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Modeling mass and density distribution effects on the performance of co-extruded electrodes for high energy density lithium-ion batteries

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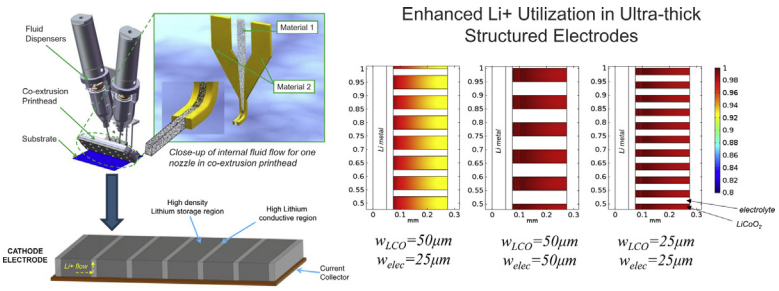
HIGHLIGHTS

- Two-dimensional finite element analysis performed on structured battery electrodes.
- Thick co-extruded $LiCoO_2$ electrodes enable a substantial improvement in energy.
- 25–100 μm width electrode fingers garner best performance at a 1C rate.
- Co-extruded electrode structures fundamentally minimize the ionic pathway for Li^+.

GRAPHICAL ABSTRACT



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ABSTRACT

Utilizing an existing macro-homogeneous porous electrode model developed by John Newman, this paper aims to explore the potential energy density gains which can be realized in lithium-ion battery electrodes fabricated with co-extrusion printing technology. This paper conducts an analysis on two-dimensional electrode cross-sections and presents the electrochemical performance results, including calculated volumetric energy capacity for a general class of lithium cobalt oxide ($LiCoO_2$) co-extruded cathodes, in the presence of a lithium metal anode, polymer separator and liquid ethylene carbonate, propylene carbonate, and dimethyl carbonate (EC:PC:DMC) electrolyte. The impact of structured electrodes on cell performance is investigated by varying the physical distribution of a fixed amount of cathode mass over a space of dimensions which can be fabricated by co-extrusion. By systematically varying the thickness and aspect ratio of the electrode structures, we present an optimal subset of geometries and design rules for co-extruded geometries. Modeling results demonstrate that ultra-thick $LiCoO_2$ electrodes, on the order of 150–300 μm, can garner a substantial improvement in material utilization and in turn capacity through electrolyte channels and fine width electrode pillars which are 25–100 μm wide.

1. Introduction

Lithium-ion batteries, in which lithium ions shuttle between an insertion cathode and anode, have emerged as the power source of choice for consumer electronics and high performance rechargeable batteries [1]. Thin film lithium-ion batteries have the potential to reach energy densities as high as 1000 Wh l^{-1} (250 Wh kg^{-1}), power densities around 2500 W kg^{-1}, and high life cycles (> 1000) [2]. In addition, thin film batteries have demonstrated good temperature stability at temperatures ranging from −40 °C to 150 °C. Given these advantages, one may conclude that building battery stacks of thin film electrodes will enable high performance, high energy density lithium-ion batteries. However, the need to add

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current collectors, separators, and other inactive components for each cell layer makes this impractical. These inactive components contribute significantly to a battery stack's mass and volume (over 50%) but not to the active electrode material. A large surface area is required for thin film batteries in order to have sufficient electrode material, especially for high discharge capacities. State of the art high power lithium-ion microbatteries with interdigitated three-dimensional nanoporous electrodes solve some of the aforementioned problems, by reducing the stack of multiple inactive components, but introduce other issues such as high manufacturing costs and trade-offs between power and energy density [3].

As an alternative to thin film batteries, one can build ultra-thick battery electrodes which provide large amounts of energy or power for a given discharge rate. However, this approach is limited by diffusion controlled lithium-ion (Li^+) intercalation, especially at high discharge rates. Ultra-thick battery anodes [4] and the electrochemical properties of ultra-thick $LiCoO_2$ cathodes prepared by screen-printing techniques [5] have been considered for high discharge capacities. However, this direction does not consider the fact that for all but the thinnest cathodes, or very low current densities, discharge capacities from 4.2 to 3.0 V are limited by the lithium diffusivity in Li_xCoO_2 and the ultimate formation of a resistive layer at the interface as the state of discharge (x) approaches 1.0. Measurements of the equilibrium open circuit potential and ac impedance upon deep discharge support this model [6].

Promoting higher diffusion for the $0.96 < x < 1.0$ phase in $LiCoO_2$ can greatly enhance the power and energy achievable by both thin film and ultra-thick batteries. However, this enhancement often requires doping and fine crystallization control of the cathode material in question to generate the required high ion diffusion at high states of charge [6]. Alternatively, reducing the lithium-ion diffusion pathway, while providing sufficient cathode mass for high discharge capacities, may significantly alleviate the problems encountered with thin film and ultra-thick electrodes. The main issue becomes how to best distribute the required mass or density of any given amount of electrochemically active material to reach the full potential of a given electrode.

Both thin film and ultra-thick electrodes offer distinct advantages but fail to yield optimal performance. Can more active material be utilized in an ultra-thick lithium-ion battery while keeping the advantages of a thin film battery? We believe the answer lies in understanding how, for a constant amount of cathode material, mass and density spatial distributions affect the performance of lithium-ion batteries. This work presents solutions, using computational results that include electrolyte diffusivity in porous media, tortuosity effects, with a systematic search for optimal mass and density distribution in $LiCoO_2$ cathodes fabricated by co-extrusion [7].

1.1. Three-dimensional (3D) battery electrodes

1.1.1. Experimental and computational studies

The benefits of expanding the dimensionality of electrochemically active material from flat to more complex geometries have been the focus of recent research with many researchers exploring a wide variety of geometries and fabrication methods. Three-dimensional (3D) battery structures significantly increase electrode surface area and in turn increase energy storage capacity. 3D batteries have the potential to transform the performance of a multitude of battery systems through structural changes rather than material changes. Any advances in new materials can always be incorporated into 3D structured batteries.

Experimentally, researchers have been investigating the benefits of 3D battery electrodes. A super ink jet printing (SIJP) system was used by Ho et al. to fabricate alkaline zinc–silver microbatteries with electrode pillar structures [8]. The fabricated electrode pillars were on the order of 40 μm tall and 10 μm in diameter located approximately 100 μm apart. The 3D electrode structures demonstrated a 60% increase in areal capacity compared to planar electrodes of a similar footprint area. Baggetto et al. explored the advantages of 3D negative electrode stacks with a micro-pore channel configuration for a solid-state battery [9,10]. This design gave a unique surface area increase over a standard battery. The authors found that further optimization of the trench dimensions ideally result in a storage capacity increase of more than five times with respect to planar electrode films. Lastly, focusing on a form of extrusion technology, micro pore channel battery structures have also been fabricated [11]. By creating a periodic pore channel array in an electrode, Bae et al. were able to reduce the effective tortuosity of an $LiCoO_2$ electrode which in turn helped retain greater capacity at higher discharge rates in thick electrodes (up to 220 μm) with pore channels for electrolyte approximately 5 μm in diameter when compared with a conventional electrode. All of the aforementioned experimental efforts demonstrate the advances of 3D structures electrodes. However, no systematic search for optimal geometries was conducted in any of these cases.

Focusing on computational modeling, researchers have also investigated the effects of 3D battery structures. Interdigitated anode and cathode electrode structures have been studied by Garcia et al. [12]. The microstructures considered consisted of a highly tortuous particle distribution with a topology of ordered branches of electrode material. Simulations of micro-structured interdigitated batteries show that the power density of a rechargeable battery can be engineered by maximizing the electrochemical driving force for intercalation while decreasing the ion transport distances of the material components. At high discharge rates, energy improvements around 37% were realized with the aforementioned structures. Zadin et al. [13] conducted finite element modeling (FEM) of electrode material utilization in a 3D microbattery structure with interdigitated anode and cathode electrodes – similar to other 3D interdigitated structure concepts [12,14]. The authors examined the influence of electrical conductivity and electrode pillar height on the overall performance of the battery. Issues with inhomogeneous lithiation were found due to differences in surface area between electrode pairs which caused non-uniform current density distributions. Zadin et al. [15] extended the aforementioned work and examined the impact of further varying the material properties and geometry profiles of the interdigitated electrode structures. It was shown that the locally high non-uniform current densities where reduced when sharp points and corners in the geometry were rounded, leading to more uniform ion concentration gradients. At the micro-scale, Smith et al. used experimentally derived cross sections of rechargeable lithium ion batteries to computationally model the effect of microstructure on the galvanostatic discharge of a $LiCoO_2|LiC_6$ cell [16]. This highly detailed level of analysis demonstrated that large inhomogeneous particle distributions led to diminished macroscopic power densities which limit the response of a lithium-ion cell. Though these computational studies provide a meaningful window into the benefits of 3D electrode structures, the important issue of mass and density distribution of the electrode remains unexplored.

1.1.2. 3D battery design principles

Design principles for 3D batteries typically focus on the geometrical and material requirements of the electrodes. Estimates of performance for 3D battery architectures indicate that an increase in the height of an interdigitated 3D battery pillar, L, results in increased energy capacity and electrode area, without an