Balancing formation time and electrochemical performance of high energy lithium-ion batteries☆

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HIGHLIGHTS

- Formation protocols are optimized to reduce time and improve cycling performance.
- The potential for Li plating during formation is addressed by post-mortem analysis.
- The slow formation leads to greater impedance rise and lower capacity retention.
- The impact of formation on SEI chemistry and thickness is characterized with XPS.

ARTICLE INFO

ABSTRACT

Most lithium-ion batteries still rely on intercalation-type graphite materials for anodes, and the formation process for them typically takes several days or even more to provide a stable solid electrolyte interphase (SEI). The slow formation step results in lower LIB production rates, requires a large number of battery cyclers, and constitutes the second highest cost during battery manufacturing. In an effort to decrease the high manufacturing cost associated with long formation times, we studied five different formation protocols in nickel-rich $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811)/graphite cells where the total formation time varied from 10 to 86 h. Electrochemical characterization and post mortem analysis show that very long formation time do not necessarily improve long-term performance while very short formation protocols result in lithium plating and poorer electrochemical performance. We find the optimum formation cycling protocol is intermediate in length to minimize impedance growth, improve capacity retention, and avoid lithium plating.

1. Introduction

The electrification of the modern transportation sector drives the growing demand for lithium-ion batteries (LIBs) [1]. To make battery packs in electric vehicles (EVs) competitive with the internal combustion engine, the driving range should be extended to 300–400 miles at an affordable cost [2]. Several strategies must be pursued in parallel to increase battery energy density while lowering cost. These include advanced cell design and engineering [3–5], high-capacity active materials [6,7], thick electrode architectures with high loading of active materials [8], and reductions in manufacturing cost [9,10].

Besides raw materials, cell formation is the most expensive step in battery manufacturing ($\approx 6\%$ of the total pack cost) [9,11]. During the first charge of a full cell, electrolyte decomposition occurs on the fresh graphite anode, forming a solid electrolyte interface (SEI). This passivation layer is electrically resistive but ionically conductive [12,13].

Table 1
Formation protocols used in this study.

Formation Protocol	Wetting Conditions	Cycling Conditions	Total Formation Time
F_86h	Tap Charge to 1.5V after vacuum seal, then rest for 6 h at 30 °C.	C/10 CCCV Charge to 4.2 V till Current < C/20 C/10 Discharge to 3.0 V, 4 Cycles Cycling at 30 °C	86 h
F_30h	Tap Charge to 1.5V after vacuum seal, then rest for 6 h at 30 °C.	C/2 CCCV Charge to 4.2 V till Current < C/20 C/2 Discharge to 3.0 V, 1 Cycle C/2 CCCV Charge to 4.2 V till Current < C/20 C/2 Discharge to 3.0 V, 1 Cycle Cycling at 30 °C	30 h
F_26h	Tap Charge to 1.5V after vacuum seal, then rest for 6 h at 30 °C.	C/10 CCCV Charge to 4.2 V till Current < C/20 C/10 Discharge to 3.0 V, 1 Cycle Cycling at 30 °C	26 h
F_10h	Tap Charge to 1.5V after vacuum seal, then rest for 6 h at 30 °C.	C/2 CCCV Charge to 4.2 V till Current < C/20, C/2 Discharge to 3.0 V, 1 Cycle. Cycling at 30 °C.	10 h
F_10h@40	Tap Charge to 1.5V after vacuum seal, then rest for 6 h at 40 °C.	C/2 CCCV Charge to 4.2 V till Current < C/20 C/2 Discharge to 3.0 V, 1 Cycle Cycling at 30 °C	10 h

The SEI acts as a protective layer to impede continuous electrolyte decomposition and solvent co-intercalation into graphitic layers during subsequent cycles [14,15]. Imperfect SEI layers could expose fresh graphite to the electrolyte, cause continuous electrolyte decomposition, and lead to graphite exfoliation [16–18]. The cell formation protocol is, therefore, essential to create a stable SEI layer and minimize active lithium loss, electrolyte depletion, and capacity fade over the lifetime of the battery.

The manufacturing cost of cell formation scales with the required length of time. Complete wetting of the active material and separator with electrolyte is typically a slow process (hours to days). After wetting, the first charge/discharge cycle(s) is at low rate to ensure formation of a robust SEI and avoid lithium plating. Typical formation protocols found in the academic literature include 3 to 5 cycles at a C-rate of C/10 to C/20 [11]. In an industrial setting, the formation protocol may be faster but remains a bottleneck for production. The formation step in battery manufacturing requires a tremendous number of battery cyclers, which occupy a sizeable footprint and consume considerable energy. Therefore, it is important to reduce formation time to increase production rate and lower cost [19].

Herein, we evaluated five different formation protocols for large-format pouch cells, where the total formation time varied from 10 to 86 h. Materials and cell design are representative of lithium-ion batteries with relatively high energy density and low cost. For example, the cathode is nickel-rich $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811), which delivers a higher capacity (> 185 mAh/g) over the same operating voltage window compared to other widely used layered cathode materials such as $LiCoO_2$ (140 mAh/g), $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (160 mAh/g), and $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (175 mAh/g) [20–22]. Moreover, replacing expensive Co with relatively cheap Ni lowers the cost of raw materials.

A graphite anode is used to match the NMC 811 cathode since graphite remains the standard active material for negative electrodes despite considerable progress towards higher-capacity materials such as metal oxides [23], graphene [24,25], Si [26] and Li metal [27]. Graphite is inexpensive and non-toxic with desirable electrochemical properties including a low average voltage, minimal hysteresis [3], flat voltage profile, and an adequate specific capacity from 350 up to 372 mAh/g [28].

The electrodes were coated with high areal loadings (> 2 mAh/cm^2), which are typical for high energy cells. While thick electrodes are important to lower the overall cell cost, they present new challenges for decreasing cell formation time. Ion transport is limited through thick electrodes, which leads to lithium plating at high charge rates [29]. Post-mortem analysis assessed the degree of lithium plating in cells that underwent the different formation protocols. Our results show that very long formation times do not necessarily improve long-term performance. Rather, we find the optimum formation cycling protocol is intermediate in length to minimize impedance growth, improve capacity retention, and avoid lithium plating.

2. Experimental

2.1. Electrode preparation

Electrode fabrication and cell build were completed at the U.S. Department of Energy (DOE) Battery Manufacturing R&D facility at Oak Ridge National Laboratory. All chemicals were provided by suppliers and used as received. Electrodes were prepared by coating slurries onto metal foil current collectors (Al for the cathode and Cu for the anode) using a pilot-scale slot-die coater (Frontier Industrial Technology). The cathode slurry contained 90 wt.% $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ powder (Targray), 5 wt.% acetylene carbon black (Denka Black), and 5 wt.% polyvinylidene difluoride (Solvay 5130) in N-methyl-2-pyrrolidone (NMP). The anode slurry contained 92 wt.% Superior SLC 1520T graphite, 2 wt.% carbon black (Timcal Super C65), and 6 wt.% polyvinylidene difluoride (Kureha 9300) in NMP. The areal capacity of the NMC 811 cathode was 2.3 mAh/cm^2 (11.5 mg/cm^2 mass loading), and the areal capacity of the graphite anode was 2.6 mAh/cm^2 (8.3 mg/cm^2 mass loading), yielding a negative to positive capacity ratio (N/P ratio) of around 1.15 in the full cells. All electrodes were calendared to 35% porosity (2.8 g/cm^3 electrode density for the cathode and 1.4 g/cm^3 for the anode) after primary drying and underwent secondary drying under vacuum at 120 °C prior to cell assembly. 1.2 M $LiPF_6$ dissolved in ethylene carbonate: ethylmethyl carbonate (EC:EMC = 3:7 by weight, SoulBrain) was used as the electrolyte and the electrolyte fill factor remained consistent through all cells. Polyolefin-based separators (Celgard) with 25 μm thickness and 39% porosity were used to build the cells. Single layer pouch cells (≈100 mAh) were assembled in a dry room (dew point of less than −50 °C and relative humidity (RH) of 0.1%).

2.2. Electrochemical measurements

All cells were first charged to 1.5 V to avoid corrosion of the Cu current collector and rested for 6 h at 30 °C or 40 °C in an environmental chamber. Next, they went through their respective formation cycles using the protocols summarized in Table 1. Following formation cycling, the cells were degassed and resealed under vacuum. All cells were tested on a Maccor battery cycler under 5 psi stack pressure in an Espec environmental chamber at 30 °C. The cells were cycled between 3.0 and 4.2 V at C/3 charge/discharge rates with a 3-h long voltage hold at the top of each charge to accelerate cell degradation. Tests for F_86h and