



Electrochemical performance of lithium-ion capacitors evaluated under high temperature and high voltage stress using redox stable electrolytes and additives



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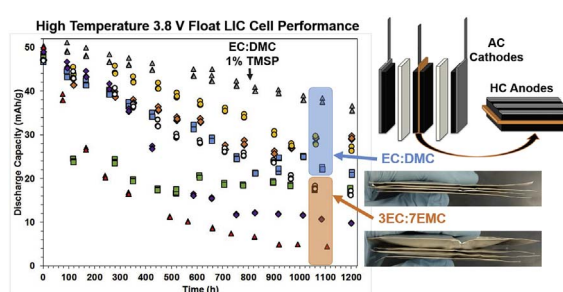
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HIGHLIGHTS

- Pre-lithiated LICs with HC anodes and AC cathodes show long term cycling stability.
- VC and TMSP additives are essential for improved performance of LICs at a 10C rate.
- VC and TMSP improve capacity retention and the specific energy/power up to 4.0 V.
- Electrolytes containing DMC yield better capacity retention at high temperatures.
- EC:DMC 1% TMSP retained 70.5% of initial performance after floating 1200 h at 65 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-ion capacitors (LICs) were investigated for high power, moderate energy density applications for operation in extreme environments with prolonged cycle-life performance. The LICs were assembled as three-layered pouch cells in an asymmetric configuration employing Faradaic pre-lithiated hard carbon anodes and non-Faradaic ion adsorption-desorption activated carbon (AC) cathodes. The capacity retention was measured under high stress conditions, while the design factor explored was electrolyte formulation using a set of carbonates and electrolyte additives, with a focus on their stability. The LIC cells were evaluated using critical performance tests under the following high stress conditions: long-term voltage floating-cycling stability at room temperature (2.2–3.8 V), high temperature storage at 3.8 V, and charge voltages up to 4.4 V. The rate performance of different electrolytes and additives was measured after the initial LIC cell formation for a 1C–10C rate. The presence of vinylene carbonate (VC) and tris (trimethylsilyl) phosphate (TMSP) were found to be essential to the improved electrochemical performance of the LIC cells under all testing conditions.

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1. Introduction

A new generation of energy storage technologies, referred to as “advanced and post lithium-ion batteries,” have the potential to address both existing and future challenges of increasingly complex energy and power systems. These energy storage technologies include Si-anode batteries, Li-S batteries, Na-ion batteries, Mg-ion batteries, Li-air batteries, solid state batteries, lithium-ion capacitors, and new hybrid battery-capacitors. Advanced and post lithium-ion batteries have been projected to comprise 10% of the entire battery market by 2026, which is valued at \$14 billion according to IDTechEx's latest research report, “Advanced and Post Lithium-ion Batteries 2016–2026: Technologies, Markets, Forecasts.” [1] Alternative technologies are needed to meet increasing demands for high energy, high power, and prolonged cycling stability for applications in electric vehicles, uninterrupted power source systems, portable power systems, voltage sag compensation, and radio communication devices [1–7].

Recently, the lithium-ion capacitor (LIC) has been proposed as a hybrid battery-capacitor that would be a suitable alternative high-power power source technology [2,3]. The conventional electrochemical double-layer capacitor (EDLC), also known as a supercapacitor, is composed of high surface area activated carbon (AC) electrodes that store energy in the double-layer formed at the interface of the porous AC electrodes and the electrolyte. Additionally, it has been reported that the activation process for AC by oxidizing agents (e.g., oxygen, steam, KOH, H₃PO₃, H₂SO₄, HNO₃, etc) introduces surface oxygen functional (SOF) groups (e.g., hydroxyl, phenol, ether, carbonyl, carboxyl, etc.) on the carbon surfaces that further contribute Faradaic pseudocapacitance [8]. The EDLC provides high power density and superior cycle performance using cost-effective and environmentally friendly electrode materials. A recent study has shown that flexible solid-state EDLC devices exhibit extreme durability under electrochemical, thermal, and mechanical stresses to preserve performance [9]. However, the energy density is relatively low (~0.5–15 Wh/kg) compared to that of lithium-ion batteries (~100–265 Wh/kg), which limits its usage in large scale energy devices [2–7]. The lithium-ion battery (LIB) is an electrochemical energy storage device that is formed using Li-intercalation materials as the positive electrode (e.g., LiCoO₂, LiMn₂O₄, LiFePO₄, etc.), carbonaceous materials as the negative electrode (e.g., graphite, hard carbon, soft carbon, etc.), and a lithium-based organic electrolyte [10–18]. The LIB displays relatively high energy density and high working voltage, and a low self-discharge in comparison to EDLC devices, but limited power density and cycle life [12,13,16,19–22]. The supercapacitor electrodes of EDLCs undergo ion adsorption/desorption during the charging-discharging process, while lithium-ion intercalation/de-intercalation occurs within the bulk of the electrodes in LIBs [2–7].

The lithium-ion capacitor (LIC) can accommodate both the non-faradaic (i.e., ion adsorption/desorption) and the faradaic (i.e., lithium insertion/extraction) processes of EDLCs and LIBs at the same time, respectively [2,3]. Typically, the supercapacitor electrode is coupled with a negative battery electrode in lithium-based organic electrolytes. The advantages of the hybrid LIC device include higher power density and longer cycle life than a LIB and higher energy density than an EDLC, as well as a higher output voltage and a wide range of operational temperatures, from –30 °C to 70 °C [6]. Factors that affect the LIC performance are the pre-lithiation process of the negative battery electrode, the carbonaceous active electrode materials, safe operational limits of the electrolyte, and the configuration of the electrodes for hybrid cell design. Activated carbon and graphite electrodes are commonly used owing to their high theoretical capacities, stable charge-discharge, natural abundance, and low cost. The battery electrode determines the power performance of the LIC as a result of the slower kinetics of lithium-ion intercalation/de-intercalation. Additionally, hard carbon anodes as the battery electrode exhibit high capacity, do not undergo intercalation-induced exfoliation, and have higher rate

capabilities compared to graphite [2–7]. Pre-lithiation of the negative battery electrode (e.g., hard carbon) for LICs is required and improves the working voltage, energy density, and cycling stability. The pre-lithiated battery electrodes exhibit better retention of the irreversible capacity and lower electrode resistance [3]. However, some of the carbonaceous materials suffer from low lithium-ion diffusion rates, may require an increased operating voltage range, and require the use of alternative electrolytes [2–7].

A key challenge facing all electrode materials are the detrimental interactions with the electrolyte over long-term cycling and at extreme conditions, i.e., decomposition, redox reactions, and corrosion [23–27]. The electrolyte is a critical component for optimizing the electrochemical performance and long-term stability of lithium-ion batteries, and thereby is critical in the development of lithium-ion capacitors. The optimal electrolyte for the desired application is highly dependent on the system of interest. Electrolytes that are stable against unfavorable reduction and oxidation at the electrode surfaces can aid in improving the overall performance of LICs. Additives are beneficial owing to their ability to improve the electrolyte stability, high temperature performance, long-term cycling performance, and decrease gas formation during cycling. The benefits of the additives are due to their ability to form solid electrolyte interphases (SEIs) between the electrode and electrolyte. Ideal anode additives reduce at higher potentials than that of the electrolyte and should exhibit high anodic stability and good cathodic reactivity. An ideal cathode additive has a lower oxidation potential than the electrolyte and should exhibit high cathodic stability and good anodic reactivity. Additives for both electrodes should exhibit good polymerizability, good thermal stability, less reactivity with lithium-ions, and less solvation behavior. The passivating SEI film that forms from the additives should ideally hinder the reactivity of the electrodes with the electrolyte, reduce the interfacial resistance, enhance the ionic conductivity, prevent electrode decomposition, and prevent HF formation [23–26,28–32].

The Army requires that power sources operate within extreme environments over long mission periods, be light weight/energy dense, and provide rapid charge capability to minimize the burden on the Soldier and meet specific high power density requirements. The objective of this investigation into LICs for Army applications is to optimize power density and high temperature lifetime through consistent cell design, electrolyte and additive development, and rigorous performance testing. The performance of the energy storage devices was evaluated in terms of the specific discharge capacity, operational voltage window, coulombic efficiency, specific power and energy, and cycling stability under various conditions using a combination of different electrolytes and additives.

2. Experimental methods

2.1. Materials and cell design

The non-aqueous electrolytes were prepared using a series of alkyl and cyclic carbonate solvents, LiPF₆ salt, and additives with known reduction and oxidation windows, as shown in Fig. 1 [23]. The electrolyte components utilized in this study were ethylene carbonate (EC), fluoroethylene carbonate (FEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and the LiPF₆ salt that were all purchased from BASF, stored in an argon-filled glovebox, and used as received (H₂O < 20 ppm). The electrolyte additive vinylene carbonate (VC) was purchased from TCI and distilled under partial vacuum and inert atmosphere, while the additive tris(trimethylsilyl) phosphate (TMSP) was purchased from TCI and used as received. The electrolyte formulations utilized in this study were 1.2 M LiPF₆ solution in a 3EC:7EMC (3:7 wt%) mixture, 1 M LiPF₆ solution in FEC:4DMC (1:4 wt %) mixture, and 1 M LiPF₆ solutions in mixtures of EC with EMC or DMC (1:1 and 3:7 wt%) [23,33]. Additionally, the VC and TMSP additives were added in 0.5–5 wt% to the electrolytes.

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