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Fabrication and evaluation of 100 Ah cylindrical lithium ion battery for electric vehicle applications

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Abstract

A total of 100 Ah class lithium ion cells with $C/LiCoO_2$ cell system for electric vehicles (EVs) was developed. EV-size lithium ion battery was developed by Sony, KERI/STC, SAFT, VARTA, Sanyo and Matsushita. GS battery and Hitachi have developed also stationary type large scale (70–80 Ah) lithium ion batteries. Lithium ion battery module for EVs was demonstrated by Sony/Nissan and KERI/STC in 1996. At present, the performance of developed EV-cells was up to 115 Wh/kg and 286 W/kg of specific power at 80% DOD. We assume our EV cells to have 248 and 242 km driving distance per one charge with DST-120 mode and ECE-15 mode, respectively. Finally, we performed safety/abuse tests of developed lithium ion cell. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium batteries; Electric vehicle; Performance; Temperature; Safety

1. Introduction

Lithium ion batteries are expected to be used as a large scale energy storage devices for electric vehicles as well as for the electric power load leveling [1]. Lithium ion cells are now considered to be most promising cells to satisfy with mid-term goal of USABC [2].

Though commercial lithium ion cells are currently using various type of cathode materials such as $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$ and a substituted transition metal oxides as typically $LiNi_{1-x}Co_xO_2$. In these cathode materials, $LiCoO_2$ is most widely used because it can be synthesized with well developed crystal structure and it is relatively stable against thermal decomposition in charged state than nickel based materials. Though spinel $LiMn_2O_4$ is promising cathode materials have benefits of lower price for large quantitative batteries such as EVs and load leveling, it could not achieve enough cycle performance now.

In previous studies, we obtained up to 120 Wh/kg and 300 Wh/l with same C/LiCoO₂ system in prismatic cell configuration [3]. However, prismatic cell had poor cycle performance caused by electrodes that have no uniform

coating edges and dimensional stability during charge and discharge. We tried to improve uniformity of electrodes with automatic winding with cylindrical cell configuration for the purpose of improving cycle performance and mass productivity.

2. Experimental

2.1. Fabrication of EV cells

The mesophase carbon fiber (MPCF) was used as an anode active material. Because MPCF anode have high capacity, higher coulombic efficiency at first cycle, high degree of graphitization and large fraction of surface area for intercalation with the radial-like texture [4].

Table 1 General features of cylindrical EV cell

General features of cylindrical EV cen		
3.8		
$73\phi \times 445$		
1.86		
117		
434		
114		
233		
-20 to 40		

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Plate I. Developed 100 Ah class lithium ion cell and module.

Though the price of Co is high, $LiCoO_2$ was used as cathode active material for the reason of easy preparation of electrodes. The cathode mixtures were prepared with 87 wt.% $LiCoO_2$, 10 wt.% carbon as conducting agent and 3 wt.% polyvinylidene fluoride (PVDF) as binder. The anode mixtures were prepared with MPCF and 7 wt.% PVDF binder. The mixtures were coated on both side of aluminum and copper foils for cathode and anode, respectively. These electrodes were wound with porous polyporphylene separator. Lithium ion cells were obtained from electrolyte filling. We used organic electrolyte such as 1 M $LiPF_6$ in EC and DEC (1:1). Then the EV cells were characterized with various test conditions. General characteristics of cylindrical EV cells are described in Table 1. Cell and module are shown in Plate I.

2.2. Evaluation of EV cells

The performance of EV cells were evaluated with several test regimes. The constant current (USABC Procedure #2) discharge was carried out with C/3 rate to determine nominal capacity of fabricated cells. Peak power (#3) was tested to determine power capability at various state of

140 120 100 80 Specific Power(W/kg) 60 4020(-20 -40 -60 -80 100 200 300 400 0 Time(sec)

Fig. 1. Dynamic stress test profile for EV batteries proposed by USABC.

charge. The constant power (#4) test was carried out with various power level to determine the Ragone plot. The variable power with DST-120 (#5B) and ECE-15 modes shown at Figs. 1 and 2 were tested. Tests were performed at $23 \pm 0.5^{\circ}$ C. Finally, safety/abuse tests were carried out.

3. Results and discussion

3.1. Capacity

Fig. 3 shows the discharge capacity of fabricated EV cells was 117 A h when charged and discharged at C/3 rate. The average discharge voltage was 3.71 V and energy density was 114 Wh/kg. Typical temperature behavior during charge and discharge is shown in Fig. 4. The center of cell container had largest change of temperature. And cathode terminal indicated smallest temperature change.

3.2. Power capability

The dynamic resistance of EV cell was measured to estimate peak power capability at a given depth of discharge (DOD). A dynamic resistance is determined based



Fig. 2. ECE-15 power profile for the EUCAR reference vehicle.



Fig. 3. Typical voltage and current profiles of EV cell at C/3 rate.

on a measurement of $\Delta V/\Delta I$ between base current and a high test current step. The changes in voltage and current are measured from a point in time just before the beginning of a 30-s current pulse. The resulting resistance is calculated as:

$$R = \Delta V / \Delta I = (V_1 - V_2) / (I_1 - I_2)$$
(1)

Where V_1 , I_1 are measured value before applying high test current and V_2 , I_2 are measured values after 29-s from high test current was applied. From these measured dynamic resistance, the peak power can be calculated based on the battery peak power calculations of USABC. That is,

Peak Power Capability =
$$(-2/9)(V_{IR Free}^2)/R$$
 (2)

Peak Power Capability $\equiv -DVL(V_{IR Free} - DVL)/R$

where VIR Free is calculated by the measured point of Fig. 5 and Eq. (1), DVL means discharge voltage limit. Fig. 6 shows this calculated and measured peak power capabilities when discharged with 400 A for 30 s at every 10% of DOD state. We assumed the peak power capability could be higher than about 350 W/kg at 80% DOD state based



Fig. 4. Voltage and temperature profiles of EV cell at C/3 rate at 50th cycle.



Fig. 5. Dynamic resistance of EV cell with DOD. High test current was 190 A.



Fig. 6. Calculated and measured power density with DOD.

on calculated peak power. The measured peak power capability at 50% DOD was 300 W/kg. To simulate electric vehicle driving behavior including regenerative braking, variable power discharge testing was carried out on the basis of dynamic stress test of USABC and ECE-15 of EUCAR. Figs. 7 and 8 show the voltage and temperature profiles of EV cell during discharge with DST and



Fig. 7. Discharge voltage and temperature profile of EV cell with DST-120 mode.



Fig. 8. Discharge voltage and temperature profile of EV cell with ECE-15 mode.

ECE-15 modes respectively. Cell temperature was changed from 22.5 to 26.5°C and 22 to 27.5°C at each mode. The resultant driving range was expected up to 248 and 242 km with passenger car with 1000 kg include battery. USABC strongly recommend to report DST power profiles at 80% DOD. So the actual driving range could be approximately 200 and 194 km at each test mode for driving simulations.

3.3. Power to energy

Our target is shown in the Fig. 9 compared with various types of battery. Driving range per a charge is 300 km with average speed of vehicle between 40 and 60 km/h. Total



Fig. 10. Cycle performance of EV cell at C/3 rate with 80% DOD.

weight of car without passenger is less than 1200 kg and maximum speed is 120 km/h. The power density is plotted on the power to energy curve (Ragone plot). It had 105 Wh/kg energy density when 200 W/kg of constant power was applied. When 400 W/kg was applied, drained energy was less than 10 Wh/kg because current limit of test equipment was 500 A. So we could see poor power property at 400 W/kg constant power condition because of current limit of tester. Current EV cells were not so optimized too enough to reduce dead volume and weight of battery components. Further improvements should extend the driving range more than 300 km, concerned with its energy density. And power capability for maximum speed and acceleration is enough to satisfy the target.



Fig. 9. USABC and G7 goal of EV battery on Ragone plot.

Table 2 Results of safety and abuse tests

Test items	Test condition	Results
Over discharge	Discharge to 0 V	No fire, no vent
Drop impact	Drop from 1.9 m height	No fire, no vent
Crush	Crush with about 150 kN	No fire, no vent
Bending	Drop of mass at 61 cm height with $(25.4 \text{ mm}\phi)$ round bar	No fire, no vent
Intrusion	Spike with 5 mm nail	No fire, vent acts
Immersion	Dipping into water for 24 h	No fire, no vent

3.4. Cycle life

Cycle performance of EV cell is shown in Fig. 10. Approximately 80% discharged capacity was achieved when EV cell was charged to 4.1 V and discharged to 3.0 V. Though fabricated EV cell had good power capability and excellent temperature performance, cycle performance was not satisfied with the result of small consumer size test cell with same electrochemical system. In the case of small size, test cell showed 20% of capacity loss after 500 cycles. We think there might be several problems exist to produce wide and long electrodes for EV-size cell. Though the almost area of electrodes had uniform thickness, it was not clear and not easy to keep uniform coating thickness of edge of electrodes for the purpose of welding tap for current collecting. So we think there were different concentration of lithium ion near the edges of electrodes. That might give rise to local overcharge and overdischarge. Cycle performance is still important subject to archive our target for EV systems.

3.5. Safety / abuse test

Hazardous conditions may occur when electric vehicles drive. Because the long term target of performance of EV batteries is too high. The safety problem was in the shadow of battery performance. However, the safety feature may be the most important issue and hindrance to realize electric vehicle.

Safety and abuse test protocols of EV cell for electric vehicles are still under developing world widely. We also performed modified safety and abuse test method based on SBA guide line for safety evaluation on secondary lithium cells (SBA G1101). Table 2 shows the results for safety and abuse test of 100 Ah EV cell. All these tests were carried out in the anti-explosive chamber made of SUS and bulletproof glasses. Control room is apart from this safety facility.

When test cell was overdischarged to 0 V and kept for one day at 0 V. It seemed nothing was happened. For drop impact test, test cells were dropped various direction onto concrete bottom from 1.9 m height. There were no fire and no vent. The SBA guide line describes force to apply 13 kN to the battery for crush test. But in the case of EV cell, we thought 13 kN was too low. It was nearly found no deformation was occurred at 13 kN. So we increase this value up to 150 kN. For the bending test, even though we thought 9.1 kg and 61 cm was too low, bending test was performed without modification of SBA. This bending test condition should be also changed. Immersion of cell into water for a day showed no change and no hazardous accident.

Intrusion tests were carried out with fully charged fresh EV cell (100% SOC). The charged capacity of fresh cell was 130 A h. The safety vent was activated after the spike passing through the EV cell. There were no fire, but the fume cased by liquid electrolyte was spouted out from cell through safety vent. It occurred suddenly and immediately when the nail spike through the container of EV cell.

4. Conclusions

A total of 100 Ah lithium ion cells was fabricated and performance of EV cells evaluated under the USABC, SBA, EUCAR test procedures. The nominal capacity was 117 Ah at C/3 rate. Energy densities of 114 Wh/kg and 233 Wh/l were obtained. Specific power density was estimated at 286 W/kg at 80% DOD. Cycle life is still our important subject to improve battery performance. EV cells of this work were safe on tested items. The safety feature must be considered when cell components and design electrochemical system are decided.

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