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Development of prismatic lithium-ion cells using aluminum alloy casing

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Abstract

Light weight prismatic lithium-ion cells for cellular phones have been developed using an aluminum alloy case. Various kinds of aluminum alloys have been examined from the view point of the electrochemical stability, mechanical strength, the ability to be laser-welded and easy formation into a casing. An aluminum alloy with 1.1 wt.% Mn was the best candidate for the casing. The energy density of the lithium-ion cell with the aluminum alloy casing was improved by about 30% compared to the conventional steel casing.

Keywords: Lithium-ion; Aluminum alloy; Manganese

1. Introduction

The quick development of the information and communication systems during the past decade has required small and portable equipment like cellular phones and note book style computers. For this type of equipment, batteries are one of the key devices as are LSI and LCD. The important requirements of the battery for these applications are reliability, compactness and minimum weight. In 1991, lithium-ion batteries were commercialized [1] and extensively used for portable equipment. The energy density of the conventional lithium-ion battery with a carbon anode and a $LiCoO_2$ cathode is around 80 Wh/kg (cylindrical AA type) compared to the theoretical value of 560 Wh/kg [2]. The difference between the theoretical and the observed value is due to the large weight contribution of the casing. To improve the energy density of the battery we should use a light-weight casing. Until now, steel containers have been used for the conventional lithium-ion battery. A light-weight metal like aluminum is quite attractive as a container. However, there are many problems with aluminum containers such as mechanical properties and sealing, in prismatic type cells. The prismatic type batteries are attractive for cellular phone and note book style computers, because of the high package density. Generally, the prismatic battery uses a thicker casing material than that for cylindrical type, because of the mechanical strength required. Therefore, the specific energy of the prismatic battery is 30% lower than that of the cylindrical one.

In this paper we have proposed the use of an aluminum alloy as the casing for the prismatic lithium-ion battery, and the cell performance and stability have been examined.

2. Experimental

Four different kinds of aluminum and aluminum alloys, namely, pure Al metal (99.6% purity), Al–Mn alloy (Mn 1.1 wt.% (w/o)), Al–Mn–Mg (Mn 1.1 w/o, Mg 1.0 w/o), and Al–Mg–Si (Mg 1.0 w/o, Si 0.5 w/o), have been used as materials for the case. The commonly used Ni plated steel ('SPCD', purity 99.4%, C 0.10 w/o or less, Mn 0.45 w/o or less) casing has been compared to the aluminum alloy casing.

Cases of various size were made using these metals. The sizes of these cases and metal thickness are as follows. Case A: Al and Al alloys thickness 0.5 mm, 5.6 mm in height, 19 mm in width and 58 mm in length; case B: Al–Mn alloys thickness 0.5 mm, 5.6 mm in height, 16.4 mm in width and 67 mm in length; case C: Al–Mn alloys thickness 0.4 mm, 5.6 mm in height, 16.4 mm in width and 67 mm in length; and case D: steel, thickness 0.4 mm, 5.6 mm height, 16.4 mm in width and 67 mm in length.

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The mechanical properties of case A prepared with Al and Al alloys were tested. The expansion rate of the case was measured under an internal pressure in the range of 0–5 kg/cm^2. The pressure was supplied by compressed air.

Prismatic test cells were prepared using Al and Al alloy cases. These cells consisted of natural graphite, a $LiCoO_2$ cathode, and a $LiPF_6$ electrolyte in ethylene carbonate and diethyl carbonate mixed solvent. $LiCoO_2$, carbon as a conductive agent and poly-vinylidene-difluoride as a binder were mixed in *N*-methyl pyrolidone (NMP). The paste was coated on both sides of an aluminum sheet and was pressed after drying. The paste mixture of natural graphite and NMP was coated on to a copper sheet, and pressed after drying. The anode and cathode sheets along with a micro porous polyethylene separator were placed into the case and then the electrolyte was poured in. The cell sealing was carried out using a laser welding method. A YAG laser with power of 200 W was used.

The cell was charged up to 4.1 V under a constant current of 1 C and then kept at a constant voltage of 4.1 V. The total charging period was 2.5 h. The discharge was carried out at constant current of 1 C to a cut-off voltage of 2.75 V. The expansion rate of the cells stored for 20 days at 60°C was examined.

3. Results and discussion

The cell casing plays an important packaging role in holding the interior cell components, and also in maintaining an interior pressure to keep a good contact between the cell components. The strength of the case is therefore an important factor in the cell performance. Fig. 1 shows the expansion rate of the case A prepared with Al and Al alloys under pressure. The expansion rate depends on the alloys mechanical properties. The lowest expansion rate is

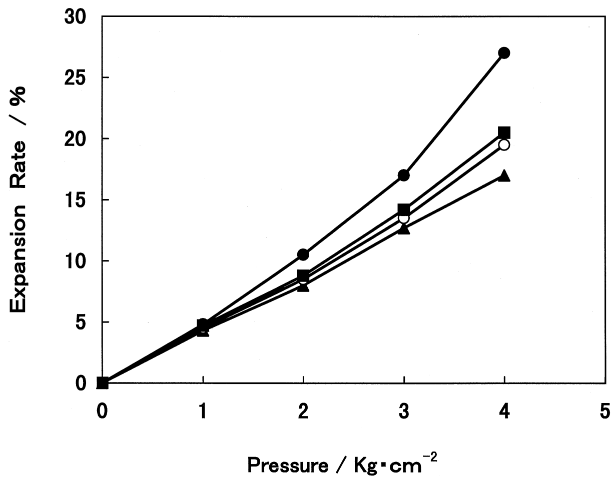

Fig. 1. Expansion rate of the case A prepared with Al and Al alloys under pressure. (●, Al; ■, Al-Mg-Si; ○, Al-Mn; ▲, Al-Mn-Mg).

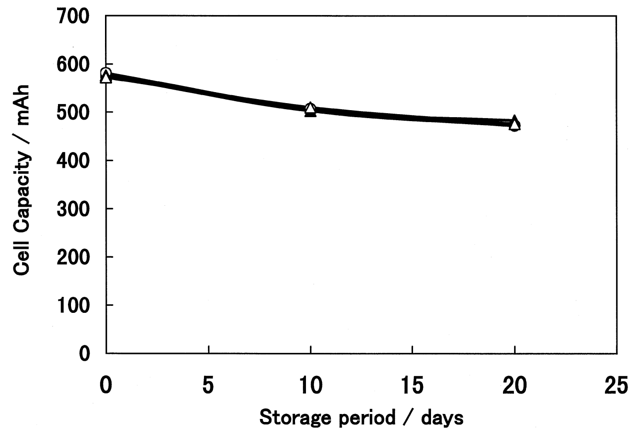

Fig. 2. Changes of cell capacity during the storage period at 60°C. (●, Al; ○, Al-Mn; △, Al-Mg-Si; ▲, Al-Mn-Mg).

observed in the Al–Mn–Mg alloy, which has the highest tensile strength, yield strength and hardness. Generally, the internal pressure of lithium-ion batteries is in the range 1–2 kg/cm^2. In this pressure range, no remarkable difference of expansion rate is observed between Al alloys and pure Al shows a slightly higher expansion rate.

The cell performances of the test cells with Al and Al alloys have been examined. The initial charge and discharge characteristic of these cells showed no change with the casing material. The cells were fully charged up to 4.1 V and stored at 60°C. At such a high cell voltage, electrochemically unstable alloys will be reduced, and the cell capacity will decrease with the storage period. Also, the open-circuit voltage at full discharge state will decrease by a small self-discharge current. In Fig. 2, the changes in cell capacity are shown as a function of the storage period. The cell capacity gradually decreases with the storage period. However, no significant difference is observed in the case of Al and Al alloys. An open-circuit voltage change during the storage period was not observed in regard to the different casing materials as shown in Fig. 3. These results suggest that these Al alloys studied in this experiment are

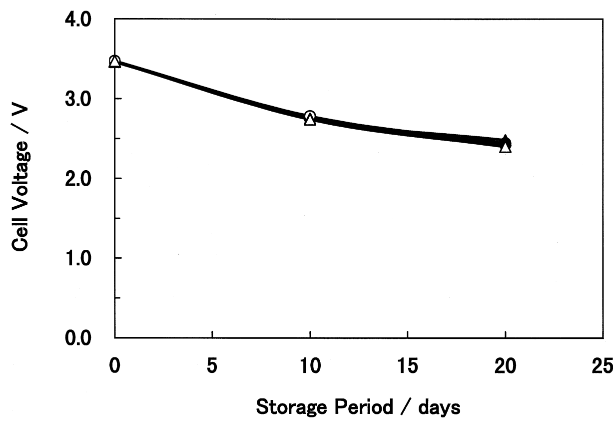

Fig. 3. Change of open-circuit voltage during the storage period at 60°C. (●, Al; ○, Al-Mn; △, Al-Mg-Si; ▲, Al-Mn-Mg).

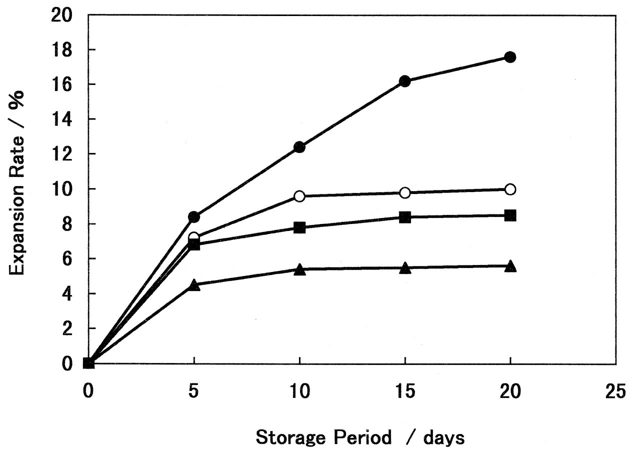

Fig. 4. Expansion rate of the cell stored at 60°C. (●, Al; ○, Al-Mn; ■, Al-Mg-Si; ▲, Al-Mn-Mg).

as stable in contact with the cathode material of $LiCoO_2$ as pure Al metal.

The mechanical strength of the case is also important in practical applications. The cells expand at a higher temperature by expansion of the cell components. Fig. 4 shows the expansion rate of the cells stored at 60°C as a function of storage period, where case A with 0.5 mm in thickness was used. The cells expand gradually with the storage period. The expansion is presumed to be caused by the bulge of both electrodes. The expansion rate depends on the casing material. The highest expansion rate is observed in pure Al, where a cell stored for 20 days at 60°C expanded by 17.5%. On the other hand, the Al–Mn–Mg alloy shows only 5.5% expansion. The expansion rate corresponds to the strength and hardness of the casing material. The tensile strength and Vickers hardness of the Al–Mn–Mg alloy are 18.5 kg/mm^2 and 93–98 respectively, compared to those of pure Al which is 7.0 kgf/mm^2 and 47. The Al–Mn and Al–Mg–Si alloys also showed acceptable expansion rate.

The other important requirement for prismatic cased lithium secondary batteries is to make a good seal. The laser welding method is more attractive to get a good seal and has been used for steel containers [3,4]. The melting point of Al is low at 660°C, compared to that of steel, 1500°C. As Al metal has high thermal conductivity and a high reflective rate of the laser beam, it is best to quickly supply a large amount of the laser beam on the welding position. The thermal expansion rate of Al metal is around twice that of steel (Al 2.39×10^{-5}, Fe 1.15×10^{-5} deg^{-1}). A conventional laser welding machine could not be used for the Al casing. We have developed a new welding machine for the Al casing to improve the focus. The details are presented in patents [5,6]. Al and Al alloy cases have been sealed by this laser sealing welding machine, and the sealing condition has been examined with the help of an optical microscope. A good seal was observed in pure Al and the Al–Mn alloy. On the other hand, we have not obtained good sealing in the Al–Mn–Mg and the Al–Mg–Si alloys by laser welding. It is not clear at this stage what properties of the alloys are effected by the laser welding. From the results of the cell expansion rate experiment and the sealing condition by laser welding, we can conclude that the Al–Mn alloy is the best candidate for the case in a lithium secondary cell using a $LiCoO_2$ cathode.

Test cells have been prepared using the Al–Mn alloy casing, where case B with the alloy of 0.5 mm in thickness and case C with the alloy of 0.4 mm in thickness were used. The cell performance of the Al–Mn alloy casing has been compared to that of the steel casing, where case D with steel of 0.4 mm in thickness was used. The characteristics of these cells are shown in Table 1. The discharge performance at different loads, temperature and cycle performance are almost the same within these test cells. However, a large expansion rate is observed in the cell using the Al–Mn alloy of 0.4 mm in thickness after charge–discharge cycling, compared to the steel casing of the same thickness. The cell using the Al–Mn alloy of 0.5

Table 1
Characteristics of test cells (cell size: $5.6 \times 16.4 \times 67$ mm)

		Material		
		Al–Mn alloy	Al–Mn alloy	Steel
Thickness of case (mm)		0.5	0.4	0.4
Initial capacity at 1 C (mAh)		390–410	410–430	390–410
Load performance: relative to 1 C capacity (%)	0.2 C	100–105	100–105	100–105
	2 C	80–95	80–95	80–95
Temperature characteristics: relative to capacity at 25°C (%)	60°C	87–93	87–93	87–93
	0°C	75–80	75–80	75–80
	−10°C	55–75	55–75	55–75
After 500 cycle	relative to initial capacity (%)	60–75	60–75	60–75
	increase of thickness (mm)	0.2–0.3	0.4–0.5	0.1–0.2
Cell weight (g)		14.5	14.1	19.0
Energy density	Wh/kg	99.3	107	75.8
	Wh/l	234	246	234

mm in thickness shows a similar expansion rate to that of the steel casing of 0.4 mm in thickness. As shown in Table 1, the energy density of the cell with the Al–Mn casing is 99.3 Wh/kg, which is about 30% higher than that of the cell with the steel casing. The high energy density for the cell with the Al–Mn alloy case is quite attractive for applications to portable equipment.

A 550 mAh practical prismatic cell using the Al–Mn alloy casing has been developed. The size of the cell was 7.6 mm in thickness, 22.0 mm in width, and 47.3 mm in length. The weight of the cell was 18 g and the energy density 110 Wh/kg. The degradation of cell capacity after 500 cycles at 1.0 C charge–discharge rate was 20–35%.

4. Conclusion

Aluminum and aluminum alloys have been examined as the casing for a prismatic lithium secondary battery using a $LiCoO_2$ cathode and a natural graphite anode. Pure Al shows some mechanical problems, and Al–Mn–Mg and Al–Mg–Si alloys show difficulty with the laser welding process. The Al–Mn alloy is the best candidate for the view of points of electrochemical stability, mechanical properties and laser welding. A prismatic cell with an Al alloy casing shows 30% higher specific energy than that with a conventional steel casing. A 550 mAh capacity practical prismatic cell with an Al–Mn alloy casing has been developed. The resulting energy density is 110 Wh/kg.

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