Lifecycle comparison of selected Li-ion battery chemistries under grid and electric vehicle duty cycle combinations

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HIGHLIGHTS

- Lifecycle of Li-ion batteries were compared under grid and electric vehicle cycles.
- Commercial $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $LiFePO_4$ (LFP) chemistries were compared.
- Multiple cells were tested under the standard testing protocol developed by DOE.
- Degradation mechanisms of different chemistries have been analyzed and proposed.

GRAPHICAL ABSTRACT
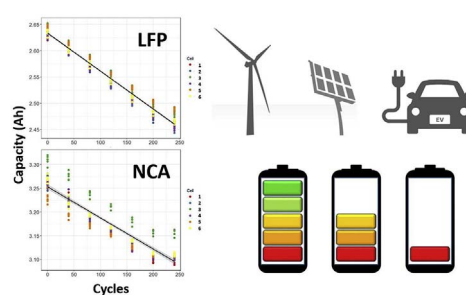
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ABSTRACT

Li-ion batteries are expected to play a vital role in stabilizing the electrical grid as solar and wind generation capacity becomes increasingly integrated into the electric infrastructure. This article describes how two different commercial Li-ion batteries based on $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and $LiFePO_4$ (LFP) chemistries were tested under grid duty cycles recently developed for two specific grid services: (1) frequency regulation (FR) and (2) peak shaving (PS) with and without being subjected to electric vehicle (EV) drive cycles. The lifecycle comparison derived from the capacity, round-trip efficiency (RTE), resistance, charge/discharge energy, and total used energy of the two battery chemistries are discussed. The LFP chemistry shows better stability for the energy-intensive PS service, while the NCA chemistry is more conducive to the FR service under the operating regimes investigated. The results can be used as a guideline for selection, deployment, operation, and cost analyses of Li-ion batteries used for different applications.

1. Introduction

The use of electricity, as the leading form of energy used today, is anticipated to grow with increasing electrification of end-uses in an effort to decarbonize global economies. Currently, about 67% of worldwide electricity generation is from fossil fuels including coal, which coproduces an average of $1\,kg\,kWh^{-1}$ of CO_2 gas, the primary contributor to climate change [1–3]. Resource constraints, environmental concerns, and the need for energy security have prompted great interest in renewable energy, particularly wind and solar power, but the intermittencies of wind and solar generation pose significant challenges to grid operators, making electrical energy storage (EES) a desirable technology option. Several energy storage technologies, including pumped hydro, compressed air, flywheels, capacitors, and batteries, are key enablers of the smart grid of the future. These technologies offer several operational benefits for grid services

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such as backup power, load leveling, frequency regulation, voltage support, spinning reserves, and regulation reserves [1,4]. However, one type of energy storage does not provide all services cost-effectively and, thus, motivating the need for a technology portfolio with various implementation strategies [1,5]. Consequently, addressing the operational value of energy storage is the main challenge faced by the storage developers for wider deployment, especially reliability and lifecycle performance that may not be fully captured within the electricity markets. The different system needs may place varying stresses on the storage technologies. Understanding the wear and tear of each storage system relative to the provision of grid services is crucially important for the selection of the right technology for the right service. Although many storage technology-specific reliability studies exist [6–11], the standardized testing protocols for stationary energy storage are not well established and available because of the complexity of grid systems. Therefore, standardized test methodologies for evaluating EES technologies based on various service duty cycles and control strategies need to be established. Hence, the U.S. Department of Energy's Energy Storage Systems (ESS) program in 2012 initiated the development of a protocol for measuring and expressing the performance of EES systems [12,13]. This effort brought together Pacific Northwest National Laboratory (PNNL), Sandia National Laboratories (SNL), industry stakeholders, and standard setting organizations to develop best practices for measuring, analyzing, and expressing ESS system performance for the following grid services: (1) frequency regulation service, (2) peak shifting, (3) wind smoothing, (4) volt-var control services, and (5) micro-grid operations (in islanded mode) [13]. This paper focuses on frequency regulation and peak-shaving services because of their high value in U.S. electricity markets. Frequency regulation dampens the momentary fluctuations in grid frequency caused by the difference between load and supply. In the United States, standards require balancing authorities to keep the operating frequency from deviating too far from 60 Hz, which is common in many countries. One of the most comprehensive frequency regulation sources publicly available is the PJM (Pennsylvania, New Jersey, Maryland) interconnection, which is named for the most prevalent states of a U.S. regional transmission organization that manages the movement of the wholesale electricity of 13 states and the District of Columbia [13,14]. The derivation of duty cycle from PJM frequency regulation signals was selected for testing because PJM represents a market in which grid storage has an existing incentive to participate.

Among energy storage technologies, Li-ion batteries, backed by their success in electric vehicles and associated mass production, have gained interest for stationary applications because of their high energy/power density and greater than 90% energy efficiency [15,16]. Currently, 77% of electrochemical ESSs operated for grid stabilization in United States use Li-ion batteries - mostly for frequency regulation service, which is a high-value market. To maximize benefits, the use of single Li-ion battery chemistry for both stationary as well as electric vehicle applications is being considered [17,18]. Because of the dual use of Li-ion batteries in electric vehicles (EVs) and in stationary applications, this study focuses on the performance and degradation of two different Li-ion battery chemistries when exposed to (1) selected grid services, (2) typical EV use patterns, and (3) a combination of grid services and EV applications, sometimes referred to as vehicle to grid (V2G). Therefore, high-energy $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA) and high-power $LiFePO_4$ (LFP) based advanced Li-ion battery chemistries were chosen for our reliability studies under three scenarios: (1) frequency regulation, and EV drive cycle coupled with either (2) frequency regulation or (3) peak shaving to understand the degradative effect of grid service that can increase lifecycle cost [17–20]. The NCA-based cell has good power and energy characteristics and has been used in EVs, but it tends to release significant amounts of oxygen from its cathode, resulting in oxidation of the electrolyte and thermal runaway [21]. In contrast, the LFP-based has been widely deployed for stationary energy storage because the LFP electrode provides high power, stability, and

does not generate oxygen during heating; thus, safer than the NCA electrode [15,16,22,23]. The reliability of these two battery chemistries was evaluated by analyzing lifecycle performance factors such as capacity/energy fade, round-trip efficiency (RTE), resistance change, and calendar aging behavior.

2. Experimental procedures

To fully compare the reliability and performance of batteries for grid services, two different commercial Li-ion batteries from leading manufacturers were chosen: cylindrical high-energy NCA cells (18650 form factor [18 mm dia., 65 mm height], 3.2 Ah, 2.5–4.2 V, C/2 charge, 4 C max. discharge) and high-power LFP cells (26650 form factor [26 mm dia., 65 mm height], 2.6 Ah, 2.0–3.6 V, 1 C rate charge, 20 C max. discharge). Both cell chemistries use graphite anode and electrolyte containing $LiPF_6$ salt in carbonate based solvent (EC/DEC for NCA cell but unspecified for LFP cell) but detailed compositions are not available. These battery chemistries were evaluated for frequency regulation (FR) grid service and use of EV batteries for FR and peak-shaving (PS) grid services, referred to as EV-FR and EV-PS, respectively.

The testing was conducted using a multi-channel battery test system (Landt Instruments CT2001B) with commercially available battery holders. The cells were placed in an environmental chamber (Tenney) and all tests were started and stopped at the same time. Due to issues regarding safety, the chamber was not operated, since in the event of cell venting, flammable gases may come in contact with the heated surface of the chamber heater coils. Hence, the temperature was not controlled, but it was monitored and recorded throughout all tests, during which the average temperature was 29.79 ± 0.62 °C (Fig. S1). For safety, tight voltage limits (2% above upper and below lower limits for each battery chemistry) and capacity limits within +0.2 Ah of cell capacity were applied. For each FR service-related test condition, six cells of each chemistry were used, and an equal number for baseline tests without the grid service were used. For each EV-FR and EV-PS test, three cells from each chemistry were used, and an equal number were used for baseline tests, for a total of 48 cells. The test matrix is shown in Table S1. The normalized (± 1 power unit or p.u.) PJM signal was provided for FR with signals of average (red) and aggressive (green) profiles based on the standard deviation of these signals from the mean (Fig. S2) [13,14].

Before designing test procedures, each cell chemistry was subjected to pulse charge/discharge to find the maximum currents leading to voltage polarization that would not exceed the voltage window specifications (Fig. S3) for safety. The cycling profiles and state-of-charge (SOC) levels of three different service scenarios of FR, EV-FR, and EV-PS services and respective baselines (BSs) are shown in Fig. 1(a–d). From voltage profile and pulse currents, the SOC level of 50% was chosen as a starting condition for FR service to avoid voltage excursion beyond the upper voltage limit, especially for NCA, which had a higher internal resistance (Fig. S3). The FR service cycle applied contains 20 average and 4 aggressive cycles over 24 h periods (Fig. 1(b)), and the highest peak power and associated currents were chosen without compromising safety (Table 1S). To quantify the effect of grid services, baseline (BS) tests were introduced to rest the battery (Fig. 1(b)) for the same duration and SOC level as that of the grid service duty cycle to distinguish differences related to calendar aging. For the EV and grid service combined scenarios (Fig. 1 (c, d)), the charge-depleting EV cycles developed by Idaho National Laboratory for plug-in hybrid EVs (PHEVs) were used (Fig. 10 of the reference) [24]. While the drive cycle was developed for a 40 kW, 12 kWh PHEV battery, for this work, the power-to-energy ratio was considered to be 1 to develop the drive cycle, keeping the same ratio of maximum charge to maximum discharge power. For the tests involving EV drive cycles, the starting SOC was set at 85%, such that the SOC at the end of the drive cycle was around 65% (Fig. 1(a)). Because the charge peak power for the EV drive cycle was only 55% of the discharge peak power, resulting in approximately 50%