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Hybrid lithium-ion capacitor with $LiFePO_4$/AC composite cathode – Long term cycle life study, rate effect and charge sharing analysis

A. Shellikeri[a,b], S. Yturriaga[b], J.S. Zheng[c,d,**], W. Cao[e], M. Hagen[a,b], J.A. Read[f], T.R. Jow[f], J.P. Zheng[a,b,g,*]

[a] Department of Electrical and Computer Engineering, Florida A&M University-Florida State University College of Engineering, FL, 32304, USA
[b] Aero-Propulsion, Mechatronics and Energy Center, Florida State University, FL, 32310, USA
[c] Clean Energy Automotive Engineering Center, Tongji University, Shanghai 201804, China
[d] School of Automotive Studies, Tongji University (Jiading Campus), Shanghai 201804, China
[e] General Capacitor LLC, Tallahassee, FL, 32304, USA
[f] U.S. Army Research Laboratory, Adelphi, MD, 20783-1197, USA
[g] Center for Advanced Power Systems (CAPS), Florida State University, Tallahassee, FL, 32310, USA

HIGHLIGHTS

- Internal hybrid LIC is realized combining $LiFePO_4$/AC cathode with hard carbon anode.
- Pre-lithiation and excess capacity of anode are key for high rate and long life.
- The EC performance, rate dependence, and cycle life of hybrid LICs were studied.
- The capacity degradation due to faradaic and non-faradaic materials was studied.

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ABSTRACT

Energy storage devices, which can combine the advantages of lithium-ion battery with that of electric double layer capacitor, are of prime interest. Recently, composite cathodes, which combine a battery material with capacitor material, have shown promise in enhancing life cycle and energy/power performances. Lithium-ion capacitor (LIC), with unique charge storage mechanism of combining a pre-lithiated battery anode with a capacitor cathode, is one such device which has the potential to synergistically incorporate the composite cathode to enhance capacity and cycle life. We report here a hybrid LIC consisting of a lithium iron phosphate ($LiFePO_4$-LFP)/Activated Carbon composite cathode in combination with a hard carbon anode, by integrating the cycle life and capacity enhancing strategies of a dry method of electrode fabrication, anode pre-lithiation and a 3:1 anode to cathode capacity ratio, demonstrating a long cycle life, while elaborating on the charge sharing between the faradaic and non-faradaic mechanism in the battery and capacitor materials, respectively in the composite cathode. An excellent cell capacity retention of 94% (1000 cycles at 1C) and 92% (100,000 cycles at 60C) were demonstrated, while retaining 78% (over 6000 cycles at 2.7C) and 67% (over 70,000 cycles at 43C) of the LFP capacity in the composite cathode.

1. Introduction

Lithium (Li)-ion battery (LIB) and electric double-layer capacitor (EDLC) are the two widely used electrochemical energy storage devices. A typical LIB is made with Li intercalated anode and Li metal oxide cathode (hence the redox process or faradaic mechanism of energy storage), while the EDLC is made with a high surface area activated carbon (AC) for both anode and cathode (hence the reliance on double layer capacitance or non-faradaic form of energy storage). As a consequence of their different energy storage mechanisms, they both are distinct in their energy and power performances. LIB has a high specific energy of 100–250 $Wh{\cdot}kg^{-1}$; however, it has a low specific power of $< 0.5\,kW{\cdot}kg^{-1}$ and a poor cycle life of < 5000 cycles. EDLC has a high specific power of $10\,kW{\cdot}kg^{-1}$ and a long cycle life over 100,000

* Corresponding author. Florida State University, 2525 Pottsdamer St., Tallahassee, FL, 32310, USA.
** Corresponding author. Tongji University, 4800 Caoan Road, Shanghai, 201804, China.
E-mail addresses: jszheng@tongji.edu.cn (J.S. Zheng), zheng@eng.fsu.edu (J.P. Zheng).

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cycles; however, it has a much lower specific energy of < 6 $Wh{\cdot}kg^{-1}$ [1–4].

Moreover, energy storage devices, which can combine the advantages of LIBs and EDLCs in a single form, are highly desirable. As a new generation of supercapacitor, the Li-ion capacitor (LIC) is an advanced energy storage device which consists of an EDLC cathode and a prelithiated anode [5–7], between which the ions shuttle during charge and discharge processes. Because of using prelithiated and low surface anode materials, the LIC can be charged to a maximum voltage as high as 4.0 V, which is much higher than that of EDLCs and comparable to LIBs.

Very recently, we have demonstrated a new hybrid energy storage device that combines the advantages of both the LIB and the LIC [8], thereby avoiding their inherent defects, while bridging the gap between the high energy densities offered by batteries and the high power densities seen in EDLCs. The fundamental difference between this hybrid LIC energy storage source and the LIC is that the hybrid LIC technology integrates two separate energy storage devices into one by synergistically combining battery and capacitor materials together to form a composite cathode. As seen from the potential profile of the hybrid cathode in Fig. 1, the non-faradaic capacitor material is initially charged electrostatically till the electrode potential reaches the redox reaction potential of the faradaic battery material, when the battery material is charged while maintaining a constant battery redox reaction potential. Once fully charged, the capacitor material is charged again till a limiting potential is reached for the capacitor material. Moreover, the composite cathode combines the double layer capacitance, which is surface limited, with the materials that store charge through redox reactions, which are limited by the charge transfer kinetics and diffusional processes, but are not limited to the material surface and hence, the bulk can be accessed, resulting in greater charge storage. This internal hybrid LIC device does not require any electric circuits for charge balancing and control when compared with the conventional external hybrid energy storage source. The energy density and power density of the hybrid cell can be designed to meet the requirements by a reasonable distribution of the ratio between LIB and LIC electrode materials in the internal hybrid LIC. For example, in a LIB/LIC internal hybrid cell in our recent work, made with a 20 wt% $LiFePO_4$ (LFP) and 80 wt% AC mixed cathode and a pre-lithiated hard carbon anode, showed the best rate performance and the specific energy increased by 40% compared with conventional LIC [9]. The LFP is a high specific capacity and high potential battery material, while the AC is a highly conductive and porous material which provides better power capability and adsorption of electrolyte, apart from contributing towards surface charge storage.

In the recent past, several studies have investigated and elaborated on the LFP/AC and other composite cathode electrode performances [10–16]. Moreover, carbon coated LFP has also been composited with CNTs to overcome the issues of low conductivity, to achieve high rate performance [17,18]. Hence, Li-ion insertion type battery material when diluted with highly conductive and double layer type capacitor materials, has proven to be very beneficial in improving rate performance. These studies indicated the beneficial effects and advantages of combining a battery material with a capacitor material as a composite cathode in varying degrees, which include high conductivity, high tap density and specific capacity by enabling accessibility to the battery materials through a highly conductive and porous capacitor material. But most of these studies were limited by the lack of long term cycle life performance analysis (few thousands) in full cell format, which is a necessity for a practical supercapacitor device.

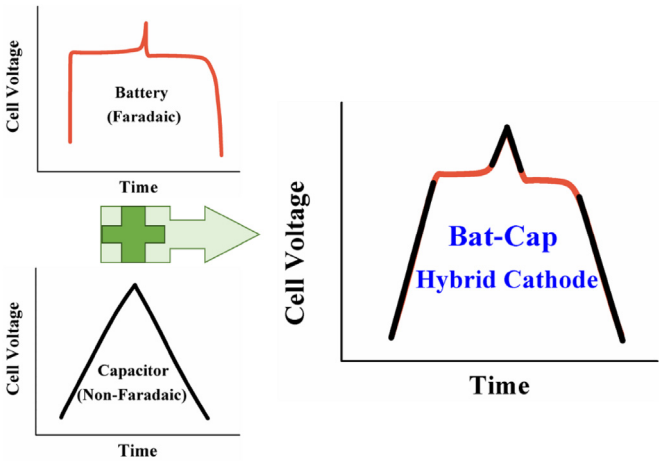

Fig. 1. An illustration of a hybrid composite cathode potential profile, combining faradaic and non-faradaic types of charge storage.

Here we report our investigation on the long-term cycle life of the internal hybrid LIC with LFP/AC as the composite cathode, showing for the first time, an extremely large cycle life of > 100,000 cycles for a LFP/AC composite cathode. To the best of our knowledge, our present work is one of the first to successfully demonstrate the performance of such a composite cathode for a large number of charge/discharge cycles in a hybrid LIC full cell format by employing three key strategies: 1) *An innovative fabrication method*: The quality of electrodes plays a crucial role in determining the performance of hybrid energy storage cells including energy, power and cycle life. We have employed a dry electrode fabrication method to produce electrodes for internal hybrid cells, the advantages being high tap density, good mechanical properties of electrode, good adhesion between electrode and current collector, and low contact resistances. 2) *Anode/cathode capacity design*: It has been shown that the cycle-life of hybrid cells is greatly influenced and limited by the anode electrode [19,20]. Moreover, the lower potential limit of the anode electrode is determined mainly by the mass capacity ratio between anode and cathode. Hence, the more the anode material in the cell, the greater is the cycle life and further is the anode potential away from the Li-plating potential of 0 V vs. Li^+/Li, but the use of excess anode also results in additional inactive material, which lowers the energy density, hence a tradeoff between energy density and cycle life, and 3) *Anode pre-lithiation strategy*: The anode electrode was pre-lithiated with Li metal source. Absence of pre-lithiation step, will engender the following effect, where the SEI formation during initial cycles will consume the Li-ions from the electrolyte, leaving it depleted and hence, some amount of active Li content from LFP is bound to be used up to replenish the depleted Li-ion counts from the electrolyte. Moreover, with the large anode to cathode capacity ratio, anode pre-lithiation is necessary to not only compensate for the lithium loss from SEI formation, but also to drive the anode potential to lower values initially during soaking process to ensure a low and narrow potential window of operation for anode. Hence, the hybrid LIC will not consume salt in the electrolyte during the charge/discharge cycles, which is crucial in ensuring long cycle life and high capacity [21–23].

Moreover, to improve the performance of an energy storage device, it is necessary to identify and characterize the different charge storage mechanisms and in case of the composite electrode, it is of paramount importance due to the presence of two charge storage mechanisms in one single electrode. Hence, we also introduce here, a unique combination of methods of high rate cycling-low rate sampling and a slope estimation method, for the estimation of the effect of rates and cycle life decay on the individual faradaic and no-faradaic components of energy storage in a single composite electrode, which can potentially help in the further optimization of composite cathodes.

2. Experimental

2.1. Electrode preparation and characterization

Commercial active materials were used for the negative and positive electrode preparation. The composite cathode (abbreviated as LFP20