

Supporting Information

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SI Text

The microbattery is capped with a PDMS cover to force the ions to travel laterally during cycling. Fig. S2A shows the optical image of such battery electrodes (immersed in electrolyte). Here, we coat half of the PDMS with gold to visualize the interface between the PDMS cover and the electrode. With a 50 \times objective, the gap between the PDMS and the electrode is estimated to be ~ 5 μm , which, however, can still provide a pathway for ions. Fig. S2B shows the same sample configuration but with an external pressure applied to the PDMS. The slightly curved interface suggests a tight contact between the PDMS and the electrode.

Modeling Microbatteries in COMSOL. Here, a simple 1D isothermal model is used to simulate the microbattery. Because of the difficulties in defining the 3D holographic electrodes and the conformal active material coatings in the simulation, we approximate the 3D Ni scaffold and its active material coatings as an ensemble of spherical particles. The diameters of the active material particles are determined by fitting the experimental capacity retentions of cathode and anode at 500 and 1,000 C (the microbattery is tested in a large electrolyte reservoir). The model contains the following elements:

- i) Ni current collectors (40% FF) that account for electronic conduction in the electrodes. Because the Ni current collector is continuous in the 3D space and the thin active material layers are conformally deposited on the Ni scaffold, the effective electronic conductivity of the electrodes is approximately equal to that of nickel.
- ii) Conductive particles and active material spheres that form the electrodes. The equivalent diameter and FF of Ni–Sn spheres in the negative electrode are 70 nm and 20%, respectively. For the positive electrode, the equivalent diameter

and FF of LMO particles are 100 nm and 30%, respectively. The electrode digit width in the simulation represents half of the dimension in experiment, because each anode (cathode) interacts with two adjacent cathodes (anodes).

- iii) Electrolyte made of 1 M LiClO_4 in 1:1 mass ratio ethylene carbonate:dimethyl carbonate. The Li^+ diffusion coefficient is $\sim 2.6 \times 10^{-10}$ m^2/s (1).
- iv) Two adjacent electrode digits are separated by 15 μm ;
- v) Equilibrium potential obtained experimentally from discharge curves of half cells to entail Butler–Volmer electrode kinetics;
- vi) Tortuosity of the electrode is calculated using a volume averaging approach for monosized objects (2).
- vii) The potentiostatic intermittent titration technique is used to measure the diffusivity of the Ni–Sn and manganese oxide. The diffusivity of the Ni–Sn varies between 9.3×10^{-18} and 8.5×10^{-17} m^2/s . The manganese oxide diffusivity varies between 1.5×10^{-19} and 1.1×10^{-16} m^2/s . In the simulation, a constant diffusivity in these ranges is used to approximate the diffusivity in the electrode materials.

Table S1 summarizes all of the parameters used in the simulations. The modeled battery is initially fully charged, where the Li^+ concentration is at its maximum in the anode and at minimum in the cathode.

Simulating Holographic Structures. The holographic structure is simulated in MATLAB by calculating the 3D interference pattern. Once the volume data are obtained, an isosurface value (equivalent to exposure threshold) is calculated for targeted volume FF. The surface area of a unit cell is obtained by subtracting the area of the side faces from that of the isosurface.

1. Verbrugge MW, Koch BJ, Schneider EW (2000) Mass transport in lithium-battery solvents. *J Appl Electrochem* 30(3):269–275.

2. Ahmadi MM, Mohammadi S, Hayati AN (2011) Analytical derivation of tortuosity and permeability of monosized spheres: A volume averaging approach. *Phys Rev E Stat Nonlin Soft Matter Phys* 83(2 Pt 2):026312.

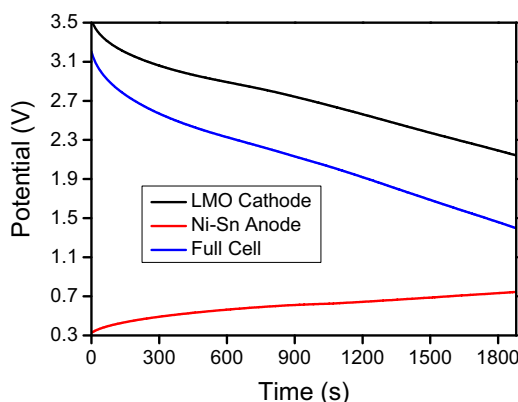


Fig. S1. Voltage profiles of a microbattery that is discharged at 1 C in a three-electrode configuration using lithium metal as the reference, where the LMO cathode cycles between 3.5 and 2.2 V versus Li/Li^+ (black curve) and the Ni–Sn anode cycles between 0.3 and 0.8 V versus Li/Li^+ (red curve). The resultant full cell cycles between 3.2 and 1.4 V (blue curve).

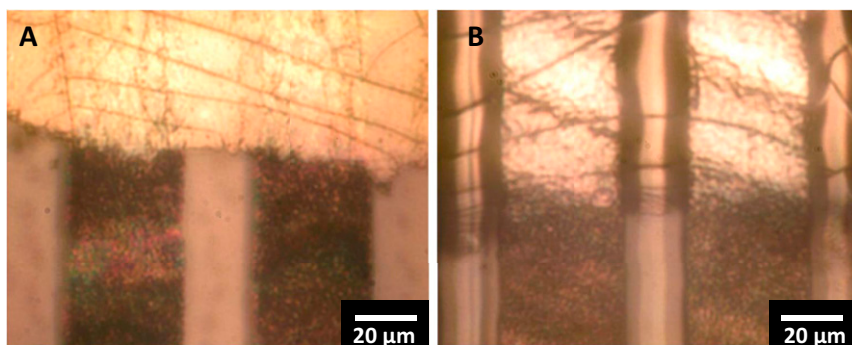


Fig. S2. Optical images of battery electrodes capped by PDMS covers. To visualize the contact between electrodes and PDMS, the top half of the PDMS surface is coated with gold. (A) No pressure applied to PDMS, and (B) external pressure applied to PDMS to ensure good contact.

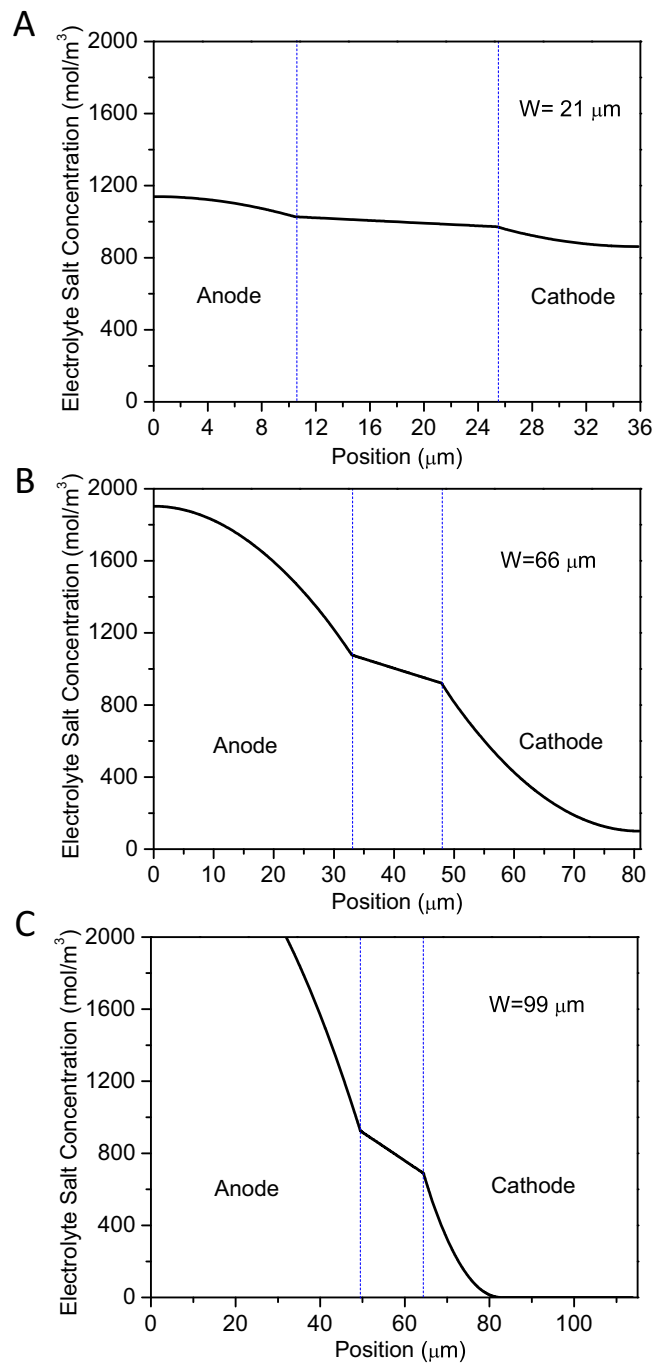


Fig. 53. Calculated electrolyte concentrations in microbattery unit cells. The simulations are conducted for three different digit widths (21, 66, and 99 μm) at the end of 20-C discharge. (A) For the cell made of 21- μm -wide digits, the electrolyte is only slightly polarized and lithium ions can fully transport from anode to cathode at the end of discharge. (B) When $W = W_c$ (66 μm), there is a large concentration gradient in the electrolyte, which nearly drops to zero on the right side of the cathode, but the ion diffusion is still sufficient to achieve a complete lithiation in the cathode. (C) As for $W = 99 \mu\text{m}$, the salt is completely depleted beyond 80 μm in the cathode, which dramatically raises the overpotential and prematurely ends the discharge.

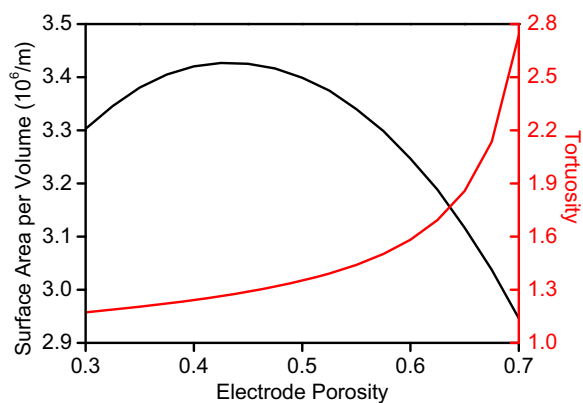
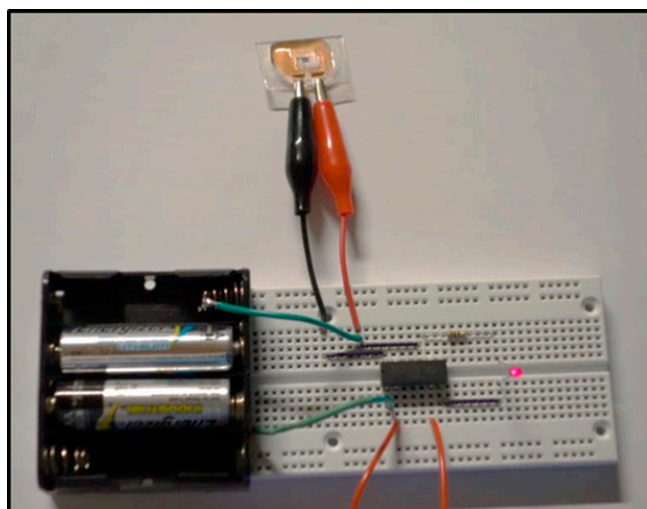


Fig. S4. Calculated surface area (black curve) and tortuosity (red curve) of battery electrode as a function of porosity.

Table S1. Values of parameters used in COMSOL modeling

Simulation parameters	Value
Solid-state Li-diffusivity of Sn	$8.5 \times 10^{-17} \text{ m}^2/\text{s}$
Solid-state Li-diffusivity of LMO	$1.1 \times 10^{-16} \text{ m}^2/\text{s}$
Ni-Sn particle diameter	$70 \times 10^{-9} \text{ m}$
LMO particle diameter	$100 \times 10^{-9} \text{ m}$
Ni-Sn electrical conductivity	$1.4 \times 10^7 \text{ S/m}$
LMO electrical conductivity	$1.4 \times 10^7 \text{ S/m}$
Salt diffusivity in electrolyte	$2.6 \times 10^{-10} \text{ m}^2/\text{s}$
Ni-Sn volume filling fraction	0.2
LMO volume filling fraction	0.3
Tortuosity of electrode	2.7



Movie S1. An LED is driven by the microbattery for 10 s.

[Movie S1](#)