Assessment of spent EV batteries for second-life application

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Abstract—Electric vehicle (EV) batteries typically retained around 70- 80% of their initial capacity at the end of their automotive life. The first batches EV batteries are hitting their retirement age and around 3 million used battery packs will be coming out from EV annually which represent around 108 GWh. Automotive companies and OEM have announced numerous projects and business models for second-life batteries, such as the stationary energy storage system (ESS) to extract additional services and revenue in post automotive life with cross-cutting benefits. The potential of second-life batteries lies in their state of health (SoH) or remaining useful life. To enable this market for second use batteries, it is necessary to demonstrate the capability of such batteries in real-world scenarios and validating the longevity of these batteries in this application is critical. This paper characterises three selected Nissan Leaf Cells/Modules disassemble from 24 KW Nissan Leaf pack that reach an end of life (EoL). The modules are tested individually to provide insight into the variation in degradation across a single battery pack and also establish the available energy at EoL via Hybrid pulse power characterization (HPPC). The result shows three data points of capacity and Ohmic resistance. Furthermore, the batteries achieved the power density of 700 W/Kg/300 W/Kg during discharge/regen in the working regions from 100% to 30% and /80% to 20% DOD respectively. Besides, the HPPC micro cycle discriminates between the strong and weak battery in 120 s.

Keywords—EoL Lithium-ion batteries, Assessment, Sorting, capacity, Electrochemical impedance spectroscopy, Hybrid pulse power characterization, reuse, second-life

I. INTRODUCTION

Battery reuse strategies in which a battery pack first serves in an automotive application, then once deemed appropriate is redeployed into a secondary market could help overcome lithium-ion battery cost barriers to the deployment of both electric vehicles (EVs) and grid-connected energy storage. Allocating retired automotive batteries in applications that are less power demanding such as energy storage systems (ESS) to mitigate the intermittency of renewables, utility peak load reduction, smart grid, grid stabilisation, low energy buildings and utility reliability. The prospect of ESS via second use batteries would improve materials efficiency, bring tremendous value to the wide range of stakeholders across the automotive and energy sectors, as well as society and environment. [1]-[4].

Although, the economic margins that make reuse batteries viable are often small, and thus several factors could affect this conclusion. The major impediment being the complexities of repurposing heterogeneous lithium-ion batteries, collection and technical labour are the primary cost element. Furthermore, non-availability of on-board diagnostics data and accurate assessments of automotive and second use battery degradation stand out in particular. Use of vehicle

diagnostics data to confirm the state of health (SoH) and absence of faulty cells in modules/battery packs before their deployment in second-life is, therefore, key to repurposing. Since the volume of end of life (EoL) batteries is likely to increase as penetration of EV/HEV increases.

Whilst, the most promising application for spent EV batteries is the ESS and perhaps power system. To enable the second-use battery market, it is necessary to demonstrate the capability of the retired batteries to adequately provide these services. In particular quantifying system response in real-world scenarios and validating the longevity of these batteries in post automotive application is critical. To this end, we acquired an EoL 24 KW Nissan Leaf battery pack that has been disassembled to the module level. Module from this pack are being tested individually to provide insight into the variation in degradation or SoH across a single battery pack and to ensure that the retired batteries meet the EoL characteristics of ESS performance targets for EVs [5] - [7].

It is necessary to present a SoH or RUL data for a value chain analysis from the lifecycle perspective to help stakeholders identify potential value opportunities. This would be achieved via a rapid testing protocol for gateway testing and sorting battery at the end of their automotive life prior to second-use. This will enable accurate identification of a battery's value and its viability for second use service. A single weak cell in a module would affect the output power and comprises the performance of the whole module. Furthermore, the failure of a cell in a battery-powered system can lead to performance deterioration, costly replacement and serious hazards [8]. Therefore, the gateway testing and sorting of second-life batteries must be rapid and accurate.

Literature classifies testing of lithium-ion batteries into three phases i.e., characterisation, life and reference performance test (RPT). Characterisation test establishes the baseline performance. Life testing establishes behaviour over time of both cycle and calendar life at various temperature, state of charge (SoC) as well as other stress conditions; whilst RPT track the evolution of performance over cell life and are performed periodically during the battery life from the beginning of life (BoL) and EoL [5]-[7]. Typical parameters denoting the degradation of lithium-ion cells are capacity depletion and resistance growth. Essentially, the capacity measures the amount of electric charge stored in a cell and defines its maximum capacity in the application under a given load. Whereas, the resistance characterises the cell dynamics.

Batteries can be sorted optically or electrically. Optical sorting involves sorting the batteries based on their shape or appearance. Electrical measurement requires sensors to establish contact with the battery and measure certain parameters, which is difficult to automate in a real-time process. Besides, most of the existing electrical methods are

not rapid in separating good cells from bad ones. For example, capacity measurement involves cycling the battery and takes several hours to complete. These techniques are unsuitable in a recycling facility where tens of thousands of batteries need to be processed every day.

Many approaches are being used to determine the SoH, of a battery e.g. Pseudo open-circuit voltage (pOCV), Incremental capacity-Differential voltage (IC-DV), electrochemical impedance spectroscopy (EIS) and differential thermal voltammetry (DTV), each approach has its strategy and advantages.

Outside these different choices, hybrid pulse power characterisation is another useful tool for determining the pulse power capability of battery in both discharge and regen regimes. EoL characteristics of energy storage system performance goals for EVs [5]- [7], targets a 700 W/Kg peak specific discharge power lasting 30 s and a 300 W/Kg peak specific regen power lasting 10 s. A minimum of 300 Wh/Kg of energy must be available within the SoC operating range capable of meeting the power goals. The goals dictate the use of HPPC to quantify the remaining available energy with obvious drawbacks of requiring tens many hours of testing.

This paper demonstrates the assessment and sorting of the EoL EV batteries with unknown history to meet the requirements of repurposing in ESS. This demonstration is accomplished via the HPPC, capacity and EIS techniques. Section II provides an overview of the characterisation methods employed and sections III discussed the results obtained. Section IV outlines the conclusions drawn from the study.

II. CHARACTERISATION

Three commercial modules A, B, C, disassembled from Nissan Leaf battery pack that reach EoL in an automotive application were selected. Each module comprises four identical pouch cells. The cells are electrically configured as 2X2 arrangement (2 in series and 2 in parallel). The cell chemistry is lithium-manganese-oxide with nickel oxide widely known as (LMO). The cells are characterized as follows:

A. Capacity Fade

This test is a time domain method that measure the battery capacity in ampere-hours. For the battery subjected to automotive use, the change in capacity from BoL to some later point in time is regarded as capacity fade and expressed as a percentage of the original capacity as in (1)

$$Q_{fade}(\%) = 100 * [1 - Q_{t1}/Q_{t0}] \quad (1)$$

Fig. 1. Capacity fade.

Fig. 2. EIS measurement.

Where Q_{t1} , Q_{t0} are the initial and the current capacities of the battery respectively. Fig. 1 shows the measured capacity of the three cells A, B, C. The test is executed base on manufacturers cycling protocol i.e. C/1 constant current - constant voltage (CC-CV) to full charge state V_{max} (4.2 V). Discharge begins following a default rest from a fully charge state and is terminated on discharge voltage limit V_{min} (4.2 V). 57 Ah, 54.5 Ah and 49.45 Ah are the measured capacities corresponding to cells A, B and C. The capacity fade of the batteries stands at 86.36%, 82.57% and 74.92%.

B. Impedance test

EIS is considered as a powerful method for investigating the operational, ageing mechanism and thermal degradation of a cell [8], [9]. EIS technique is a frequency response method which typically measures cell impedance along a range of frequencies (i.e. KHz to mHz). The test can be performed in either potentiostatic or galvanostatic mode by simply perturbing the cell voltage and measuring the cell current or vice versa. The cell impedance is computed as in (2)

$$Z = \frac{\tilde{V}}{\tilde{I}} = \frac{\Delta V \cdot e^{j\omega t}}{\Delta I \cdot e^{j(\omega t + \Phi)}} \quad (2)$$

A Shift in Nyquist spectra from left to the right indicate an aged or degraded cell. In other words EIS is characterisation tool used to infer ageing mechanism of a cell. Fig 2. Illustrate the Nyquist spectra of the three cells. As can be seen, the Ohmic resistance of the cells are 0.95 Ω , 0.98 Ω and 0.86 Ω .

C. HPPC test

Fundamentally, HPPC is a measure of battery's dynamic power capability over its useable voltage ranges incorporating a discharge and regeneration current pulses. The HPPC procedure determines this ability by applying current waveforms as shown in Fig. 1 to the battery under test, the response to this stimulus is used to determine power capability. The test comprises of 30s discharge, 40s rest and immediately followed by 10s regen; together these make up one complete HPPC micro cycle. Between each pair of the micro cycle, the battery is discharged to the next 10% depth of discharge (DoD) level based on the operating capacity. It is worth noting that the current values are relative and the micro cycle is not charged balance.

A HPPC is executed on each module at 0.1 SoC interval (constant current C/3 discharge segments) starting from 1.0 to 0.1, each interval is followed by one hour rest to allow the battery to attain electrochemical and thermal equilibrium before discharging to the next SoC. The HPPC micro cycle and complete current profile is shown in Fig. 3a. To achieve conservative estimate of pulse resistances a low current HPPC

Fig. 3. HPPC cycling and analysis of second-life batteries

[] is adopted during the test. Fig. 3b illustrate the voltage vs time of the three cells. As can be seen, the 10s regen pulse appeared as a spike in the waveform whilst the 30s discharge pulse is clear. A close up of the HPPC microcycle is also shown. Following each HPPC microcycle is the 10 % capacity removal followed by the one-hour default rest prior to the application of the subsequent HPPC micro cycle. Fig. 3c illustrate the OCV of the cells as a function of the individual cell DoD. OCV between each 10% increment can be estimated by straight-line interpolation. The shift in OCV between the cells is apparent and clearer towards the nominal voltage of the batteries. The pulse resistance of each cell is calculated during discharge/regen pulses corresponding to the DoD by dividing the change in voltage during the 30s discharge and 10s regen periods by the applied current using (3).

Fig. 3d shows the plot of the discharge and regen resistance calculated using (3) as a function of the DOD. As can be seen, the 10s regen resistances are slightly shifted to the right compared to the 30s discharge resistances due to the inclusion of the 30s discharge regime during the HPPC micro cycle when determining the percentage of the rated capacity removed. Furthermore, there are minor differences between the discharge and regen resistances. It is apparent as the cell

$$R_{discharge/regen} = \frac{\Delta V}{I_{discharge/regen}} \quad (3)$$

discharges the resistance increases. From these resistance values and the OCVs, the maximum pulse power capability of each cell can be determined using equation (4) and (5).

$$P_{discharge} = \frac{V_{min}(OCV_{discharge} - V_{min})}{R_{discharge}} \quad (4)$$

$$P_{regen} = \frac{V_{max}(V_{max} - OCV_{regen})}{R_{regen}} \quad (5)$$

Where $OCV_{discharge}$ and OCV_{regen} are the OCVs of the battery immediately prior to applying either the discharge or regen pulse. V_{min} , V_{max} are the minimum and maximum terminal voltages limits within which the battery is cycled.

Fig. 3e shows the discharge and regen pulse power capability of the three cells as a function of DoD of the cells, and Fig. 3f shows the discharge and regen pulse power capability of the cells as a function of the cumulative energy removed from the cells. This is achieved with the assumption that the capacity removed from the constant power discharge and subsequent HPPC test are equivalent.

Having obtained the pulse power capabilities, the total cell useable energy as a function of power level the device is being operated can be determined. The useable energy is the amount of energy that a cell can accept or deliver when it is being cycled at a certain power level. The battery size factor (BSF) of a target application can then be determined using the useable energy as a function of power.

III. DISCUSSION

Most battery performance analysis tools use Coulomb counting to estimate the SoH of a battery. The energy flowing in-and-out of a battery is measured and stored in an accessible register. The content of the register is then compared with subsequent measurements to predict the SoH of the battery. The major shortcoming is losing accuracy when the battery is randomly cycled and integral errors accumulating over time.

The leading SoH indicator of a battery is its capacity. Estimating the capacity of a battery on the fly is complex. The best approach is to read the capacity through the charge/discharge cycle. The result obtained is accurate and noninvasive. The downside is the battery must often be removed from service to determine the capacity and the cycling takes 2 - 3 h to complete for the commercial Nissan leaf module tested in this case.

EIS test measures Ohmic internal battery resistance to verify the loading characteristics. The resistance reading does not correlate with capacity. EIS performs rapid testing on a battery by scanning with multiple frequencies to generate Nyquist spectra. The horizontal axis reveals the real battery Ohmic impedance and the vertical represent the imaginary impedance. Movement of impedance spectra from left to right denotes ageing. Fig. 4 illustrate the closed up of the three batteries impedance spectra showing the two domains of Nyquist plot entitled migration and charge transfer corresponding to high and mid-range frequency scales respectively. The mid-frequency range called charge transfer displays valuable characteristic explaining the kinetics of the battery that tells the SoH reference. As can be seen cell B denote higher Ohmic resistance than all the remaining cells. A rapid test shouldn't take a long time i.e. from few seconds to no more than 5 minutes, but scanning all the three frequency regions (i.e 3 KHZ - 10 mHz) in this case takes about 15 m. Test duration can be shortened by scanning only the high and mid-frequency regions.

HPPC measures the mobility of ion-flow between cathode and anode at different DoD by applying discharge/regen pulses and evaluating the voltage response. As can be seen from Fig. 3b battery A appears firm and has quick recovery than battery B and C. Battery C shows softness and sluggish recovery in comparison to battery A and B. Furthermore, all the three batteries meets the requirement of EoL ESS performance target by achieving the power density of 700 W/Kg during discharge in the working regions from 100% to 30% DOD. Similarly, the cells meet the regen target by achieving 300 W/Kg from 80% to 20% DoD.

The technique involves measuring the DC resistance of the battery due to current perturbation and consequent drop in voltage. The voltage drop is largely due to contribution of pure Ohmic and bulk electrolyte resistance of the battery, double layer capacitance, charge transfer resistance and polarisation resistance.

Fig. 4. Close up of migration and charge transfer regions.

There is a clear distinction between the discharge and regen pulse power capability despite the similarity in values of discharge and regen pulse resistances. This could be as a result of overpotential due to driving high current during cycling. Table I summarises the selected SoH determination techniques and duration required to perform each test.

TABLE I. SUMMARY OF SELECTED SOH METHODS AND DURATION

S/N	SoH Methods	Duration (m)
1	Capacity	120/C ₁
2	AC Impedance EIS	15
3	HPPC microcycle	2

IV. CONCLUSION

In this research, three different battery SoH measurement techniques were employed to measure the SoH of three LMO 66 Ah module for rapid EoL assessment/sorting. From comparison of the results, it has been shown that each technique provide different insight into a particular aspect of degradation across module/cell. The leading SoH indicator is the capacity measurement which account for capacity fade as the battery age. On one hand the EIS display all the individual resistance contribution and phase transformation in an electrochemical cell. On the other hand HPPC provides information of resistance degradation during discharge/regen pulses. The pulse resistance allows pulse power capability during HPPC microcycle and available energy of the battery to be determined as a performance indicator of ESS at EoL. In addition, Both EIS and HPPC can be parametrised into an equivalent circuit model (ECM) and have potential to be used for rapid testing using algorithms with parameters serving as lookup tables.

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REFERENCES

- [1] G. Eason, B. Noble, and I. N. Sneddon, "Battery second life: Hype, hope or reality? A critical review of the state of the art," J. Ren.& Sustain. Energy Rev., vol. 93, pp. 701-718, Oct 2018.
- [2] Pinsky N, Gaillac L, Mendoza A, Argueta J, Knipe T. Performance of advanced electric vehicle batteries in stationary applications. In: Proceedings of the 24th annual international telecommunications energy conference; 2002. p. 366-72
- [3] Pinsky N. Electric Vehicle Battery 2nd Use Study. Tech. rep., Argonne National Laboratory, Electrochemical Technology Program; 1998.
- [4] Cready E, Lippert J, Pihl J, Weinstock I, Symons P, Jungst RG. Technical and economic Feasibility of applying used EV batteries in stationary applications. Tech. rep., andia National Laboratory; 2003.
- [5] J. P. Christopsen, "Battery Test Manual for Electric Vehicles," INL Rev. 3, vol. 93, pp. 1-50, June 2015
- [6] Battery Test Manual for Plug-In Hybrid Electric Vehicles, INL pp. 1-54, March 2008.
- [7] FreedomCAR 42V Battery Test Manual, INL pp. 1-54, April 2003.
- [8] S. Lambert, M. Armstrong P.S. Attidekou, P.A. Christensen., J. D. Widmer, C. Wang, and K. Scott, "Rapid Nondestructive-Testing Technique for In-Line Quality Control of Li-Ion Batteries," IEEE Trans. Ind. Electron, vol. 64, pp. 4017-4026, May 2017.
- [9] P.S. Attidekou, S. Lambert, M. Armstrong, J. Widmer, K. Scott, and P.A. Christensen, "A study of 40 Ah lithium ion batteries at zero percent state of charge as a function of temperature," J. Power Source, vol. 269, pp. 694-703, Dec 2014.