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Calendar life study of Li-ion pouch cells

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Abstract

A calendar life study was conducted on lithium ion pouch cells which were stored under float charge condition at five temperatures. The half cell study showed that the anode experienced severe loss of the active material, especially at high temperatures. The capacity fade mechanisms were then proposed. The capacity fade at low temperatures could mostly be caused by the loss of lithium inventory to side reactions and impedance increase. The capacity fade at high temperatures demonstrated a two-regime pattern. The fading mechanisms in the first regime could be similar to those at low temperatures. The capacity fade in the second regime could be dominated by the severe loss of active carbon material. The impedance rise plays a minor role in the second capacity fade regime.

Keywords: Calendar life study; Capacity fade; Loss of active carbon

1. Introduction

The calendar life of lithium ion batteries is an important factor in the evaluation of their dependability, stability and cost. The calendar life study defined in the PNGV battery test manual [1] is designed to evaluate the cell degradation as a result of the passage of time with minimal usage. Several national labs and groups [2–9] have studied the storage of lithium ion batteries. For example, Broussely et al. [2] concluded that lithium oxidation on the negative electrode is a major side reaction affecting the cell capacity on storage at high temperatures. Wright et al. [5] observed a square root of time dependence of the cell resistance after long time storage. Asakura et al. [7] observed that a 15 °C increase in temperature and 0.1 V increase in charging voltage could cut the cell life in half under floating charge conditions.

In this work, the capacity fade of lithium ion pouch cells was studied under float charge condition at different temperatures. Half cell studies on the used electrodes were conducted to understand more about the capacity fade of these cells. The capacity fade mechanisms were then proposed and discussed based on the findings from the full cell tests and half cell studies.

2. Experiments

Ten lithium ion pouch cells received from Nation Reconnaissance Office were used in the calendar life study. Each cell consisted of four (double-sided) positive electrodes and five (three double-sided and two single-sided) negative electrodes. The active material of the positive and negative electrode is $LiCoO_2$ and carbon (mesocarbon micro-bead), respectively. One molar $LiPF_6$ in a quaternary solvent mixture of EC, PC, EMC and DEC was used as the electrolyte. The double-sided positive electrodes were contained in bags made with separators. Three double-sided negative electrodes were sandwiched between four positive electrodes, while the two single-sided negative electrodes covered the outer positive electrodes. The entire assembly of anodes, cathodes and separators were enclosed by proprietary material to make a pouch cell. The pouch cells were vacuum degassed and mechanically clamped between two aluminum plates (for each cell) when they were shipped to our lab. The name plate capacity of these cells was 1.656 Ah and the experiment charge and discharge C rate currents were determined based on the nameplate capacity of the cell ($C = 1.656$ A).

The cells were stored at five different temperatures: 5, 15, 25, 35, and 45 °C. The test procedures and the sequence were summarized in Fig. 1. The procedures consisted of rate capability test, storage at float charge condition and monthly capacity

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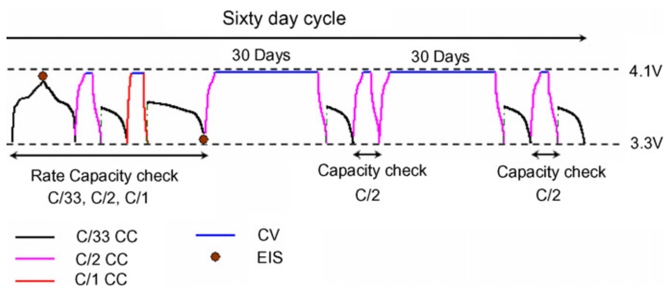

Fig. 1. Test procedures for the calendar life study.

check. The sequence was rate capability test, storage for 30 days, capacity check, storage for 30 days and capacity check. After one sequence was finished, another sequence would start with the rate capacity test. The designed procedures would be helpful to build a model from the experiment data. That is, the data from the rate capability tests could be used to formulate the model while the data from the monthly capacity checks could be used to validate the model. In the rate capability tests, three current rates were used to evaluate the performance of the cells. They were *C*/33, *C*/2 and *C*/1 rates. At *C*/33 rate, a constant current (CC) protocol was used to charge and discharge the cells. At *C*/2 and *C*/1 rates, CC–CV (constant voltage) protocol was used to charge the cells. A two stage CC protocol was used to discharge the cells, that is, *C*/2 or *C*/1 rate followed by *C*/33 rate. The voltage window for the rate capability tests was 3.3–4.1 V. Electrochemical impedance spectroscopy (EIS) measurements were also taken at the end of the rate capability tests. The frequency range for the impedance measurement was 10 kHz to 0.1 Hz and the amplitude of the input signal was 10 mV. The rate capability tests and EIS measurements were both performed at the storage temperatures. During storage, the cells were stored under a trickle charge condition to maintain the cell potential at 4.1 V. All the experiments were done in the Tenney environment chambers and the battery testing hardware was the Arbin BT-2000 testing system. The data were collected using the MitsPro software provided by Arbin.

Half cell studies were performed on the used electrodes harvested from the aged cells to understand the capacity fade in individual electrodes. The residual capacity and the intrinsic capacity of used electrodes were measured. One pouch cell from each temperature was first discharge to 3.0 V at room temperature with a small current to ensure a complete discharge. Then they were opened inside an argon filled glove box. Carbon disc electrodes of diameter 5/8 in. were punched out of the single-sided carbon electrode sheets inside the glove box to prevent any possible reactions of lithiated carbon with air. For the double-sided $LiCoO_2$ cathodes, one side of the electrode coating was scratched off the current collector plate by hand outside the glove box before they were used to make disc electrodes of diameter 5/8 in. Coin cells of type CR2025 were made with $LiCoO_2$ or carbon disc electrode as working electrode and lithium foil as counter electrode. The $LiCoO_2$ coin cells were first discharged to 2.0 V to measure the residual capacities. Another charge and discharge cycle between the voltage window 2.0–4.3 V measured the intrinsic (reversible) capacities of the $LiCoO_2$ coin cells. The carbon coin cells were first charged to 2.0 V to measure the residual capacities. Another discharge and charge cycle between the voltage window 0.01–2.0 V measured the intrinsic capacities of the carbon coin cells.

3. Results and discussion

3.1. Calendar life data

The pouch cells stored at 5, 15 and 25 °C were tested for 18 months. At the end of the calendar life study, they had a capacity fade percentage of around 17%, 20% and 62%, respectively. The cells stored at 35 and 45 °C were tested for 14 and 10 months, respectively. The capacity fade percentage of the cells reached more than 90% at the end of storage test.

The discharge capacities measured at *C*/33 rate in the rate capability tests are presented in Fig. 2. Because of the small current used, the impedance effect would be minimized and the measured discharge capacities reflect the true cell capacities. The capacity fade at low temperatures is mostly linear with time, but nonlinear at high temperatures. Cells stored at high temperatures experience an accelerated capacity fade after a few months of storage. When they approach the end of life, the capacity fade slows down. The pattern is consistent with the results found in a previous study [8] where cells are stored at 35 °C under both float charge condition and open circuit condition.

Three different current rates were used in the bi-monthly rate capability tests to measure the cell performance. The discharge capacities at different current rates are presented in Fig. 3 for selected temperatures. The capacities measured at high rates appear to fade in a similar pattern as those measured at low rates. However, a close examination of these experimental data reveals that the capacity fade mechanisms could be different for different temperatures. A detailed discussion on possible capacity fade mechanisms is presented in Section 3.3.

Fig. 4 compares the pre-monthly and monthly cell capacities measured at *C*/2 rate at different temperatures. A two stage

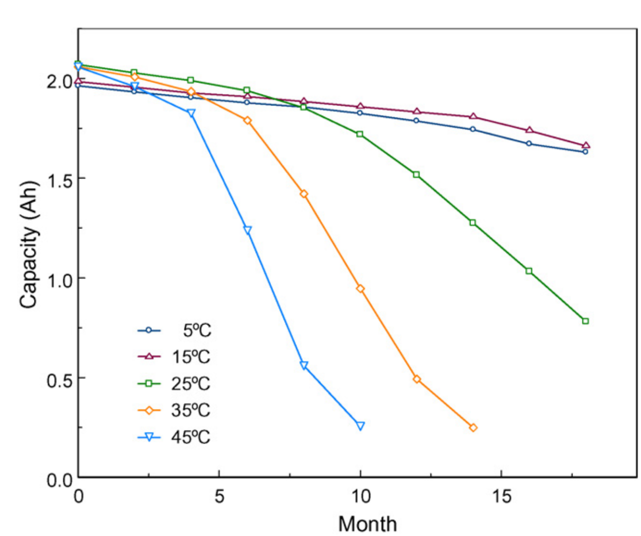

Fig. 2. Capacity fade at *C*/33 rates for different temperatures.