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Improving the specific energy of Li-Ion capacitor laminate cell using hybrid activated Carbon/$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ as positive electrodes

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HIGHLIGHTS

- LIB/LIC hybrid cell consists of NMC/activated carbon cathode and hard carbon/Li.
- The specific energy of hybrid cell is 50% higher than that of Li-ion capacitor.
- The cycle life of internal hybrid cells is over 20,000 cycles.

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ABSTRACT

In this work, we investigated the performance impact of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NMC) as an additive to activated carbon (AC) electrodes within a high-performance Li-ion capacitor (LIC) fabricated with activated carbon positive electrodes (PEs) and hard carbon negative electrodes (NEs) having lithium thin films as Li sources loaded on the surface of the negative electrodes. The NMC additive impact in initial testing showed an increase in specific energy of the LIC of nearly 50.5% with a 32% maximum specific power loss. Contrary to its typical low rate battery decay at high rate cycling the cell having a hybrid PE is still able to maintain over 90% capacity at a 0.7C rate after 11,000 cycles at rate of 18C and an additional 9000 cycles at a rate of 36C. We conclude at high rate cycling minimal impacts occurs to the NMC properties which can be seen with low rate intercepts.

1. Introduction

In an ever technologically advancing age, the need for power and performance from electronic devices only continues to grow. Throughout the growth of the past few decades the demand for energy storage devices has grown exponentially. In today's market, two devices types can be seen heavily extending into the market, lithium ion batteries (LIBs) and lithium ion capacitors (LICs). LICs are often in use for their unique qualities of long cycle life (over 100,000 cycles), and high specific power but unfortunately, they suffer from low specific energy most only reaching a maximum of 15 Wh kg^{-1}. LIBs have nearly all the opposite traits, possessing high specific energy, but suffering from low specific power and cycle life (500–3000 depending on material used in cells).

Naturally, these two varying devices leave a gap between them when looking at a Ragone plot graphing power density against energy density. This area would allow for a diversity of situations and problems to be solved could a device enter this range. That idea, has been pursued by many throughout the decades looking for a combination of the two devices internally or externally connecting into a system capable of falling between the two regions these devices encompass [1–4]. These devices were often attempted by connecting a device/electrode of LIBs material with one of LICs material. This union of these two devices is not without its own issues, often having voltage range limitations, or material breakdown issues impacting performance.

This all lead to a natural progression of going from serial or parallel connection of LIBs and LICs devices to a combination of materials to attempt to find that perfect blend. Hybrid energy storage device

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research in attempts to produce an LIC which utilizes a LIB's negative electrode and an Electric Double-Layer Capacitors (EDLCs) positive electrode has had many research done looking to find the limitation of long cycle life, energy density, and power density [5–31]. In this work, we explore the fabrication of a hybrid positive electrode to see the additive properties of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NMC) on a more readily used activated carbon (AC) electrode. The most significant advantages of NMC are high specific capacity and high voltage. Although internal hybridization of materials is being researched, the additive benefit is still unknown based on controlled quantities of additives. In previously works, people were pairing entire electrodes of LIB material with an entire electrode of LIC material [32,41,42]. In this work, an important difference between the hybrid cell in this study and previous works is that we used a pre-lithiated anode. The capacity of the anode in our hybrid cells is several times that of the capacity of the cathode; therefore, pre-lithiation is necessary. The tradeoff for the high capacity of the anode (extra weight of anode) is a lower energy density but high cycle life. We are controlling the amount of NMC in the cathode like a material additive to an already proven LIC laminate cell system [32–35]. The effects of the additive have proven to provide a unique trade off in performance. In time, this trade off may allow for the creation of a device able to step into that gap between these two traditional devices and allow for a much smaller device for numerous applications compared to traditional systems requiring both LIBs and LICs. This device would be able to perform typically like any other LIBs or LICs of those materials but when necessary would be able to utilize the additive material in order to increase the necessary characteristic that the LIB or LIC couldn't otherwise.

In this paper, the cell design of the new generation hybrid energy storage device will be described in detail. The electrochemical performance including energy density, maximum power density and cycle life of the hybrid device will be reported. The comparison of electrochemical performance between the hybrid device and traditional LIC will also be included.

2. Experimental

$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NMC) powder was purchased from MTI Corporation, USA. All single-side coated NMC/AC electrodes were prepared by laminating a dry powder mixture of NMC, AC and the polytetrafluoroethylene (PTFE) as the binder (AC:NMC:PTFE = 75:25:6.4) on to an Al foil substrate with a thickness of 20 μm. Making an electrode by a dry process, electrode and binder powders were mixed by a high-speed blender, where the binder was fiberized to form a matrix to support the electrode particles to form an electrode film. The free-standing, continuous electrode film was formed by pressing the uniformly mixed powders together through the gap between two heated rolls of a roll-mill. Then the free-standing electrode films were laminated onto a substrate such as a current collector with conductive coating layers on both surfaces. This dry powder mixture allows for better control of the electrode properties and is environmentally friendlier than tradition wet-method electrode fabrication because it doesn't require solvents and the film can be modified into a desired range before lamination. After the dry powder films were fabricated the films were dried at 120 °C for 12 h in an oven under vacuum. All the hybrid electrodes' active layer thicknesses were around 100 μm after the compression process. The final thickness of the electrode was controlled by the gap of two rolls and the pressure between two rolls. All the hybrid electrodes were additionally dried at 120 °C overnight in a vacuum oven and then transferred into a glove box (The conditions of the glove box were less than 1 ppm oxygen and moisture). For the LIC and hybrid cells, additional double-side coated 100% AC and hybrid NMC/AC (25:75) positive electrode sheets were prepared by the same procedures mentioned above. The active layer thickness of the double-side coated PEs was around 200 μm. The negative electrode preparation has been described previously [31]. Briefly, the double-side coated NE was made with hard carbon on copper (Cu) foil current collector with thickness of 10 μm and supplied by General Capacitor LLC. The active layer thickness of NEs is around 180 μm. All the electrode sheets were dried at 120 °C under vacuum first and then transferred to a dry room environment with - 45 °C Dew Point and punched out into 4.6 cm × 4.6 cm (active area) for NE and 4.5 cm × 4.5 cm for PE with additional 1.5 cm × 1.5 cm tab. Thin lithium foils were used to prelithiate hard carbon NE and the method has been described in an earlier report [35]. The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC): dimethyl carbonate (DMC) at a ratio of 1:1 by weight (LP30, SelectiLyte ™, Merck Electrolyte) and the separator for the laminate cells was polypropylene (PP) based material.

LIC laminate cell LIC200R and hybrid laminate cell (HLC) with NMC:AC (25:75) as PEs were fabricated in the dry room by stacking 7 double-sided lithium thin films pre-loaded NEs, 6 double-sided PEs and 2 single-side PEs. The schematic representation of the laminate cells was shown in the earlier report [35]. Both the Al and Cu substrates from the electrodes were welded to the Al and nickel (Ni) tabs. Then the cell core was placed in an aluminum lamination formed case that was sized for the cell's core's dimensions after the stacking and welding processes. The laminate cells were filled with electrolyte to a targeted level based on cell core size. After electrolyte was impregnated, the cells were vacuum sealed in the glove box using a vacuum sealer. The laminate cells then entered a formation process before any evaluation. After the formation cycle, the laminate cells were de-gassed and sealed again under vacuum. The capacitance and DC-ESR were obtained by charging-discharging the LIC200R and HLCs under a constant current of 80 mA and 4 A. Each current was done to both cells for 3 cycles with 15 s rest time between each charge and discharge step. After the initial capacitance, DC-ESR, and the electrochemical impedance spectrum (EIS) of the cells were recorded using a Gamry Instruments Reference 3000 Potentiostat. The frequency range was from 0.01 Hz to 10^6 Hz and the amplitude was 10 mV. After EIS testing, both LIC200R and HLC were charged and discharged under the currents of 80 mA, 0.2 A, 0.5 A, 1 A, 2 A and 4 A to study the performance under various rates. Additionally, the three HLC were put under cycling performance testing. The HLCs were charged and discharged under constant currents of 0.5 A, 2 A, and 4 A for various cycles to obtain the cycling performance under various charge-discharge rates. The higher rates of 2 A and 4 A were periodically intercepted with a low rate of 80 mA for a period in order to see the high-rate cycles impact on the battery material. These low rate intercept cycles allow for a baseline comparison of battery material utilization across any number of cycles. In this study, we did an initial baseline of 80 mA and 2 A rate. Then after 8000 2 A cycles another 80 mA C & DC-ESR intercept test was taken for comparison. Incrementally, every 3000 cycles an additional 80 mA intercept was taken. This continued till 11,000 cycles in total had passed. Then the rate was increased to 4 A for each 3000 cycles set before an additional intercept was performed. The electrochemical performances of LIC200R and HLC were tested by an Arbin BT-2000 Battery Testing Unit and laminate cells were clamped with acrylic plates under a constant pressure of 10 kg during all testing.

To investigate the surface morphology of NMC powder, 100% AC electrode and hybrid NMC/AC (25:75 wt%) electrode, a field emission scanning electron microscope (SEM) (JEM-ARM200 cF) was used. Powder and electrode samples were prepared and scanned under 10 kV condition resulting in images with 2000 × magnification of the desired surfaces.

3. Results and discussion

The SEM images of the NMC powders, 100% AC electrode and NMC:AC (25:75 wt%) hybrid electrode is shown in Fig. 1. It can be observed from Fig. 1(a) that the NMC powder shows an average particle size of 10 μm and well-crystallized particles with uniform spherical-like morphology. The 100% AC electrode in Fig. 1(b) shows an average particle size of 5 μm and a porous structure. The 100% AC electrode's