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Non-Planar Electrode Architectures for Ultrahigh Areal Capacity Batteries

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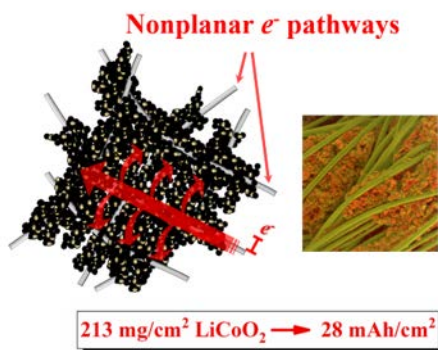
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TOC Graphic

Abstract: We report on the design of a battery electrode architecture in which ion and electronic transport pathways are continuous, and span the entire volume of a thick, non-planar electrode. It is shown that for a range of active materials conductivities, the length scale for electronic transport in such an architecture can be tuned by simple manipulations of the electrode design to enable good access to the active material. The benefits of such electrodes for basic science research and practical lithium metal batteries are demonstrated in low-N:P ratio cells in which a conventional (300- 800 μm) Li foil is successfully cycled with LiCoO₂ cathodes with high areal capacities (10- 28 mAh/cm²).

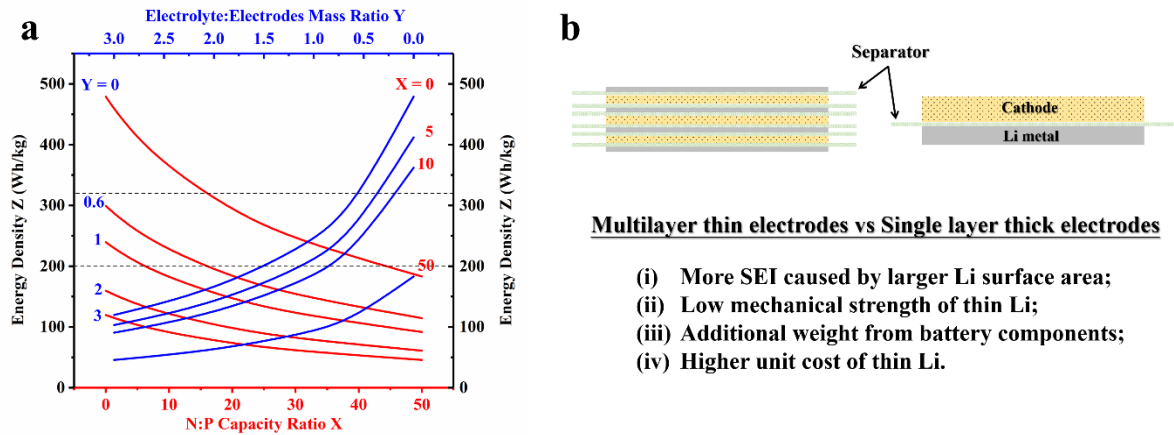


Figure 1. Rationale for using high areal capacity cathodes in Li metal battery. (a) Energy density of Li-LCO battery; Red curves and blue curves report dependencies of energy density on negative:positive (N:P) capacity ratio and electrolyte: electrodes mass ratio, respectively. (b) Comparison between multilayer thin electrode configuration (left) and single layer thick electrode configuration (right).

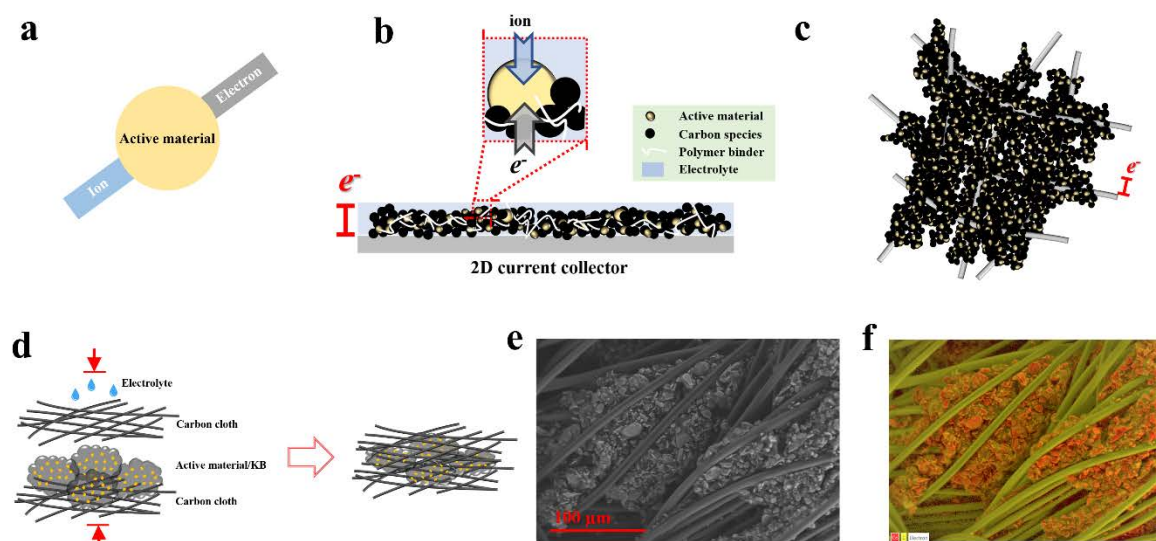


Figure 2. Design principles and fabrication of nonplanar high areal capacity electrodes. (a) illustration of the principle that active material particles need to be both electronically and ionically wired. Illustration of the electron transport length scale in (b) 2D/planar electrode and (c) Non-planar electrode based on carbon cloth; (d) illustration of the fabrication of a non-planar cathode. (e) SEM image and (f) EDS mapping of a non-planar LCO cathode (red for cobalt; yellow for carbon).

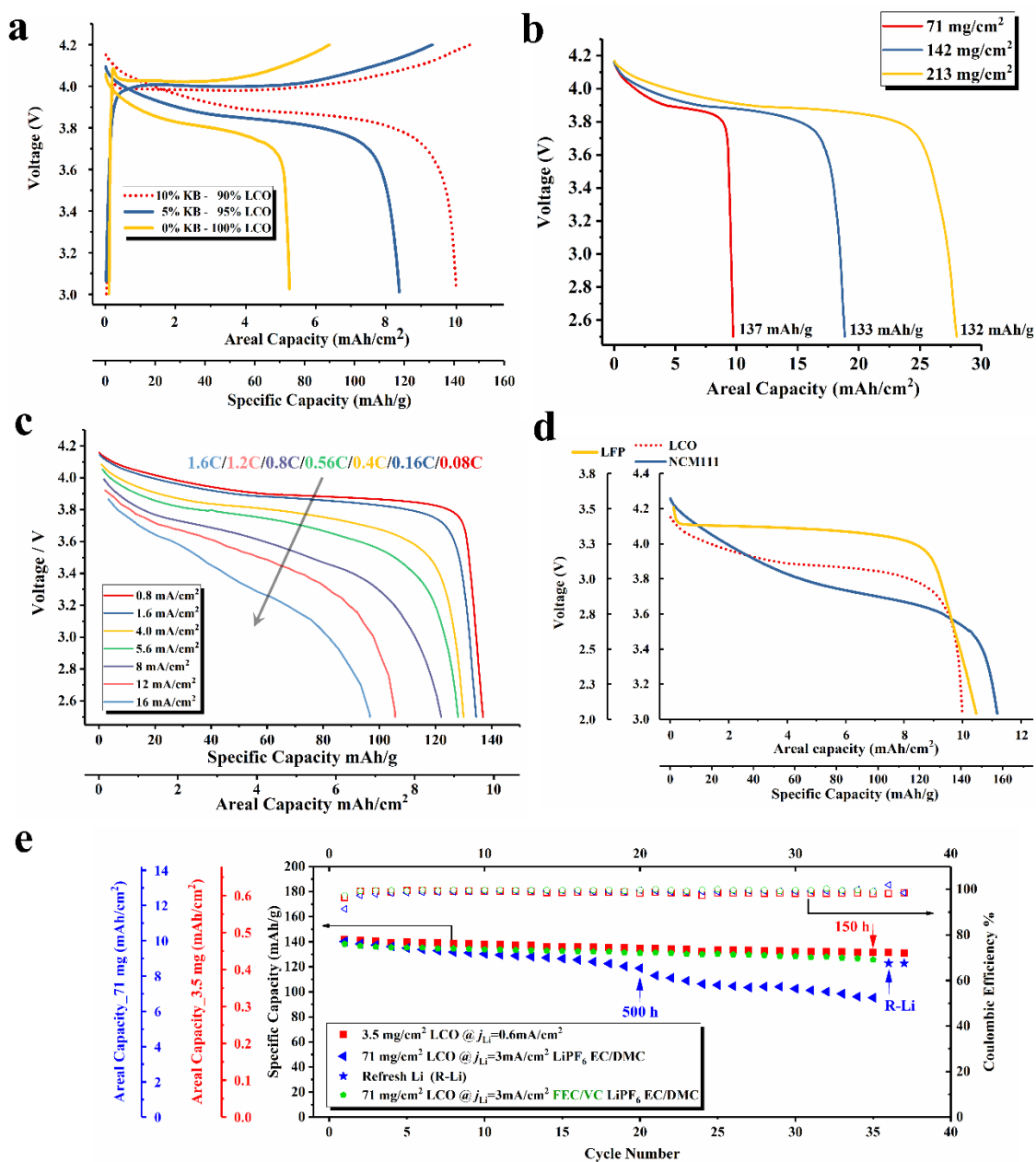


Figure 3. Electrochemical performance of nonplanar high areal capacity electrodes. (a) Charge/discharge profiles of LCO electrodes with different KB carbon contents; (b) discharge voltage profiles of non-planar LCO cathodes with 71, 142 and 213 mg/cm² loading; (c) discharge voltage profiles of 71 mg/cm² LCO cathode at different current density. (d) discharge profiles of

71 mg/cm² non-planar LCO, LFP and NCM₁₁₁ cathodes. (e) cycling performance of a Li || LCO full cells with N:P ratio = 4:1. Current density = 0.8 mA/cm² in (a), (b) and (d).

Rechargeable batteries based on the Li metal anode have reemerged as an area of intense scientific and practical interest in the last decade.^{1,2} The source of this interest is on the one-hand obvious — the specific capacity of the Li anode is one order of magnitude higher than graphite (3860 v.s. 372 mAh/g) and the standard potential for reducing Li ions in solution to the metal ($\text{Li}^+ + \text{e}^- \rightarrow \text{Li(s)}$) is fully (200-300)mV lower than the corresponding intercalation reaction with graphite to form LiC_6 . The interest is on the other hand problematic because the practical energy density of a battery is dependent not only on the anode chemistry, but also on subtle and often ignored parameters, including the negative to positive electrode capacity ratio (N:P ratio), electrolyte to electrodes mass ratio and weight of other battery components, e.g. separator, etc. **Fig. 1A** (see also **Supplementary Note 1**) highlights the tradeoffs between the oftentimes conflicting design parameter choices that must be made in creating Li metal batteries (LMB) that live up to the promise offered by the anode. The figure shows that a Li metal cell that uses a conventional intercalating cathode can only truly outperform a conventional Li-ion battery when the N:P ratio is kept below 5:1. Unfortunately, because some fraction of Li in the battery will inevitably be lost to parasitic reactions in forming the Solid Electrolyte Interface (SEI) on the metal anode and because the specific capacity of Li metal is about 20 to 30 times higher than that of conventional intercalation Li-ion cathode (usually around 150 mAh/g), it is extremely difficult to evaluate Li

metal anodes under the stringent N:P conditions that will be required to establish practical cell viability.

Of the conventional approaches towards increasing the N:P ratio in an LMB, strategies which (a) use a thin Li foil (e.g. as created by roll pressing or Physical Vapor Deposition (PVD)) to lower the areal capacity of the anode,³ or (b) utilize cathode architectures that introduce non-planarity and thereby higher areal capacity are the most practiced. Comparing the two approaches, the disadvantages of the former are as plentiful as they are fundamental, as illustrated in **Fig. 1B**. First, as the Li foil becomes thinner, more of the active material in the anode is present at the interface with the electrolyte, meaning that a greater fraction of the active anode mass is loss in creating the SEI on Li (See Li plating/stripping efficiency in **Fig. S1**). Second, the mechanical robustness of anode will deteriorate, meaning that its ability to accommodate cyclic volume changes associated with the large change in specific volume associated with the reversible reaction ($Li^+ + e^- \leftrightarrow Li$) during charge and discharge cycles. Third, the weight of the current collector, separator and the electrolyte needed to wet these battery parts will correspondingly increase. Finally, the cost of fabricating thin Li anodes by either approach will add substantially to the overall unit cost. Currently, most conventional cathode structures are based on 2D/planar deposition on a thin metallic current collector, e.g. Al foil. Due to the limited electron transport length scale, the areal loading is rarely higher than 20 mg/cm² which corresponds to an areal capacity of 2~3 mAh/cm². For a 3 mAh/cm² cathode, if the N:P ratio is set to 3:1, the resulting thickness of Li foil is 25 μm, whose commercial availability remains limited. Physical vapor deposition, rather than the conventional casting and rolling procedure, will be necessary to prepare Li foil with this thickness, which makes batteries of this type uncompetitive in terms of cost and ability to be scaled up. For the aforementioned reasons, designing a novel electrode structure that can accommodate a high

areal mass loading of active material and can thus offer a high areal capacity comparable with Li foil is a competitive viable route towards high energy density LMB.

Maier and co-workers recently proposed a simplified, but elegant physical analysis of ion and electronic transport in a heterogeneous electrode (**Fig. 2A**) and on that basis introduce instructive size-based design rules for creating electrodes that enable high active materials utilization at reasonable rates ⁴. In such a design, the “wiring” required for good electron transport is realized by at least two types of contact junctions at different scales: (i) the contact between active particle and small conductive carbon species, e.g. Super P, Ketjen Black; and (ii) the contact between active particles/carbon composite and current collector. In an electrode based on 2D planar current collector, the areal mass loading is limited by the electron transport at the second length scale, i.e. the contact between the composite and the current collector (**Fig. 2B**). In practice, polymeric binder is added to maintain the physical integrity of the composite and its attachment to current collector. As this length scale increases, i.e. the composite becomes thicker, it can become physically detached from the current collector ⁵.

The main concept that guides our study is that a porous, electronically conductive matrix, able to support high loading of active material particles and full infiltration of a liquid electrolyte provides a mechanism for constraining electron and ion transport length scales below the critical values (**Fig. 2C**) for any arbitrary thickness of the electrode ^{6,7}. Previously, non-interwoven dispersed carbon fiber, as a long range electron conducting agent, has been shown to be effective in enhancing electrode rate performance ⁸. We evaluate the concept here using a commercial carbon cloth comprised of interwoven carbon fibers as the electron transport medium. Nonplanar carbon matrix is a group of promising current collectors for high areal capacity liquid-based conversion-type cathode, e.g. polysulfides⁹, iodine¹⁰. For these electrodes, the liquid-based chemistries play

an crucial role in the functioning of the electrodes, in which active material can diffuse and homogenize within the electrode during cycling. While, for intercalation cathode materials that rely on solid reaction, the active material in powder form needs to be homogeneously dispersed into the pores of carbon cloth matrix before battery cycling, which poses difficulties for high areal capacity intercalation-type cathode. To address this issue, we utilize a powder-compaction technique (see **Fig. 2D** and **Fig. S2**) in which a composite of nano-sized, commercial battery-grade active materials particles, e.g. LCO, LFP, etc., with a carbon conductivity aid is loaded in the electrolyte-free dry state into the carbon framework. In this strategy, low contact stresses produced by periodically agitating the composite powder were found to be sufficient to break apart any particle aggregates⁷ formed in the composite powder (SEM images available in **Fig. S3**) to enable high fill ratios. Once exposed to a liquid electrolyte, capillary forces draw the electrolyte into the interparticle region to enable fast, complete, and nearly optimal (electrolyte to electrodes mass ratio = 0.6:1) wetting of the active material interfaces by a process analogous to wicking¹¹ (rheological properties available in **Fig. S4**). The electrodes are integrated into coin cells by applying a fixed pressure in the range of 100~150 bar using a crimper. The mechanical robustness of carbon cloth (tensile strength 345 MPa) due to the interwoven nature maintains the physical integrity of the electrode under the pressure applied. The active material is retained within the matrix by friction force; the electrode architecture is binder-free. **Fig. 2E** reports the morphology of the fabricated electrode and its corresponding elemental distribution information is probed by EDS mapping (**Fig. 2F**). A consequence of the large capillary and compression forces exerted on the composite material during electrolyte infusion and cell assembly, respectively, the LCO/KB composite is observed to fill the space between carbon fibers.

Results from galvanostatic charge-discharge experiments reported in **Figure 3** illustrate the electrochemical characteristics of the electrodes. Specifically, for a high loading of 71 mg/cm² LCO cathode with 10% KB manifests a discharge capacity of 138 mAh/g specific capacity, and a 10 mAh/cm² areal capacity is achieved. Of note is that the N:P ratios in these batteries are only 4:1, although these experiments use a 750 µm thick Li foil, underscoring the potential benefits of the cathodes for evaluating features of the Li anode under realistic conditions for achieving high cell-level energy densities. When the KB carbon content is decreased from 10 wt% to 5 wt% to 0 wt%, the specific capacity, i.e. the utilization rate of LCO, correspondingly decreases from 138 to 118 to 74 mAh/g, and the voltage hysteresis increases from 0.16 to 0.23 to 0.24 V (**Fig. 3A**). The results can be understood in a straightforward manner. As the carbon content is lowered, the electron conduction within the KB/LCO composite is weakened and LCO particles are insufficiently electronically wired to the system to utilize the full electrode capacity. It is noticeable, however, that the active material utilization rate of LCO is as high as 50% even without any KB black, which is attributed to the intrinsic high electronic conductivity of LCO particles ($10^{-1} \sim 10^2 \text{ S/cm}$)¹². The results in **Fig. 3B** show that the strategy can be used to create cathodes with even higher areal mass loading, as high as 213 mg/cm² for a capacity of 28 mAh/cm². These capacities are to our knowledge among the highest reported for a functional LCO cathode^{6,13-15}. Due to the large pressure applied that removes residue porosity, the volumetric energy density is not significantly compensated by the usage of a nonplanar matrix in the high areal mass loading cathodes (See thicknesses and volumetric energy density in **Supplementary Table S1**).

A well-known beneficial attribute of the LCO cathode is that the theoretical specific capacity can be improved by charging to a higher voltage. We find that by charging to 4.5 V, specific and areal capacities are 188 mAh/g and a 13.3 mAh/cm², respectively, are achieved (**Fig. S5**). **Fig. 3C**

reports the effect of current density on the voltage profiles for the 71 mg/cm² LCO cathodes. When discharged at 8 mA/cm², a specific capacity of 122 mAh/g and an areal capacity of 8.7 mAh/cm² are observed, suggesting that the electronic wiring of LCO particles is effective. When the current density is further increased, ion transport within the solid particles can limit the rate performance (characteristic relaxation time $\tau \approx L^2 / D_{Li \text{ in LCO}} = \frac{(10 \times 10^{-4} \text{ cm})^2}{10^{-9} \text{ cm}^2 \text{ s}^{-1}} = 10^3 \text{ s}$)^{4,12}. In addition to LCO particles, whose intrinsic electron conductivity is high, the electrode architecture should also be compatible with other cathode chemistries, including LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ and, most challengingly, LiFePO₄ that is reported to have a conductivity of only $10^{-8} \frac{\text{S}}{\text{cm}}$.¹² The results reported in **Fig. 3D** show that irrespective of the active material electronic conductivity, cathodes that deliver near theoretical capacities are achieved in each of these cases. On this basis, we tentatively conclude that the both the electrode architecture reported here and the fabrication method may serve as a generic platform for upscaling the mass loading of a generic cathode material, without compromising homogeneity of the materials distribution. To evaluate the latter of these two features of the cathodes, we performed X-ray absorption near edge structure (XANES) analysis of conventional planar (8 mg/cm²) and non-planar (90 mg/cm² LiFePO₄ cathodes. The results reported in **Fig. S6** show that the oxidation state of the transition metal is unchanged, confirming that distribution of LiFePO₄ is as uniform and the active material is as electrochemically accessible even at the rather high mass loadings achieved in the non-planar electrode configuration.

The galvanostatic cycling performance of the Li || high loading LCO full cells are reported in **Fig. 3E**. The conditions used for the test provide an extreme test for the Li anode, i.e. at a low N:P capacity ratio = 4:1, a high current density $j_{\text{Li}} = 3 \text{ mA/cm}^2$ and a high lithium throughput = ~30 mAh/cm² per (dis)/charge. To specifically evaluate these effects **Fig 3E** compares the cyclability

of the bare Li-LCO full cell using a commercial 1M LiPF₆ in EC/DMC as electrolyte with cycling studies in electrolytes containing additives such as FEC that are known to reduce at the Li anode to generate LiF.¹⁶⁻¹⁹ After 20 deep cycles, which corresponds to approximately 450 hours of continuous cycling and an accumulated Li throughput of ~1350 mAh/cm², the capacity retention is 84% in the control electrolyte. After 35 deep cycles, the capacity retention is 69%. To understand the origin of the capacity loss, the cycled battery was opened and the Li foil replaced by a fresh anode. Results also reported in **Fig 3E** show that this change resulted in restoration of the initial discharge capacity, indicating that the fading is associated with the Li anode. In addition, we pair a low-loading non-planar LCO cathode, which is fabricated via the same procedure, with Li foil, and the capacity retention is 93% after 35 cycles. These results confirm that the extreme cycling condition for Li metal leads to the capacity fading. In electrolytes containing 10%FEC/2%VC as additives, 91% of the original capacity is retained after 35 deep cycles, corresponding to 840 hours of cycling at 3 mA/cm². Consistent with previous reports, post-mortem morphology characterization by SEM (**Fig. S7**) shows that the FEC/VC additive facilitates more compact, less dendritic deposition of Li. This finding underscores the importance of the new cathode architectures as a tool for evaluating electrolyte and separator chemistries for stabilizing Li anodes under practical conditions where the Li throughput per cycle is high.

In summary, by designing the electron wiring length scales in electrode, we successfully demonstrate a non-planar electrode architecture that enables battery cathodes with areal capacity as high as 28 mAh/cm². We show that the cells can be cycled stably against a Li anode over a range of current densities and that because of the high Li throughput (10~30 mAh/cm²) per (dis)/charge, the cells provide an important tool for evaluating long-term stability of Li metal

anodes. Future work should focus on stabilizing the Li metal anode under high Li throughput and high current density condition.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

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Materials and methods, detailed calculation of energy density, Li metal plating/stripping Coulombic efficiency measurements, details about fabrication of non-planar cathodes and coin cell assembling, SEM morphology of electrode composites, rheological measurements, discharge voltage profiles of LCO charged to different voltages, XANES data, SEM images of cycled Li metal and table summarizing the parameters of nonplanar LCO cathodes.

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