Mechanism of gas build-up in a Li-ion cell at elevated temperature

Kyoung Hee Lee[1], Eui Hwan Song, Jin Young Lee, Bok Hwan Jung, Hong S. Lim[*]

Corporate R&D Center, Samsung SDI Co., Ltd., Giheung 449-902, South Korea

Abstract

A study has been made of the swelling behaviour at 90 °C, due to gas evolution, of pouch-type Li-ion cells that contain $LiCoO_2$ (LCO) or $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (LNMCO) as the cathode and an artificial-graphite material as the anode. Swelling of the LCO cell is dominated by the reaction at the cathode at cell voltages above 4 V, but is dominated by the reaction at the anode below 4 V. Results of gas composition analyses and the voltage dependence of the swelling indicate that the swelling in the charged state might be due to oxidation of the electrolyte at the cathode, and that in the discharged state to reduction of the electrolyte at the anode by lithium from the lithiated graphite. By contrast, swelling of LNMCO-cathode cells, may be dominated by the cathode at cell voltages above 3.2 V since swelling of the LNMCO-cathode is far greater than that of the anode, even in the low-voltage region.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Lithium-ion cell; Swelling; Gas evolution; Lithium cobalt oxide; Electrolyte oxidation

1. Introduction

Swelling of the prismatic or pouch-type cell packaging of a Li-ion cell by gas evolution at elevated temperatures (85–90 °C) has been brought to our attention since such swelling deforms the packaging and might even damage the device or equipment that is powered by this type of cell [1–3].

Although it is important to understand the mechanism of such gas evolution and control the swelling behaviour, available related information is sparse. Understanding the effects of the cathode material and high-voltage charging (above 4.2 V) will be particularly important since there have been intensive efforts to develop cathode materials with high specific energy [4]. As a part of such efforts, many Ni-base lithium intercalation compounds have been studied extensively [4–7] to take advantage of the fact that their specific energy is higher than that of $LiCoO_2$, as well as to seek the possibility of charging them at a higher voltage than 4.2 V to increase the useable specific energy [8–11].

In the present paper, the swelling behaviour at 90 °C of pouch-type cells, which contain $LiCoO_2$ (LCO) or a Ni-base compound $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (LNMCO) as the cathode

material is studied, in order to obtain a better understanding of the gas evolution mechanism and the factors that affect it.

2. Experimental

The Li-ion test cells had a nominal capacity of 780 or 800 mA h and were of the pouch design. The cells employed LCO or LNMCO as the cathode active material. Artificial-graphite material served as the anode and 1.3 M $LiPF_6$ in organic carbonate solution as the electrolyte. All test cells were packaged in a sealed pouch of aluminium-polymer laminated foil. The swelling test was performed by storing test cells at various states-of-charge (SoCs) at 90 °C for 4 h in an air oven. The degree of swelling is reported as the swollen pouch thickness as a percentage of the initial value. The measurements were made at the maximum thickness position, i.e., usually the centre of the broad face of the cell. Swelling of electrode-only pouches was also measured by a similar technique.

The fully charged state (100% SoC) was obtained by charging a fully discharged cell at the 0.5C rate to 4.2 V, followed by additional constant voltage charging for total time of 2.5 h. The fully discharged state (0% SoC) was obtained by discharging a fully charged cell at the 0.5C rate to 2.75 V. An intermediate SoC was obtained by discharging the fully charged cell at the 0.5C rate for a calculated period of time to the desired SoC. In order to determine

---

the individual contributions of the cathode and anode to the swelling individual electrodes were removed from a test cell at a given value of SoC. The electrode-only pouches were prepared by hermetically sealing each electrode in a pouch bag without washing or drying. The size of the pouch packaging was approximately the same as that of the original cell. Pouches containing only an individual cathode or anode were subjected to a swelling test in a manner similar to that described above for full Li-ion cells. The degree of swelling was calculated with respect to the thickness of the original cell rather than to the initial electrode pouch so that the swelling of electrode pouches and cells can be compared directly. Electrode potential is reported as a 'voltage' since it refers to the cell open-circuit voltage prior to disassembly of the test cell.

Chemical analyses of gases were performed by means of a Agilent Model 6890 gas chromatography. Linear sweep voltammetry was conducted on a coin-type cell, which comprised the sample cathode and a Li–metal counter/reference electrode, and used a CHI Model 700A Potentiostat at a scan rate of $10\,\mathrm{mV\,s^{-1}}$.

3. Results and discussion

The swelling test of a 780 mA h LCO-cathode cell was carried out over the full range of SoC (0–100%). Swelling values are plotted against the SoC and the open-circuit voltage of the cell is shown in Fig. 1. The swelling is constant at approximately $9 \pm 1\%$ of the initial thickness for SoCs between 0 and about 80% and for open-circuit voltages between 3.2 and 4 V, but increases sharply above 80% SoC or 4 V. The swelling approaches 40% at 100% SoC.

Similar swelling tests to those reported in Fig. 1 were also performed using pouches containing only a cathode or an anode. The swelling values for the individual cathodes and anodes are plotted against SoCs (Fig. 2) and cell voltages (Fig. 3). The LCO-cathode pouch exhibits little swelling below 80% SoC or 4 V, but the swelling increases sharply as the SoC is increased to over 80% or the voltage to above 4 V. This indicates that these two values are threshold values for the gas evolution reaction. By contrast, the swelling of the anode pouch is substantial (an average value of 14%) below 80% SoC, but becomes almost negligible above this value of the SoC, as shown in Fig. 2. These results suggest strongly that swelling above 80% SoC or 4 V is entirely due to a reaction at the cathode, while that below 80% SoC is entirely due to one at the node. The reaction at the cathode must be an oxidation reaction of the electrolyte since its rate increases as the potential becomes less negative. The reaction at the anode is likely to be an electrochemical reduction or a chemical reaction of the electrolyte with lithium from the anode.

The sum of the swelling values of LCO-cathode and anode pouches at various SoCs is compared with those of a full Li-ion cell containing these electrodes (Fig. 4) in order to
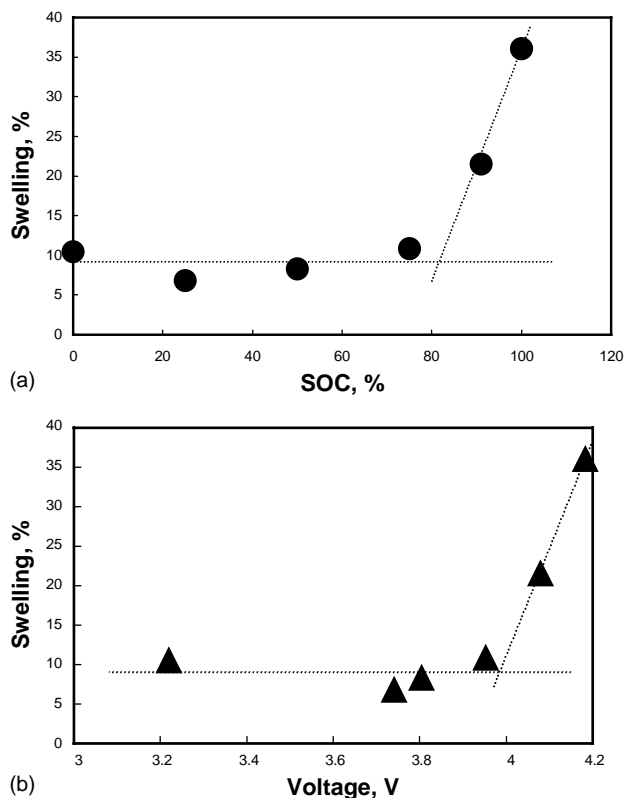

Fig. 1. Plots of swelling values of 780 mA h LCO-cathode Li-ion cells, against (a) SoC and (b) cell open-circuit voltage.

ascertain if a direct comparison of the swelling of the electrode pouches against that of the cell is valid or not. Given the uncertain error in the swelling measurements, the sum of the swelling values of the electrode pouches are in reasonable agreement with those of the cell. This finding indicates that the swelling value of the individual electrode pouches is a valid indication of their contributions to the swelling of cells.

Gas samples from the pouches containing a fully charged cathode or a fully discharged anode after the 90 °C-swelling test were analysed, as shown in Table 1, in order to gain an understanding of the gas evolution reactions that are the main reasons for cell swelling. The gas composition of a
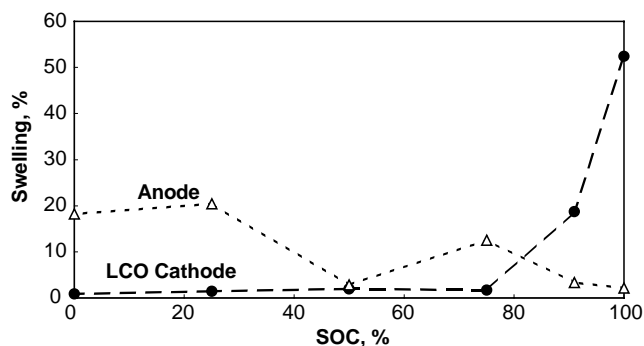

Fig. 2. Swelling of LCO-cathode and anode pouches after 90 °C-storage test at various SoCs.
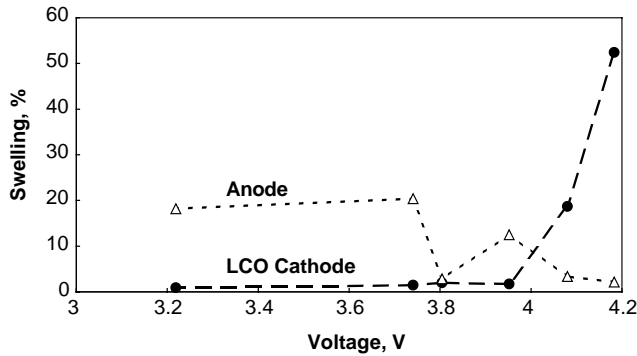
Fig. 3. Swelling of LCO-cathode and anode pouches after 90 °C-storage test at various cell open-circuit voltages.
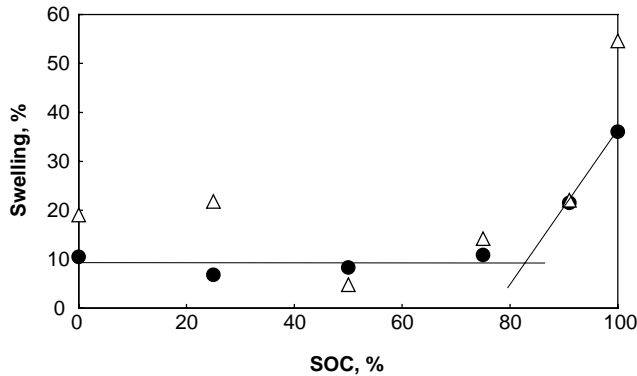

Fig. 4. Comparison of sum of swelling values of LCO-cathode and anode pouches with swelling of a cell; filled circles for cell and open triangles for sum of anode and cathode pouches.

Li-ion cell in a fully charged state should be similar to that of the cathode pouch since the gas evolution reaction should be entirely due to the reaction at the cathode. By contrast, the gas composition in a fully discharged state should be similar to that of the anode pouch. It also appears to be reasonable to assume that the gas composition for the charged cell above 80% SoC may be roughly the same as that of the cathode pouch whereas the composition below 80% SoC should be the same as that of the anode pouch. Since the main gas composition in the charged state is CO_2, the swelling above 4 V (or 80% SoC) might be due to oxidation of the electrolyte at the LCO-cathode, as suggested earlier [12,13], while the swelling below 4 V (or 80% SoC) might be due to a reduction of the electrolyte at the lithiated anode [14]. Evolution of CO gas might occur only at elevated temperature (90 °C) since

Table 1
Analysis of gases (%) from pouches containing the cathode at 100% SoC and the anode at 0% SoC after swelling test (90 °C; 4 h)

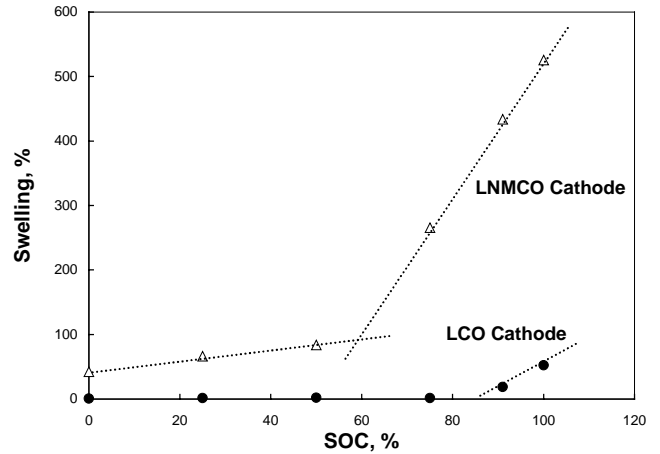| Gas component	Cathode pouch	Anode pouch
CO_2	75.1	18.7
CO	22.8	66.7
C_2H_4	2.1	7.9
CH_4	–	6.1
H_2	–	0.6

Fig. 5. Comparison of swelling of cathode-only pouch containing LNMCO-cathode material with that of LCO-cathode after 90 °C, 4 h storage test as function of SoC.

its presence was not reported at room temperature during reduction of the electrolyte [14]. A detailed mechanism of the gas evolution is not understood well, especially with respect to the low-swelling of the anode pouch in a fully charged state.

The threshold voltage of approximately 4 V for the swelling of the LCO-cathode (Figs. 1(b) and 3) appears to be related to the threshold voltage of about 3.9 V for capacity fading on storage, and is also similar to the threshold value of charge cut-off voltage for capacity fading on cycling [15]. Since these voltage values match well with one another, the gas evolution reaction during the swelling test may be similar to that of capacity fading. In other words, the reaction above 3.9–4 V is predominantly an oxidation reaction at the cathode [15], whereas that below 3.9–4 V is mainly a reduction reaction at the anode [12].

3.1. Effect of cathode material

The swelling behaviour of a LNMCO-cathode pouch is quite different quantitatively from that of a LCO-cathode,
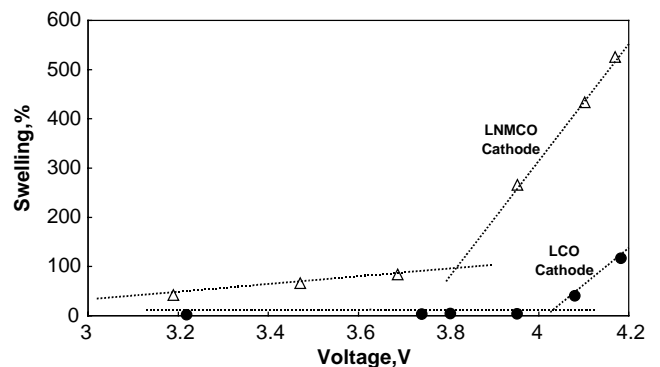

Fig. 6. Comparison of swelling of cathode-only pouch containing LNMCO-cathode with that of LCO after 90 °C, 4 h storage test as function of electrode potential.

as shown in Figs. 5 and 6. Although both cathodes display a low-swelling SoC or voltage region with a threshold above which swelling increases sharply with further increase in SoC, an SoC-independent swelling region is not found with the LNMCO-cathode pouch. The swelling of the LNMCO-cathode pouch in all regions is at least an order of magnitude higher than that of the LCO-cathode pouch. Thus, the gas evolution rate of the cathode is much higher than that of the anode. The SoC and voltage threshold values (60% SoC and 3.8 V, respectively) of the LNMCO-cathode pouch are significantly lower than those of the LCO-cathode (80% SoC and 4 V). This suggests that the acceleration of the gassing reaction at the former cathode commences at a much lower voltage than that of the latter. Swelling of the LNMCO-cathode pouch (42–84%) in the low-swelling region below the threshold is also much larger (3–6 times) than that of the anode pouch in the same region (14%).

These observations also indicate that the swelling in a Li-ion cell containing the LNMCO-cathode is dominated by the cathode at all SoC regions, while that of the LCO-cathode at low SoCs below 80%, is dominated by the anode.

In order to determine the characteristic potential for electrolyte oxidation at the two different cathodes, linear sweep voltammetry experiments were carried out using a coin-type cell that comprised cathode samples at 20, 45 and 60 °C. The positive-going scan of LCO- and LNMCO-cathodes are shown in Fig. 7. A sharp increase in oxidation current, e.g., at 60 °C, is shown at about 4 V for the LCO-cathode and at about 3.5 V for the LNMCO-cathode. The threshold voltage of 4 V for the current is in good agreement with the dependency of swelling on the electrode potential of the LCO-cathode. The value for the LNMCO-cathode is rather difficult to correlate quantitatively with the swelling behaviour.
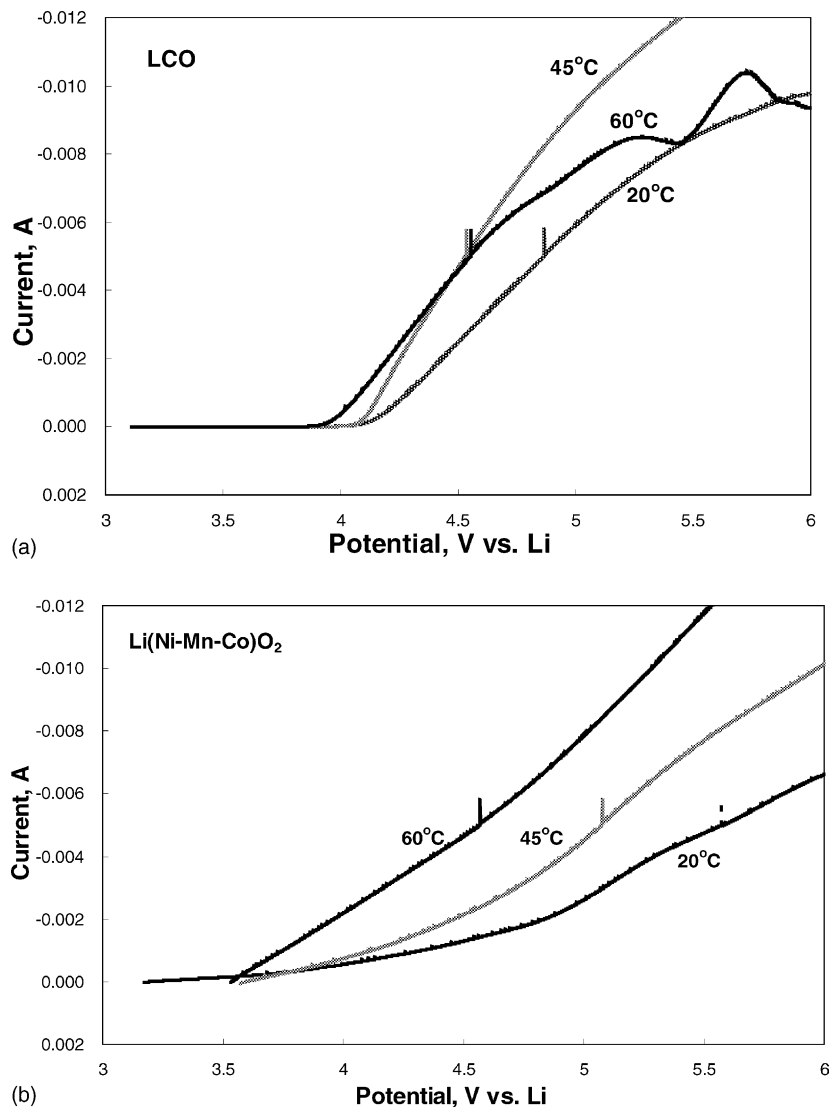

Fig. 7. Linear sweep voltammetry curves of LCO- and LNMCO-cathodes.

4. Conclusions

The gas evolution reaction of the LCO-cathode cell is dominated by an oxidation reaction at the cathode in the high potential region above 4 V, while it is dominated by a reaction at the anode below 4 V. The gas that mainly causes cell swelling in the fully charged state is CO_2, while that in the fully discharged state is CO. The gas compositions and the potential dependence indicate that swelling in the charged state may be due to the oxidation of electrolyte at the cathode, and in the discharged state may be due to the reduction of electrolyte at the anode by lithium from the lithiated graphite. The swelling of a LNMCO-cathode cell, however, may be dominated by the cathode in all potential regions above 3.2 V since the swelling caused by the cathode is far greater than that caused by the anode even in the low-voltage region.

References

[1] K.-H. Lee, E. Song, H.S. Lim, Proceedings of the 203rd Meeting of the Electrochemical Society, Paris, France, April 27–May 2, 2003, Abs. 110.

[2] N. Takami, T. Ohsaki, H. Hasebe, M. Yamamoto, J. Electrochem. Soc. 149 (2002) A9.

[3] A.B. Gavrilov, R.M. Brey, T.I. Movchan, K.E. Page, J. DeMatteis, J.D. Abbot, A.J. Naukam, Proceedings of the 203rd Meeting of the Electrochemical Society, Paris, France, April 27–May 2, 2003, Abs. 88.

[4] J.-M. Tarascon, M. Armand, Nature 414 (2001) 359.

[5] J. Cho, G.B. Kim, H.S. Lim, J. Electrochem. Soc. 146 (1999) 3571.

[6] J. Cho, H.S. Jung, Y.C. Park, G.B. Kim, H.S. Lim, J. Electrochem. Soc. 147 (2000) 15.

[7] H.-J. Kweon, S.J. Kim, D.G. Park, J. Power Sources 88 (2000) 255.

[8] T. Ohzuku, Y. Makimura, Chem. Lett. (2001) 642.

[9] Z. Lu, D.D. MacNeil, J.R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A200.

[10] Z. Lu, L.Y. Beaulieu, R.A. Donaberger, C.L. Thomas, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A778.

[11] N. Yabuuchi, T. Ohzuku, J. Power Sources 119–121 (2003) 171.

[12] M. Broussely, S. Herreyre, P. Biensan, P. Kasztejna, K. Nechev, R.J. Staniewicz, J. Power Sources 97–98 (2001) 13;
M. Broussely, et al., Proceedings of the 200th Electrochemical Society Fall Meeting, San Francisco, CA, September 2–7, 2001, Abs. 128.

[13] K. Kanamura, T. Umegaki, M. Ohashi, S. Toriyama, S. Shiraishi, Z. Takehara, Electrochim. Acta 47 (2001) 433.

[14] A.M. Andersson, M. Herstedt, A.G. Bishop, K. Edstrom, Electrochim. Acta 47 (2002) 1885.

[15] S.S. Choi, H.S. Lim, J. Power Sources 111 (2002) 130.