Journal of Power Sources 196 (2011) 10213–10221

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Calendar and PHEV cycle life aging of high-energy, lithium-ion cells containing blended spinel and layered-oxide cathodes

J. Belt[a], V. Utgikar[b], I. Bloom[c,*]

[a] Idaho National Laboratory, 2525N. Fremont, Idaho Falls, ID 83415, United States
[b] University of Idaho, Department of Chemical Engineering, 1776 Science Center Drive, Idaho Falls, ID 83402, United States
[c] Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439, United States

ARTICLE INFO

Article history:
Received 23 June 2011
Received in revised form 15 August 2011
Accepted 16 August 2011
Available online 22 August 2011

Keywords:
PHEV battery testing
Performance degradation
Curve-fitting
Calendar life
Charge-sustaining cycling
Charge-depleting cycling

ABSTRACT

One hundred seven commercially available, off-the-shelf, 1.2-Ah cells were tested for calendar life and CS cycle- and CD cycle-life using the new USABC PHEV Battery Test Manual. Here, the effects of temperature on calendar life, on CS cycle life, and on CD cycle life; the effects of SOC on calendar life and on CS cycle life; and the effects of rest time on CD cycle life were investigated. The results indicated that the test procedures caused performance decline in the cells in an expected manner, calendar < CS cycling < CD cycling. In some cases, the kinetic law changed with test type, from linear-with-time to about t^2. Additionally, temperature was found to stress the cells more than SOC, causing increased changes in performance with increasing temperature.

1. Introduction

Lithium-ion batteries continue to attract much interest in applications where high specific or volumetric power or energy is required. High-energy lithium-ion batteries are also being considered for automotive applications by the U.S. Department of Energy-supported U.S. Advanced Battery Consortium (USABC) [1]. The batteries usually consist of a metal-oxide positive electrode, a carbon negative electrode, and an organic electrolyte containing dissolved lithium salts.

Layered-oxide cathodes, such as $Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O_2$, represent good candidates for automotive applications because of their high specific capacity [2]. However, the cycle life of this oxide was not as high as desired [3]. On the other hand, spinel oxides, such as $LiMn_2O_4$, are also viable candidates. These oxides are low-cost and have fast kinetics, which makes the oxide suitable for high-power applications [2]. The spinels were reported to have lower specific capacity than the layered oxides [2] and to degrade rapidly due to manganese dissolution [3–6]. There have been reports in the literature that blending these two materials produced a composite with the benefits of both [7–12].

Two U.S. Department of Energy national laboratories, Argonne National Laboratory (ANL) and Idaho National Laboratory (INL), continue to collaborate to understand the causes of performance decline in lithium-ion batteries. Results from this collaboration using three positive electrode materials—$LiNi_{0.8}Co_{0.2}O_2$, $LiNi_{0.8}Co_{0.1}Al_{0.1}O_2$, and $Li_{1.05}(Mn_{1/3}Co_{1/3}Ni_{1/3})_{0.95}O_2$—are given in Refs. [13–18].

The procedures outlined in the USABC test manuals [19–21] are intended to show the promise of a technology versus a set of performance and cost targets. No knowledge of the actual battery chemistry is needed. Thus, the evaluation of cells concentrates on their performance and life and how their life is affected by SOC, time, temperature and type of test. Calendar and cycle life tests were performed to determine the aging characteristics of the blended cathode material under plug-in hybrid electric vehicle (PHEV) testing conditions [19]. It should be noted that the calendar tests in the PHEV and hybrid-electric vehicle (HEV) [20] manuals are essentially the same. The cycle life test is more complex, depending on what is to be learned. Instead of just one cycling mode of operation, charge-sustaining, as in an HEV, the PHEV operates in charge-depleting (CD) as well as charge-sustaining (CS) modes, as shown schematically in Fig. 1. In the CD mode of operation, the battery powers the vehicle directly; the internal-combustion engine is not used at all. After a while, the battery energy becomes exhausted. At this low state of charge, the PHEV will operate in CS mode, similar to that of a hybrid-electric vehicle.

* Corresponding author. Tel.: +1 630 252 4516; fax: +1 630 252 4176.
E-mail address: ira.bloom@anl.gov (I. Bloom).

0378-7753/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2011.08.067

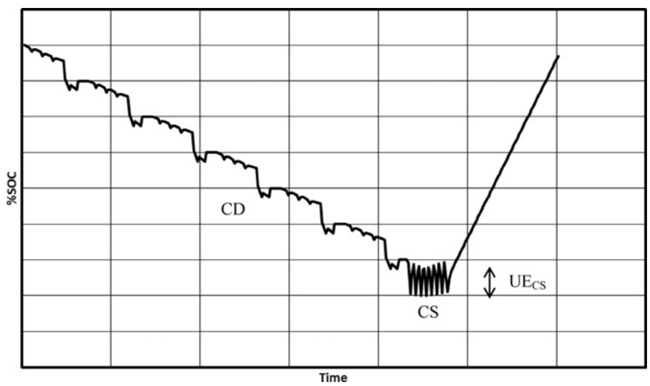

Fig. 1. Schematic showing the two PHEV operating modes, charge-depleting and charge-sustaining (after Ref. [19]). In charge-depleting mode, the internal-combustion engine is not used; energy from the battery alone powers the vehicle. The charge-sustaining mode is similar to that of the HEV; the power from the battery supplements that from the engine. The abbreviation, UE_{CS}, shown in the figure, is the SOC window from which the usable energy in CS mode is based.

The PHEV-related test methods and protocols are new and have not been validated. The objective of work below, in part, is to validate that the test methods stress the battery as expected. In the study described below, the effects of temperature on calendar life, on CS cycle life, and on CD cycle life; the effects of SOC on calendar life and on CS cycle life; and the effects of rest time on CD cycle life were investigated using commercially-available, 18650-size cells. The results of this work will help elucidate the additional stresses on the battery when it is cycled.

2. Experimental method

2.1. Testing

One hundred-seven commercially-available, off-the-shelf, 1.2-Ah, 18650-size cells were used in this work. These cells contained a physically-blended Li–Ni–Mn–Co layered-oxide and Li–Mn–O spinel cathode, an organic electrolyte, and a carbon anode. The test matrix is presented in Table 1. All cells were charged using the manufacturer's recommended algorithm: charge at 1.2 A to 4.2 V, followed by a potentiostatic hold at 4.2 V for a total charge time of 2 h or until the current drops below 50 mA.

Before the start of the aging tests, all cells were characterized in terms of their 10-kW rate capacities and by the hybrid-pulse power characterization (HPPC) test at 30 °C. The cell groups were aged as shown in Table 1 and the performance was averaged for each group. The cells tested at temperatures higher than 30 °C were heated to the test temperature and allowed to equilibrate for 8 h before the aging period began. Every 32 days, testing was stopped and the cells were allowed to rest at 30 °C for at least 8 h. Changes in cell performance were measured by repeating the characterization tests at 30 °C (a reference performance test, or RPT). Testing was then resumed for a total of 10 RPTs.

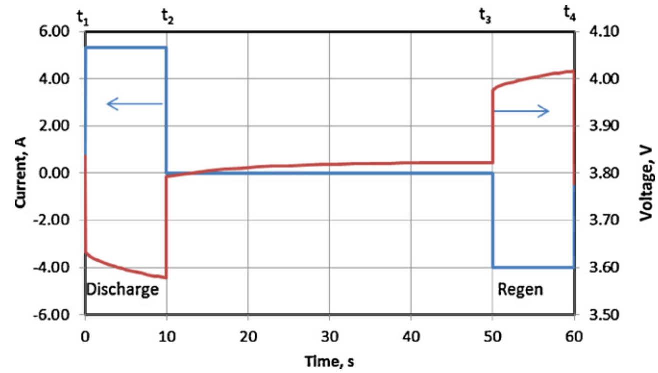

Fig. 2. HPPC profile and voltage response for a typical cell.

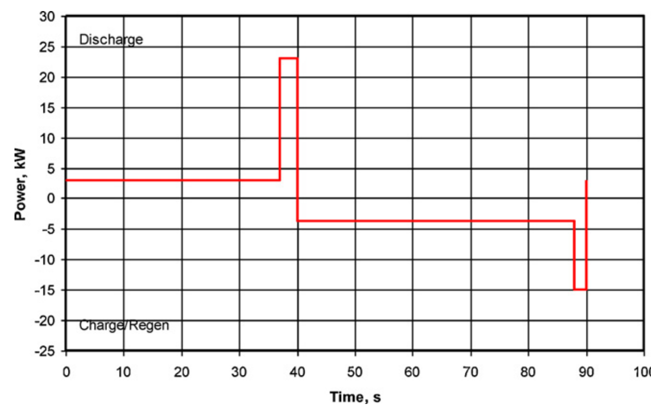

Fig. 3. Charge-sustaining cycling profile [19]. The power levels given on the vertical axis are divided by the BSF to yield the actual power levels used to test a given battery. The unscaled profile removes 50 Wh during the discharge portion of the cycle; the regen portion charges the battery with 46.2 Wh of energy, producing a net removal of 3.8 Wh.

The HPPC test was a constant-current test and consisted of removing 10% of the rated capacity at the C/1 rate, resting for 1-h and applying the test profile. This test sequence was repeated for a total of 9 profiles. Fig. 2 shows the HPPC test profile and the voltage response of a typical cell. For the cells tested, the discharge current in the HPPC profile was 5.3 A, and the regeneration (regen) current, 4.0 A.

Based on the initial HPPC results, the average, calculated battery-size factor (BSF) was 1400 cells. The BSF was used to scale the CS and CD cycle profiles to accommodate the capabilities of the test cells. The generic CS and CD cycle profiles [19] are given in Figs. 3 and 4, respectively. In this experiment, all SOCs for aging were defined in terms of cell potentials: 3.69, 3.89, and 4.09 V for 30, 60, and 90% SOC, respectively. For CS cycling, the battery was discharged to the target SOC at the $C/1$ rate and allowed to rest for

Table 1
Test matrix used in this work. Each entry in the table represents the number of cells tested under that condition.

Test	Temperature, °C				SOC		Rest time, min		
	30	40	50	60	30	90	0	20	40
Calendar life (60% SOC)	10	5	5	4					
Calendar life (30 °C)					5	5			
CS cycle life (60% SOC)	9	5	5	5					
CS cycle life (30 °C)					5	5			
CD cycle life (15-min rest time)	9	5	5	5					
CD cycle life (30 °C)							5	5	5