



# A hybrid three-dimensionally structured electrode for lithium-ion batteries via 3D printing



Jie Li<sup>a</sup>, Ming C. Leu<sup>a</sup>, Rahul Panat<sup>b</sup>, Jonghyun Park<sup>a,\*</sup>

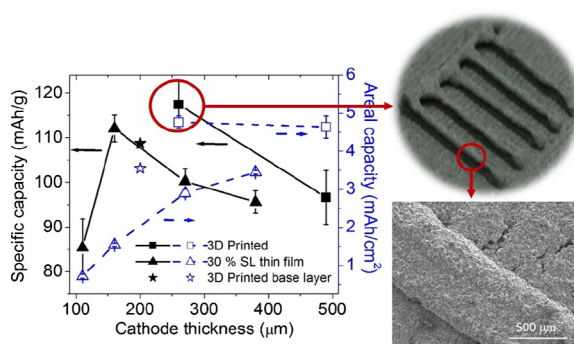
<sup>a</sup> Department of Mechanical and Aerospace Engineering, Missouri University of Science and Technology, Rolla, MO 65409, USA

<sup>b</sup> School of Mechanical and Materials Engineering, Washington State University, Pullman, WA 99164, USA

## HIGHLIGHTS

- The new 3D battery has high areal/specific capacity, which overcomes the trade-off between the two in conventional batteries.
- Superior battery performance is achieved via a new hybrid structure that has advantages of the conventional and 3D structure.
- Conventional li-ion battery paste is optimized for extrusion-based 3D printing without the need of complex solvent processes.

## GRAPHICAL ABSTRACT



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## ABSTRACT

New hybrid 3D structure electrodes with a high aspect ratio are fabricated through extrusion-based additive manufacturing to achieve high mass loading. This new 3D printed battery exhibits both high areal and specific capacity, thus overcoming the trade-off between the two of the conventional laminated batteries. This excellent battery performance is achieved by introducing a hybrid 3D structure that utilizes the benefits of the existing laminated structure and three-dimensional interdigitated structure. In addition, conventional battery paste components are used optimally to fit the 3D printing process, which eliminates the need for a complicated solvent preparation process required for a typical 3D printing process for battery applications. Using the CR2032 coin cell, the general assembly problem that occurs at the 3D structured electrodes is solved, which means that the proposed hybrid 3D structure can easily be added to the existing lamination structure. This innovative design and fabrication process demonstrates the high areal energy and power density, which is a critical requirement for energy storage systems in transportation and stationary applications.

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## 1. Introduction

Despite remarkable advancements in lithium ion batteries (LIBs), during the past several decades, a higher energy and power density is

still required for portable devices, transportation, and stationary applications [1–3]. In order to satisfy these demands, besides developing new materials, it is necessary to enhance battery performance via optimizing battery electrode structures because they significantly affect the transport of species and their reactions [4,5]. In general, gravimetric capacity ( $\text{mAh} \cdot \text{g}^{-1}$ ) is one of the most utilized metrics in LIB studies as it describes the capacity that a material can deliver. However, in practice,

\* Corresponding author.

E-mail address: [parkjonghy@mst.edu](mailto:parkjonghy@mst.edu) (J. Park).

the actual amount of materials in an electrode determines the energy and power of a LIB. Accordingly, high mass loading is another important requirement for various applications. One simple strategy for achieving high mass loading is the addition of more materials, which means increasing the thickness of electrodes. Unfortunately, this approach limits the transport of ions and electrons, resulting in poor power performance and bad utilization of materials [4]. A better option is to make electrodes smartly, so that a more facile transport of the species will be possible [6,7]. Conventional modern batteries, which are based on laminated composite electrodes, are fabricated via a paste casting process that involves mixing the constituent materials and coating them onto a current collector. In a composite electrode structure, the electrode thickness, porosity, and mass loading are the key factors for increasing areal capacity ( $\text{mAh} \cdot \text{cm}^{-2}$ ) and maximizing usage of materials. After a certain thickness, however, the electrode shows poor power performance [4].

Three-dimensional (3D) batteries have been considered to be a new solution for improving battery performance [3,6,7]. Battery electrodes with 3D nanoarchitectures have been successfully synthesized for almost two decades [8–16]. Some of the nanomanufacturing methods (e.g., lithography tools) are expensive and time-consuming. However, additive manufacturing has several advantages, as compared to other manufacturing tools; because it can provide an inexpensive and flexible manufacturing process that includes more complex geometry designs and a wider selection of materials [17,18]. Therefore, the additive manufacturing technique appears to be a very promising method for fabricating 3D battery structures [7,19–22]. However, the preparation of the proper composition and rheology of paste is demanding because of several requirements, including preventing clogging of the nozzles, promoting a bond between each filament, and keeping the controlled feature geometry after deposition [23–25]. For LIB applications, in particular, the use of paste chemical components is a critical factor in battery performance, since more binders inside the paste would decrease ionic and electronic conductivity. In this respect, conventional tape casting pastes have the advantage that they do not mix unnecessary components in pastes, which has been commercially used for LIB fabrication for decades.

Currently, 3D structures are being thoroughly studied for LIB applications, but most of these studies are focused on microbatteries [7, 19–22]. Further, a strategy of adopting the advantages of the conventional laminated structure and the 3D digital structure has not been considered. In this paper, a novel hybrid 3D structured electrode was developed to overcome the limitations of conventional laminated composite electrodes via an extrusion-based additive manufacturing technique. The principal goal of this work was to utilize the out-of-plane dimension of the 3D structured electrode, so that power and energy density could be further enhanced with short ion transport distances and an increased surface area as compared to the conventional laminated structure. The rheology of the conventional tape casting paste with different solids loadings (SL) was tested for the reliability of printing onto a controlled hybrid 3D feature of an electrode, without adding unnecessary chemical components.

## 2. Materials and methods

### 2.1. Materials and paste preparation

In this work, a  $\text{LiMn}_2\text{O}_4$  (LMO) paste was used to fabricate a hybrid 3D structure electrode. Two different solids loading pastes were prepared by first mixing 85.5 wt% LMO powder (MTI, 13  $\mu\text{m}$ ) with 6.5 wt% carbon black (CB, Alfa Aesar) and 8 wt% Polyvinylidene fluoride (PvdF, Sigma-Aldrich), and that was then dispersed in *N*-Methyl-2-pyrrolidone solvent (NMP, Sigma-Aldrich) for 30% SL and 15% SL paste, respectively. The paste was mixed with a SpeedMixer (FlackTeck Inc.) at 2000 RMP for 20 min at room temperature. The paste rheology was measured by a viscometer (Brookfield model HB) equipped with a

CAP-52Z cone spindle at 25 °C. The viscosity ( $\eta$ ) was recorded as a function of RMP (0.5–5) which corresponded to the shear rate ( $10\text{--}1000 \text{ s}^{-1}$ ) logarithmically, and the shear stress was calculated based on measured viscosity and shear rate.

### 2.2. Electrode fabrication and cell assembly and test

An Extrusion Freeform Fabrication (EFF) system was used (Fig. 1) to deposit the paste in a 3D structure. An aluminum foil piece (5 cm  $\times$  5 cm) was fixed on a substrate heated to 120 °C prior to printing, which was used as a current collector after assembly. The deposition system was a home-built extrusion-based additive manufacturing system, which consisted of a motion subsystem, a real-time control subsystem, and extrusion devices, which were controlled by Labview 2012 software. The system contained three linear axes, Daedal 404 XR (Parker Hannifin, Rohnert Park, CA) driven by three stepper motors (Empire Magnetics, Rohnert Park, CA) and was able to print up to three different materials. In this research, a single extruder was used to extrude the LMO paste.

The paste was loaded into a 50  $\text{cm}^3$  plastic syringe (EXELint) with a 200  $\mu\text{m}$  nozzle (EFD Inc.), and extruded with 100 N extrusion force onto a substrate that moved along the XY-axes. The hybrid 3D structure consisted of two parts: a base part and a digital structure part (Fig. 2). First, a base layer was printed to cover the current collector as a conventional laminated structure and the thickness of this base layer was optimized to yield the highest specific capacity (without 3D structure). Next, a digital structure, with a different number of layers, was printed on the top of the base layer to increase the specific surface area. All the fabricated structures were examined via scanning electron microscopy (SEM, Hitachi S4700).

A CR2032 coin cell (Wellcos Corp.) was used to assemble a battery (Fig. 3) in an argon-filled glove box (Mbraun). LMO was used as a cathode, Li foil as an anode, and commercial PP/PE/PP membrane (Celgard) as a separator; the battery was filled with liquid electrolyte 1 M  $\text{LiPF}_6$  EC:DMC 1:1 (Sigma-Aldrich).

The electrochemical behavior of the assembled batteries was measured from 3 V to 4.2 V by using a battery testing station (IVIUMnSTAT, Ivium Tech). The specific capacity and areal capacity were measured under a 0.1 C-rate, and then the cycling performances were conducted with 0.1C, 0.2C, 0.5C, and 1C per three cycles. Battery impedance was also measured via an electrochemical impedance spectroscopy (EIS) at 3.5 V open circle voltage.

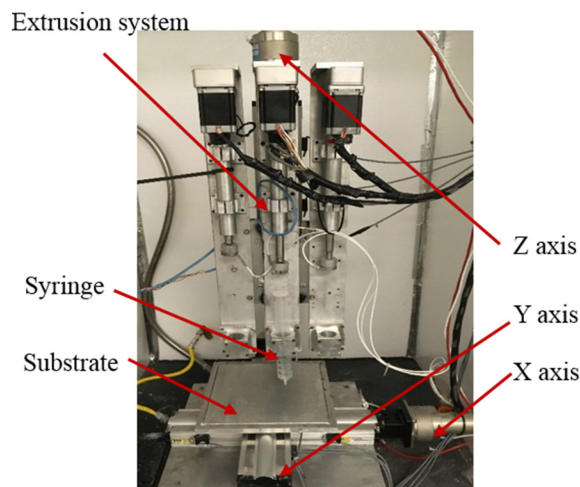


Fig. 1. Extrusion Freeform Fabrication machine overview.

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