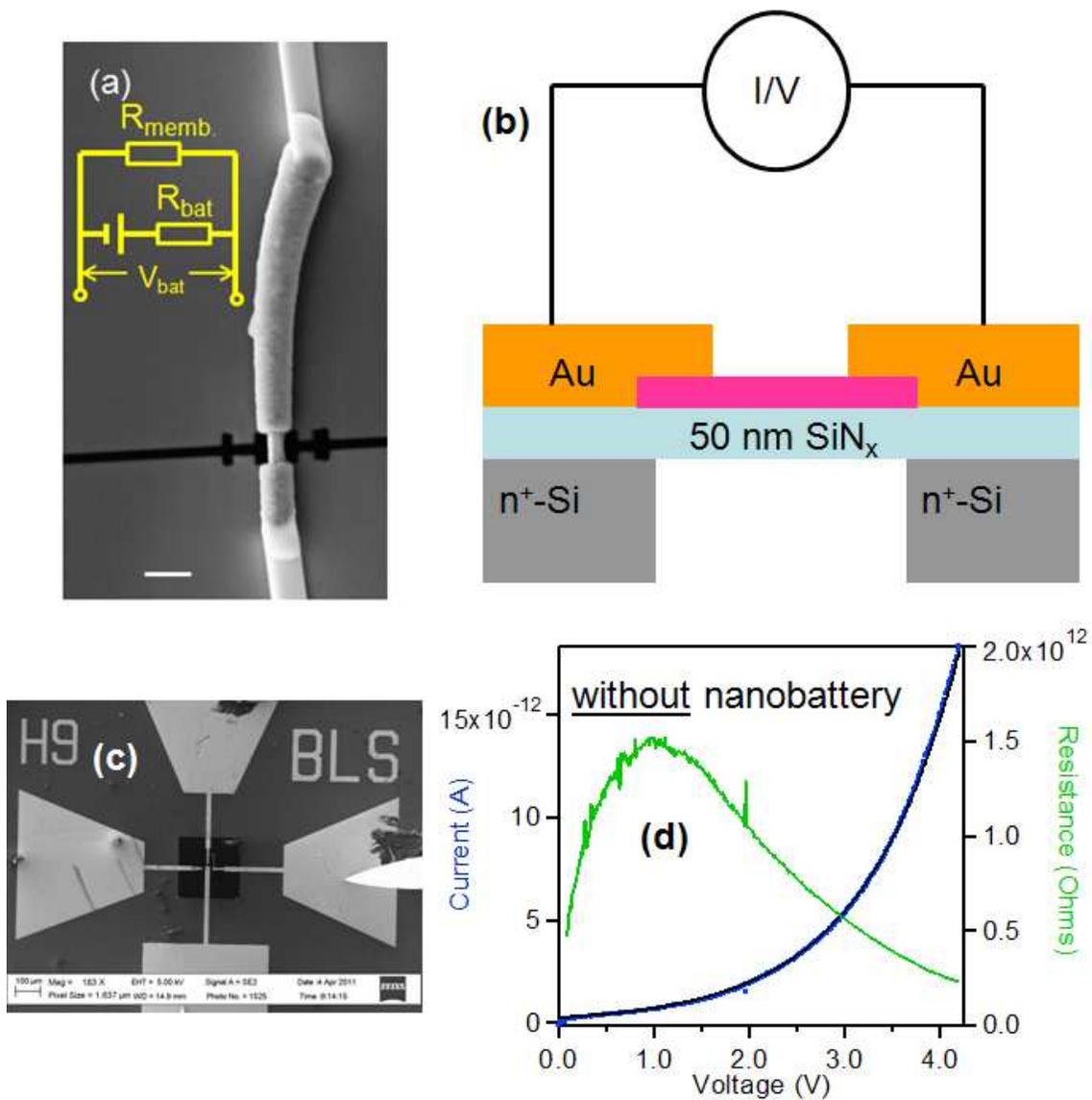


Figure S3 (a) FESEM image of a NWLIB on a SiN_x membrane with a schematic of the equivalent circuit, R_{memb} and R_{bat} are both voltage dependent; (b) schematic of the in situ biasing chip; (c) FESEM of the chip showing the Au contact pads; (d) I-V characteristics (blue) and effective resistance (green) for a Si chip without a nanowire.

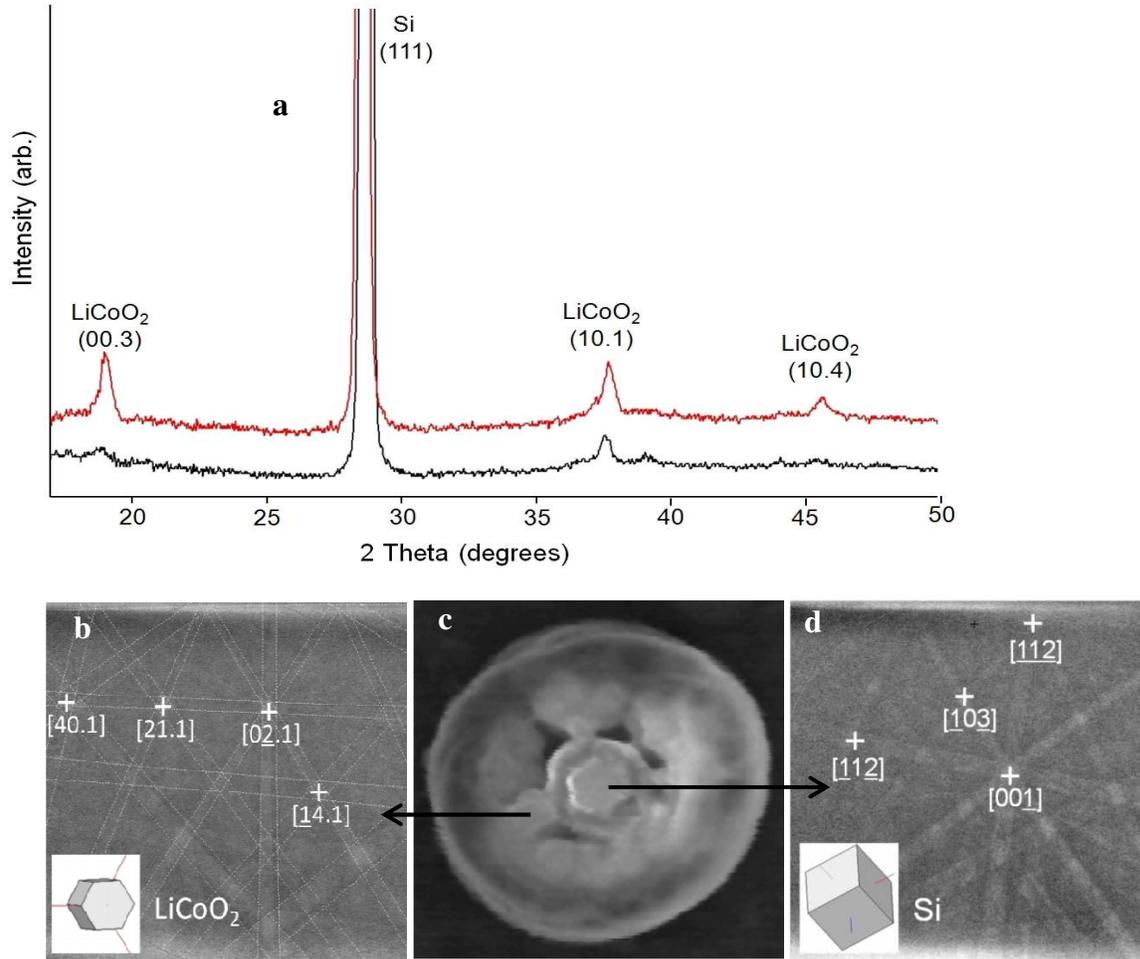


Figure S4. (a) XRD Ω - 2θ scans from the NW battery array. Phases detected: Si (substrate and NWLIBs, red curve) and LiCoO₂, while peaks from LiPON and thin Ti/Pt/Ti layers were not registered. LiCoO₂ indices correspond to the hexagonal phase (R-3m; PDF#75-0532) with lattice parameters $a=2.817$ Å and $c=14.052$ Å. Removal of NWs from substrate (black curve) has dramatically reduced (003) peak intensity, which implies that the observed texture in scan (a) is associated with LiCoO₂ shell on Si NWs. The LiCoO₂ texture in the shell was confirmed by EBSD analysis. EBSD patterns of the LiCoO₂ crystallites (b) and a Si nanowire (d), obtained from the cross-sectioned NWLIB (c) as indicated by arrows. Inset with simulated orientation of LiCoO₂ unit cell in (b) indicates that the (00.3) plane has preferred orientation nearly parallel to the Si (111) plane: the misorientation angle between [00.3] and [111] is 8°.

Model for space-charge limited conduction with traps

The general model for space-charge limited transport with traps describes electron transport via drift together with Poisson's equation for the electric field:

$$J = e\mu nE$$

$$\partial \frac{dE}{dx} = \rho(x) = -e(n - n_0) - e \sum_j (n_{ij} - n_{j,0})$$

Here n_0 is the equilibrium density, and the sum in the 2nd term is over trap states, labeled by j , and e is the magnitude of electron charge. $n_{j,0}$ is the equilibrium density of the j^{th} trap state. We assume a continuous distribution of trap energies:

$$D(E) = \left(\frac{N_t}{k_b T_c} \right) \exp \left[\frac{(E - E_c)}{k T_c} \right].$$

We further assume that the trap space charge density is

much larger than the injected charge density, so that $\rho(x) \approx N_t [F(x), F_0]$. Here

$F(x)$ is the quasi-Fermi level and F_0 is the equilibrium Fermi level. N_t is simply the occupied trap density at position x :

$$N_t [F(x), F_0] = \int_{F_0}^{F(x)} \left(\frac{N_t}{k_b T_c} \right) \exp \left[\frac{(E - E_c)}{k T_c} \right] dE.$$

As described in the text, important parameters in the solution are: $\ell = \frac{T_c}{T}$ and

$$\Gamma = \left(\frac{N_t}{n_0} \right) \left(\frac{n_0}{N_c} \right)^{1/\ell}.$$

Using the regional approximation method leads to 3 distinct regimes

in the current-voltage relation (expressed in terms of $V_0 = \frac{en_0 L^2}{\partial}$):

1. For $V < V_0 \frac{\Gamma(\ell+1)^2}{\ell(2\ell+1)}$, $J = \frac{e^2 n_0^2 \mu L}{\partial} \frac{1}{2A} \left[1 - \sqrt{1 - \frac{4\partial AV}{en_0 L^2}} \right]$, where

$$A = \frac{\ell^2}{\Gamma(\ell+1)(2\ell+1)}.$$

The low voltage end of this regime corresponds to simple

Ohmic Transport.

2. For $V_0 \frac{\Gamma(\ell+1)^2}{\ell(2\ell+1)} < V < \frac{4}{3} V_0 \left(\frac{\Gamma(\ell+1)^2}{\ell(2\ell+1)} \right)^{1/\ell-1}$, there is not an explicit $J-V$ relation.

The solution is described through implicit relations involving the variables v, w , and u . v and w are related to J and V according to:

$$J = \frac{e^2 n_0^2 \mu L}{\partial} \frac{1}{w}$$

$$V = \frac{e n_0 L^2}{\partial} \frac{v}{w^2}$$

The $J-V$ relationship is extracted via the parametric equations in u :

$$w = \frac{1}{2} \left[\frac{2\ell}{\Gamma(\ell+1)} \right]^{2\ell/(\ell-1)} + \frac{\ell}{\Gamma(\ell+1)} \left[u^{(\ell+1)/\ell} - \left(\frac{2\ell}{\Gamma(\ell+1)} \right)^{(\ell+1)/(\ell-1)} \right]$$

$$v = \frac{1}{3} \left[\frac{2\ell}{\Gamma(\ell+1)} \right]^{3\ell/(\ell-1)} + \frac{\ell}{\Gamma(2\ell+1)} \left[u^{(2\ell+1)/\ell} - \left(\frac{2\ell}{\Gamma(\ell+1)} \right)^{(2\ell+1)/(\ell-1)} \right]$$

At the onset of this regime, the current-voltage relation can be approximated by:

$$J \approx N_c \mu e^{(1-\ell)} \left[\frac{\partial \ell}{N_t (\ell+1)} \right]^\ell \left(\frac{2\ell+1}{\ell+1} \right)^{(\ell+1)} \frac{V^{(\ell+1)}}{d^{(2\ell+1)}}$$

3. For $V > \frac{4}{3} V_0 \left(\frac{\Gamma(\ell+1)^2}{\ell(2\ell+1)} \right)^{1/\ell-1}$, we recover trap-free space charge limited transport:

$$J = \frac{9}{8} \partial \mu \frac{V^2}{d^3}.$$

For the current-voltage relation during the downward voltage sweep, we assume that all of the traps are occupied so that we may treat the problem as a trap-free insulator. We find that approximating the total current as the sum of thermal and SCLC current matches the exact solution well. The current-voltage relation is therefore simply:

$$J = ne\mu \frac{V}{d} + \frac{9}{8} \partial \mu \frac{V^2}{d^3} \text{ over the entire voltage range.}$$

We next comment on using a one-dimensional model for the cylindrical geometry of the nanowire battery. The inner wire radius r_1 is approximately 345 nm, while for the

thin layer the LiPON thickness d is 110 nm. The validity of the 1-d model can be checked by expanding the cylindrical solution in powers of $\frac{d}{r_1}$. For illustration, in the

Ohmic regime the current-voltage relation is:

$$J(r_1) = e\mu n \frac{V}{r_1 \log \left[1 + \frac{d}{r_1} \right]} \approx e\mu n \frac{V}{d} \left(1 + \frac{1}{2} \left(\frac{d}{r_1} \right) + \dots \right).$$

A similar (though more involved) analysis applies for the SCLC regime. We therefore estimate that values obtained with the one-dimensional model are within 30% of those obtained from the full cylindrical model, and is sufficient to capture the qualitative features of the electron transport.