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Millimeter-scale lithium ion battery packaging for high-temperature sensing applications

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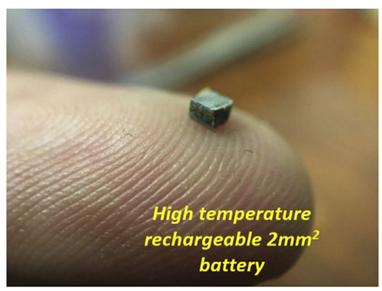
HIGHLIGHTS

- Fabrication process for miniatured Li-ion batteries with high temperature stability.
- Validated the assembled power sources for high temperature sensing applications.
- Thermally stable electrochemical active materials and packaging components.
- Compatible for energy harvesting, solar cell charging at room temperature.

GRAPHICAL ABSTRACT



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ABSTRACT

Continuously growing and miniaturizing autonomous electronic devices and sensors for large temperature window is mostly depends on stability and performance of power-up systems. The net achievable power and energy densities of such miniatured rechargeable energy storage systems are largely dominated by internal hardware and external packaging materials. Similarly, temperature stability of electrochemically active materials and packaging components is also crucial to realize desired activity at few millimeter scale devices. Herein, we explore energy storage devices at tunable miniatured scale by selecting optimal electroactive materials, thermally stable packaging components, and their fabrication process. Further, an assembled device is subjected to evaluate its energy and power density per foot-print-area along with other key electrochemical parameters such as internal resistance, self-discharge, and thermal stability. Detailed studies reveal that the presently packaged millimeter size rechargeable batteries (2 mm–5 mm) have the ability to work up to 120 °C with minimal load loss and compatible with energy harvesting renewable source of the solar cell.

1. Introduction

In recent years, electronic industries are breaking previous boundaries of integration and functional density towards miniaturization in autonomous self-powered microdevices. These micro/nano machines are suitable to operate as well as interconnect in different environments to provide, process and store information without having any connection to power grids [1]. The autonomous devices should operate continuously without any power obstacle in natural, industrial or in-vivo applications of the human body [2–5]. As self-directed systems are shrinking day by day, energy storage systems have to be flexible with respect to dimensional constraints so that they can be integrated into the miniaturized devices [6]. International Technology Roadmap for Semiconductor (ITRS) has forecasted that the power consumption in semiconductor industries will be big concern [7–9]. As electronic circuit shrinks, it requires higher chip operating frequencies, higher

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interconnects resistance and capacitance, as well as gate leakage, contribute to increasing power requirement in microprocessor unit [10,11]. However, in last decade large effort has been undertaken to develop semiconductor-based micro-electro-mechanical system (MEMS) sensor technology to match up the load for making portable devices [12]. Innovations in the miniaturization of autonomous electronic devices and sensors demand miniaturization of power technologies [11]. For harvesting the energy in these devices, few strategies have been commenced which include study of energy conversion devices (piezoelectric generators, photovoltaics, thermoelectric, thermostatic, etc) and energy storage devices (batteries) [13–15]. However, these energy conversion systems require an intermittent source of the power which can store energy such as batteries. Therefore, battery is the main power source in autonomous system and the improvement of miniaturized energy storage system with large volumetric density is of essential importance for MEMS-based sensors that deliver power at vigorous environment conditions [16]. However, present miniaturized batteries have several serious limitations including areal energy (near μAh cm^{-2}), size (around 80 mm^2) and thermal stability (up to 85 °C) [17]. In addition, several micro-sensors acquiring real-time information related to pressure, temperature, etc., at extreme environmental conditions demands highly reliable rechargeable miniaturized batteries sustaining temperatures beyond 100 °C, works at high pressure and deliver power in the order of few mAh cm^{-2}. Thus, miniaturized rechargeable batteries which can readily embed with microsystem and works at extreme conditions are a requirement of present autonomous devices in various industries.

By considering these problems, here we present packaging of miniaturized rechargeable lithium batteries by using "3D printing" casings for high temperature (~120 °C) autonomous sensing applications. Miniaturized batteries contain electrochemically active components which must be protected from moisture, air, and mechanical stresses, therefore, packaging the battery components within millimeter configuration is extremely challenging for high-temperature applications. In addition, these batteries having millimeter size components need to be assembled in the inert atmosphere which further complicates the process. Hence, tackling previously mentioned issues, a process flow has been developed to fabricate miniaturized batteries in the small domain by reducing a number of required components compared to conventional coin cell battery. Packaged miniaturized batteries in small geometrical dimension (2–5 mm) show minor self-discharge, long lifetime and high volumetric capacity at high temperature (120 °C). Moreover, to show integrability of the miniaturized batteries for typical autonomous sensor, room temperature solar cell charging and discharging at 120 °C in terms of different duty cycle has been performed.

2. Methods

2.1. 3D printing components

Grade 316 stainless steel components for packaging millimeter size batteries were fabricated by using 3D printing technique from GPI prototype and manufacturing services. This metal 3D printing is also called as a direct metal laser sintering (DMLS) where laser beam melt (20–40 micron layers) metal powder to create metal parts. This additive manufacturing process is similar to conventional 3D printing except metal powder (i.e., stainless steel) is spread on the platform and converted into solid parts by melting it locally using a focused laser beam.

2.2. $LiFePO_4$/C cathode by spray coating method and lithium (Li) anode coating

Spray ink is prepared by mixing the synthesized powder with super P carbon black and polyvinylidene fluoride (binder) respectively, and the mix was treated with N-Methylpyrrolidin-2-one (NMP) solvent to form an ink. The ink is filled in the spray gun and applied uniformly on bottom cases and then dried it out. The ratios of NMP and electrode mixtures, spray time, drying temperature, etc. are optimized to get the desired coating of $LiFePO_4$/C cathode on respective bottom cases. On the other hand, the conformal coating of Li on the stainless steel (SS) lid is done inside the inert environment (Glove Box). Solid Li is placed on the top of projection and press it at high temperature to get a conformal coating.

2.3. Quartz separator and RTIL electrolytes injection

Separator (GE Healthcare, Life Scinces, Quartz microfiber filters) cut into square pieces according to area of cup and systematically was placed on the top of the cathode material. Afterward, optimized amount of the electrolyte consists of 1 M of bis(trifluoromethylsulfonyl)amine lithium salt in 1-Propyl-1-methylpiperidinium bis(trifluoromethanesulfonyl)imide was used to properly wet separator and cathode material.

2.4. Epoxy for hermetically sealing

Generally, urethane epoxies are used to protect integrated circuits (IC) from chemical, moisture, salts, biologic organisms, atmospheric contaminates and at the same time to provide mechanical strength. Herein, we have used urethanes epoxies (Oxirane, 2,2-[(1-methylethylidene) bis(4,1phenyleneoxymethylene)] bis,homopolymer) to seal our millimeter batteries. The important characteristics of this epoxy are, it cures at room temperature, provide conformal coating, and sealed hermetically. Also, limestone is used as another main component in this epoxy to reduce the coefficient of temperature expansion. Moreover, it has been found that chemically resistant to most of the organic solvents and thermally stable up to 200 °C.

2.5. Electrochemical performance

CR2032-type coin cell and miniaturized batteries were fabricated with above optimized materials inside the glove box and performed charge-discharge and electrochemical impedance test on SP-200 potentiostat Biologic and Arbin instruments.

2.6. Solar cell charging

Solar cell charging circuit was designed to charge miniaturized batteries from the solar cell. USB/DC/solar lithium battery charger - v2 from adafruit was utilized for getting constant current output from the circuit. Output current in this circuit can be tuned with a respective resistance connected across it.

3. Results and discussion

3D printers are gaining tremendous popularity in almost every industry due to its rapid prototyping of parts and machines by using Computer-Aided Design. This additive manufacturing technique is simple and shown its potential by manufacturing big houses to small extremely complicated human organs [18–20]. Therefore, we utilize "3D printing" technique (Direct metal laser sintering) to fabricate miniaturized battery casings by maintaining material properties (316 stainless steel) for electrochemistry compatibility. Representative miniaturized battery casing contains two parts of 316 stainless steel, bottom case to hold the cathode material whereas the top case contains anode material, an extrusion has been added to the top case which aids sufficient contact pressure between the anode and cathode material as shown in Fig. 1. At first, the optimized design had a wall thickness of 500 μm in 3 × 3 mm^2 domain (Supplementary Fig. S1) which was later reduced to 200 μm in the 2.25 × 1.7 mm^2 size casings as illustrated in Fig. 1(a) and (b). The requirement of the thinner wall is to increase the overall area of the cup which leads to enhanced areal capacity by