Impedance spectroscopy characterization of lithium batteries with different ages in second life application

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***Abstract*— The aging behavior of lithium cell has a profound impact on its performance in terms of energy, power efficiency and capacity fade, especially when it is considered in End of Life (EOL) in automotive field. Lithium battery is considered in EOL if at 85-80% of nominal capacity. Today, the reusing of Electric and Hybrid Vehicles EOL batteries on less-demanding grid connected energy storage applications, giving them a second use/life, is an interesting solution to reduce high potential cost of lithium batteries. Currently, there is a lack of investigation of the performances of these second life batteries. In this paper, authors show the results of the impedance spectroscopy of 20 Ah lithium NMC batteries after EOL, exactly at 100, 85, 80, 60 and 50% of rated capacity, in a wide range of frequency: 450 mHz to 3.5 kHz. By results, there are many way to correlate battery state of health and battery impedance spectroscopy, especially when the battery is in second life.**

Keywords*— *Lithium cell, Impedance spectroscopy, State of health, Second life battery, grid connected energy storage applications, Randles model.

I. INTRODUCTION

Nowadays, battery electric and hybrid vehicles (EVs and HEVs) have a role central to play in Europe's transition from fossil fuels to renewable energy, reducing the greenhouse gas emissions. Lithium batteries, due to high power and energy capability, high efficiency long cycle and calendar life, are established in the automotive market. There is a large scale production and technical improvement for lithium batteries [1][2]. Nevertheless, their high cost is one of the major impediment to increase the market share of EVs and HEVs. Among several solutions, e.g. recycling [3], development of advanced electrode materials and electrolyte solutions [4], the reuse of EV/HEV Li-Ion batteries after their End-Of-Life (EOL), giving them a second life, is one of the major promising solution to decrease the high cost of these batteries today. EV and HEV lithium batteries are considered in EOL if at 85-80% of nominal capacity. Second-life batteries are still expected to be capable of storing, delivering substantial energy and to meet the requirements of a stationary applications. Today, car manufacturers are using the second use option in an attempt to expand their portfolio and enter in the stationary battery market. In cooperation with utility companies, they are launching several battery second life pilot projects. Summary of these projects is presented in [5]. Currently, several studies are focused on the analysis of the economic, technical and environmental matters of battery second life [6][7]. However, there is an increasing need to investigate in depth the potential of using second life batteries for stationary. One of the key challenge related to second life batteries is that the battery behavior and in particular the aging phenomena after first life are not clear known for the different battery chemistries. Therefore, there is a lack of reliable and accurate battery models to assess the applicability of second life batteries into stationary applications. Battery models can be divided in many groups. Electrical models depending on a Thevenin equivalent circuit, adding many R-C groups in series, are usually used, because they solve the trade-off between model complexity and accuracy [8][9]. In literature these models are so-called Electrical Circuit Models (ECMs). However, ECM accurately describes the electrical behavior of the battery while presenting limited physical meaning in its parameters. Instead, many chemical-physical properties of lithium batteries can be observed by Electrochemical Impedance Spectroscopy (EIS) technique [10]. EIS consists of measuring battery impedance in a wide range of frequency. Analyzing several electrochemical battery internal processes with different frequencies, there is the possibility to assess battery SOC [11] in low frequency, internal temperature [12] and SOH [13][14] in high frequency. This paper is focused on the analysis of battery SOH based on EIS measurement at different states of battery ageing and battery SOC. In particular, four different EOL Li-Ion Nickel-Manganese-Cobalt (NMC) batteries with different SOHs will be under test, measuring impedance and analyzing their chemical-physical properties in the following frequency range: 450 mHz to 3.5 kHz. The paper is structured as follows: Section

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variation and the internal temperature excursion very low [10], but maintaining the SNR between measured signal and noise high [16], thus ensuring good accuracy and that the battery system could be considered as LTI system. In this work, current amplitude value is equivalent to 0.3C, where C is the current battery capacity. The DSpace MicroLabBox DS1202 has been used as battery voltage, current and temperature data measurement and acquisition, with a sample time of 20 kHz.

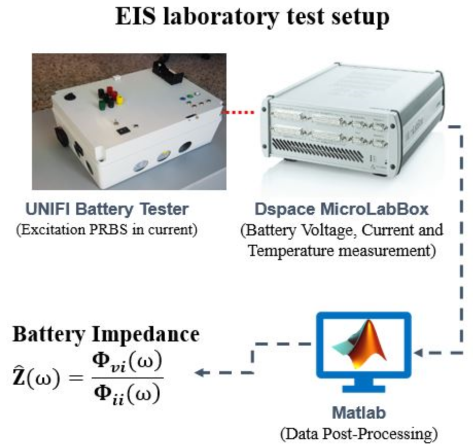

Fig. 2. Laboratory test & measurement setup.

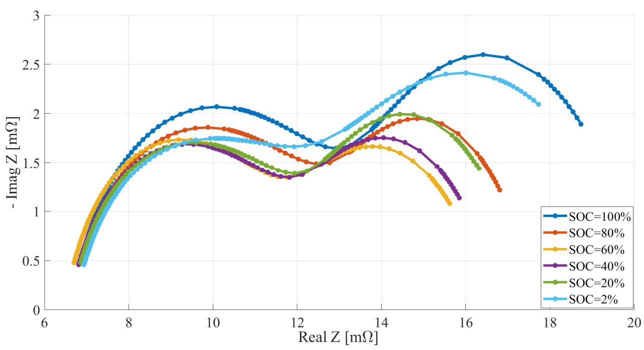

Fig. 3. Measured battery impedance results on cell #5 (SOH 60%) at different SOC.

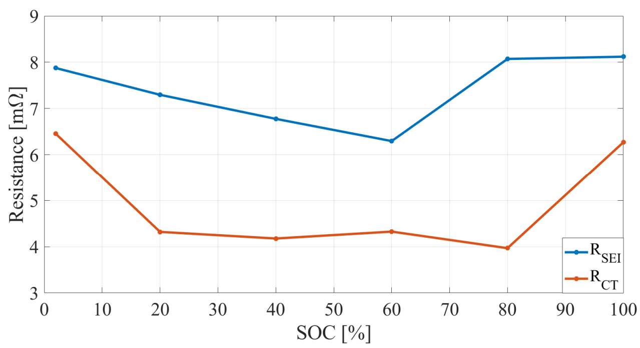

Fig. 4. Dependence of battery SEI resistance and charge-transfer resistance (R_{SEI}, R_{CT}) at different SOC (cell #5, SOH=60%).

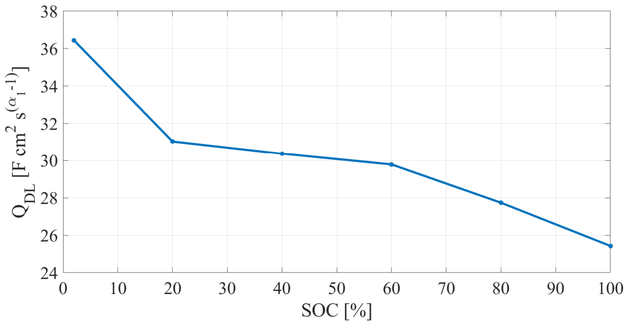

Fig. 5. Dependence of battery double layer capacitance at different SOC (cell #5, SOH=60%).

IV. Results

A. Analysis of battery EIS results at various SOC

In this subsection, the relationship between battery impedance spectra with battery SOC is discussed. EIS test are performed on NMC cells with lab-test setup shown in Fig.2 (more details in [23]), using PRBS excitation signal [16]. Every EIS test is performed with a SOC variation less than 2% and without temperature variation, thus working in the fixed operating condition. In Fig.3 the evaluated impedance spectra for the cell with SOH 60% are shown for 6 different battery SOC. The shape of the impedance is similar for all the SOC values. In particular, many considerations should be highlighted at low frequency: it's noticeable that the amplitude of the semi-ellipses becomes very high at the extreme part of the battery SOC window (2%, 100%). In particular, the amplitude of the second semi-ellipse (defined by the R_{CT}, CPE_{DL}) increases, revealing an increase of charge-transfer resistance, as shown in Fig.4, similar to other cell chemistries [12][24]. Moreover, in Fig.4, the increase of the R_{SEI} is observed, whose value was smaller than R_{CT} when the cell was in the begin of life [25]. Finally, the double layer capacitance increases, when battery SOC is decreasing, as shown in Fig.5.

B. Dependence of battery EIS results at various SOH

As mentioned in the introduction, EIS analysis allows us to extrapolate much information about current battery chemical-physical properties and battery SOH. Fig.6 shows the results of evaluated battery impedance spectra on the cells under test at fixed SOC=60%. It's noticeable that a decrease of battery SOH, so a battery degradation, implies a shift to the right of the impedance spectra in the Nyquist diagram with respect to the real impedance axes. This behavior corresponds to an increase of the ohmic resistance R_{Ω} proportional to the battery capacity degradation, as it happens in its first life [13][14][25]. Moreover, an increase of the two semi-ellipses arcs are noticeable, in according to [11][12], more noticeable as SOH decreases. In particular, the length of the two ellipses semi-axes approximately corresponds to the sum of the SEI and charge-transfer resistance (R_{SEI}, R_{ct}) [18], so an increase of ellipses semi-axes corresponds to the increase of (R_{SEI}, R_{ct}) over battery lifetime. This phenomenon is present also in the first life of the battery [25], but becomes more evident in the second life, especially for the increasing of R_{SEI}. Since the aging effects are difficult to evaluate directly

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