Influence of Long-term Equalization Processes on the Voltage Based Self-discharge Measurements in Li-Ion Cells

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Lithium-ion batteries have become a key player in the field of energy storage for various applications ranging from mobile phones to electric vehicles. Large battery packs contain Battery Management Systems (BMS), including voltage balancing circuits, which keep in series connected cell blocks from drifting apart. Different self-discharge rates are usually claimed to be the main factor of such voltage imbalances. However, the process of self-discharge is not completely understood yet. A common way to determine self-discharge is to measure the voltage decrease over time when the cell is in an equilibrated state. Correlating the slope of this voltage decrease (i.e. dU/dt) with the inverse differential analysis of the open circuit potential curve (i.e. dQ/dU) reveals the self-discharge current of the cell (i.e. dQ/dt). This current represents the sum of all side reactions occurring within the cell on the half-cell potentials. In this work, this method is more closely investigated regarding the long-term voltage equalization and possible associated measurement inaccuracies. Within this study, 13 fresh cylindrical 18650 cells comprising an NMC cathode and a graphite anode were investigated. First, dU/dQ characteristics of each cell were determined in order to choose significant state of charge (SOC) levels, as shown in Fig. 1. After discharging the cells to the SOC of interest, all cells were rested until dU/dt became negative. Subsequently, a small discharge pulse of 0.00027% of the nominal capacity at C/30 was applied in order to determine an exact value of the dU/dQ quotient. Finally, the cell voltages were measured over a period of 90 days at an ambient temperature of 25 °C. The comparison between the dU/dQ characteristics determined during a constant current discharge at C/30 and by applying a small C/30 discharge pulse after the cells were completely relaxed is shown in Fig. 1. Whilst both curves reveal a similar trend, the exact values of dU/dQ derived from the pulsed measurement differ by the factor of two from the continuous measurement for several SOCs. Such discrepancy is most likely caused by a polarization of the cell, which is not constant during discharge. Fig. 2 shows the calculated self-discharge currents over the corresponding SOC range. The different curves shown in the Fig. 2 are based on varying dU/dt quotients taken from different times during the period of 90 days. It can be shown that the self-discharge current is overestimated for SOCs larger than 50% and underestimated for SOCs lower than 30% when the chosen resting time for determining dU/dt is too short. Such behavior indicates long-term equalization processes, which might be caused e.g. by the overlap of the anode (ca. 3.3% in capacity in this case) with differing lithiation compared to the active area of the anode.

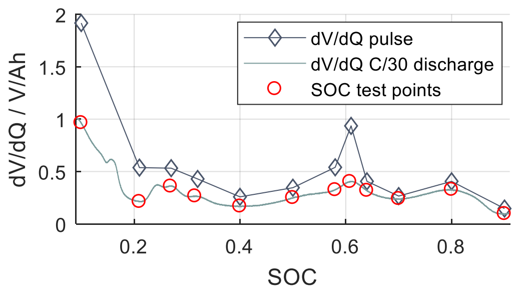

Fig 1. dV/dQ comparison

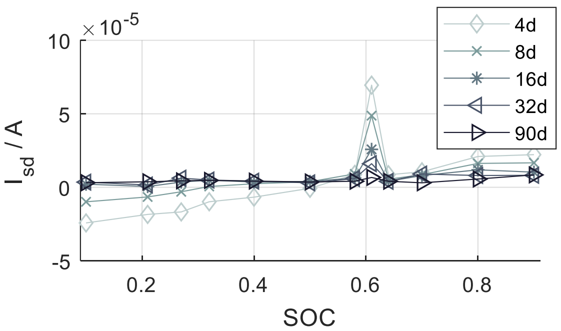

Fig 2. I_{sd} at different resting times