Improved safety and mechanical characterizations of thick lithium-ion battery electrodes structured with porous metal current collectors

Daniel J. Noelle[a,*], Meng Wang[b], Yu Qiao[a,b]

[a] Program of Materials Science and Engineering, University of California – San Diego, La Jolla, CA, 92093, USA
[b] Department of Structural Engineering, University of California – San Diego, La Jolla, CA, 92093, USA

HIGHLIGHTS

- Porous metals current collectors enable thick electrodes with high aerial capacity.
- Interpenetrating phase composite electrodes show very safe short circuit responses.
- Optimizing electrode thicknesses with device-centric design minimizes inherent risk.
- Increased thickness composite electrode structures impart greater bending stiffness.
- Mechanically-robust electrodes support next-generation structural battery designs.

ARTICLE INFO

ABSTRACT

Porous metal current collectors enable the fabrication of thick electrode structures with improved safety margins and unique mechanical properties. Interpenetrating phase composite $LiCoO_2$ cathodes and graphite anodes with large active material loadings are formed using advanced slurry processing techniques with a submersible ultrasonic horn. Full cells with $600\,\mu m$ thick electrodes demonstrate high aerial capacity of $16.7\,mAh.cm^{-2}$, improving energy density by 22% with respect to volume versus reference cells using traditional laminate composite electrode stacks. External shorting and nail penetration testing show notably suppressed joule heating currents, limiting peak temperature accrued to just 25% of the reference. Shear testing and three-point bending of individual electrodes and stack assemblies elucidate the greater role of the binder phase in the mechanical response, and that extensive characteristics such as thickness can be more influential than the intensive properties of the materials. Optimization of electrode thicknesses to balance rate capability with abuse safety is discussed, and opportunities for multifunctional application as load-bearing structural components are considered. Improved battery safety characteristics are demonstrated by reorienting the inherent components of the cell, without altering the chemical make-up, emphasizing the profound influence of structural design.

1. Introduction

Structural lithium-ion battery (LIB) designs present opportunities to increase the energy density of LIB-powered devices by undertaking both electrochemical and mechanical load-bearing functions, without modifying the underlying LIB chemistry [1]. By using energy-storing LIBs to give a device its structural form, overall mass and volume can be reduced to improve performance if the LIBs can sustainably fulfill both tasks [2,3]. Multifunctional design could aid in lightweighting of electric vehicles to extend driving range capabilities or reduce the size of personal electronics to make them easier to carry [4–6]. However, structural applications make LIBs more susceptible to physical damage,

which could induce dangerous short circuit events leading to thermal runaway. As such, multifunctional LIBs with greater degrees of device integration demand more robust mechanical properties and greater margins of safety against abuse [7].

Porous metal current collectors (also referred to as metal foam current collectors) can serve as electrically-conductive structural reinforcements to enable thick electrode orientations with high aerial capacity [8–11]. When filled with an electroactive matrix of energy-storing active materials, conductive additives, and adhesive polymer binders, interpenetrating phase composite (IPC) electrode structures with unique mechanical characteristics are formed [12,13]. Unlike traditional laminate composite (LC) electrodes using 2D metal foil

current collector substrates, which are coated with electroactive matrix layers on each side typically with thicknesses on the scale of 50–100 μm [8], porous metal current collectors offer a 3D foundation. In an IPC orientation, active materials can be retained close to the nearest porous metal current collector surface even when the overall electrode thickness is much larger, ensuring electron conduction uniformity and achieving high aerial loading of the electroactive matrix [9]. High capacity IPC electrodes allow for fewer bilayers to be used in cell construction compared to traditional LC electrodes, reducing the need for nonelectrochemical support components such as separators, which helps increase the volumetric energy density [14,15].

Current collectors have a significant role in short circuit discharge electrical kinetics and the electroactive matrix layer thicknesses have a notable influence on ion transport dynamics [16,17]. Upon physical damage of traditional LC electrode multilayer assemblies, direct contact between the metal foil current collectors is often the major cause of thermal runaway [18]. Electrons will rapidly discharge across low-resistance pathways afforded by the electrically-conductive metals, moving in tandem with lithium-ions travelling short distances through the electrolyte within the thin, porous electroactive matrix layers. As the electrons and the ions recombine in the cathode's active material particles, liberated joule heat can cause temperature to accrue to dangerous levels in a matter of seconds [19]. The metal foil current collectors dictate the ultimate strength of the LC electrodes, and strategic weakening of the metal foil has been shown to greatly improve safety in impact testing [20]. Thus, restructuring of the electrodes with porous metal current collectors into IPCs without strong homogeneous metal layers, as well as longer ion transport lengths, may exhibit improved safety characteristics.

The mechanical properties of the IPC electrodes are categorically different from traditional LC electrodes. In LC electrodes, the high tensile modulus metal foil component is thin, and located at the center of the structure where it imparts only low flexural stiffness to the electrode structure [21]. The porous metal current collector in heterogeneous IPC orientation reinforces the electroactive matrix throughout the thickness [12,13]. Additionally, flexural stiffness tends to increase with larger thickness components. High flexural stiffness is critical to minimizing deflection to maintain form and function when subject to mechanical loading. With these mechanical performance and safety design considerations, IPC electrodes with porous metal current collectors are investigated.

2. Experimental

2.1. Electrode processing

Porous metal current collectors were generously provided by Sumitomo Electric Industries, Ltd. The cathode's aluminum foam current collector (Al Celmet) had an initial thickness of 1.0 mm, porosity of ∼95%, and pore density of ∼45 PPI. The anode's copper foam current collector (Cu Celmet) had an initial thickness of 1.0 mm, porosity of ∼94%, and pore density of ∼105 PPI. They were filled with high-density LIB electrode slurries by hand using a spatula, and then dried under vacuum at 80 °C for 24 h. Once dry, the IPC electrodes were calendered to 600 μm thicknesses using a generic rolling press containing 2 rollers with 7.62 cm diameter in a single passthrough motion. The electrodes were cut into 1.98 cm^2 circular discs, which were subsequently characterized using a Fischer Scientific mass balance.

The high-density LIB electrode slurries, containing active materials, conductive additives, and adhesive binders, were prepared by dispersion and homogenization in processing solvents using a QSonica Q55 Sonicator with 3.2 mm diameter submersible ultrasonic horn in 10 mL Pyrex beakers (25 mm diameter, 33 mm height). Systematically applied ultrasonic power at a frequency of 20 kHz was controlled, such that standing wave resonance was maintained throughout the mixing processes. The ultrasonic friction and processing solvent cavitation was

used to heat the slurry while mixing, and active stirring by hand with the horn tip ensured temperature uniformity during the homogenization process and upon cooling, as monitored by 2 type-K gage-40 thermocouples affixed to opposite sides of the beaker, connected to a Digi Sense 20250-02 Temperature Logger. The processes yielded slurries with appropriate casting viscosities at room temperature. Details of optimized power application, slurry temperature, and mixing event progression during the processes are given in section 3.1.

For cathode, LiCoO$_2$ (LCO, Lectro Plus 100, FMC Lithium), carbon black (CB, C-Energy Super C45, TIMCAL), and polyvinylidene fluoride (PVDF, MW ∼534,000 powder, Sigma Aldrich) were dispersed in the ratio of LCO:CB:PVDF 93:3:4 w:w:w totaling 10.8 g into 3.6 g of N-methyl-2-pyrrolidone (NMP, anhydrous 99.5%, Sigma Aldrich). LCO, CB, and PVDF powders were premixed using a mortar and pestle prior to dispersion in NMP.

For anode, graphite (TIMREX SLP30, TIMCAL), CB, carboxymethylcellulose sodium salt (CMC, medium viscosity, Sigma Aldrich), and styrene-butadiene rubber (SBR, MTI Corporation) were dispersed in the ratio of graphite:CB:CMC:SBR 93:2:2:3 w:w:w:w totaling 3.15 g into 3.5 g of deionized water (DI). The CMC salt was first dissolved in DI water. The SBR liquid was subsequently mixed in solution at 80 °C for 1 h using a Corning PC-420D Stirring Hot Plate. Then, graphite and CB powders were fully mixed into the solution using a glass stir bar prior to ultrasonic agitation. Graphite and CB powders were premixed using a mortar and pestle before being added to the DI/CMC/SBR solution.

2.2. Electrochemical performance and abuse characterization

LIR2032 format full cells were constructed for electrochemical characterization and short circuit abuse testing of the IPC electrode assemblies. The electrode stacks were assembled in uniaxial orientation using one cathode disc, one anode disc, one trilayer separator layer (Celgard 2320), and a copper foam spacer used to secure electrical and thermal contact with the cell case. The electrodes and separators were submerged in 1 M LiPF$_6$ EC:EMC 1:1 w:w electrolyte (BASF Selectilyte LP50), and subjected to reduced pressure atmosphere of 85 mmHg at room temperature for 3 min, ensuring complete wetting prior to cell construction. Cells were sealed using an MTI Corporation MSK-100 hydraulic press with CR20XX crimping die set inside an MBraun LABStar glovebox with water-free argon atmosphere (H$_2$O < 0.5 ppm).

Galvanostatic analysis was carried out using a Neware BTS4000-5V10 mA Battery Analyzer. Cycling was performed at 0.38 mA cm^{-2} constant current rate between 3.0 V and 4.2 V, which took ∼45 h after the initial two conditioning cycles for each charging step and discharging step, denoted here as the C/45 current rate for this IPC cell system. Discharging rate capabilities at constant currents of 0.75 mA cm^{-2}, 1.12 mA cm^{-2}, 1.50 mA cm^{-2}, and 1.88 mA cm^{-2} following 0.38 mA cm^{-2} constant current charging steps were also evaluated.

The mass and dimensions of galvanostatic-conditioned electrode stack assemblies and components were measured in the discharged state with a Fischer Scientific mass balance and displacement micrometer inside the glovebox. Measurements were made immediately upon deconstruction using the MTI Corporation MSK-100 hydraulic press with CR20XX disassembling die set. These measurements were taken to evaluate energy density accounting for electroactive matrices, current collectors, separator, and saturated electrolyte mass internal to the stack, while excluding mass and volume contributions from cell cases, connecting tabs/spacers, and electrolyte external to the stack.

The LIB cells were subjected to external shorting and nail penetration testing, performed using the same testing procedures described in Ref. [16]. In external shorting, current response was directly measured using a Neware BTS3000-5V6A Battery Analyzer upon discharge with a 110 mΩ resistor. Nail penetration was performed using a 2.7 mm diameter, 38 mm long 304 stainless steel nail. In both experiments cell temperature response was documented using type-K gage-40 thermocouple affixed to the cell case by polyimide tape. Cells used in abuse