Journal of Power Sources xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Power Sources

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

Effect of overcharge on $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$/graphite lithium ion cells with poly(vinylidene fluoride) binder. III — Chemical changes in the cathode

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HIGHLIGHTS

- 1.5 Ah NMC532/graphite pouch cells were systematically overcharged and their cathodes characterized in the discharge state.
- The bulk crystal structure of the NMC532 cathodes was retained at all SOC.
- Li loss was observed above 140% SOC.
- Formation of a thin C and O rich CEI layer through cathode-electrolyte reactions was observed.

ARTICLE INFO

Keywords:
Lithium ion batteries
Overcharge
XPS
SEM
XRD
NMR

ABSTRACT

1.5 Ah pouch cells based on $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ cathodes and graphite anodes, both containing poly (vinylidene fluoride) (PVDF) binders, were systematically overcharged to 100, 120, 140, 160, 180, and 250% state of charge (SOC), at which point they vented. The cells were subsequently discharged to 0% SOC and disassembled under an inert atmosphere for characterization. A combination of X-ray photoelectron spectroscopy (XPS), scanning-electron microscopy (SEM), energy-dispersive spectroscopy (EDS), ^{6}Li SSNMR, and X-ray diffraction (XRD) analysis of the NMC532 cathodes indicates the formation of a thin C- and O-rich cathode electrolyte interphase layer, progressive Li loss above 140% SOC, and retention of the bulk crystal structure at all states of charge.

1. Introduction

Interest in electrochemical energy storage, and in particular, in lithium-ion related technologies, has seen an enormous growth over the last couple of decades due to the increasing popularity of portable consumer electronics, power tools, and lately, electric and hybrid vehicles and grid storage [1]. A great deal of attention is being paid to increasing the energy density of different technologies, in particular to overcoming the “range anxiety” of electric vehicles and to meet the ever-increasing demands of portable electronics. However, service lifetime and device cost are also important parameters. And device safety is a non-negotiable condition for the widespread implementation of any technology, as exemplified by the newsworthiness of any lithium-ion battery incident.

One strategy that can be used to increase the performance of an existing technology is to broaden the operation voltage window of the electrochemical couple to access more of its Li inventory. However, this approach has been shown to adversely affect the lifetime of the device. A corresponding strategy that can be used to increase the lifetime of a device, albeit at an increased cost, is to over engineer it to meet the end-of-life specifications at the expense of a built-in buffer. Therefore, understanding the effect of the state of charge (SOC) on the aging

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https://doi.org/10.1016/j.jpowsour.2017.12.061
Received 14 September 2017; Received in revised form 8 November 2017; Accepted 20 December 2017
0378-7753/

Please cite this article as: Bareño, J., Journal of Power Sources (2018), https://doi.org/10.1016/j.jpowsour.2017.12.061

behavior has the potential to not only extend the service life of different electrochemical energy storage technologies, but also to lower costs through reduced overhead.

Additionally, as individual cells are cycled at higher average voltages, it becomes increasingly easy to push them into overcharge. Overcharge occurs when the SOC of a lithium-ion cell is taken beyond the design limit (defined as 100% SOC). As a condition that has the potential to both adversely affect a device's lifetime and to trigger the catastrophic failure of a device, it has been broadly studied, especially from an electrochemical and thermal point of view [2,3].

Finally, just as overcharge accelerates cell aging through capacity loss and impedance rise, aging also increases the probability of overcharge. As a Ni-Mn-Co oxide (NMC) v. graphite cell ages, and as a consequence of Li inventory depletion, the operating voltage of the cathode (v. Li/Li^+) steadily increases [4], making it easier to overdelithiate the cathode at high SOC. Correspondingly, the lower cutoff potential becomes increasingly dominated by the anode voltage rise (v. Li/Li^+) upon delithiation, making it easier to push the anode into overdischarge conditions at low SOC. While mild overdischarge conditions have been shown to be benign for several chemistries [5–7], the destabilization of the anode solid electrolyte interphase (SEI) at high anode voltage (v. Li/Li^+) can also result in cell gassing and rupture events.

During the charge cycle of a cell, Li is extracted from the cathode and intercalated at the anode. The voltage of the cathode (v. Li/Li^+) increases, making it more oxidant, and the voltage of the anode decreases, making it more reducing. Side reactions at both electrodes consume Li, reducing the capacity of the system and increasing impedance. If too much Li is extracted from a layered NMC oxide cathode, its crystal structure is destabilized resulting in changes of crystal structure (starting at particle surfaces and propagating through the bulk), oxygen loss from the oxide structure, and an exothermic reaction with the electrolyte [8,9]. Conversely, if too much Li is transferred to a carbon-based anode, it can become irreversibly trapped in the carbon crystal structure [10]. Eventually, it will deposit on, rather than intercalate into the carbon, sometimes growing dendrites and enhancing parasitic reactions with the electrolyte [6,11]. Depending on the nature of the carbon, this excess Li can sometimes be stripped and transferred back to the cathode upon cell discharge [12]. Whether the anode is overlithiated or the cathode overdelithiated during charge depends on the cell design (N/P ratio and rated capacity for 100% SOC) and cycling rate [13,14].

Therefore, capacity fade, due to Li-consuming reactions and loss of active material, and impedance rise, due to changes in cathode crystal structure and SEI growth on the anode, are the main consequences at low levels of overcharge [15]. At higher states of delithiation, the cathode reacts with the electrolyte [16,17] and, at higher temperatures, becomes thermally unstable [18,19]. For both processes, the onset temperature is lowered at a higher cathode SOC. While cathode decomposition will generate enough gasses for the cell to vent [20], thermal runaway is precipitated by SEI decomposition and reformation at the anode, which is initiated when the anode reaches a high enough temperature due to the heat generated by the cathode reactions [21–24].

A significant amount of work has been carried out, focused on mechanistic and materials-level understanding of aging mechanisms in lithium-ion cells. Additionally, there are several studies focusing on cell-level electrical and thermal responses to different abuse conditions, like overheating, overcharging, nail penetration, etc. However, a thorough understanding of the materials-level mechanisms operating during overcharge events is still lacking. Therefore, we have embarked on a collaborative effort between Argonne National Laboratory (Argonne), Sandia National Laboratories (SNL), and Oak Ridge National Laboratory (ORNL) to fill this gap and develop a fundamental understanding of the physical and chemical changes occurring during stepwise overcharge of NMC532/graphite cells.

First, a set of 1.5 Ah pouch cells based on NMC532/graphite chemistry and N-methylpyrrolidinone (NMP)-soluble binders were made at the DOE Battery Manufacturing R&D Facility (BMF) at ORNL. These cells were then delivered to the Advanced Cell Testing Facility at SNL and charged to 100, 120, 140, 160, 180, and 250% SOC; with 250% SOC resulting in cell venting [25]. Then the cells were discharged to 0% SOC and shipped to Argonne for teardown and post-test characterization. This paper, the third paper in a series, focuses on X-ray diffraction (XRD), solid-state nuclear magnetic resonance (SSNMR), and X-ray photoelectron spectroscopy (XPS) characterization of the abused cathodes. Microstructural characterization of the anodes in the same cells can be found in Ref. [25], while chemical characterization of the anode surfaces is presented in Ref. [26].

2. Experimental

The electrodes studied in this work are harvested from the same 1.5 Ah NMC532/graphite pouch cells described in Refs. [25] and [26]. These cells were fabricated at the DOE Battery Manufacturing R&D Facility at ORNL, subjected to overcharge abuse tests at the Advanced Cell Testing Facility at SNL, and characterized at the Post-Test Characterization Facility at Argonne.

The cell cathodes are double-sided laminates consisting of 90 wt% of $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$ (NMC532), 5 wt% Denka carbon black (powder grade) and 5 wt% NMP-soluble binder (polyvinylidene fluoride PVDF, Solvay Solef® 5130). The loading density of the cathode is 12.5 mg cm^{-2}. The cathode material was spread on 15 µm-thick aluminum foil (MTI Corporation) and calendared to 50 µm thickness on each side, corresponding to 40% porosity. Similarly, the anodes are double-sided laminates containing 92 wt% A12 graphite (ConocoPhillips), 2 wt% carbon black (C-NERGY Super C65, Imerys Graphite & Carbon), and 6 wt% NMP-soluble binder (PVDF, Kureha 9300). The loading density of the anodes is 6.5 mg cm^{-2}. The anode material was spread on 9 µm-thick copper foil (MTI Corporation) and calendared to 48 µm thickness on each side, corresponding to 37% porosity. The separators are Celgard 2325. And the electrolyte is a 1.2 M solution of $LiPF_6$ in ethylene carbonate:diethylcarbonate (3:7 by wt). The negative-to-positive capacity ratio of the cells is N/P = 1.1.

After formation by charging/discharging at the C/20 rate between 2.5 and 4.2 V for 4 cycles, the cells were shipped to the Advanced Cell Testing Facility at SNL. A Bitrode battery tester was used to carry out the overcharging as well as to discharge them after the overcharge test. A constant current charge rate of 1C (1.5A) was applied to the cells to reach the desired state of overcharge. Cells were set to 100% (no overcharge), 120%, 140%, 160%, 180%, and 250% SOC (failure, compliance voltage of 20 V met). The overcharge was followed by a 30-min rest and a discharge at the 1-C rate to 2.5 V. If the cell exceeded a voltage of 2.8V after a 30-min rest, then a subsequent discharge was performed. Depending on the level of overcharge, multiple discharges were performed in an attempt to remove capacity and reduce voltage in order to satisfy shipping requirements.

The cells were then shipped, in the discharged state, to the Post-Test Characterization Facility at Argonne for tear-down and examination. Here, the cells were disassembled and the electrodes were sampled under inert atmosphere conditions and (unless otherwise specified) lightly washed twice by gentle swirling, for one minute each time, in excess dimethyl carbonate to remove the electrolyte residue and salt deposits from the surface.

XRD. Unwashed samples of cathode laminates were encased in Kapton® tape in an inert atmosphere glovebox and transferred to a separate laboratory for XRD examination. A Rigaku Miniplex diffractometer was used to collect XRD θ-2θ patterns using Cu Kα radiation (λ = 1.5418 Å).

SEM. Rinsed pieces of the positive electrodes were placed in an airtight holder, which was based on the design published by ORNL [27]. The spring-loaded lid was secured with two screws. The sealed