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The storage degradation of an 18650 commercial cell studied using neutron powder diffraction

Po-Han Lee[a], She-huang Wu[a,*], Wei Kong Pang[b], Vanessa K. Peterson[b,c]

[a] Department of Materials Engineering, Tatung University, No.40, Sec. 3, Zhongshan N. Rd., Taipei City 104, Taiwan, ROC
[b] Institute for Superconducting and Electronic Materials, University of Wollongong, NSW 2522, Australia
[c] Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organization, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia

HIGHLIGHTS

- Storage capacity losses of a cell are diagnosed with incremental capacity analysis.
- Losses of Li inventory and active materials are estimated.
- Capacity loss is strongly affected by the depth-of-discharge of cell during storage.
- *In operando* neutron powder diffraction is used to study cell degradation.

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ABSTRACT

Commercial 18650 lithium ion cells containing a blended positive electrode of layered $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ and spinel $Li_{1.1}Mn_{1.9}O_4$ alongside a graphite negative electrode were stored at various depth-of-discharge (DoD) at 60 °C for 1, 2, 4, and 6 months. After storage, the cells were cycled at C/25 at 25 °C between 2.75 and 4.2 V for capacity determination and incremental capacity analysis (ICA). In addition to ICA analysis, the mechanism for capacity fade was investigated by combining the results of neutron powder diffraction under *in-situ* and *operando* conditions, in conjunction with post-mortem studies of the electrodes using synchrotron X-ray powder diffraction and inductively-coupled plasma optical emission spectroscopy. Among the cells, those stored at 25% DoD suffered the highest capacity fade due to their higher losses of active Li, NMC, and LMO than cells stored at other DoD. The cells stored at 0% DoD shows second high capacity fade because they exhibit the highest of active LMO and graphite anode among the stored cells and higher losses of active Li and NMC than cells stored at 50% DoD.

1. Introduction

Lithium-ion batteries are often charged to high states of charge (SoC) and stored at various depth of discharge (DoD) after use. A personal electric vehicle (EV), for example, spends most of its time in parking mode, which may cause capacity loss of the battery due to storage at different DoDs, especially at elevated temperature. Most analyses of cell fade are based on post-mortem investigations of capacity loss of the electrodes, electrolyte, and separator by disassembling the cell and examining samples using various spectroscopic or microscopic methods [1–5]. The effects of the cell disassembly on analysis results can be avoided using *in-situ* methods, with incremental capacity analysis (ICA), differential voltage analysis (DVA), and electrochemical impedance spectroscopy (EIS) all demonstrated as powerful techniques to obtain information of aging mechanisms without cell disassembling [6–11]. However, these methods can't provide the details of the electrode structural changes upon cycling. Neutron powder diffraction (NPD) has been proven effective as *in-situ* method for the study of the crystalline structure study of commercial lithium-ion batteries due to its lower interaction with testing materials, higher penetration, and higher sensitivity towards Li and neighboring transition metals than X-ray based techniques [12–21]. However, relatively few reports on the aging of Li-ion batteries have been published using NPD [16,21–23]. Shiotani et al. focused on the degradation of a lithium ion battery prepared with $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ and graphite using NPD. *In-situ* neutron diffraction studies were conducted for cells before and after degradation tests at their charged and discharged states or during discharge [21]. *Operando* (real-time during cell operation) results were collected to investigate electrode deterioration, with results suggesting that loss of active positive electrode occurred, as evidenced by a lower discharge

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[*] Corresponding author.
E-mail address: shwu@ttu.edu.tw (S.-h. Wu).

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capacity and smaller changes in the *c* lattice parameter of the electrode compared with that for the electrode within a fresh cell. Dolotko et al. studied the fatigue processes of Li_xCoO_2 using NPD and electrochemical analysis [16]. Changes in the Li occupancy, Li_xCoO_2 lattice parameters, and weight ratio between LiC_{12} and LiC_6 were monitored as a function of battery fatigue. The loss of active lithium in the cell was considered to be the primary reason for fatigue of the Li-ion battery, with the most obvious scenario for the loss of lithium suggested as trapping in the solid electrolyte interphase (SEI). Sharma and Peterson used *in-situ* NPD to understand the effects of overcharging on the phase evolution of graphite within a $LiCoO_2$//graphite commercial cell. During overcharge, the graphite converted to single-phase of LiC_6, in contrast to the mixed LiC_{12} and LiC_6 phase composition usually found [13].

Cells with composite positive electrodes comprising a mixture of two or more individual lithium intercalation compounds balance energy and power densities, and are expected to be viable candidates for large-format energy storage systems. Although storage aging studies of lithium-ion batteries are presented previously [1,2,24–31], only few focus on blended positive electrode materials [1,32–36], as a result of the complexity of the analysis of the degradation mechanism [1,32]. Recently, Keil et al. conducted an experimental study of the aging of electrodes with differing lithium ion intercalation states using a fine SoC resolution [31]. Their results revealed a strong dependency of calendar aging on the graphite electrode, and that a cell with a blended positive electrode stored at a given DoD means that the individual phases within that electrode are stored at different DoDs.

In this study, the structural changes and amount of lithium in electrodes of a commercial 18650 battery containing a composite positive electrode of layered-type $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) and spinel-type $Li_{1.1}Mn_{1.9}O_4$ (LMO) paired with a graphite negative electrode after storage at 0, 25, and 50% DoD at 60 °C for 6 months were obtained using *in-situ* high resolution and real-time *operando* NPD. These results and those of post-mortem analyses are used to validate incremental capacity analysis results for charge/discharge curves performed at C/25 after storage.

2. Experimental

Commercial 18650 lithium ion cells containing a blend of $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC) and $Li_{1.1}Mn_{1.9}O_4$ (LMO) as well as graphite with a nominal capacity of 2.15 Ah were obtained from a well-known global company. The characteristics of this cell are shown in a previous study [37]. 90 commercial cells with discharge capacities of 2207 ± 3 mAh at C/25 rate were selected by following the method introduced by Dubarry et al. for storage studies [11]. At first, the charge/discharge capacities of each cell were determined within cutoff voltages of 2.75 and 4.2 V at C/25 with a 1 h rest between charge/discharge switching. After the cells were discharged to various DoDs of 0, 25, 50, 75, and 100%, they were stored in a temperature-controlled chamber (Yih Der, LE-509RD, Taiwan) at 60 °C for 1, 2, 4, and 6 months. Three cells were used in each test condition. After storage, the cells were moved to room temperature (25 °C) for 12 h rest followed by discharging at C/25 to 2.75 V for residual capacity determination and another single cycle for capacity determination. After the electrochemical tests, one set of the 6-month storage-aged cells were disassembled at their discharged state in a glove box for post-mortem studies. The electrodes were dried in the vacuum oven at room temperature for 24 h without solvent washing to avoid any changes on the electrode surface. The composition and crystalline structure of the stored positive electrodes was analyzed with the samples scraped or punched from the center of the positive electrodes at 15 cm from the end of jelly rolls using inductive coupled plasma-optical emission spectrometry (ICP-OES, Optima 2100, PerkinElmer, USA) and synchrotron X-ray diffraction at beam line BL12B2 at SPring-8, Japan, with a wavelength (λ) of 0.6886(3) Å over $2\theta = 2$ and 54°, calibrated with the standard reference material (National Institute of Standards and Technology (NIST) LaB_6 660b). Negative electrodes were studied using X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALAB 250) with samples punched from the center of the negative electrode at 15 cm from the end of the jelly rolls. To understand structural changes and determine the Li^+ content in electrodes at their fully charged and discharges states, the two sets of cells stored at 0, 25, and 50% DoD at 60 °C for 6 months were charged with a constant current-constant voltage (CC-CV) mode at C/10 to 4.2 V and then held until the current was lower than C/25. One set of cells was then further discharged to 2.75 V and alongside a fresh cell, studied using ECHIDNA [38], the high-resolution neutron powder diffractometer at the Open Pool Australian Light-water (OPAL) research reactor at the Australian Nuclear Science and Technology Organization (ANSTO). NPD data were collected within over $2\theta = 6.5$ to 163.95° with a step size of 0.125° using a neutron beam with a wavelength of 1.6219(3) Å, determined using the LaB_6 NIST Standard Reference Material 660b. *Operando* NPD studies were performed using WOMBAT [39], the high-intensity neutron powder diffractometer at ANSTO, with a neutron beam of wavelength of 2.4167(1) Å determined using the Al_2O_3 NIST Standard Reference Material 676, using a fresh cell and the discharged 6-month storage-aged cells cycled galvanostatically using a postentiostat/galvanostat (Autolab PG302N) at a current of 215 mA (~C/10) with a constant voltage charging at 4.2 V until the current was smaller than 86 mA (~C/25). Data were continuously obtained at room temperature with a collection time of 3 min per pattern during charging and discharging within $2\theta = 15.0$ and 135.9°. The lattice parameters of the samples at their charged and discharged states were obtained using Rietveld analysis of the synchrotron X-ray and the high-resolution neutron diffraction data, and sequential refinement using the high-intensity NPD data with the GSAS II program [40].

3. Results and discussion

The discharge capacities determined at C/25 after storage under various conditions are shown in Fig. 1. The capacity loss is 9.7, 17.2, 7.3, 3.9, and 0.9% for cells stored at 0, 25, 50, 75, and 100% DoD, respectively, under 60 °C for 6 months. Cells stored at 50% DoD at 25 °C, exhibiting 1.0% capacity loss after storage for 6 months, are also shown for comparison. For cells stored at 60 °C, the capacity loss increases exponentially with storage duration as per previous reports [41,42], instead of linearly as per our previous study on the storage capacity fade of cells with identical chemistry [37], except the cells stored at 100% DoD. It can be attributed to the storage DoD may vary with storage duration in this study due to storage aging, whereas the cells in our previous study were reset their storage DoDs to their pre-set values intermittently. It can also be found that the capacity loss decreases with increasing storage DoD for cells stored for the same duration, with the exception of those stored at 25% DoD. Cells stored at 25% DoD have the highest capacity fade and fade rate amongst all cells stored at the same duration at 60 °C up to six months. These results are

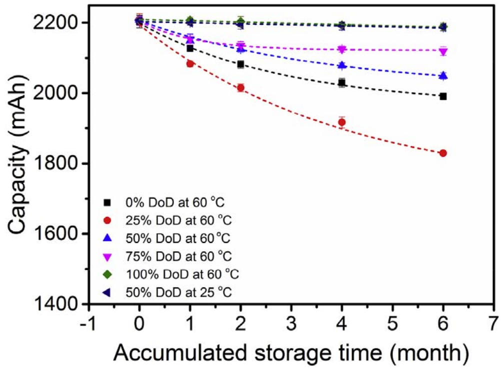

Fig. 1. Discharge capacity under C/25 at 25 °C after storage at various DoD at 60 °C for various durations compared with discharge capacity of cells stored at 50% DoD at 25 °C.