Development of Rechargeable Thermal Batteries

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Abstract

In this work, a rechargeable thermal battery (RTB) system, enabled by a thermally activated electrolyte formulation and a custom integrated heating method, was developed and demonstrated. The RTB was scaled from several mAh cells up to 7 Ah cells and a functional multi-cell battery pack. The cell parameters were optimized for high rate performance, achieving >12.5 kW/L. Cells configured for high energy density operation delivered >840 Wh/L. Over 25 cycles of rechargeable operation was demonstrated. Multiple formulations of a novel, low-melting point solid electrolyte that enables on/off functionality between 80 – 140 °C and enables long-term storage with minimal capacity fade were demonstrated. The developed prototype represents a significant step forward from traditional thermal battery systems which are single-use and require very high operational temperatures (>200°C).

Key Words

rechargeable thermal battery; high power; high energy; battery; directed energy weapons

Introduction

Thermal batteries are primary, reserve-type electrochemical energy sources capable of supplying high power output upon activation with a single-use pyrotechnic heating element, necessitating replacement for multi-use applications.[1,2] Thermal batteries are often employed for military applications (such as missile and torpedo systems), usually as a power source for guidance, propulsion, and safe/arm applications.[3] Directed energy weapons (DEWs) are an evolving class of technology with applications in missile defense and incapacitation of enemy vehicles, among others.[4] DEW devices require a high-power electricity source sustained over several minutes to function and thus are an ideal application for thermal batteries; however, they would benefit from the ability to recharge the battery for subsequent use. Constantly replacing single-use thermal batteries would be costly and generate significant amounts of waste.

Traditional thermal batteries typically utilize a stacked pellet construction and a molten-salt electrolyte that is solid at room temperature (allowing for storage of the battery in an inert state) and liquid after activation (facilitating discharge of the battery).[1,2] The irreversibility of the system stems from both the melting of the electrolyte and the single-use nature of the pyrotechnic heating element. Additionally, due to the fragility of the pellet electrodes, the high operational temperatures, and challenges preventing short-circuiting during shock or vibration, the engineering of the thermal battery system is a challenging technical problem that requires consideration of each component as well as the overall battery pack.[1,2,5-7] Rechargeability would represent a significant advancement over state-of-the-art single-use commercial devices, and a robust, rechargeable solution that addresses each of these technical challenges doubly so.

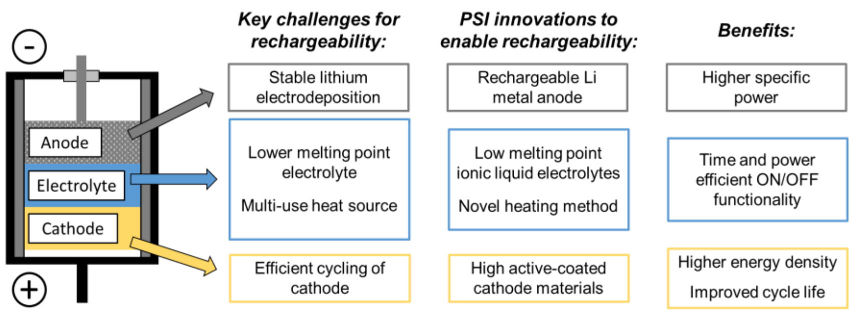

Figure 1. Overview of PSI technologies integrated to create a state-of-the-art rechargeable thermal battery.

Imperia Batteries, a division of Physical Sciences Inc., has successfully demonstrated a rechargeable thermal battery (RTB) with a high energy density (840 Wh/L) that is capable of delivering >12,700 W/L for high power applications with temperature dependent on/off functionality. Imperia's RTB leverages the high energy and power density of lithium metal batteries combined with a novel electrolyte formulation that enables on/off functionality through temperature-modulated conductivity. This technology is well-suited for applications that require intermittent high power pulses over long periods of time. Figure 1 presents a schematic view of Imperia's RTB system highlighting the key innovations and capabilities of the technology.

Results and Discussion

Traditional thermal batteries are activated by melting a solid electrolyte at high temperatures (>200ºC) with a single-use pyrotechnic heating element, preventing continued or repeated use. In order to enable a mutli-use thermal battery, the electrolyte needs to have a well-defined temperature at which the mixture becomes conductive. Several approaches have been demonstrated in the literature.[8-12]

The strategy employed in this work utilizes low melting point organic salts combined with traditional lithium salts with a non-flammable, non-carbonate solvent. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) is used as the primary electrolyte component, so the TFSI anion was selected as the anion for the low melting point organic salt component. A range of cations were considered and candidates were selected based on literature reports of on/off ionic conduction behavior ca 90°C in mixtures of LiTFSI and the candidate organic salts.[13] This approach enables operation at 100ºC instead of 200ºC, requiring less startup energy.

By combining this thermally activated electrolyte (TEL) with other lithium ion and lithium metal cell technologies including a patented cathode coating that improves specific power and energy density and an anode-less cell design where lithium metal is deposited from the cathode, Imperia is able to produce high energy density lithium metal batteries with temperature dependent on/off functionality. This on/off functionality is demonstrated at the coin cell scale in Figure 2. At the operating temperature, the system delivers over 690 Wh/L with 97-99% cycle-to-cycle efficiency. When the temperature is reduced to 40 ºC, solidification of the electrolyte prevents operation. This inactivity below the operation temperature represents the inert state of the battery and is ideal for long-term storage. Upon reheating to the operating temperature, the system returns to the previous charge/discharge behavior. The resulting RTB benefits from the high specific power, energy density of traditional lithium metal batteries and the inert storage capabilities of a thermal battery while being able to cycle ca. 25 cycles.

Imperia has demonstrated RTB performance in 7 Ah pouch cells, with energy density of 840 Wh/L during a 1C discharge (Figure 3). Additionally, the capacity fade of the full-scale cells during extended cycling was tested. Cells were cycled at 80% depth of discharge. Cells were charged at a 1C nominal rate and discharged at 85ºC and a rate of 1C between 4.3 V and 3.55 V (80% DOD as determined by the percentage of the total capacity at the given voltage). The results are summarized in Figure 4.

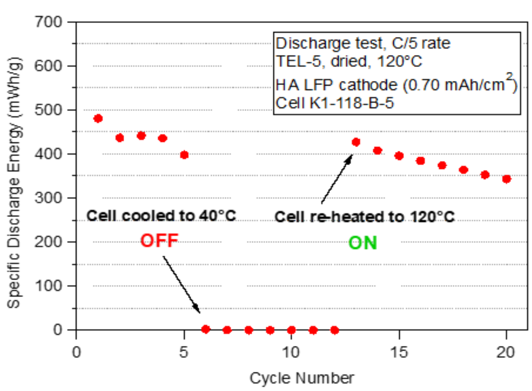

Figure 2. Specific energy delivered in the activated state, cooled to the inert state, and reheated to the operating temperature.

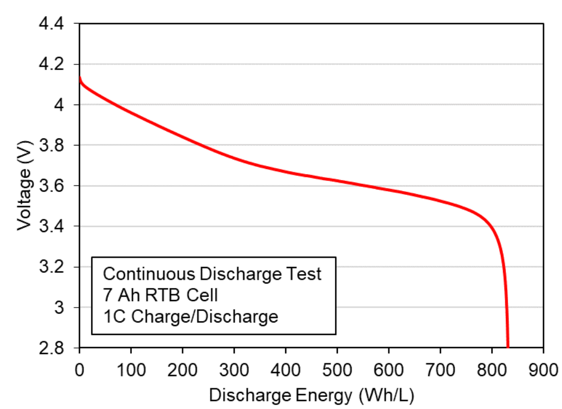

Figure 3. Specific discharge energy of a 7 Ah RTB cell operated using custom PCB heating.

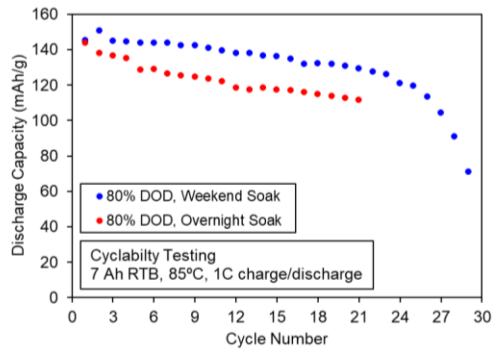

Figure 4. Discharge capacity as a function of cycle number for a cell cycled 80% DOD after soaking overnight (red) and over a weekend (blue).

Imperia has shown that the RTBs can deliver high power discharge pulses up to 54C a (current densities greater than 100 mA/cm2). Figure 5 shows the pulse power density delivered for an RTB discharged with 1 second pulses of increasing current. Imperia's RTB supports high rate discharge pulses up to a power density of 12.7 kW/L. Following the discharge pulse, the system shows rapid recovery of the voltage within milliseconds after the end of the pulse, indicating low internal resistance and the ability to support subsequent high power pulses. The current design can be further modified to achieve a power density as high as 13.5 kW/L.

In order to quickly and efficiently activate the system, Imperia has developed a novel heating technique that can be efficiently integrated into the battery pack design. An integrated circuit and board matching the dimensions of the current battery configuration was fabricated. The custom heater is capable of heating a 7 Ah RTB to operating temperature in under 90 seconds, utilizing 2.84 Wh. Additionally, the activation power efficiency improves as battery pack size and capacity increases.

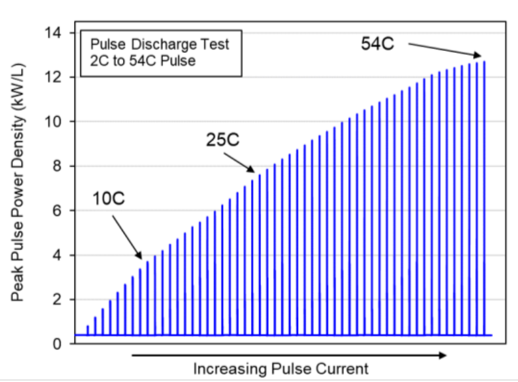

Figure 5. Pulse power density as a function of 1 second pulse rate from 1C to 54C.

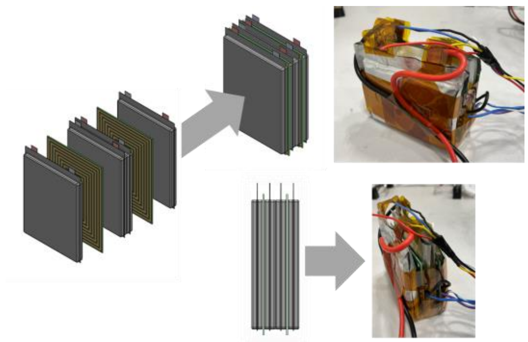

Figure 6. (left) Schematic and (right) Photographic depictions of the front (top) and side (bottom) views of 2S2P RTB battery pack with 2 integrated PCB heating boards.

The lithium deposition and discharge profile of a 7 Ah RTB heated with the novel heating method are characteristic of the battery type and indistinguishable from those resulting from a system heated with a conventional oven.

To demonstrate the ability of the cells to be integrated into a rechargeable thermal battery unit, a demonstration unit was produced. To assemble the battery pack, four 7 Ah cells were configured in a 2S2P battery pack, creating a 14 Ah pack with a nominal voltage of 10.8 V. The assembly also integrated two novel heaters after the first and third cells. This battery pack is shown in Figure 7. The battery pack reached operating temperature (as measured on the cell exterior) using the built-in heating system within 110 seconds. After being heated to the activation temperature, the battery pack was successfully charged and discharged using a power source and a programmable load, respectably. This demonstration proves that these technologies can be straightforwardly combined into a prototype rechargeable thermal battery device. By leveraging lithium ion and lithium metal cell designs, high capacity cathode materials, and lithium metal anode technologies, the rechargeable thermal battery is capable of high energy and power densities. By leveraging custom electrolyte blends of lithium salts and low melting point organic salts, temperature dependent on/off behavior was demonstrated. When this electrolyte was paired with a custom heating method, the battery could be quickly and reliably activated and de-activated. Further development work will focus on customization of these technologies towards a specific application – optimizing activation time, total energy density, peak power delivery, and size to match application needs. In the conference talk corresponding with this article, these results as well as potential applications and impacts will be discussed.

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