ELSEVIER

Journal of Power Sources 101 (2001) 196–200

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Development of a plastic Li-ion battery cell for EV applications

K.N. Han[a,*], H.M. Seo[a], J.K. Kim[a], Y.S. Kim[a], D.Y. Shin[a],
B.H. Jung[a], H.S. Lim[a], S.W. Eom[b], S.I. Moon[b]

[a]*Energy LAB, Samsung SDI Co. Ltd., San 24-1 Sungsung-Dong, Chonan City, Chungchongnam-Do 330-300, South Korea*
[b]*Korea Electrotechnology Research Institute, Changwan City, Khungsangnam-Do, South Korea*

Received 28 November 2000; accepted 31 January 2001

Abstract

Large plastic Li-ion (PLI) cells (25–28 Ah) have been fabricated for electric vehicle (EV) applications. The 28 Ah cells show high specific energy (160 Wh/kg), high specific power (526 W/kg), excellent round-trip energy efficiency (92%), and a low self-discharge rate (6% in 30 days). A 25 Ah cell of an earlier design has a good cycle-life of up to 750 cycles at 100% depth-of-discharge (DOD) to 80% of its initial capacity. Cycle-life tests of a 28 Ah cell of a later design is in progress. Preliminary safety tests have also been carried out using 6 Ah cells of a similar electrode design. These give very encouraging results for the development of a safe, high-energy PLI battery for EV duty.

Keywords: Li-ion; Plastic Li-ion; EV battery; Safety test

1. Introduction

Development of a useful zero-emission electric vehicle (EV) is desirable for many metropolitan areas in order to reduce air-pollution problems, since the major portion of this pollution originates 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 which will provide a driving range that is competitive with that of an internal combustion engine vehicle. The objective of the present work is to develop such a battery. The main performance goals in the present work are specific energy over 150 Wh/kg, specific power over 300 Wh/kg at 80% depth-of-discharge (DOD), and a cycle-life of greater than 1000 cycles at 80% DOD.

We have chosen a plastic Li-ion cell [1,2] as the base cell technology for the following reasons: (i) the highest specific energy has been demonstrated with the Li-ion chemistry among long cycle-life, ambient-temperature batteries; (ii) the thin prismatic cell configuration is expected to make thermal management easier than with a cylindrical cell; (iii) improved thermal management will enhance the safety of the battery.

2. Cell fabrication and test procedures

The cathode and anode active materials were $LiCoO_2$ and synthetic graphite material, respectively. These materials were fabricated into thin films with Super P carbon black, a binder of poly(vinylidene flouride-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 $LiPF_6$ solution in ethylene carbonate (EC)–dimethyl carbonate (DMC)–ethylmethyl carbonate (EMC) base solvents. The cathodes (23.6 cm × 13.0 cm) were fabricated by laminating two cathode films containing 65–73% active material by weight with an expanded-metal aluminum current-collector between the films. The anodes (24.0 cm × 13.3 cm) were also prepared by laminating two films containing 65% active material with an expanded-metal copper current-collector between the films. An anode of 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.

A 2 Ah bi-cell which contained 65% active material in the electrode film and a 2.2 Ah bi-cell which contained 73%

---

[*] Corresponding author. Tel.: +82-41-560-3760; fax: +82-41-560-3789.
E-mail address: honglim@samsung.com (K.N. Han).

0378-7753/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0378-7753(01)00672-3

Fig. 1. The 28 Ah cell.

active material had dimensions of approximately 240 mm × 133 mm for the electrochemically active area. Nominal 25 and 28 Ah cells were fabricated by stacking 13 bi-cells of 2 and 2.2 Ah, respectively, in a package similar to that shown in Fig. 1. The dimensions of the 25 and 28 Ah cells were 250 mm × 150 mm × 9.2 mm and 250 mm × 150 mm × 8.7 mm, respectively. These cells, on average, weighed approximately 645 g for the 25 Ah cells and 685 g for the 28 Ah cells. The 2 Ah test cells were composed of a single 2 Ah bi-cell and the 6 Ah test cells of three 2 Ah bi-cells.

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

Specific power tests were undertaken at the ambient temperature as follows. The test cell was charged at the *C*/3 rate to 4.2 V, followed by additional charging at this voltage to a current cut-off at the *C*/20 rate, and then held at open-circuit for 60 min. The cell was discharged at a baseline current (I_1) of *C*/3 for 30 s prior to starting the power capability measurements by applying a high-rate discharge current (I_2) at the 3*C* rate. The cell was discharged at this rate for 30 s, 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. The cell was then discharged at the *C*/3 rate to 90% state-of-charge (SOC) (or 10% DOD). The last three steps of the 3*C*-rate discharge, the open-circuit period, and the *C*/3-rate discharge were repeated for subsequent 10% DOD steps to a final 90% DOD (or 10% SOC) state. The peak power at each SOC was calculated from Eqs. (1) and (2) using the measured voltage and the discharge current values [3,4], i.e.

$$P_{\text{peak}} = \frac{2}{9}\frac{V_{oc}^2}{R} \tag{1}$$

where

$$R = \frac{V_1 - V_2}{I_2 - I_1} \tag{2}$$

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

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

3. Cell performance

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

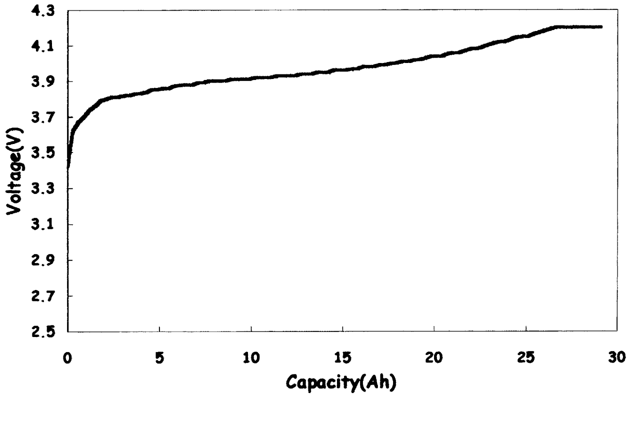

Fig. 2. Typical charge voltage curve of 28 Ah cell at *C*/3 rate at ambient temperature.

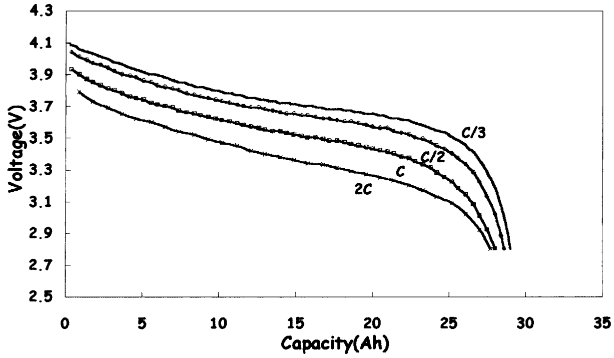

Fig. 3. Discharge voltage curves of a 28 Ah cell at *C*/3, *C*/2, 1*C*, and 2*C* rates at ambient temperature.

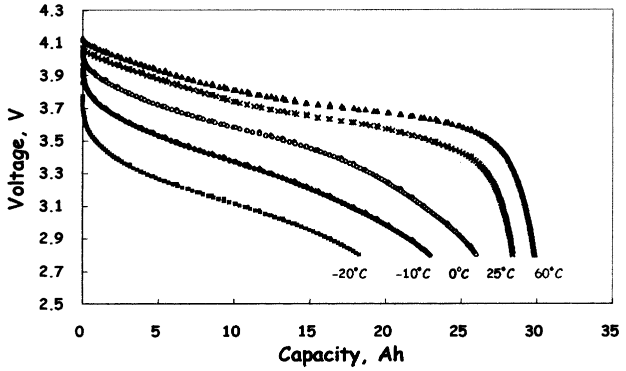

Fig. 4. Discharge voltage curve of 28 Ah cell at *C*/3 rate at various temperatures, 25, 60, 0, −10, and −20°C.

Typical discharge voltage curves for 28 Ah cells at various temperatures (60, 25, 0, −10, and −20°C) are shown in Fig. 4. These cells display good capacity values at both high and low temperatures. The values are 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 presented in Fig. 5. The specific power and the cell internal resistance of an early 25 Ah cell, an improved 25 Ah cell, and a 28 Ah cell are shown in Fig. 6. The overall performance data of the cells are summarized and compared in Table 1. The 28 Ah design has significantly higher specific energy and energy density, and a significantly lower self-discharge rate than the 25 Ah design.

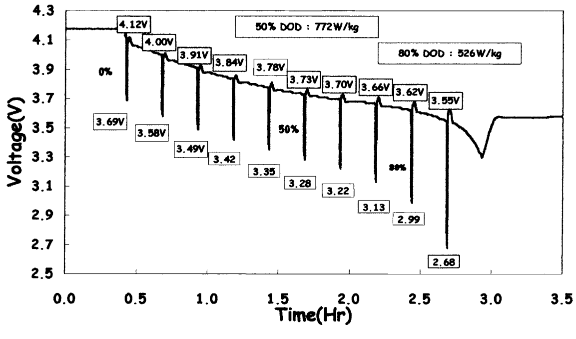

Fig. 5. Cell voltage curves for specific power measurements of 28 Ah cell at ambient temperature.

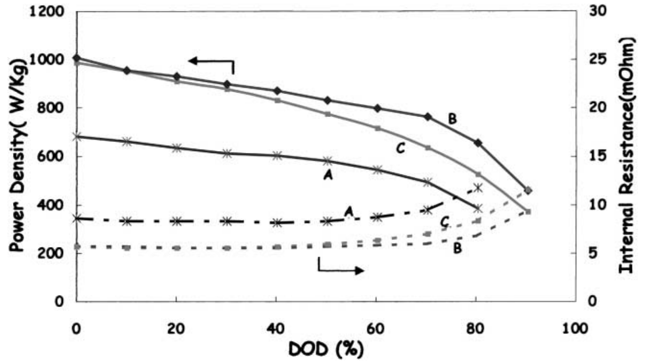

Fig. 6. Specific power and internal resistance at ambient temperature of: (A) early 25 Ah cell; (B) improved 25 Ah cell; (C) improved energy 28 Ah cell.

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.

The 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. One of the 2 Ah cells retained 89% of its initial capacity after 862 cycles, the other 85% after 645 cycles. 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% capacity after 690 cycles and 90% after 400 cycles, respectively. To date, the cause of the inferior performance of cell A is not known. The 28 Ah cell C retained 94% capacity after 100 cycles. These results are very encouraging for meeting long-term performance goals of 1000 cycles at 80% DOD.

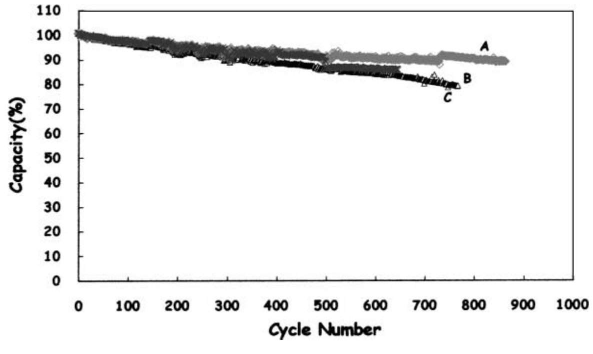

Fig. 7. Cycle-life of two 2 Ah cells (A and B) and 25 Ah cell (C) at 100% DOD at ambient temperature.

Table 1
Overall performance data of 25 and 28 Ah cells

	25 Ah cell	28 Ah cell	US DOE goal[a]
Relative capacity under various experimental conditions (%)			
$C/3$, 25°C	100 (25.0)	100 (29.8)	
$C/3$, 60°C	98.0 (24.5)	95.2 (28.4)	
$C/3$, 0°C	95.7 (24.0)	87.2 (26.0)	
$C/3$, −10°C	–	76.8 (22.9)	
$C/3$, −20°C	71.6 (17.9)	61.1 (18.2)	
$C/2$, 25°C	99.6 (25.1)	99.6 (28.6)	
$1C$, 25°C	98.4 (24.8)	96.9 (28.0)	
$2C$, 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
Specific power at 80% DOD (W/kg)	658	526	300
Self-discharge in 30 days (%)	15	6	<15[b]
Cycle-life at 80% DOD			
Cell A	690	–	1000
Cell B (after 400 cycles)	90%	–	1000
Cell C (after 100 cycles)		94%	1000
Cycle-life at 100% DOD (after 766 cycles)	79%	–	

[a] US DOE target values for the year 2000 for a Li-polymer battery [3–5].
[b] In 48 h.

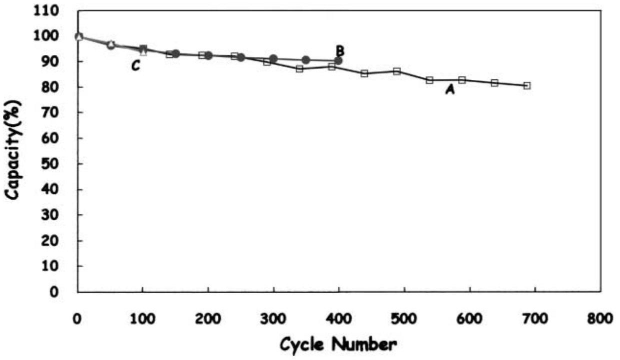

Fig. 8. Cycle-life of two 25 Ah cells (A and B) and 28 Ah cell (C) at 80% DOD at ambient temperature.

4. Safety tests

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: (i) external short-circuit, overcharge, and high-current charge tests for electrical abuses; (ii) impact, nail penetration, and crush tests for mechanical abuses; (iii) heating tests for environmental abuse. The external short-circuit tests were performed by shorting the fully charged cell through a conducting wire of less than 5 mΩ in resistance. The overcharge tests included charging a fully discharged cell at the $1C$ rate for up to 2.5 h. The high-current charge tests included charging a fully discharged cell at the $4.5C$ rate to 100% SOC. The impact tests involved dropping a weight of 9.1 kg from a height of 61 cm on to a 0.79 cm diameter steel bar which was placed on a fully charged test cell. The nail penetration test comprised penetration of a 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 h or longer. The crush test involved squeezing a fully charged test cell between two parallel steel plates at a force of 13 kN. The heating tests were performed by heating fully charged test cell at a rate of 5 ± 2°C/min to 130°C, and then keeping the cell at that temperature for 60 min.

The cells passed all the tests except for the overcharge test. Under the overcharge test, all five cells became swollen and eventually burst into flames at an overcharging point between 105 and 150% of the cell capacity. These results were expected from those of similar tests on other Li-ion cells without current breaker devices such as a PTC device. The present cells are expected to pass the tests when a PTC device is attached to each cell. Although, all the cells passed the requirements for the high-current charge tests (at $4.5C$), one of the five cells released gas without a flame and the temperature rose above 150°C while that of the other cells stayed below 100°C. The $4.5C$ rate of charging used in this test may be close to, or a little higher than, the upper limit for safe operation of the cells.

5. 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 applications. A 25 Ah cell of an earlier design showed a good cycle-life of up to 750 cycles at 100% DOD to 80% of its initial capacity. Cycle-life tests of a 28 Ah cell are still in progress and show good performance after 100 cycles. Preliminary safety tests using 6 Ah cells have given very encouraging results for the development of a safe, high-energy density, PLI battery for EV applications.

Acknowledgements

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

References

[1] F.K. Shokoohi, et al., in: Proceedings of the 37th Power Sources Conference on Bellcore's Plastic Lithium-Ion Battery, Cherry Hill, NJ, 17–20 June 1996.

[2] C. Schmutz, et al., in: S. Megahed, B.M. Barnett, L. Xie (Eds.), Proceedings of the Electrochemical Society on a New Rechargeable Plastic Li-Ion Battery, Pennington, NJ, Vol. 28, 1994, p. 330.

[3] USABC Electric Vehicle Battery Test Procedures Manual, Revision 2, Vol. 26 Part A, January 1996, Procedure #3 Peak Power Test.

[4] SAE Publication, SAE, J1798 issued in January 1997.

[5] R.A. Sutula, et al., Electric and hybrid vehicle energy storage R&D programs for the US Department of Energy, in: Proceedings of the 16th International Electric Vehicle Symposium, Beijing, China, 12–16 October 1999.