Journal of Power Sources 328 (2016) 81–90

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Characterizing rapid capacity fade and impedance evolution in high rate pulsed discharged lithium iron phosphate cells for complex, high power loads

Derek N. Wong [a], David A. Wetz [b, *], John M. Heinzel [c], Azzam N. Mansour [d]

[a] Materials Science and Engineering Department, The University of Texas at Arlington, 501 West First St, Arlington, TX 76019, USA
[b] Electrical Engineering Department, The University of Texas at Arlington, 416 Yates St, Arlington, TX 76019, USA
[c] Naval Surface Warfare Center, Carderock Division, 5001 S. Broad St., Philadelphia, PA 19112, USA
[d] Naval Surface Warfare Center, Carderock Division, 9500 MacArthur Blvd., West Bethesda, MD 20817, USA

HIGHLIGHTS

- Performance of $LiFePO_4$ cells for powering high rate pulsed loads is investigated.
- Only pulsed cells show rapid capacity fade and no longer accept high rate charge.
- Nyquist curve separates in pulsed cells indicating degradation of diffusional processes.
- Cathodes experience minimal loss of active material in both the bulk and surface.
- Anodic surface films are rich in LiF for cells which have been pulsed discharged.

ARTICLE INFO

Article history:
Received 27 June 2016
Received in revised form
18 July 2016
Accepted 2 August 2016

Keywords:
Pulsed power systems
Lithium-ion
High rate cycling
Electrochemical impedance spectroscopy
Surface films

ABSTRACT

Three 26650 $LiFePO_4$ (LFP) cells are cycled using a 40 A pulsed charge/discharge profile to study their performance in high rate pulsed applications. This profile is used to simulate naval pulsed power loads planned for deployment aboard future vessels. The LFP cells studied experienced an exponential drop in their usable high-rate recharge capacity within sixty cycles due to a rapid rise in their internal resistance. Differential capacitance shows that the voltage window for charge storage is pushed outside of the recommended voltage cutoff limits. Investigation into the state of health of the electrodes shows minimal loss of active material from the cathode to side reactions. Post-mortem examination of the anodic surface films reveals a large increase in the concentration of reduced salt compounds indicating that the pulsed profile creates highly favorable conditions for $LiPF_6$ salt to break down into LiF. This film slows the ionic movement at the interface, affecting transfer kinetics, resulting in charge buildup in the bulk anode without successful energy storage. The results indicate that the use of these cells as a power supply for high pulsed power loads is hindered because of ionically resistant film development and not by an increasing rate of active material loss.

1. Introduction

More than ever before, lithium-ion batteries (LIBs) are being considered for deployment as prime power supplies or as short-term energy storage modules for high power electrical systems [1,2]. Applications range everywhere from simple consumer electronics to advanced electrical loads that will one day be used upon naval ships. In several instances, LIBs may be required to provide capacitor-like performance in which they act more like power dense storage than the energy dense storage they are traditionally designed to be. The US Navy expects LIBs to be capable of sourcing loads that have unconventional cyclic demands while still maintaining their recoverable energy storage. As these systems become more prevalent, it is increasingly important to understand the capabilities of LIBs when they are cycled under high rate pulsed

* Corresponding author.
E-mail addresses: derek.wong@mavs.uta.edu (D.N. Wong), wetz@uta.edu (D.A. Wetz), john.heinzel@navy.mil (J.M. Heinzel), azzam.mansour@navy.mil (A.N. Mansour).

http://dx.doi.org/10.1016/j.jpowsour.2016.08.013
0378-7753/

profiles that are well outside their normal operational range.

The Navy is currently researching a number of applications that will require LIBs to both source and sink high power. The charge and discharge modes, respectively, will each last approximately a few seconds and they will be switched repetitively within a single cycle. While some domestic applications demand high rate transient operation from their batteries, none published are equivalent to those being studied by the Navy. The closest would be hybrid electric vehicles (HEVs) that use secondary cells, mainly lithium-ion or nickel metal hydride (NMH) chemistries [3–5], as their primary power supply for driving the electric motors. While the load profile of an HEV requires high power, the rate at which the batteries are operated will nearly always stay well below their maximum ratings so that safety and cycle life for the consumer is maximized. Additionally, the duty cycle of an HEV's transient profile is quite long compared to those the Navy is interested in Ref. [4]. In order to meet the size and weight restrictions aboard their mobile platforms, the Navy will require their battery to be operated at its manufacturer's maximum allowable rating. Operation near the top of the cell's capabilities stresses them both electrically as well as thermally and introduces new phenomena and challenges that must be understood and overcome. In the Navy's applications, safety remains most critical but size and weight of the battery are often considered more important than cycle life. If high rate pulsed operation brings a reduction in cycle life, it is valuable to understand what capacity fade characteristics are unique to it. This need for understanding is what has prompted the work discussed here.

The reader may question why the Navy is pursuing batteries as a possible prime power source for use in high rate applications if their cycle life is significantly reduced. Typically, the Navy has relied upon large diesel powered motor-generator sets to supply a ship's electrical power. As the Navy's electrical requirements increase and their load profiles become more transient in nature, it will become surprisingly more inefficient to use only the ship's motor-generator as a power source. Rapidly ramping on and off a rotational generator's output severely effects its power quality pushing both the voltage and the harmonic distortion well outside of the ratings of the MIL-SPEC-1399 power system standards. On top of the impact to power quality, this type of operation is also fuel inefficient, leading to higher fuel consumption. One proposed solution for improving both efficiency and power quality involves pairing the generator with a hybrid energy storage module (HESM) that utilizes both LIBs and ultra-capacitors to maximize both energy density and power density [6–8]. The ultra-capacitors allow for fast power delivery to the load while the LIBs allow for more pulses from the HESM under a single charge. The HESM is able to act as an augmenting power supply to the motor-generator and as a load to the motor-generator so that a base load can always be maintained.

When sizing the LIB for use within a HESM, several different chemistries can be initially considered however, the unique power profile quickly starts to eliminate many of the available options. Historically, applications utilizing batteries as their prime power source have cycled them under continuous charge and discharge profiles at relatively low to modest rates well below the cells' maximum ratings. These metrics are vastly different from the rapidly transitioning load requirements of interest to the Navy. The energy dense chemistries typically used in consumer electronics, such as NMH and $LiCoO_2$, are less than ideal for safe and reliable operation within high-pulsed power loads because of the high internal heat generated as well as the high rates of recharge required. These chemistries become unstable at high temperature and the risk/reward is not worth it. A more stable battery chemistry, such as $LiFePO_4$ (LFP), is becoming a popular choice for variable high power loads, however knowledge of their degradation behavior in a high rate pulsed profile is very limited. It is imperative that the degradation behavior of this commercial high power battery chemistry be better characterized under these conditions so that behavior can be predicted and cells can be reengineered to perform under this harsh loading.

A literature search yields very few publications in which the capacity fade of LFP cells have been studied at high rates above their nominal rating [3–6]. Within the bodies of work found in the literature, there is no significant discussion of the aging mechanisms that this type of operation induces within the cells. Instead, the authors present data that shows how capacity fade is accelerated with only speculations as to why aging occurs from a chemical and materials level perspective. In the work presented here, LFP cell degradation has been characterized at rates of up to 15C in both continuous and pulsed modes of operation. The cells were studied using both destructive and non-destructive methods to identify and compare the fundamental mechanisms which lead to reductions in capacity and charge acceptance in high rate continuous and pulsed modes. In this study, $LiFePO_4$ cells of the 26650 form factor are being investigated as a viable cell for use in the Navy's future high-rate, pulsed power systems. The cyclic profile studied here was developed in collaboration with scientists from the US Navy to simulate the types of loads anticipated aboard future vessels [9–11]. The objective of this study is to evaluate the cell's performance under high rate pulsed conditions and to study how the profile fundamentally degrades the anode and cathode host structures, respectively.

2. Experiment

2.1. Experimental cell, test plan, and setup

In the work presented here, four identical commercially available off the shelf lithium-iron-phosphate ($LiFePO_4$) cells have been studied. The anode is composed of graphite using carboxymethyl cellulose and styrene-butadiene rubber as a binder. The cathode is a $LiFePO_4$ bound with polyvinylidene fluoride (PVDF) and mixed with carbon black. The electrolyte is a 1:1:1 mixture of EC:DEC:DMC solvents with 1 M of $LiPF_6$ conducting salts. Three of these cells were cycled using a high rate pulsed profile while the fourth was cycled using a high rate continuous profile. All of the cells used are of the 26650 form factor and the manufacturer's data sheet properties are presented in Table 1.

Prior to any high rate evaluation, each of the LFP cells studied was cycled five times the nominal 1C rate (2.6 A) using a constant current (CC) discharge and a constant current - constant voltage (CC-CV) recharge procedure between 2.5 V and 3.65 V, respectively. Next, a 'baseline' procedure was performed in which the cell was cycled once at the 1C rate using the same CC discharge and CC-CV recharge procedure used the initial five cycles and each cell's impedance was measured using electrochemical impedance

Table 1
List of specifications for the lithium iron phosphate test cell used in this study.

26650 lithium iron phosphate test cell	
Capacity	2.6 Ahrs
Nominal voltage	3.2 V
Charge cutoff voltage (recommended)	3.65 V
Charge cutoff voltage (maximum)	4.1 V
Discharge cutoff voltage (recommended)	2.5 V
Discharge cutoff voltage (minimum)	2.0 V
Recharge current (recommended)	2.6 A
Recharge current (maximum)	5.0 A
Continuous discharge current (maximum)	42 A
Pulsed discharge current (recommended for 30 s)	26 A
Pulsed discharge current (maximum for 30 s)	50 A