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# Novel estimation method of operating life in lithium-ion pouch cells

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ABSTRACT

Herein, a novel operating life (OL) test method was evaluated with 200 mAh pouch-type lithium-ion batteries. By combining the calendar life (CL) test with intermediate pulse power cycling, more realistic life prediction was possible, which encompassed real operation of batteries accompanying with thermal acceleration. Larger capacity decrease and resistance increase of pouch cell were observed in the OL test, which was well explained using the SEI film growth model. After dissemble of pouch cell, capacity loss and resistance increase mostly occurred within anode, reflecting that SEI film growth on anode surface was highly attributable to cell degradation.

## Introduction

Recently, the lithium-ion battery (LIB) has been applied to hybrid electric vehicles (HEVs), plug-in HEVs, and EVs due owing to their high energy and power [1–7]. In general, life performance becomes more significant for these application since automobile energy sources should certificate over 10 years of life. Besides the typical cycle life, which is assessed by constant current–constant voltage (CC–CV) charging and CC discharging, calendar life (CL) has been used for prediction of battery life. Generally, CL can be evaluated using life acceleration by thermal degradation of LIB cells. In this method, typically, LIB cells at half state-of-charge (SOC) are stored at the designed temperatures, from ambient temperature to 60 °C. After storage for a certain time, their capacity is measured using CC–CV mode and DC-resistance is also evaluated based on the voltage drop, and the available power is estimated from the obtained voltage drop and the available voltage limit of the full cell. After setting the SOC to half-value again, the storage at a certain temperature is repeated. Using the Arrhenius relationship obtained from the high temperature results, the expected cell life at ambient temperature can be estimated. However, the CL test is based only on life expectation under the assumption of battery storage without real operation, which is unrealistic for practical applications of LIBs. When considering the operation of LIB cells under regular driving conditions, it is reasonable that the CL test is insufficient to obtain an actual life prediction.

As a typical evaluation method of LIBs operation installed within HEVs, pulse power energy efficiency has been used [8]. Regarding the pulse power operation, the specification for batteries in HEVs requires guaranteeing 90% energy efficiency during $1.5 \times 10^5$ cycles for 10 years. Typically, this energy efficiency pulse cycling experiment is conducted using the minimum power assist (25 Wh) efficiency test profile for pulse power cycling of the US Advanced Battery Consortium (USABC) method [8,9]. According to this method, the goal of round-trip efficiency should be higher than 90%, and the applied power should be scaled to satisfy the 25 Wh energy goal with 15 kW peak power system. This pulse cycling can represent the real utilization of the battery after installation in HEVs. Hence, it is worthwhile to include this pulse power cycling to simulate a real operation.

To suggest a more advanced prediction method of battery life, herein, the CL test is combined with intermediate power pulse cycling which can simulate 10 year life expectation. When considering the daily operation of conventional cars, they are stored under charged state at the parking place and operated during morning and night for regular driving. Hence, the CL can simulate the storage state at the parking place, which can be accelerated by thermal degradation. In addition, the pulse cycling test can represent the usual car operation. Thus, it is highly reasonable to suggest a more advanced life prediction method by a combination of CL and an intermediate pulse cycling, which can be called operating life (OL) test. In our investigation, small sized pouch LIB cells with 200 mAh capacity, which are designed in the

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similar electrode fabrication condition to HEV battery, are utilized as LIB cells. Using 200 mAh LIB cells, the CL test results are compared with those of the OL to demonstrate the validity of our proposed OL test method at 40 and 55 °C.

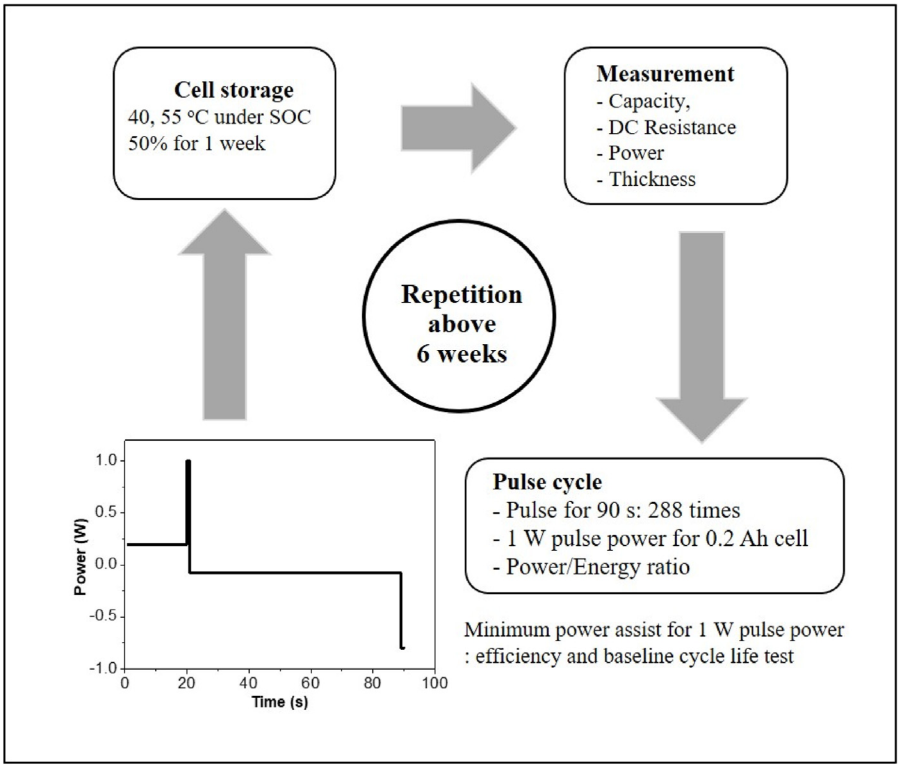
## Experimental

The lithium manganese oxide (LMO) cathode of the pouch cells was fabricated by mixing spinel $LiMn_2O_4$, a conducting agent (super P), and a polytetrafluoroethylene (PVDF) binder in the ratio of 9:0.5:0.5 wt/wt/wt. The spinel material as cathode material in a LIB was prepared by a solid–state reaction of $MnO_2$, $Li_2CO_3$, and $Al_2O_3$ at 870 °C under air atmosphere. For the anode, artificial graphite of a spherical shape from the company Daeback was mixed with Super P and a PVDF binder in the ratio of 9.5:0.25:0.25 wt/wt/wt. The electrode fabrication method was identical to that previously reported in the literature [10–12]. Pouch-type lithium ion batteries were constructed using the prepared anode and cathode. The electrode loading was approximately 0.85 mAh $cm^2$, and the designed cell capacity was about 200 mAh. Ni and Al taps were used to connect the anode and cathode, respectively. After placing the anode, cathode, and separator on the right position within the pouch cell, 0.5 mL of 1 M LiPF6 EC/DMC electrolyte was added, and the cell was vacuum-sealed. The battery-grade electrolyte of high purity (purity >99.9%) was purchased from the company Technosemichem.

For the electrochemical experiment of pouch cells, their capacity was measured at 0.1C rate (0.2 A) from 3.5 to 4.3 V in the first charge–discharge using a WBCS3000 cycler (Wonatech). After this formation process, the cell was degassed and re-sealed under vacuum. The CL test was conducted using an identical method to that in our previous report. According to the UCABC method a hybrid pulse power characterization (HPPC) test was conducted using 5C pulse current (~1 A) at 50% SOC. After storage at 40 and 55 °C, capacity change and resistance increase were obtained by the HPPC test. As for the OL test, 288 times pulse cycling using 1 W pulse power was applied to the stored pouch cells every 1 week, following the minimum power assist protocol for energy efficiency. This process was repeated for 8 weeks. After the OL test, the pouch cell was disassembled, and the individual electrodes were separately obtained. The morphology of electrodes was analyzed using scanning electron microscopy. Furthermore, the obtained cathode and anode were re-constructed as working electrodes in a coin half-cell.

## Results and discussion

As shown in Scheme 1, our method employed the intermediate pulse cycle process as an additional life acceleration protocol with the normal CL measurement process. For this purpose, 200 mAh cells were stored at 40 and 55 °C under SOC 50% for 1 week to accelerate cell degradation. After this storage, the change in cell performance was evaluated using the capacity measurement from the normal galvanostatic charge–discharge, DC resistance, and available power from the HPPC test, and cell thickness. After this, the pulse cycling experiment was conducted using the minimum power assist (25 Wh) efficiency test profile for pulse power cycling of the USABC method [9]. According to this method, the goal of round trip efficiency should be higher than 90% and the applied power should be scaled to satisfy the 25 Wh energy goal with 15 kW peak power system. This performance target can be converted into 1.8 mWh energy and 1.1 W peak power. In our approach, 1.0 W was used as peak power in our 200 mAh pouch cell. Moreover, the required specification for the application of LIB cells into HEVs should guarantee 90% energy efficiency during $1.5 \times 10^5$ cycles for 10 years, which can be converted into 288 cycles for 1 week [1,4,8,13]. Therefore, after cell storage at high temperature and following the measurement of cell performance,



**Scheme 1.** Operating life prediction.