전기자동차용 plastic Li-ion battery

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전기자동차용 **Plastic Li-ion** 전지 개발

한규남, 서현미, 김재경, 김용삼, 신동엽, 정복환, 임홍섭
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Abstract

Large plastic Li-ion (PLI) cells (25 to 28-Ah) were fabricated for an EV application. The 28-Ah cells showed high specific energy (160 Wh/kg), high specific power (526 W/kg), excellent round-trip energy efficiency (92%), and low self-discharge rate (6% in 30 days). A 25-Ah cell of an earlier design showed good cycle life of up to 750 cycles at 100% DOD to 80% of its initial capacity, while cycle life test of a 28-Ah cell of a later design is in progress. Preliminary safety tests were also carried out using 6-Ah cells of a similar electrode design giving very encouraging results for development of a safe high-energy density PLI battery for EV application.

Introduction

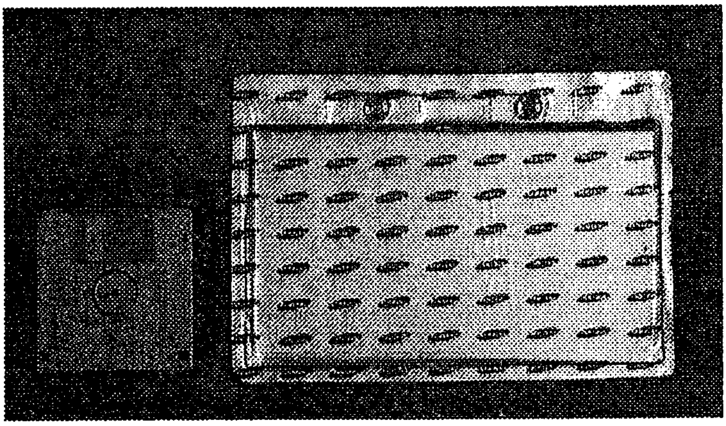
Development of a useful zero-emission electric vehicle (EV) has been desired in many metropolitan areas in order to reduce the air pollution problems since the major portion of the pollution is originated from automobile emissions. As it is well known that the main deterrent for the development of such a vehicle is the lack of availability of a high energy battery for long enough driving range to compete with an internal-combustion-engine vehicle. The objective of the present work is to develop a high specific energy battery for an EV application. Our main goals for the battery performaance in the present work were the specific energy over 150 Wh/kg, the specific power over 300 Wh/kg at 80% DOD, and cycle life greater 1,000 cycles at 80% DOD.

We have chosen a plastic Li-ion cell (1,2) as the base cell technology for the following reasons: (a) The highest specific energy has been demonstrated with the Li-ion chemistry among long cycle life ambient temperature batteries. (b) Its thin prismatic cell configuration might make its thermal management easier than a cylindrical cell. (c) Improved thermal management will enhance the safety of the battery.

Cell Fabrication and Test Procedures

The cathode and anode active materials were $LiCoO_2$ and a synthetic graphite material. The cathode and anode films were made of the respective active material, Super P carbon black conductive aid, the binder polymer of poly(vinylidene fluoride-co-hexafluoropropylene) copolymer (PVDF-HFP), and a plasticizer of dibutylphthalate (DBP). The separator was made of PVDF-HFP copolymer, silicate powder and DBP which was later removed by extraction. The electrolyte was a LiPF6 solution in ethylene carbonate (EC)-dimethyl carbonate (DMC)-ethylmethyl carbonate (EMC) base solvents. Cathodes (23.6 cm x 13.0 cm) were fabricated by laminating two cathode films containing 65 to 73% active material by weight with an expanded-metal aluminum current collector between the films. Anodes (24.0 cm x 13.3 cm) were also prepared by laminating two anode films containing 65% active material with an expanded-metal copper current collector between the films. The anode having a 73%-composition was prepared by a slightly modified process. Unit bi-cell laminates having a cathode/separator/anode/separator/cathode layer structure were fabricated by heat-laminating the component sheets together. The bi-cells were prepared by extracting DBP using either ether or methanol followed by drying, adding the electrolyte and packaging.

Both of 2-Ah bi-cell which contained 65% active material in the electrode film and 2.2-Ah bi-cell which contained 73% active material had dimensions of approximately 240mm x 133mm for the electrochemically active area. Nominal 25-Ah and 28-Ah cells were fabricated by stacking thirteen 2-Ah and 2.2-Ah bi-cells, respectively, in a package similar to one shown in Fig. 1. The dimensions of the 25-Ah and 28-Ah cells were 250mm x 150mm x 9.2mm and 250mm x 150mm x 8.7mm, respectively. These cells weighed on the average approximately 645 g for the 25-Ah cells and 685 g for the 28-Ah cells. 2-Ah test cells were made of a single 2-Ah bi-cell and 6-Ah test cells three 2-Ah bi-cells.



<Fig. 1. A picture of a 28-Ah cell>

Standard capacity tests were carried out as follows: At 25°C, cells were charged at C/3 rate to 4.2V followed by additional charging at constant voltage at 4.2V to the current cut-off at C/20 rate. They were discharged at C/3 rate to 2.8V. The energy efficiency value was calculated from total energy for discharge to 2.8V divided by the total energy for charging for the third cycle of three standard capacity measurements. Average discharge voltage value was calculated from total energy for discharge to 2.8V (Wh) divided by the total charge (Ah). For the discharge rate capability test, fully charged cells using the standard method as described above were discharged at various rates to 2.8V. Temperature effect on discharge capacity was evaluated by charging fully discharged cells using the standard charge regime at 25°C followed by soaking them at the respective test temperature for a minimum of 3hrs and then discharging them at C/3 rate to 2.8V. Cycle life tests for 100%-depth of discharge (DOD) cycles were carried out by charging and discharging cell at C/3 rate between voltage limits of 4.2 and 2.8V at ambient temperature of 23 to 24°C. Cycle life tests for 80%-DOD cycles were carried out also at ambient temperature by charging and discharging cell at C/3 rate but discharging the cell only to 80% DOD for each cycle. Capacity measurements during the life test were carried out once after every 50 cycles by full discharge to 2.8V instead of 80% DOD.

Specific power tests were carried out at the ambient temperature as follows: The test cell was charged at C/3 rate to 4.2V followed by additional charging at constant voltage at 4.2V to the current cut-off at C/20 rate and then open circuited for 60 min. The cell was discharged at the baseline current (I_1) of C/3 for 30 seconds prior to starting the power capability measurement by applying high-rate discharge current (I_2) of 3C rate. The cell was discharged at 3C rate for 30 seconds followed by an open circuit period of 1 min. The discharge voltage (V_1) prior to the application of the high-rate discharge current, the voltage (V_2) at the end of the high rate discharge and open circuit voltage (V_{oc}) were recorded for calculation of the peak power. Then, the cell was discharged at C/3 rate to its 90% state of charge (SOC) (or 10% DOD). The last three steps of 3C rate discharge, open circuit period and C/3 rate discharge were repeated for subsequent 10% DOD steps to the final 90% DOD or 10% SOC state. The peak power at each SOC was calculated by equations [1] and [2] using the measured voltage and the discharge current values (3).

$$P_{peak} = 2/9\ V_{oc}^2/R \qquad [1]$$

$$\text{Where } R = (V_1 - V_2) / (I_2 - I_1) \qquad [2]$$

Self-discharge rates were evaluated by measuring the retained capacity by C/3 rate discharge after open circuit storage of a fully charged cell for 30 days at the ambient temperature.

Safety tests were carried out using conventional safety test procedures and the equipment at the Korea Electrotechnology Research Institute which is fully equipped for the battery safety tests. Samples for each test category included five samples of 6-Ah cells which contained three 2-Ah bi-cells.

Cell Performance

A typical charge voltage curve of a 28-Ah cell at ambient temperature is shown in Fig. 2. Discharge voltage curves of a 28-Ah cell at C/3, C/2, 1C, and 2C rates are shown in Fig. 3. The average discharge voltages at these rates are 3.66, 3.60, 3.50, and 3.36V, respectively. The cell had high discharge rate capability showing the capacity value at 2C rate over 95% of the value at C/3 rate.

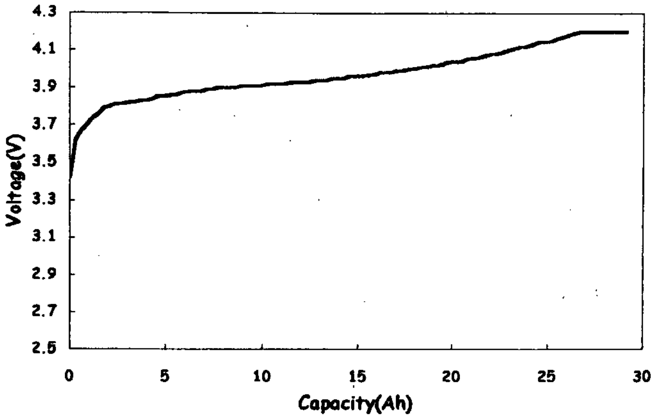


Fig. 2. A typical charge voltage curve of a 28-Ah cell at C/3 rate at ambient temperature.

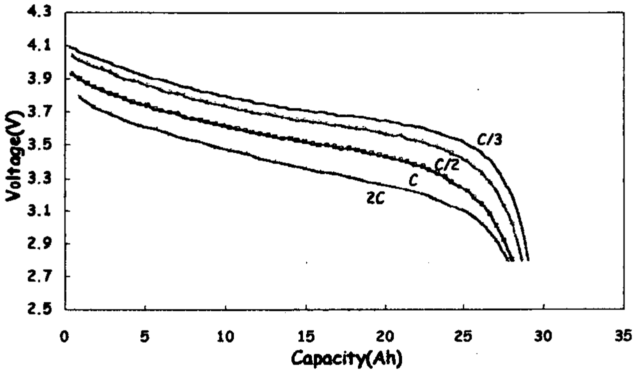


Fig. 3. Discharge voltage curves of a 28-Ah cell at C/3, C/2, 1C, and 2C rates at ambient temperature.

Typical discharge voltage curves of the 28-Ah cells at various temperatures (60, 25, 0, -10, and -20 °C) are shown in Fig. 4. These cells show good capacity values both at high and low temperatures. The values were over 95% at 60 °C and over 60% at -20 °C of that at the ambient temperature. Cell voltage curves for the specific power measurements are shown in Fig. 5. Specific power and cell internal resistance of an early 25-Ah cell, an improved 25-Ah cell, and a 28-Ah cell are shown in Fig. 6. Overall performance data of the 28-Ah and 25-Ah cells are summarized and compared each other in Table 1. The 28-Ah design showed significantly higher specific energy and energy density and significantly lower self-discharge rate than the 25-Ah design.

However, the 25-Ah design is superior to the 28-Ah design in low-temperature performance, specific power and energy efficiency. It is mainly due to the fact that the internal resistance of the 25-Ah cell is lower than that of the 28-Ah cell, especially, when as the cell is discharged more than a half of the capacity as shown in Fig. 6. This difference in the resistance might be due to reduced amount of the electrolyte in the 28-Ah cell because of reduced pore volume in the electrode due to more compact electrode design compared with the 25-Ah cell.

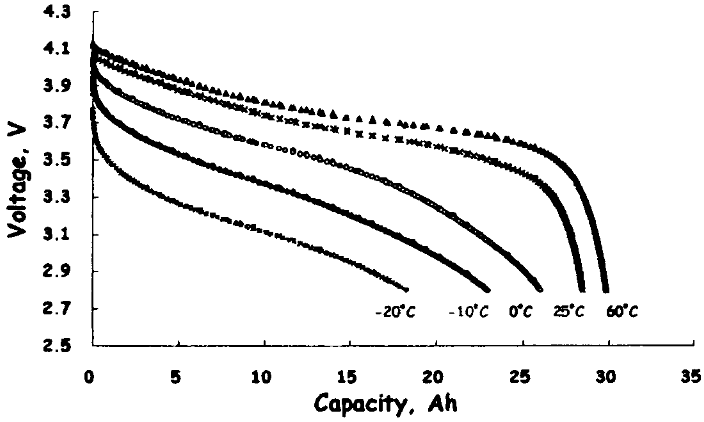


Fig. 4. Discharge voltage curve of a 28-Ah cell at C/3 rate at various temperatures of 25, 60, 0, -10, and -20 °C.

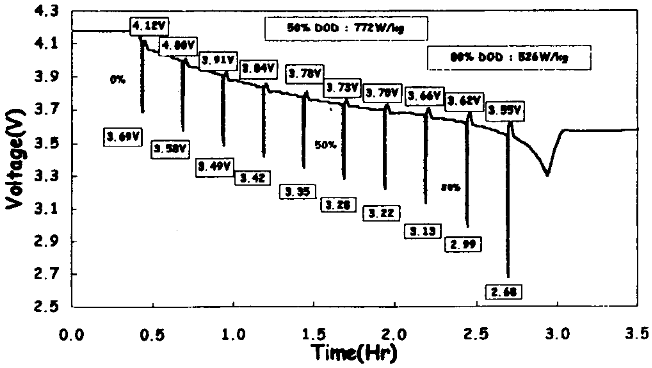


Fig. 5. Cell voltage curves for specific power measurements of a 28-Ah cell at ambient temperature.

Table 1. Overall performance data of the 28-Ah and 25-Ah cells

	25-Ah Cell		28-Ah Cell		US DOE Goal*
Relative Capacity, % (Ah)					
at C/3; 25 °C,	100	(25.0)	100	(29.8)	
at C/3; 60 °C	98.0	(24.5)	95.2	(28.4)	
at C/3; 0 °C	95.7	(24.0)	87.2	(26.0)	
at C/3; -10 °C	-	-	76.8	(22.9)	
at C/3; -20 °C	71.6	(17.9)	61.1	(18.2)	
at C/2; 25 °C	99.6	(25.1)	99.6	(28.6)	
at 1C; 25 °C	98.4	(24.8)	96.9	(28.0)	
at 2C; 25 °C	91.3	(21.5)	95.6	(27.7)	
Energy Efficiency, %	94		92		80
Specific Energy, Wh/kg	141		160		135
Energy Density, Wh/l	262		336		195
Sp. Power @80% DOD, W/kg	658		526		300
Self Discharge in 30 days, %	15		6		<15% in 48h
Cyc. Life @80% DOD, Cell A	ca. 690 cycles		-		1000
Cell B**	90%@400 cycles		-		1000
Cell C**			94% @100 cycle		1000
Cyc. Life @100% DOD**	79% @ 766 cycles		-		

* US DOE target values for the year 2000 for a Li-polymer battery (3).

** % capacity retained after cycling.

Cycle life performance at 100% DOD at ambient temperature is shown in Fig. 7 for two 2-Ah cells and a 25-Ah cell of earlier fabrication. The two 2-Ah cells retained 89% of its initial capacity after 862 cycles and 85% after 645 cycles, respectively. The 25-Ah cell retained 79% after 766 cycles. The performance at 80% DOD at ambient temperature is shown in Fig. 8 for two 25-Ah cells and a 28-Ah cell. The two 25-Ah cells, A and B, retained 80% after 690 cycles and 90% of the capacity after 400 cycles, respectively. The performance of the cell, A, was inferior to others by an unknown reason. The 28-Ah cell, C, retained 94% after 100 cycles in a continued test. These performance, overall, are very encouraging for meeting our long-term goal performance of 1000 cycles at 80% DOD.

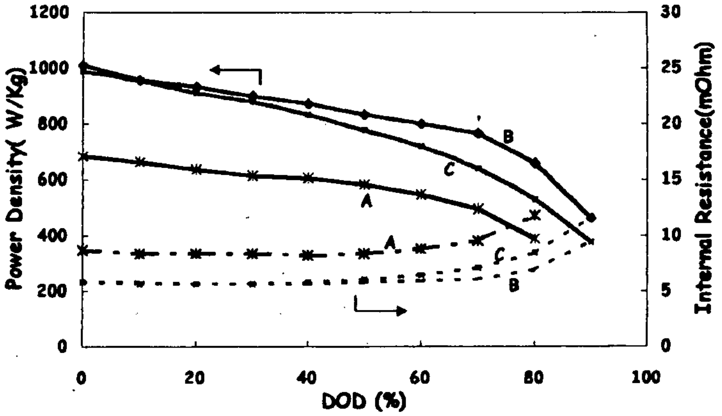


Fig. 6. Specific power and internal resistance at ambient temperature of an early 25-Ah cell (A), an improved 25-Ah cell (B), and an improved energy 28-Ah cell (C).

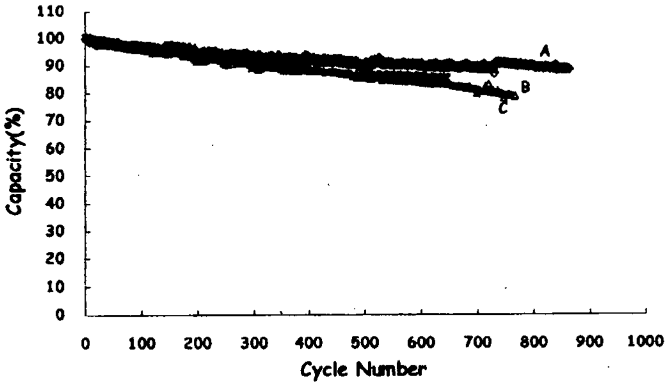


Fig. 7. Cycle life performance of two 2-Ah cells (A and B) and a 25-Ah cell (C) at 100% depth of discharge at ambient temperature.

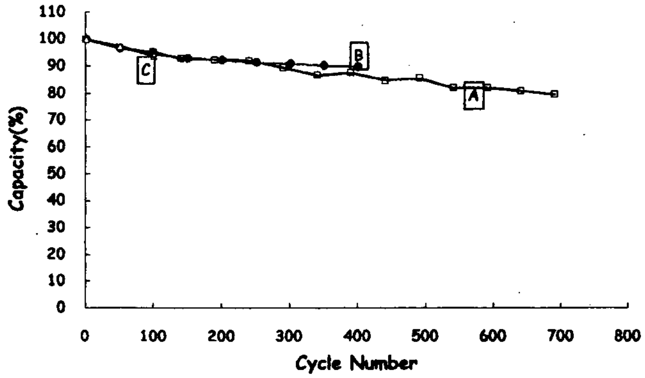


Fig. 8. Cycle life performance of two 25-Ah cells (A and B) and 28-Ah cell (C) at 80% depth of discharge at ambient temperature.

Safety Test

Preliminary safety tests were carried out using 6-Ah cells which did not have any cell protection devices such as positive temperature coefficient (PTC) current breakers. The safety tests included, (1) external short-circuit, (2) overcharge, and (3) high current charge tests for electrical abuses, (4) impact, (5) nail penetration and (6) crush tests for mechanical abuses, and (7) heating test for the environmental abuse. The external short-circuit tests were carried out by shorting the fully charged cell through a conducting wire of less than 5 mΩ in resistance. The overcharge tests included charging of a fully discharged cell at 1C rate for up to 2.5 hours. The high current charge tests included charging of a fully discharged cell at 4.5C rate to its 100% SOC by the rated capacity. The impact tests were carried out by dropping a weight of 9.1kg from the height of 61cm onto a 0.79-cm diameter steel bar which was placed on a fully charged test cell. The nail penetration test included penetration of 0.5-cm diameter nail through the middle of a fully charged test cell perpendicular to the electrode surface and then observing the results for 6 hours or longer. The crush test included squeezing a fully charged test cell between two parallel steel plates at the force of 13kN. The heating tests were carried out by heating a fully charged test cell at the rate of 5±2 °C/min to 130 °C and then keeping the cell at the temperature for 60 min.

All tests passed requirements without a problem with exceptions of the overcharge test. All five cells for the overcharge test ended up with swollen pouch eventually bursting into flame at the overcharging point between 105 and 150% of the cell capacity.

The results were expected from similar tests of other Li-ion cells without a current breaker device such as a PTC device. Present cells are expected to pass the tests when a PTC device is attached to the cell. Although all cells passed the requirements for the high current charge tests (at 4.5C), one out of five cells released gas without a flame and the cell was heated over 150 °C while the other cells stayed below 100 °C. The 4.5C rate of charging of this test might have been close to or a little higher than the upper limit for safe operation of the cells.

Concluding Remarks

High specific energy (160 Wh/kg), high specific power (526 W/kg at 80% DOD), excellent round-trip energy efficiency (92%), and low self-discharge rate (6% in 30 days) have been demonstrated with a 28-Ah PLI cell for EV application. A 25-Ah cell of an earlier design showed good cycle life of up to 750 cycles at 100% DOD to 80% of its initial capacity, while cycle life test of a 28-Ah cell is in progress showing good performance after 100 cycles. Results of preliminary safety tests using 6-Ah cells gave very encouraging results for development of a safe high-energy density PLI battery for EV application.

Acknowledgement

We would like to acknowledge joint financial support of this work by Korea Automotive Technology Institute through a G7 project and Samsung SDI Company.

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