Journal of Power Sources 403 (2018) 56–65

Contents lists available at ScienceDirect

Journal of Power Sources

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

Cost of automotive lithium-ion batteries operating at high upper cutoff voltages

Shabbir Ahmed*, Stephen E. Trask, Dennis W. Dees, Paul A. Nelson, Wenquan Lu, Alison R. Dunlop, Bryant J. Polzin, Andrew N. Jansen

Electrochemical Energy Storage Department, Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL, 60439, United States

HIGHLIGHTS

- Cathode materials were tested at upper cutoff voltages (UCV) up to 4.7 V vs. Li/Li^+.
- Specific capacities of NMC811, manganese-rich LMRNMC improved the most at high UCV.
- The BatPaC tool used high-UCV properties to estimate pack energy densities and cost.
- The LMRNMC and the NMC811 offer the lowest cost at high UCVs.

ARTICLE INFO

Keywords:
Upper cutoff voltage
High-energy high-voltage
Lithium ion battery cost
Specific energy
Battery cost
Cathode

ABSTRACT

The potential for operating automotive battery packs at high upper cutoff voltages (UCV) has been explored using preliminary data on eight cathode materials. The pack level energy density, specific energy, and battery cost are calculated using the spreadsheet tool BatPaC. The tool used experimental data for some cathode materials such as the lithiated oxides of nickel manganese cobalt (NMC), nickel cobalt aluminum (NCA), layered lithium- and manganese-rich nickel manganese cobalt (LMRNMC). The half-cell data were obtained at UCVs between 4.2 and 4.7 V vs. Li/Li^+. The experimental data showed LMRNMC with the highest lithiation capacity gain, increasing from 176 $mAh{\cdot}g^{-1}$ at 4.2 V to 260 $mAh{\cdot}g^{-1}$ at 4.7 V; this advantage is partly offset by its lower average voltage. Assuming optimized cell materials/design and an area-specific impedance of 12 $\Omega{\cdot}cm^2$ for all the materials, the BatPaC results indicate that the specific energies or energy densities of the battery electric vehicle (BEV) and plug-in hybrid electric vehicle (PHEV) battery packs with the LMRNMC and NMC cathodes can exceed 180 (BEV) and 160 (PHEV) $Wh{\cdot}kg^{-1}$ at UCV > 4.6 V vs. Li/Li^+. The costs of these battery packs are lowest at UCV = 4.7 V (vs. Li/Li^+); estimated at 135–145 and 210–220 $\${\cdot}kWh^{-1}$ for BEV and PHEV packs, respectively.

1. Introduction

The United States Advanced Battery Consortium (USABC) goals for commercial vehicles in 2020 are to use electric vehicle (EV) batteries with useable specific energy of 235 and 350 $Wh{\cdot}kg^{-1}$ at the system and cell levels, respectively (Table 1 [1]). The corresponding price targets are 125 and 100 $\${\cdot}kWh^{-1}$. A number of cathode materials have attracted the attention of automotive manufacturers and suppliers and are in various stages of commercial development or deployment. These include the lithium nickel cobalt aluminum oxides (NCA), the lithium nickel manganese cobalt oxides (NMC), and the lithium manganese-rich NMC (LMRNMC) oxides. The development of the cathode materials has been reviewed elsewhere [2–5].

The cell voltage cycle window affects the capacities and capacity retention of lithium ion cells with NMC cathodes. Klett et al. [6] have shown that raising the lower cutoff voltage (LCV) lowers the initial capacity but increases the capacity retention. On the other hand, the loss in capacity retention that accompanies the higher UCV is not as severe as that observed in lowering the LCV. Gilbert et al. [7] have observed a sharp capacity fade at UCV above 4.3 V (vs. graphite), which correlate well with the Mn and Li content in the graphitic anode. They found that at UCV > 4.3, the capacity fade data fits well with a power dependence of time ($t^{0.76}$). High UCVs around 4.7 V have been reported to lead to a loss in cell performance due to side reactions between the cathode and the electrolyte, and the formation of inter- and intragranular cracks in the particles [8–11].

* Corresponding author.
E-mail address: ahmeds@anl.gov (S. Ahmed).

https://doi.org/10.1016/j.jpowsour.2018.09.037
Received 24 July 2018; Received in revised form 7 September 2018; Accepted 14 September 2018
0378-7753/

Table 1
USABC goals for CY2020 Commercialization [1].

End of Life Characteristics at 30 °C	Units	System Level	Cell Level
Useable Energy @ C/3 Discharge	kWh	45	
Useable Energy Density	$Wh{\cdot}L^{-1}$	500	750
Useable Specific Energy	$Wh{\cdot}kg^{-1}$	235	350
Price at 100 K units per year	$\${\cdot}kWh^{-1}$	125	100

The US Department of Energy's Vehicle Technologies Office has funded the development of a spreadsheet-based techno-economic tool that is available for researchers to explore the effects of material properties and design specifications on the size, weight, and cost of an automotive battery pack [12]. It is populated with default properties for 6 electrode combinations that include NCA, NMC, lithium iron phosphate (LFP), and lithium manganese oxide (LMO) for the positive electrode and graphite and lithium titanate (LTO) for the negative electrode. BatPaC uses material properties such as the specific capacity, density, porosity, cell voltage (full-cell), area specific impedance (ASI), among many others. The user may use an alternate value for any property or material prices. The tool requires selection of the type of vehicle: all electric (BEV), plug-in hybrid (PHEV), high-power hybrid (HEV-HP), micro hybrid (micro-HEV); and specification for the energy storage capacity (kWh) and the power (kW) for the battery pack. More details of the pack design (e.g., number of cells, series-parallel configurations, etc.) and the production process (number of packs produced per year, etc.) can be entered as needed.

The objective of this paper is to compare the potential of 8 cathode active materials when operated at high UCVs, at the pack level based on some properties measured using coin cells. The pack level characteristics include energy density, specific energy, and the costs of automotive (PHEV and BEV) cells and packs, using the BatPaC spreadsheet tool. The properties used for the pack designs include the cathode active material specific capacities and voltages, which were measured with half-cells. The experimental data were collected on 8 cathode active materials with UCVs between 4.2 and 4.7 V vs. Li/Li^+.

BatPaC assumes that these batteries will be built in the future and therefore many of the technological hurdles (cycle life, raw material sourcing, manufacturing challenges, etc.) will have been resolved. Considering the variability of pack designs, we suggest a greater emphasis on the observed trends in the presented results, instead of the absolute values of the reported results.

2. Experimental

All electrodes in this study were fabricated at Argonne's Cell Analysis, Modeling, and Prototyping (CAMP) Facility, with the exception of the NCA. The NCA cathodes were fabricated by Saft using CAMP-supplied NCA powder. The cathodes contain the active material, carbonaceous additives to enhance electronic conduction, and polyvinylidene fluoride (Solvay 5130 PVdF) binder to ensure coating cohesion and adhesion to the 20 μm aluminum current collector. The electrode compositions were not optimized for any specific application or targeted performance.

Half-cells were fabricated using CR2032-type coin cell hardware for each cathode material listed in Table 2. The cells contained the cathode (1.54 cm^2), Celgard 2325 (PP/PE/PP) separator, and Li-metal counter electrode (1.91 cm^2) (lithium metal chip purchased from MTI). The cathode and separator were vacuum dried overnight at 120 °C and 60 °C, respectively. All cells were assembled in a dry room environment or argon-filled glove box and flooded (100 μL) with 1.2 M $LiPF_6$ in EC:EMC [3:7 wt%] (Tomiyama), called the Gen2 electrolyte henceforth. This is a well-studied general purpose electrolyte and provides a baseline for comparing the cathode materials at different voltages. It has demonstrated acceptable low and high-temperature performance; however, it has not been optimized for high voltage cycling. It contained no additives or co-solvents. Some of the experimental rate data that is later presented in this paper may be at least partly due to the degradation of the electrolyte [13] [14]. To limit the electrolyte decomposition at these higher voltages, the half-cells were subjected to a limited number of cycles to get the best possible data without having the electrolyte or the lithium metal anode limiting the performance.

All cycling tests were performed at 30 °C using a MACCOR Series 4000 Test System; the cycling procedures are detailed in Table 3. Each cathode material was used to fabricate 24 half coin cells, where 4 cells were tested at each UCV (namely 4.2, 4.3, 4.4, 4.5, 4.6, 4.7 V vs. Li/Li^+). [The full-cell voltage used in the BatPaC simulations were set at 0.1 V lower than the above.] All cells had a lower cutoff voltage (LCV) of 3.0 V vs. Li/Li^+, except for LMRNMC which had a LCV of 2.5 V vs. Li/Li^+. The LMRNMC half-cells were formed to 4.7 V to "activate" the material. This voltage window study focuses on cell capacities of the cycle 1 delithiation (C/10 charge), cycle 5 lithiation (C/20 discharge), and cycle 8 lithiation (C/10 discharge) information collected from these half-cells. The specific capacity ($mAh{\cdot}g^{-1}$) and the specific energy ($mWh{\cdot}g^{-1}$ or $Wh{\cdot}kg^{-1}$) for the cathode materials are based on the mass of the oxide material. The data reported below are values averaged from the 4 data points for each combination of UCV and cathode material.

Each coin cell was subjected to a total of 20 cycles (~300 h) as shown in Table 3.

In addition to the specific capacity and specific energy, the impedance plays a critical role during the charge/discharge of the cells and is reported as $\Omega{\cdot}cm^2$. Electric transportation applications require the capability to tolerate discharge and charge pulses at high currents for short durations. The hybrid pulse-power capability (HPPC) test is one testing method that provides important impedance characteristics by calculating the area specific impedance (ASI) as shown in Equation (1) [15].

$$ASI\ (\Omega{\cdot}cm^2) = \frac{abs(Voltage_{OCV} - Voltage_{10s}){\cdot}Electrode\ Area\ (cm^2)}{Pulse\ Current\ (Amps)} \quad (1)$$

Table 2
Cathode materials in the electrodes of the tested coin cells (14 mm diameter or 1.54 cm^2). Porosity values were calculated using the electrode composition, thickness of calendered coating, coating loading, and crystal densities of the materials. *Active Material, [a]Timcal C45, [b]Timcal Super P Li, [d]Timcal SFG-6, [e]Solvay 5130 PVDF.

Active Material	Material Supplier	Electrode Composition Wt.%	Coating Loading $mg{\cdot}cm^{-2}$	Calendered Coating Thickness μm	Porosity %	Coating Density $g{\cdot}cm^{-3}$
NCA	Toda	86*/4[d]/2[b]/8[e]	11.6	45	30.8	2.73
NMC111	Toda	90*/5[a]/5[e]	11.2	40	32.0	2.80
NMC433	Toda	90*/5[a]/5[e]	12.6	45	31.5	2.79
NMC442	Toda	90*/5[a]/5[e]	11.8	43	33.0	2.73
NMC532	Toda	90*/5[a]/5[e]	11.3	42	33.5	2.70
NMC622	ECOPRO	90*/5[a]/5[e]	10.0	38	35.5	2.64
NMC811	Targray	90*/5[a]/5[e]	9.7	40	40.6	2.43
LMRNMC	Toda	92*/4[a]/4[e]	6.4	26	36.1	2.46