



Review

Improvement of flexible lithium battery shelf life by pre-discharging

Seung-Gyu Lim^a, En Mei Jin^b, Xing Guan Zhao^b, Kyung-Hee Park^b,
Nam-In Kim^a, Hal-Bon Gu^{b,*}, Bok-Kee Park^c

^a Rocket Electric, R&D Center, 758 Ilgok-dong, Buk-gu, Gwangju 500-866, Republic of Korea

^b Department of Electrical Engineering, Chonnam National University, 300 Yongbong-dong, Gwangju 500-757, Republic of Korea

^c Department of Electrical Engineering, Howon University, 727 Impi-myeon Wolha-ri, Gunsan 573-718, Republic of Korea

ARTICLE INFO

Article history:

Received 30 July 2010

Received in revised form 8 November 2010

Accepted 8 November 2010

Available online 13 November 2010

Keywords:

Flexible lithium battery

Gel electrolyte

Pre-discharging

ABSTRACT

Poly (methyl methacrylate) (PMMA)-based gel electrolyte has been used in flexible lithium batteries. These batteries are flexible and less than 0.5 mm thick, which make them suitable as power sources for smart cards and radio frequency identification (RFID) tags. We investigated the electrochemical properties of flexible lithium batteries using an impedance analyzer and potentiostat/galvanostat to evaluate the electrical capacities. To prevent the formation of gas by decomposition of electrolyte solvent, the batteries had to be pre-discharged about 5% of theoretical MnO₂ capacity. Of the three kinds of pre-discharging methods, especially, battery two-step pre-discharging method was performed showed the best electrical properties after storage at 60 °C for 60 days.

Published by Elsevier B.V.

Contents

1. Introduction	6631
2. Experimental	6632
2.1. Positive electrode plate formation	6632
2.2. Negative electrode plate formation	6633
2.3. Preparation of the gel electrolyte	6633
2.4. Fabrication of the cell	6634
3. Results and discussion	6634
3.1. Linear sweep voltammetry (LSV) test of gel electrolyte	6634
3.2. Open circuit voltage (OCV) variation according to the amount of pre-discharging	6635
3.3. Cell thickness variation	6635
3.4. Cyclic voltammetry (CV) and discharge pattern	6635
3.5. AC impedance	6635
4. Conclusions	6635
Acknowledgments	6635
References	6635

1. Introduction

Since the early 1980s, non-aqueous primary batteries with Li anodes and MnO₂ positive electrodes have been widely used in commercial applications due to their high energy density, good rate capability, low temperature performance, long shelf life, and competitive cost [1–5]. Other desirable features of MnO₂

materials are an increased safety margin to over-charge conditions compared to Co or Ni based Li-ion batteries. This is due to the stable nature of Mn(IV), which is a common oxidation state for Mn and one that retains oxygen [6]. Currently, lithium polymer batteries using gel electrolytes are attracting much attention as these can be in various forms such as thin flexible plastic film with high energy density and reliability [7–11].

There has been extensive research on the physical and electrochemical properties of gel electrolytes [12–16] but comparatively little research on practical polymer batteries using gel electrolytes themselves [17–19].

* Corresponding author. Tel.: +82 62 530 1746; fax: +82 62 530 0077.

E-mail addresses: hbg@chonnam.ac.kr, kujie@naver.com (H.-B. Gu).

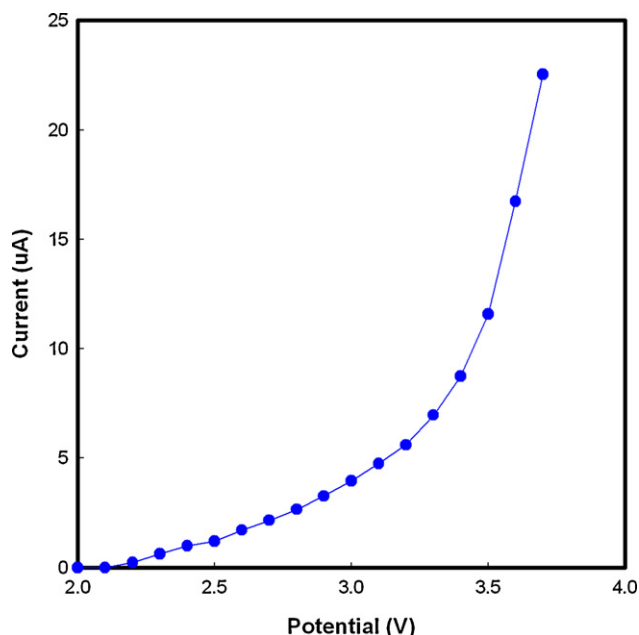


Fig. 1. Electrochemical stability window of gel electrolyte obtained by linear sweep voltammetry (sweep rate = 1 mVs^{-1}).

Despite the advantages of flexible lithium batteries, the swelling of pouch cells during storage has resulted in serious problems related to their commercial use [20].

Preliminary investigations have suggested that the swelling of pouch cells during storage are associated with gas generated by decomposition of the electrolyte solvent [21–25]. Propylene carbonate (PC) is the most commonly used solvent. In this case, CO_2 gas generation is responsible for the swelling [22,24,25].

Considering these limitations, we examined various pre-discharging methods to improve electrical properties after long term storage of flexible lithium batteries.

To accomplish this, we performed tests including linear sweep voltammetry, cyclic voltammetry, and impedance analysis.

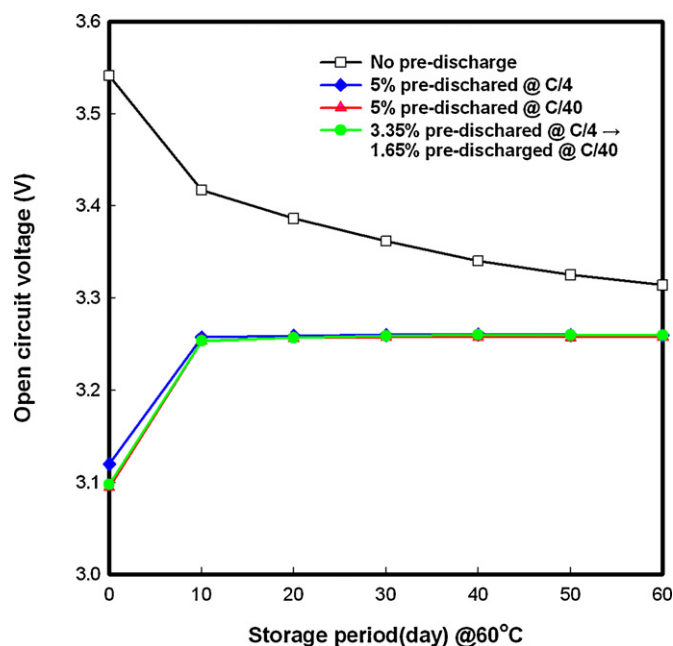


Fig. 3. OCV variation according to pre-discharging current and method.

The proposed flexible lithium primary batteries have a wide range of application where thin, flexible power sources are required, as in the case of active and semi-active RFID sensor tags [26].

2. Experimental

2.1. Positive electrode plate formation

Binder solution was prepared using N-methyl pyrrolidone (NMP) to melt 8 wt% polyvinylidene fluoride (PVDF) powder. 53.1 wt% electrolytic manganese dioxide (EMD, Mitsui Mining), 2.4 wt% of acetylene black (AB), and 44.5 wt% of binder solution

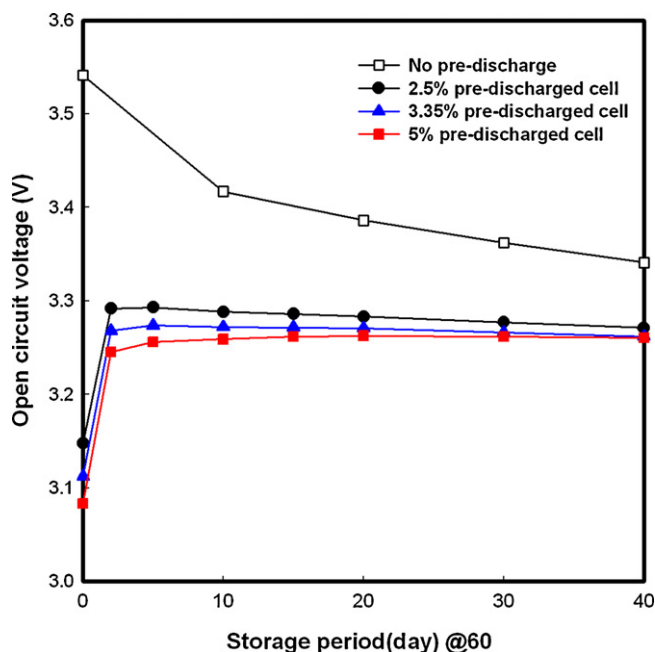


Fig. 2. OCV variation according to amount of pre-discharging.

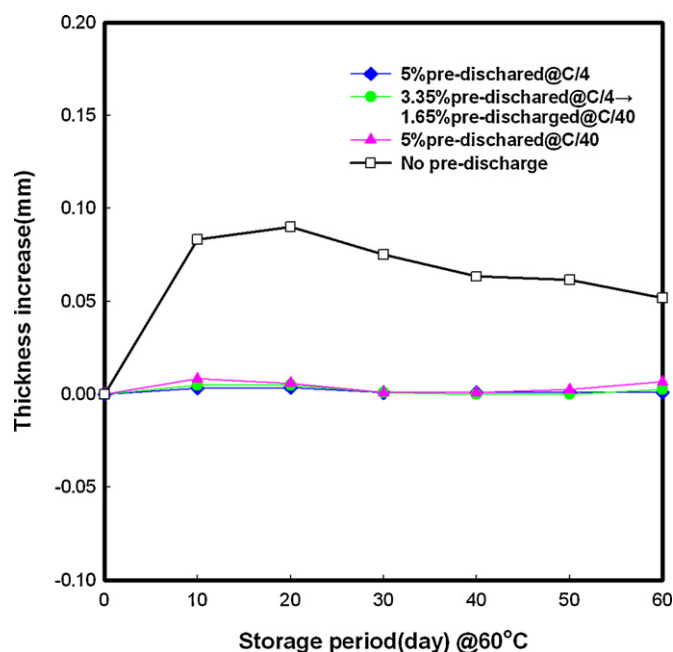


Fig. 4. Cell thickness variation according to discharge current and pattern.

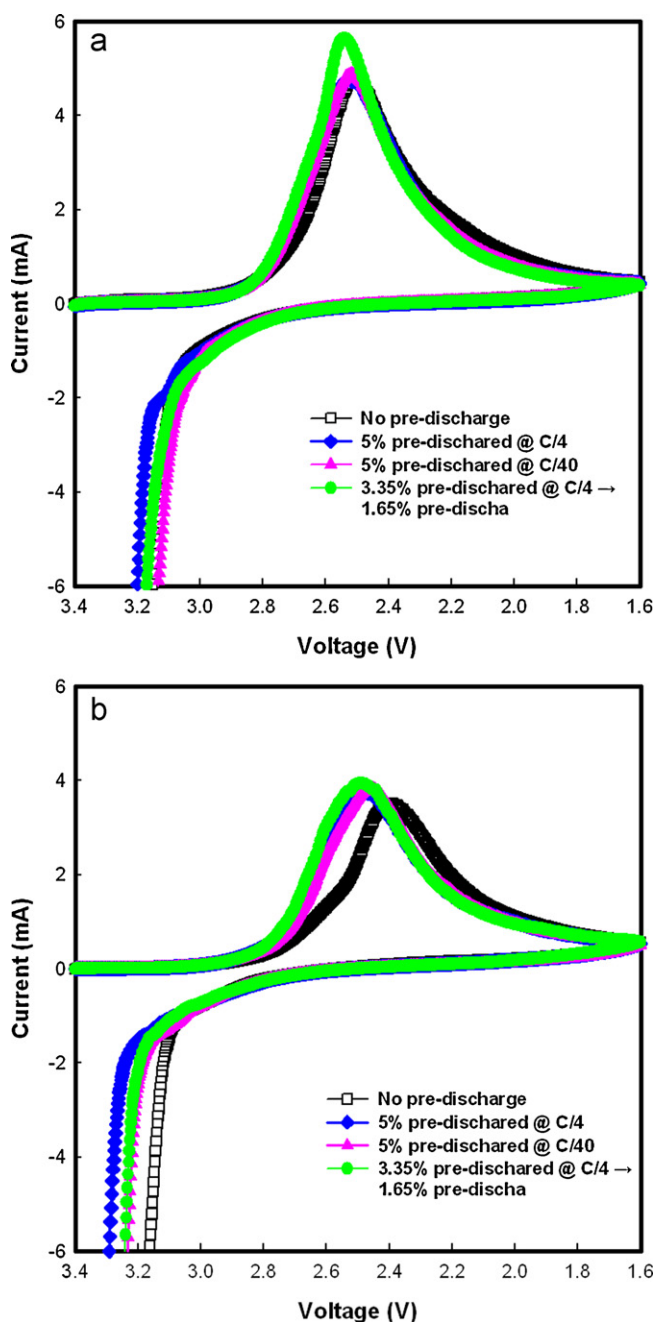


Fig. 5. Cyclic voltammogram according to discharge current and pattern before storage (a) and after storage at 60 °C for 60 days (b).

were mixed for 5 h using a planetary mixer. The resulting homogenized slurry was coated on Al foil that had been used as a current collector. The resulting product was dried in an oven at 120 °C for 30 min and placed in a vacuum drying oven at 120 °C for 1 hr. The dried mixture was pressed by a roll press and cut into small pieces (2.2 cm × 3.35 cm) to use as positive plates.

2.2. Negative electrode plate formation

50 μm-thick lithium metal was cut into 2.2 cm × 3.35 cm-sized pieces and pressed on a 30 μm-thick stainless steel sheet.

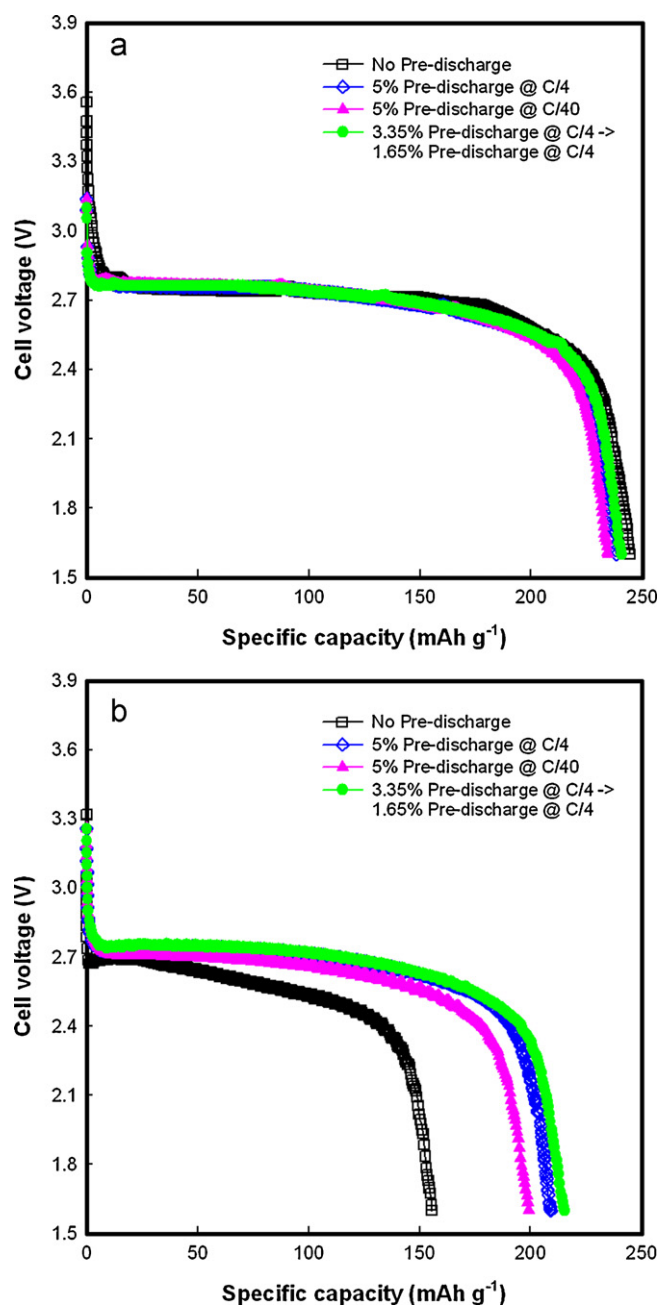


Fig. 6. Typical discharge profile according to discharge current and pattern before storage (a) and after storage at 60 °C for 60 days (b) (load current and cut-off voltage were C/20 and 1.6 V).

2.3. Preparation of the gel electrolyte

Gel electrolyte was synthesized from propylene carbonate (PC, Sigma-Aldrich), PMMA (Sigma-Aldrich, Mw = 120 K), and lithium bis (trifluoromethylsulfonyl) imide (LiTFSI, Sigma-Aldrich). The PC was pre-treated using a molecular sieve to eliminate moisture contained in the original solvent. The PMMA was dried under a vacuum at 80 °C for 24 h, and the LiTFSI was dried under a vacuum of approximately 10 mmHg at 120 °C for 24 h. Then, we obtained liquid electrolyte by dissolving 0.75 M of LiTFSI in PC solvent. The gel electrolyte was prepared by melting 15 wt% of PMMA in liquid electrolyte. Finally, the obtained gel electrolyte was sieved by passing it through a stainless steel mesh (#325).

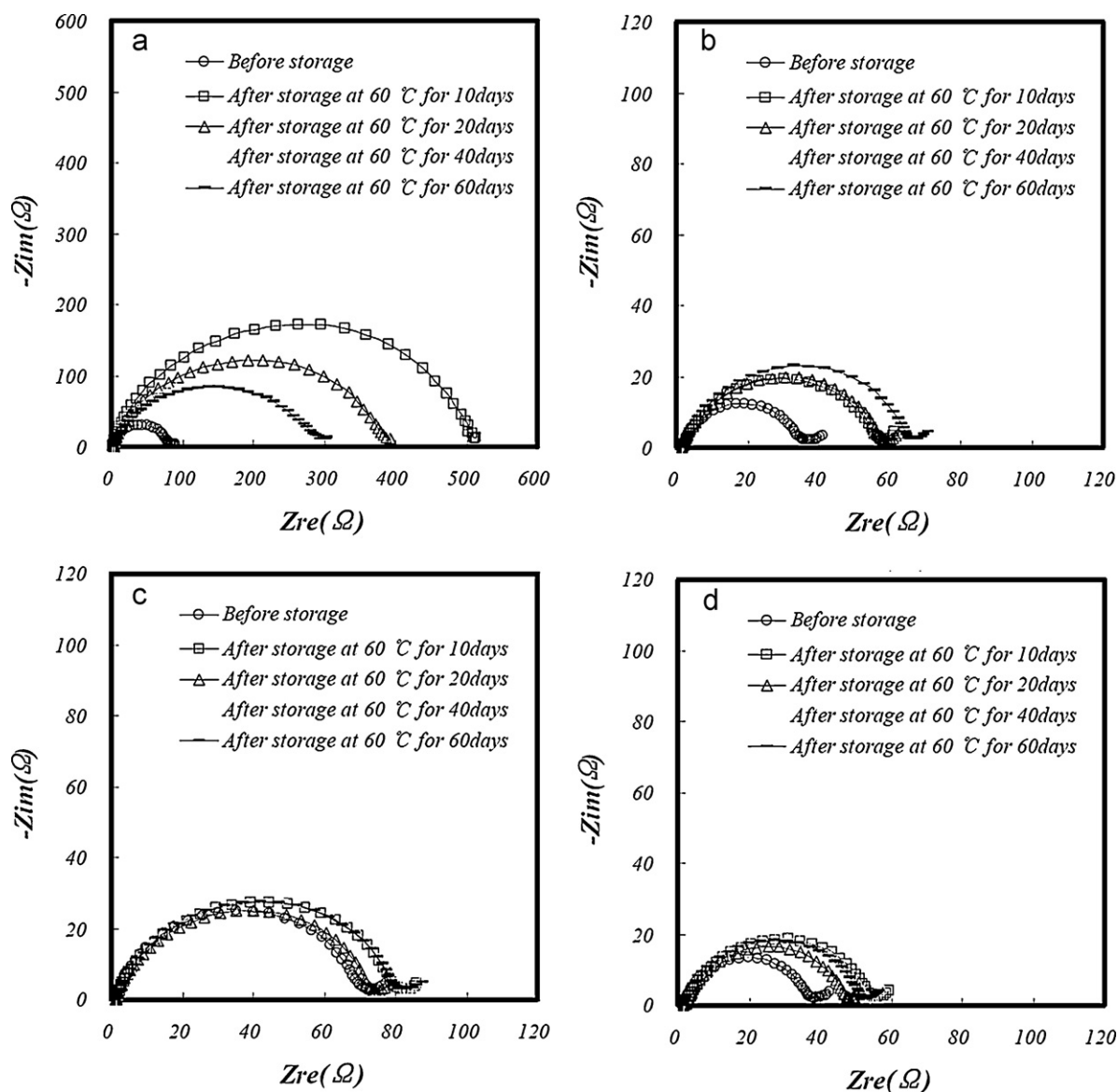


Fig. 7. AC impedance variation of “no pre-discharging” (a), “5% pre-discharging at C/4” (b), “5% pre-discharging at C/40” (c), and “3.35% pre-discharging at C/4 → 1.65% pre-discharging at C/40” (d) lot versus time.

2.4. Fabrication of the cell

Gel electrolyte was coated over the positive plate and then a non-woven polypropylene separator was positioned on gel electrolyte. The negative plate was also positioned on the separator, and the stacked electrodes were covered with a heat-confusable laminated film (pouch) that constituted the exterior material for the cell.

The cell was sealed under a vacuum condition to make a film-like flexible lithium battery. The surface area of the cell was about 14.1 cm², the thickest part of the cell was not more than 0.48 mm, and the average thickness was 0.45 mm. All fabrication took place in a dry room with a dew point lower than −34 °C.

A linear sweep voltammetry test was carried out with a potentiostat/galvanostat. The measurement sample was prepared by sandwiching the gel polymer electrolyte with a polypropylene fabric separator between two stainless steel electrodes. The cyclic voltammetry test was carried out using the potentiostat/galvanostat. The test cell was assembled by sandwiching gel electrolyte between a positive electrode plate and a negative elec-

trode plate. The alternating current (AC) impedance was measured with an impedance spectrum analyzer (IM6, Zahner Elektrik, location) with a frequency range of 100 mHz to 1 MHz and an amplitude of 10 mV.

3. Results and discussion

3.1. Linear sweep voltammetry (LSV) test of gel electrolyte

The electrochemical stability window of gel electrolyte was examined, and the result is shown in Fig. 1. One of the important properties of a flexible lithium battery is the voltage limitation of its electrochemical stability window. As shown in Fig. 1, we assumed that the gel electrolyte used in this experiment was electrochemically stable at less than approximately 3.3 V. If the cell voltage is kept at a level greater than 3.3 V, decomposition reactions of the electrolyte solvent will occur, gases will accumulate, and the cell will swell.

3.2. Open circuit voltage (OCV) variation according to the amount of pre-discharging

To control cell voltage within the stable range, a pre-discharging method was applied after cell assembly. After assembly, the initial cell voltage was about 3.55 V. The voltage of the test cells was reduced by changing the pre-discharge conditions from 2.5% to 5%, based on the theoretical capacity of MnO_2 [27]. These cells were kept at 60 °C in a drying oven. Over time, the OCV of the no-pre-discharged cells decreased gradually from the initial voltage. However, pre-discharged cells of over 2.5%, based on the theoretical capacity of MnO_2 , were controlled under 3.3 V for 40 days at 60 °C. This result is shown in Fig. 2.

To study the effects of pre-discharging current and the proposed method, we fixed the pre-discharging amount at 5% based on the theoretical capacity of MnO_2 , and three different discharge methods were used.

In the first approach, a high rate of discharge current ($C/4$) was applied to the cell to induce pre-discharge. Secondly, a low drain of discharge current ($C/40$) was used on the cell to induce pre-discharge. Finally, a two-step pre-discharging method was applied in which the cells were pre-discharged by a high rate current in the first step, followed by pre-discharging again by a low drain current. The results are shown in Fig. 3. The OCV of all attempts was controlled at less than 3.26 V for 60 days.

3.3. Cell thickness variation

The thickness variation of the test cells kept at 60 °C was observed, and the results are shown in Fig. 4. There was no significant variation in the cell thickness for all the conditions except for the no pre-discharging lot. These observations confirm that reducing the cell voltage to less than 3.26 V prevented gas formation due to decomposition reactions in the cell.

3.4. Cyclic voltammetry (CV) and discharge pattern

To stabilize the pre-discharged cell, we examined the electrochemical test after two weeks from the date of pre-discharging process at room temperature. We obtained the peak voltage and current value at the initial stage by performing a CV test. The results are shown in Fig. 5. From the results, it is clear that the two-step pre-discharged cells had higher output current than at other conditions. In addition, the pre-discharging process enhanced cell stability so that the cells showed good performance with long shelf life. The discharge patterns, as shown in Fig. 6 support the CV test results. Test cells are discharged at $C/20$ to 1.8 V at 21 °C. The initial discharge capacities are similar each other, but after long term storage at high temperature, we could observe obvious difference between pre-discharged cells and no pre-discharged cell in Fig. 6. After storage at 60 °C for 60 days, pre-discharged cells are maintained their capacities until 85%, but no pre-discharged cell is kept only 64% compare to initial capacities. We could also see that the two-step pre-discharging gives better performance than other methods.

This enhancement in performance can be explained by a porous solid electrolyte interface (SEI) layer newly formed by pre-discharge on lithium metal. After cell assembly, a dense passivation film is formed. The pre-discharge process breaks the passivation film and derives the formation of a porous SEI layer. The pre-discharging process not only prevents decomposition of the electrolyte but also forms a stabilized porous film on the lithium electrode.

3.5. AC impedance

The AC impedance of test cells was measured to determine the internal resistance of the cells. The result is shown in Fig. 7. Before storage at 60 °C, pre-discharged cells by high rate current had lower charge transfer resistance than pre-discharged cells by low drain current. This is an evidence of the destruction of passivation film by high rate pre-discharging. Pre-discharging by low drain current lead some positive effects on internal resistance of cells, but the effects were less pre-discharging by high rate current. Two-step pre-discharging gives the smallest interfacial resistance. This could be because a high rate pre-discharging current brings the destruction of passivation film formed on lithium metal, and then a low drain pre-discharging current induces a new and porous layer on the reaction site. This beneficial layer will have a decisive effect on the properties of long-term storage. The impedance data was consistent with the CV results.

4. Conclusions

A pre-discharging process after cell assembly prevents gas formation in the cell, and gives long-term stability to a flexible lithium battery. From LSV data, we confirmed that the gas formed in the cell during the storage period came from the decomposition of electrolyte. Although it used the same amount of pre-discharging on the cell, the high drain pre-discharging method resulted in better electrical properties than the low drain pre-discharging method. Two-step pre-discharging (low drain pre-discharging after high drain pre-discharging) resulted in the formation of a beneficial SEI layer. The beneficial SEI layer formed by pre-discharging prevented lithium corrosion due to the reaction of lithium with the electrolyte. Therefore, their interfacial resistance of two-step pre-discharging cells were smaller than others during the storage period. As a result, cell performance improved appreciably.

Acknowledgments

This research was financially supported by the Ministry of Education, Science Technology (MEST) and Korea Industrial Technology Foundation (KOTEF) through the Human Resource Training Project for Regional Innovation.

References

- [1] H. Ikeda, S. Narukawa, *J. Power Sources* 9 (1983) 329–334.
- [2] M. Thackeray, *Prog. Solid State Chem.* 25 (1997) 1–71.
- [3] H. Ikeda, M. Hara, S. Narukawa, US Patent No. 4 133 (1979) 856.
- [4] D. Linden, *Handbook of Batteries*, McGraw-Hill Handbooks, New York, 1995, p. 14.
- [5] G. Pistoia, *J. Electrochem. Soc.* 129 (1982) 1861.
- [6] C.S. Johnson, *J. Power Sources* 165 (2007) 559–565.
- [7] S. Sreepathi Rao, K.V. Satyanarayana Rao, Md. Shareefuddin, U.V. Subba Rao, S. Chandra, *Solid State Ionics* 67 (1994) 331–334.
- [8] J.R. MacCallum, C.A. Vincent (Eds.), *Polymer Electrolyte Reviews*, vol. 1 and 2, Elsevier Applied Science, London, 1989.
- [9] B. Scrosati (Ed.), *Application of Electroactive Polymers*, Chapman & Hall, London, 1989.
- [10] M. Wakihara, *Materials Science and Engineering* R33 (2001) 109–134.
- [11] Y. Matsuda, M. Morita, H. Tsutsumi, *J. Power Sources* 43/44 (1993) 439–443.
- [12] I. Selvaraj, S. Chaklanobis, Y. Chandrasekhar, *J. Electrochem. Soc.* 142 (1995) 366.
- [13] K.M. Abraham, M. Alamgir, *J. Electrochem. Soc.* 106 (1990) 1657.
- [14] P.E. Stallworth, J. Li, S.G. Greenbaum, F. Croce, S. Slane, M. Salomon, *Solid State Ionics* 73 (1994) 119.
- [15] B. Huang, S. Wang, X. Huang, R. Xue, L. Chen, *J. Electrochem. Soc.* 144 (1) (1997) 44.
- [16] M. Alamgir, K.M. Abraham, *J. Power Sources* 54 (1995) 40.
- [17] Y. Aihara, M. Kodama, K. Nakahara, H. Okise, K. Murata, *J. Power Sources* 65 (1/2) (1997) 143.

- [18] S. Kakuda, T. Momma, G.B. Appetecchi, B. Scrasati, T. Osaka, J. Electrochem. Soc. 142 (1995) L1.
- [19] F. Boudin, X. Andrieu, C. Jehoulet, I.I. Olsen, J. Power Sources 81/82 (1999) 804.
- [20] J. Wolfenstine, M. Shictman, J. Read, D. Foster, W. Behl, J. Power Sources 91 (2000) 118–121.
- [21] T.B. Atwater, L.E. Branovich, A.G. Pellerino, Proceedings of the 38th Power Sources Conference, Cherry Hill, NJ, 1998, p. 45.
- [22] K. Almond, S. Wessel, L. Marcoux, Proceedings of the 38th Power Sources Conference, Cherry Hill, NJ, 1998, p. 131.
- [23] H. Christopher, M. Brundage, L. Branovich, A. Pellegrino, S. Slane, T. Atwater, J. DiCarlo, Proceedings of the 37th Power Sources Conference, Cherry Hill, NJ, 1996, p. 342.
- [24] J. Wolfenstine, D. Foster, W. Behl, S. Gilman, Army Research Laboratory Technical Report No. 1805. Adelphi, MD (1998) 27.
- [25] P.R. Mosses, M.J. Turchan, A.H. Taylor, R.M. Mank, H.V.H. Venkatesetty (Eds.), Lithium Batteries, The Electrochemical Society, Pennington, NJ, 1981, p. 333.
- [26] Y.-G. Lee, J.D. Kim, S.H. Kim, K.M. Kim, J. Power Sources 195 (2010) 3715–3719.
- [27] J. Whitacre, R. Yazami, A. Hamwi, M.C. Smart, W. Bennett, G.K. Surya Prakash, T. Miller, R. Bugga, J. Power Sources 160 (2006) 577–584.