



Short communication

Development of an Aluminum-laminated Lithium-ion battery for Hybrid electric vehicle application

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ABSTRACT

We have developed a lithium ion cell using an aluminum-laminated sheet casing for its container, and we estimated the reliability of the heat-sealing for the casing and the life characteristic for the cell. The tensile strength of the heat-sealed margin soaked in electrolyte solvent was found to fade in proportion to square root of the soaking time. The weight loss of dummy cells was in proportion to the storage time, which implies that the solvent molecules diffuse through the aluminum-laminated sheet, namely in the layer of polypropylene resin which heat-sealed the cell. The specific energy for the prototype cell with capacity of 2 Ah was 57 Wh kg^{-1} , which was 30% higher than that of our previous cylindrical can-type cell with capacity of 3.6 Ah. The specific power was 3800 W kg^{-1} at 25°C , which was 25% higher than that of our previous cell. These results indicate that the mass reduction by introducing the aluminum-laminated casing enhanced the specific energy and power effectively without any loss of reliability or life characteristics.

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1. Introduction

Lithium ion batteries have been applied to many portable electronic applications such as cellular phones, personal computers, and PDA's because of their high specific energy and power. They are also expected to be used for automobiles to cope with various environmental issues. Since the first commercialization of a hybrid electric vehicle (HEV) by Toyota in 1997, HEV's powered by an internal combustion engine and a motor (or motors) have been thought to be one of the most promising applications for lithium ion batteries. Many kinds of HEV's have been commercialized after that. Hitachi group was the first to develop a lithium ion battery for HEV application, namely, a commercial vehicle, in 2000 [1,2]. However, more power and energy are required for lithium ion batteries to successfully apply them to automotive applications. We have developed an advanced lightweight and high-power lithium ion cell by substituting an aluminum-laminated (Al-laminated) sheet casing for a cylindrical metal can. The reliability of the Al-laminated sheet sealing and the cell performance were evaluated and are presented in this paper.

2. Experimental

2.1. Reliability test of Al-laminated sheet

2.1.1. Mechanical strength test

Adhesion strength at the sealing margin of the Al-laminated cell was measured to evaluate the deterioration of sealing reliability for the cell. Test pieces formed by heat-sealing Al-laminated sheets were soaked in carbonate solvent. The storage temperature was elevated to accelerate the deterioration of the sealing. The Al-laminated sheet, a product of Showa Denko Package Co., Ltd., had a three-layer structure of nylon/aluminum/polypropylene. The sheet was cut into $15 \text{ mm} \times 50 \text{ mm}$ pieces. The two pieces were stacked each facing the polypropylene side to form a test piece by heat-sealing. The heat-sealed margin was maintained to be $15 \text{ mm} \times 10 \text{ mm}$. The heat-sealing condition for the heat-sealer, Semi-Auto Gas Packer N2C-1, Shinwa Machinery Co., Ltd., was set at a temperature higher than the melting temperature of polypropylene for 10 s. The test pieces prepared as described above were put in another Al-laminated casing with electrolyte solvent and heat-sealed. The casings were stored in isothermal chambers set at 25°C , 50°C or 80°C .

The test pieces were taken out after certain time intervals, washed in distilled water, dried at room temperature, and used for peel test to measure the peeling tensile strength. Each test piece was set on the test machine, Autograph AGS-H, Shimadzu, Ltd., putting

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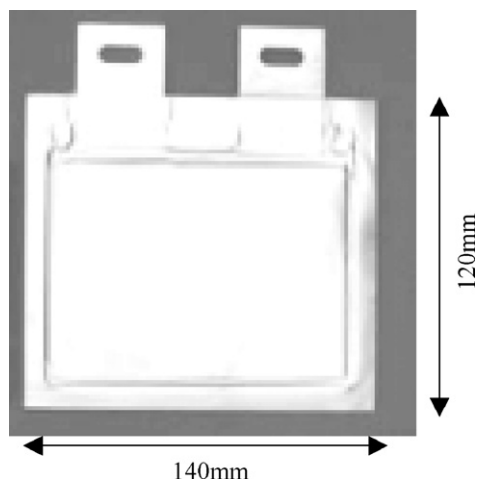


Fig. 1. Photo of single cell.

the heat-sealed margin at the center of the sample stage, and was pulled in opposite directions. The maximum load was recorded as peeling tensile strength.

2.1.2. Solvent loss test

We used dummy cells to evaluate the sealing reliability of the Al-laminated sheet cells. Fig. 1 shows the appearance of the cell, which contains a polypropylene board (100 mm × 80 mm × 3 mm) instead of electrodes and 18 g of mixed carbonate solvent (EC/DMC/EMC = 1/1/1 in volume). After heat-sealing in vacuum, the cells were stored at 25 °C, 50 °C, 60 °C or 80 °C, and the weight change was measured every 30 days.

2.2. Cell performance test

The specification for the cell developed in this study is listed in Table 1. The active material for the positive electrode was lithium manganate, and that for the negative electrode was amorphous carbon. Both electrodes were stacked with a separator between them, and the stack was contained in an Al-laminated sheet casing with electrolytic solution of 1 M lithium hexafluorophosphate (LiPF₆) dissolved in a carbonate mixture. They were heat-sealed in vacuum. The appearance for the cell is the same as Fig. 1. The designed capacity for the cell was 2.0 Ah.

The rated capacity was defined as the discharge capacity between 4.1 V and 3.0 V at 2.0 A discharge and 25 °C. Power capability for 5 s was calculated according to the procedure described by Horiba [3]. The test cell was conditioned by charging at 1 CA in constant current–constant voltage mode for 2.5 h in total. Direct current resistance (DCR) was calculated from the 5 s voltages after constant current discharge at 5 CA, 10 CA and 20 CA. Output power

Table 1
Specification of the laminate cell

Dimensions	
Depth	140 mm
Width	120 mm
Thickness	5 mm
Electrode	
Positive	Li–Mn spinel
Negative	Amorphous carbon
Solvent	Organic carbonate mixture
Li salt	LiPF ₆
Electrode arrangement	Stacking
Nominal capacity	2 Ah

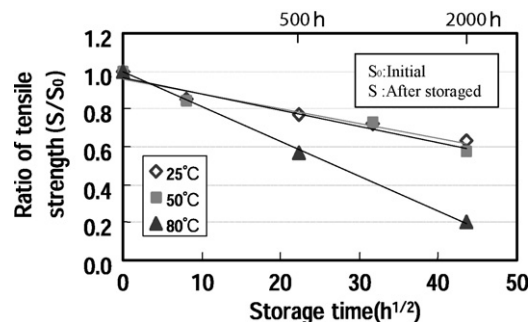


Fig. 2. Variation of tensile strength under various storage conditions.

capability was determined as the product of a discharge limit voltage of 2.5 V and extrapolated maximum current down to the limit voltage which was given by a straight line based on OCV (open circuit voltage) and the DCR. This procedure was iterated at every 10% SOC (state of charge). Input power capability was also determined in the similar manner to that mentioned above, although the input limit voltage was 4.2 V. The performance data for our previous 3.6 Ah can-type cylindrical cell with the same cell chemistry [1,2] (denoted as “Gen1 cell” hereafter) was used as a reference in discussing the results for the cell developed in this study.

The Al-laminated cells were stored at 50% SOC and 50 °C to accelerate the storage test. The cell was cooled at room temperature for 12 h and discharge capacity and power capability were measured according to the procedure mentioned above every 30 days.

3. Results and discussion

3.1. Mechanical strength

Fig. 2 shows time dependency of deterioration of peeling tensile strength. The tensile strength faded in proportion to square root of storage time at any temperature. After the test, the test pieces were observed to be broken not at the heat-sealed margin but at the interface of Al foil and polypropylene layer. It is, therefore, supposed that the tensile strength deterioration was caused by a similar mechanism to the oxide film growth on the surface of metal, called as tarnishing reaction [4], which proceeds in proportion to square root of time and the rate determining step of which is diffusion of oxygen molecules in the film. The mechanism supposed above is shown schematically in Fig. 3. The inner layer of polypropylene, commonly used as a separator material in lithium ion batteries, is not expected to react or dissolve with polar solvent such as organic carbonates. The tensile strength deterioration accordingly seems to be caused by the invasion of the solvent into the interface between the aluminum foil and the polypropylene sheet. Consequently, the tensile

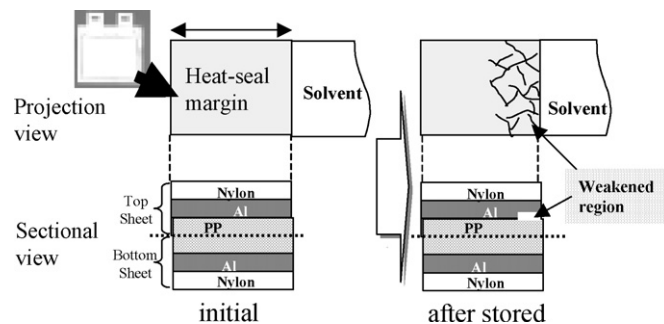


Fig. 3. Structure changing model during storage.

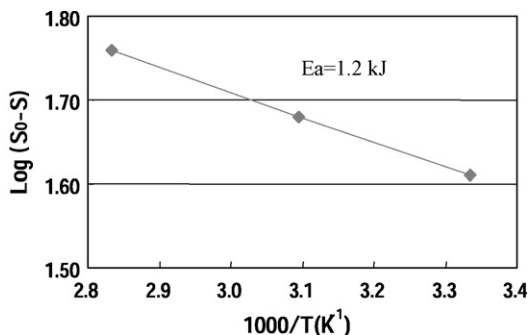


Fig. 4. Arrhenius plot of tensile strength after 200 h storage.

strength deterioration proceeds along the direction of adhesion face.

Fig. 4 is an Arrhenius plot of the tensile strength after 200 h storage. It reveals good linear relationship, which implies that there is no side reaction to change the dominant deterioration mechanism in this temperature range, although the deterioration was accelerated as the temperature rose. This means that a temperature-accelerated life test is thus suggested to be capable for this temperature range. The activation energy was estimated to be 1.2 kJ mol⁻¹, which is much lower than that for metal dissolution into acid (16.9 kJ mol⁻¹) [5]. The strength fading, therefore, seems to be caused not by the dissolution of the adhesive interface but by the gradual invasion of the solvent into the interface. This elucidation agrees well with the deterioration model shown in Fig. 3.

3.2. Solvent loss through Al-laminated sheet

Fig. 5 shows the weight loss ratio of the dummy cells after storage at various temperatures. At 80 °C, the weight loss reached 23% after 20,000 h storage. Though this large loss might sound like a serious issue, storage at 80 °C is merely an accelerated test condition. The heat-sealing was sound and there was no apparent breakage of the sealing or drip of the solvent observed even at this point of time. The weight changed in proportion to time at all temperatures, which is a different result from the tensile strength which changed in proportion to square root of time. The weight loss, therefore, seems to be caused by the diffusion of the solvent molecules through the heat-sealed material, polypropylene, layer with stable diffusion path during the test, while the tensile strength was in proportion to square root of time, suggesting the growth of deterioration in adhesive area. The weight loss rate, therefore, is expected to be in proportion to the cross section of the heat-sealed margin and to keep a constant value as far as the temperature is constant,

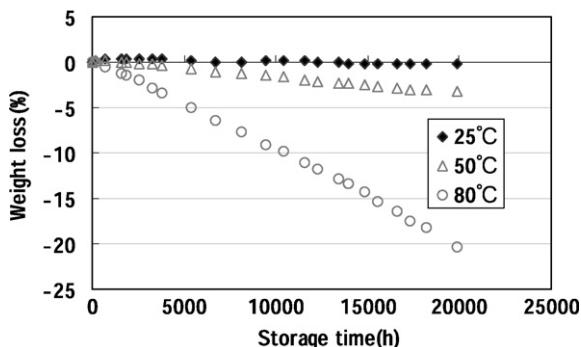


Fig. 5. Weight loss of model cell under various storage conditions.

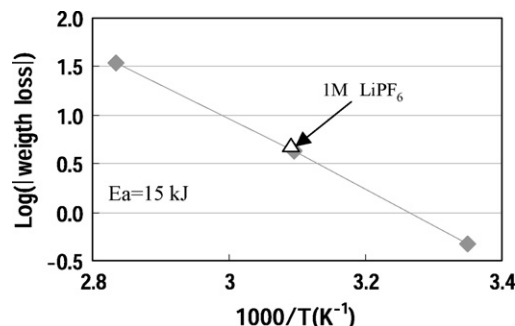


Fig. 6. Arrhenius plot of weight loss after 20,000 h storage.

namely there is no mechanical damage to form a through-hole for the solvent molecules to diffuse through.

Fig. 6 is an Arrhenius plot of weight loss after 20,000 h storage at various temperatures. The plot shows good linearity, and the activation energy was estimated to be 15.1 kJ mol⁻¹. This value is the same order of 33.1 kJ mol⁻¹ [6], which is the activation energy for water vapor to diffuse in a membrane of cellulose acetate. The weight loss, therefore, seems to be caused simply by the diffusion of the solvent into the heat-sealed layer without a side reaction to vary the activation energy within the temperature range measured. And an acceleration test is suggested to be capable within this test temperature range. Since Fig. 5 shows straight lines, we can evaluate the acceleration factors. The factor for 50 °C is 15 based on the loss at 25 °C, and that for 80 °C is 92. The weight loss after 20,000 h storage at 50 °C corresponds to 34-year storage at 25 °C and that at 80 °C to 210-year storage. The weight loss value at 80 °C is, therefore, enough acceptable to support 10-year calendar life of laminated lithium batteries for HEV applications in which average surrounding temperature seems lower than 30 °C.

At 50 °C, an additional test was conducted by dissolving LiPF₆ into the solvent to be 1 M. The weight loss after 20,000 h at 50 °C was around 3%, and the result is shown as a triangle in Fig. 6, which shows good agreement with the data for the case without LiPF₆. This agreement indicates that LiPF₆ salt in the solvent does not change the solvent molecule diffusion into polypropylene layer substantially.

3.3. Cell performance

The specific energy for the prototype cell was 57 Wh kg⁻¹, which was 30% higher than that for the Gen1 cell [2]. This result shows the merit of weight reduction by the adoption of Al-laminated sheet cell structure. Power capability of the cell is shown in Fig. 7 together with the data for the Gen1 cell as a reference [2]. The

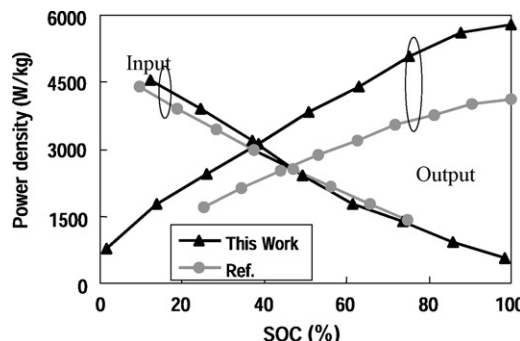


Fig. 7. 5 s pulse power capability for the single cell at 25 °C.

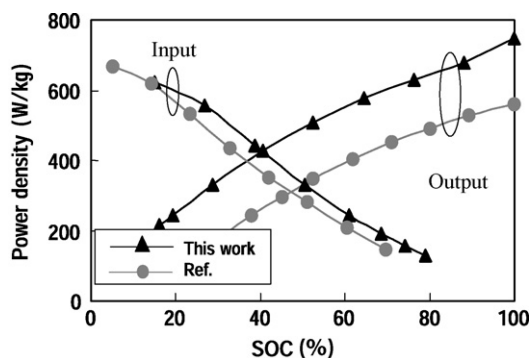


Fig. 8. 5 s pulse power capability for the cell at -30°C .

Al-laminated cell showed 25% higher output power than the reference cell, though the input power was almost the same. The reason why the input power did not increase is supposed to be caused by the difference of the capacity ratio between negative and positive electrodes. Even if we use electrodes of same specification, same electrolytic solution and same separator, the ratio will not be identical because of difference of the electrode arrangement for the wound can-type and stacked laminate-type cell. Since the capacity ratio of the negative electrode increased in this case, the input power for the cell seems to be controlled by the positive electrode capacity. The increment in power had almost the same ratio as that for specific energy, which explicitly proved that the increment was supported by the weight reduction of the cell structure. Fig. 8 shows low temperature power capability at -30°C . Even at this low temperature, the Al-laminated cell showed higher power capability than the Gen1 reference like at 25°C .

Fig. 9 shows the capacity fading in storage at 50% SOC and 50°C . Our Al-laminated cell showed a similar tendency to that of the Gen1 reference. The DCR change for the same test is shown in Fig. 10. DCR for both cells increased gradually up to 140% around 200 days after, and reached pseudo-saturation after that. To sum up, Figs. 7–10 show that Al-laminated cell structure did not cause any specific degradation, such as deterioration of Al-laminated sheet, or swelling by gas evolution. And the cell performance degradation seems to be controlled by the same mechanism as that of the Gen1 cell, i.e., the intrinsic degradation caused by the cell chemistry itself. Therefore, the degradation caused by the Al-laminated cell structure itself must be limited, and it will not lower the weight reduction merit for the structure.

Fig. 11 compares the power capability at 25°C before and after storage for 250 days at 50% SOC and 50°C . Both output and input power capabilities decreased, mainly because of the incre-

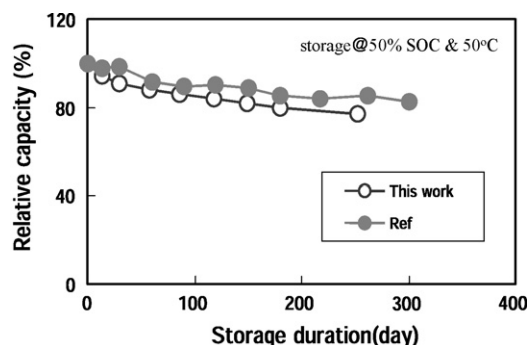


Fig. 9. Storage performance of cell on relative capacity.

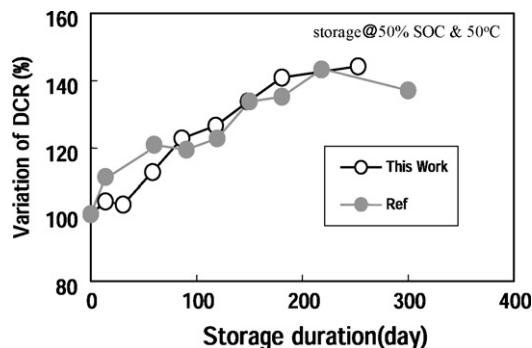


Fig. 10. Storage performance of cell on DCR (at 100% SOC).

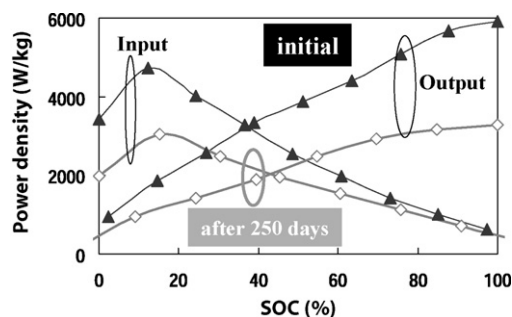


Fig. 11. 5 s pulse power capability change by at 50% SOC and 50°C .

ment of DCR. The output power capability at 50% SOC changed from 3800 W kg^{-1} to 2200 W kg^{-1} . The DCR increment for the period was 40%, which suggests power fading from 3800 W kg^{-1} to 2700 W kg^{-1} , so the rest of the 500 W kg^{-1} loss is thought to be caused by other reasons, other than the DCR increment. In other words, more than two-thirds of the power fading is controlled by DCR. Similar result was observed in a can-type cell of identical cell chemistry. When a cell was tested in a certain pulse cycle mode for 300,000 cycles at 50°C , the DCR increased from $4.2\text{ m}\Omega$ to $8.7\text{ m}\Omega$ and the 5 s output power changed from 600 W to 244 W. The increment of DCR suggests that the output power changes from 600 W to 290 W. There is 50 W difference between the measured and the predicted by DCR, the most of the power fading, however, can be attributed to the DCR increment.

The power fading mechanism for our cell in detail is not analyzed here. It was reported that lithium manganate (lithium manganese spinel) dissolved into electrolytic solution and deposited on the surface of negative electrodes during storage at high temperatures [7,8]. This mechanism will surely increase DCR of the cell. Another study claimed that dissolution of manganese increased the ratio of Mn^{4+} ions, thereby reducing the lattice constant and discharge capacity [9]. The degradation of our cell after storage at 50°C for a long time, therefore, must be caused by the dissolution of manganese as some previous works claimed. It will be our future work to suppress the manganese dissolution by applying certain additives into the electrolytic solution or surface modification of active materials according to the degradation mechanism discussed above.

4. Conclusion

We have developed a lithium ion cell using an Al-laminated sheet casing, and evaluated its reliability for heat-sealing and cell performance. Dummy cell test results proved good heat-sealing reliability; that is, the cells suffered no leakage of electrolytic

solution even after 20,000 h storage at 80 °C. Weight reduction of the Al-laminated cell structure supported the specific energy and power increment by 30%. Power fading after storage at higher temperatures for a long time still remains to be solved. Modification of the electrolytic solution or the positive active material is expected to be the key to improve the power fading.

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