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Effect of electrode manufacturing defects on electrochemical performance of lithium-ion batteries: Cognizance of the battery failure sources

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HIGHLIGHTS

- Battery electrode manufacturing defects alter the electrochemical performance.
- Agglomeration, pinholes, non-uniform coatings, metal contamination were evaluated.
- Agglomerations, and non-uniform coating showed substandard performance.
- Microstructural analysis is correlated with poor performance in defective electrodes.

ABSTRACT

During LIB electrode manufacturing, it is difficult to avoid the certain defects that diminish LIB performance and shorten the life span of the batteries. This study provides a systematic investigation correlating the different plausible defects (agglomeration/blisters, pinholes/divots, metal particle contamination, and non-uniform coating) in a $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ positive electrode with its electrochemical performance. In addition, an infrared thermography technique was demonstrated as a nondestructive tool to detect these defects. The findings show that cathode agglomerates aggravated cycle efficiency, and resulted in faster capacity fading at high current density. Electrode pinholes showed substantially lower discharge capacities at higher current densities than baseline NMC 532electrodes. Metal particle contaminants have an extremely negative effect on performance, at higher *C*-rates. The electrodes with more coated and uncoated interfaces (non-uniform coatings) showed poor cycle life compared with electrodes with fewer coated and uncoated interfaces. Further, microstructural investigation provided evidence of presence of carbon-rich region in the agglomerated region and uneven electrode coating thickness in the coated and uncoated interfacial regions that may lead to the inferior electrochemical performance. This study provides the importance of monitoring and early detection of the electrode defects during LIB manufacturing processes to minimize the cell rejection rate after fabrication and testing.

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1. Introduction

Highly efficient, cost-effective energy-storage devices are needed for *plug-in* electric vehicles (PHEVs) to compete with vehicles powered by internal combustion engines [1,2]. Lithium-ion battery (LIB) technology has proven its superiority over all other energy storage technologies in powering consumer electronics and is the leading candidate for implementation in electric vehicles (EVs) [3,4]. Several efforts have been made to enhance the

performance of current LIB systems to meet the needs of EVs as per the US Advanced Battery Consortium LLC, requirements [5,6].

In addition, the cost for a PHEV battery should be reduced to $125/kWh, and the power density should be increased simultaneously from 400 to 2000 W/L by 2022 [6]. Reducing the LIB manufacturing cost remains a challenge in the current LIB industries [7,8], and detailed attention to fundamental and applied science is required. Strategies for overcoming manufacturing costs include implementing low-cost processing and adequate quality control (QC) tools to reduce the scrap rate in larger format batteries [9–12].

Our group at Oak Ridge National Laboratory has demonstrated that adapting aqueous processing instead of N-methylpyrrolidone (NMP) processing for cathode coating (slurry) mixing could reduce the battery cost by 10% per watthour [7,13]. In addition, we recently reported the implementation of QC techniques on a slot-die coating instrument to reduce the scrap rates in larger format cells associated with LIB manufacturing [14]. A laser caliper system was mounted on the slot-die coating line to monitor the wet thickness of the coated electrodes (inhomogeneity in electrode thickness results in variation in electrode balance locally and affects the state of charge during cell test). An infrared (IR) thermography technique was also utilized to detect very small flaws in the dried electrodes that might hamper the performance of LIBs (flaws generated during coating that are not visible to the unaided eye and not with the aid of an optical microscope) [14]. The motivation behind implementing IR thermography was that, if electrode flaws and contaminants could be detected in-line near the particular processing steps that generate them, then the electrode material could be marked as unusable, and the processing protocol could be adjusted to eliminate the defects timely. The defective electrodes can be discarded ahead of the cell manufacturing steps and thus could reduce the cell scrap rate in larger format cells significantly.

In addition to the QC tools [11,12,14] an understanding of correlations between the flaws and the electrode's performance are indispensable to establishing pass/fail criteria for the electrodes. In this report, we present a thorough investigation of the correlations between the electrochemical performance of LIBs and the different defects in the LIB positive electrodes. Further, microstructural analyses of non-defective baseline (baseline) and defective electrodes were carried out to obtain some insights into the mechanisms behind the detrimental influence of the defects. To accomplish this, various types of defects were generated on a Ni–Mn–Co based positive electrode (LiNi$_{0.5}$Mn$_{0.3}$Co$_{0.2}$O$_2$ or NMC 532), and the electrode underwent electrochemical cycling. We chose "NMC 532" as the positive electrode material because it is a promising cathode material for EV application [15]. This work addressed the following important scientific questions:

i) What are the defects that might be created during the electrode manufacturing processes?
ii) What is the effect of those defects on LIB charging and discharging cycles?
iii) How do the defects alter the coulombic efficiency, power (rate capability) and lifetime (cycle life) of LIBs?
iv) Are any microstructural changes responsible for the diminished performance of an LIB manufactured with the defective NMC 532 electrodes?

2. Experimental

2.1. Materials and cell assembly

NMC 532 powders were purchased from Toda America Inc. The electrodes were fabricated at the U.S. Department of Energy (DOE) Battery Manufacturing R&D facility at Oak Ridge National Laboratory. Active NMC 532 powder (90 wt %), Polyvinylidene fluoride (Solvay 5130, 5 wt %), and carbon black (Denka, 5 wt %) were dispersed in N-Methyl-2-pyrrolidone with a planetary mixer (Ross PDM-1/2). Cathode was fabricated by applying the slurry to one side of a 15 μm thick Al foil with a slot-die coater (Frontier Industrial Technology, Inc.). The wet coating thickness was 118.5 μm, and the solid loading was 15 mg/cm^2. The anode was fabricated using A12 natural graphite (ConocoPhillips, A12) with A12 graphite, PVDF (Kureha 9300), and super P Li in 92/6/2 wt%. The anode loading is 8.0 mg/cm^2 and the electrode balance is 1.1(N/P) when coupled with the NMC532 cathode.

Full coin cells were built from uncalendered electrodes. The cells were assembled by using 0.5 inch diameter disks of the NMC 532 cathode and the A12 graphite anode, and 0.55 inch diameter Celgard 2325 separator. Defect-free cathode material was used to fabricate baseline specimens; test specimens were fabricated from defective cathode material (see the "Results" section for a description of the different types of defects that are considered for this study). A 1.2 M solution of LiPF$_6$ in ethylene carbonate (EC)–ethyl methyl carbonate (EMC) (3:7 ratio by weight) (BASF®) was used as the electrolyte. Electrochemical cycling was carried out by using a BioLogic VSP potentiostat controlled with EC-Lab software (V. 10.02).

2.2. Electrochemical testing

The assembled full coin cells were tested for rate performance and cycle-life testing. Rate performance tests were carried out in the voltage window of 2.2–4.2 V at 0.05C, 0.1C, 0.2C, 1C, 2C, 5C (where 1C = 160 mA/g). The cycle life tests were performed at high C- rate (0.5C/–2C, and 0.5C/–5C). For calculating statistics and error, five representative full coin cells from each baseline and defective electrodes were considered for every electrochemical experiment. The error in each data point was computed based on the T-distribution formula with a degree of freedom of 4 and a 95% confidence limit.

2.3. IR thermography

IR thermography was employed on the NMC 532 electrodes to demonstrate its value as a non-destructive evaluation (NDE) technique. We used an FLIR SC-8200 IR camera with a 25 mm lens (no filters or extender rings) and a 6000 J Hensel flash system at ~60% flash power. The camera has a resolution of 1024 by 1024 pixels and a wavelength range of 3–5 μm. Line scans were performed to obtain the emissivity results from both defective and baseline electrodes.

2.4. Microstructural characterization

Cells were disassembled for microstructural analysis after 0.5C/–2C cycle-life testing. Scanning electron microscope (SEM) images were obtained in a Carl Zeiss Merlin SEM operating at 15 kV for imaging and energy-dispersive. The EDS results were obtained with a system from Bruker Nano GmbH using an XFlash 5030 detector. The cross-sectional images were collected by a Hitachi S3400 SEM operated at 10 kV.

3. Results

3.1. Generation of different types of defects

Different types of defects Fig. 1(a, c, e) that were artificially