Journal of Power Sources 296 (2015) 46–52

Contents lists available at ScienceDirect

Journal of Power Sources

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

Fast and slow ion diffusion processes in lithium ion pouch cells during cycling observed with fiber optic strain sensors

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HIGHLIGHTS

- Better cell utilization and life key to encourage broader Li-ion battery adoption.
- Residual electrode strain build-up is critical cell issue for performance and life.
- Cell strain overshoot at high SOC, rest recovery observed with fiber-optic sensors.
- Correlation of the cell strain overshoot/relaxation to SOC and temperature is characterized.
- Origins, implications of issue for longer cell life, utilization also discussed.

ARTICLE INFO

Article history:
Received 23 April 2015
Received in revised form
6 July 2015
Accepted 8 July 2015
Available online xxx

Keywords:
Sensing
Intercalation
Battery management systems
Ion diffusion
Fiber optic sensors
Excess volume

ABSTRACT

Cell monitoring for safe capacity utilization while maximizing pack life and performance is a key requirement for effective battery management and encouraging their adoption for clean-energy technologies. A key cell failure mode is the build-up of residual electrode strain over time, which affects both cell performance and life. Our team has been exploring the use of fiber optic (FO) sensors as a new alternative for cell state monitoring. In this present study, various charge-cycling experiments were performed on Lithium-ion pouch cells with a particular class of FO sensors, fiber Bragg gratings (FBGs), that were externally attached to the cells. An overshooting of the volume change at high SOC that recovers during rest can be observed. This phenomenon originates from the interplay between a fast and a slow Li ion diffusion process, which leads to non-homogeneous intercalation of Li ions. This paper focuses on the strain relaxation processes that occur after switching from charge to no-load phases. The correlation of the excess volume and subsequent relaxation to SOC as well as temperature is discussed. The implications of being able to monitor this phenomenon to control battery utilization for long life are also discussed.

1. Introduction

In recent years, the market for alternative drive technologies such as electric vehicles (EVs) and hybrid electric vehicles (HEVs) has experienced considerable growth. However, the widespread adoption of these green mobility options is still limited by factors such as high costs, battery lifetime, driving range anxiety and the susceptibility to unexpected failures. Effective control and management of cell charge and discharge by battery management systems (BMS) is essential for good performance [1–3]. Current BMS rely on monitoring conventional external parameters such as voltage, current and external temperature, typically with one measurement made per group of 2–10 cells, to estimate state of charge (SOC) and state of health (SOH). The use of these weakly informative parameters limits the estimation accuracy of SOC and SOH and contributes to over-conservative usage and over-engineering of a battery pack [2]. Using additional informative

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http://dx.doi.org/10.1016/j.jpowsour.2015.07.025
0378-7753/

cell parameters such as internal temperature or electrode volume change due to lithium intercalation has the potential to improve SOC/SOH estimation accuracy, which in turn can lead to optimal battery-pack design and capacity utilization. However, available options to sense these internal parameters are limited by the corrosive and electrically noisy environment of batteries and demanding constraints on potential sensors such as cost, size, non-invasiveness, and robustness. Fiber optic (FO) sensors exhibit a small form-factor, immunity to electromagnetic interference and electrostatic discharge, and multiplexing capabilities. These attributes make them attractive candidates for reliable state monitoring in battery packs [4,5].

In this study, a particular class of FO sensors, fiber Bragg grating (FBG) sensors sensitive to temperature and strain were externally attached to lithium ion pouch cells. The potential of FBG sensors as a promising solution for monitoring cell parameters such as strain and temperature was already discussed in our previous work [6]. Multiple charge and discharge cycles demonstrated the excellent repeatability of the FBG strain signal and indicated consistent features in the strain signal that provide additional information about the cell state. FBGs can also be used for directly monitoring electrode strain and temperature inside the cell; results from such internal configurations accomplished by our team will be reported elsewhere in the future. In the present work, a more detailed understanding of the external FO sensing signal in relation to the underlying electrochemical processes is explored.

The functional principle of lithium-ion batteries is based on lithium intercalation. The insertion/release of lithium ions into/from the electrode active materials is associated with structural changes of the electrode active materials and consequently with volume change. In general, the volume change is predominantly caused by the anode material. Thus, the battery expands during charge and contracts during discharge [7–9]. Previous experiments indicated an overshooting of the volume change (also referred to as “excess volume change” within this paper) at the end of charge and volume relaxation in the subsequent no load phase. The impact of these overshoots has to be elucidated with regard to the utility of the strain signal as input parameter for BMS.

Similar characteristics at the end of charge of lithium ion batteries are reported by Lee et al. [8]. They noted a thickness change that was heavily increasing at the end of the constant current (CC) charge phase. The increase diminished during the constant voltage (CV) charging phase and the thickness started to relax. They explained this behavior with a non-uniform intercalation/de-intercalation at high SOC. Wang et al. [10,11] reported a similar excess volume change at the end of charge and a volume relaxation in the subsequent rest phase. They attributed these effects to the slow diffusion of lithium ions in the active material and the slow structural change in the outer region of the electrode particle. As observed from extended cycling experiments in Refs. [10,11], this excess volume change can lead to residual strain build up over time, affecting cell performance and life. Therefore, monitoring and controlling this phenomenon can be very useful to maximize cell life and performance in cutting-edge applications such as xEVs and satellite batteries since electrode volume change is identified as a key mechanism for capacity fading [10,11].

In this work, various charge experiments were performed to investigate a correlation of the overshooting volume change and the amount of intercalated lithium ions. In particular, this paper focuses on the strain relaxation processes that occur after switching from charge to no-load phases. The relaxation phenomena was measured at various temperatures and approximated by a decaying exponential function to explore the temperature dependence of the underlying process.

2. Experimental setup

Commercial LG Chem lithium-ion pouch cells are used for our experiments. The cathode is a blended material composed of spinel/NMC (nickel manganese cobalt oxide) while the anode material is a blended material with graphite. The nominal capacity of the cells is 15 Ah.

Two FBG sensors are used to monitor cell state in our experimental set-up as shown in Fig. 1. FBG sensors exhibit a periodic modulation of the refractive index along the core of the fiber. This modulation is inscribed into silica fiber and acts as a Bragg mirror reflecting a certain wavelength, known as the Bragg wavelength, of the incoming light. The fibers are coated with polyimide, and the core and cladding diameters are 9 μm and 125 μm, respectively. The Bragg wavelengths for the two FBGs are 1555 nm and 1560 nm. While for this initial study two separate optical fibers with FBGs are used, in principle, for deployed architectures the two FBGs can be multiplexed on the same optical fiber.

As cells undergo charging and discharging, the electrodes' volumes experience changes, which manifest as strain on the cell surface. In addition, the cell temperature also changes due to thermic electrochemical reactions and resistive heating. Two FBG sensors are used in order to measure both the temperature changes as well as cell strain due to electrode volume change. The first FBG is bonded at two points to the surface of the pouch cell with epoxy. The bonding lengths are approximately 1 cm. This FBG responds to both strain and temperature changes. The strain is caused due to electrode volume change, as well as thermal expansion or contraction. The second FBG, also referred to as the *reference* FBG sensor, is loosely attached to the cell skin with a heat conducting paste. As such, it is sensitive only to temperature changes. The wavelength shift due to the strain from the electrode volume change alone is recovered by subtracting the wavelength shift observed with the bonded FBG multiplied by a suitable constant from the wavelength shift observed by the reference FBG. The constant factor is determined empirically by conducting a calibration experiment in an environmental chamber where the cell is heated to various temperatures but not electrically cycled.

The reflected wavelength peaks of the FBG sensors are monitored by a commercial readout, the National Instruments™ PXIe-4844 optical sensor interrogator (OSI). The accuracy of the measured peak wavelength of the FBG sensors is ~1 pm. A programmable battery analyzer is used to run defined charge and discharge cycles. The standard cycle employed here consisted of charging at a constant current of 7.5 A to a cutoff voltage of 4.15 V, charging at a CV of 4.15 V to a cutoff current of 750 mA and discharging at a constant current of 7.5 A to a cutoff voltage of 3.0 V. The rest time between charge and discharge was set to 2 h.

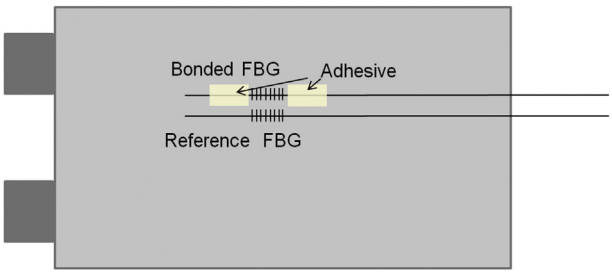

Fig. 1. Schematic of the experimental setup for monitoring strain and temperature of Li-Ion pouch cells by Fiber Bragg Grating sensors. Bonded FBG sensor is attached with an adhesive to monitor strain and temperature. Reference FBG sensor is loosely attached with heat conducting paste.