

Short communication

Electrolyte loss and dimensional change of the negative electrode in Li powder secondary cell

Ju Ho Chung^a, Woo Sung Kim^a, Woo Young Yoon^{a,*}, Sang Won Min^b, Byung Won Cho^c

^a Division of Material Science and Engineering, Korea University 1, 5-Ka, Anam-dong, Sungbuk-gu, Seoul 136-701, Republic of Korea

^b Department of Electronics and Communications, Kwangwoon University, 447-1, Wolgye-dong, Nowon-gu, Seoul 139-701, Republic of Korea

^c Eco-Nano Research Center, Korea Institute of Science and Technology, Seoul, 130-650, Republic of Korea

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Abstract

The amount of electrolyte lost in a Li powder electrode cell was measured quantitatively and compared with that in a Li foil electrode cell. The electrolyte consumption in the powder electrode cell was 30% less than that in the foil electrode cell after 50 cycles. The change in thickness of the Li electrode was also directly measured using an electro-micrometer. After 20 cycles, the variation in thickness of the powder electrode was less than 3% of its initial dimension and amounted to only 30% of that of the foil electrode. The small variation in the thickness of the electrode and small electrolyte loss were due to the porous character of the powder electrode and the stable and homogeneous SEI of the emulsified Li powders. © 2006 Elsevier B.V. All rights reserved.

Keywords: Lithium metal secondary cell; Lithium powder; Thickness change; Electrolyte consumption

1. Introduction

As far as a cycling efficiency is concerned, lithium metal secondary batteries using a compacted lithium powder electrode as the negative electrode material have been reported to be better than those using a lithium foil electrode [1]. It is known that the dendrite growth and dead lithium cause not only cycling efficiency deterioration but also safety problem [2]. In previous works, the suppression of dendritic formation in the lithium powder cell was observed [3,4] and it was ascertained that the safety problem induced by lithium dendrite can be lessened by using lithium powder electrodes. However, there are several requirements which need to be satisfied before their commercial use can be envisaged.

Among these requirements, the physical properties of the electrodes, such as the changes in their thickness during cycling, are of particular importance. In the case of lithium foil electrodes, the lithium ions are usually dissolved first from the surface in regular sequence during discharge and this causes the electrode to decrease in thickness. On the other hand, the thickness of the electrodes increases again, making them even thicker

than their initial dimensions, during the next charge, because lithium ions are deposited sparsely on the surface. This change in thickness of the lithium foil electrodes has a harmful effect on the efficiency and duration of the battery [5].

Another requirement for the commercial use of lithium metal secondary batteries is that the electrolyte should not become exhausted during cycling [5]. The surface film of the lithium electrode is usually broken down during discharge, causing the lithium to be exposed to and therefore react with the electrolyte, which in turn causes the amount of electrolyte consumed to be increased. This continuous reaction between the lithium electrode and the electrolyte would eventually result in a shortage of electrolyte.

The object of this study is to observe macroscopically and quantitatively the changes in the thickness of the lithium powder electrodes and the amount of electrolyte in the powder electrode cell during cycling. The changes in impedance of the cells during cycling were also used to examine and uphold the electrolyte consumption of the cells.

2. Experimental

To investigate the electrochemical properties of the Li electrode, a lithium–lithium half-cell was assembled in a beaker

* Corresponding author. Tel.: +82 2 32903274; fax: +82 2 9283584.

E-mail addresses: wyyoon@korea.ac.kr, cjhtiger@korea.ac.kr (W.Y. Yoon).

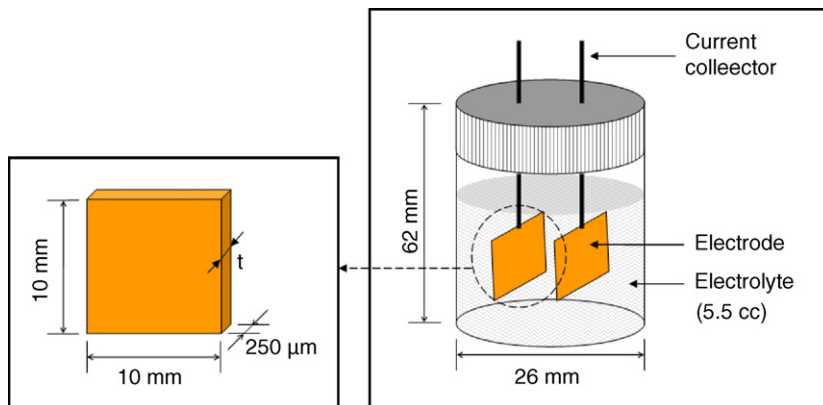


Fig. 1. Construction of a beaker cell. Each cell cycle consisted of passing a charge of 7.36 C cm^{-2} at 1 mA cm^{-2} .

(Fig. 1). Two kinds of Li electrodes (Li foil and Li powder) were used as working electrodes. The Li foil electrodes had dimensions of $10 \text{ mm} \times 10 \text{ mm} \times 250 \mu\text{m}$. The Li powders were produced using the droplet emulsion technique (DET) [3,6], and had a particle diameter of approximately $10 \mu\text{m}$. To make the powder electrodes, the Li powders were compacted by applying a pressure of approximately 15 MPa. The compacted powder electrodes had dimensions which were equal to those of the foil electrodes. The surface area of the powder electrode had been measured by the Brunauer–Emmett–Teller (BET) method and the Linear Sweep Voltametry (LSV) test directly and was reported in refs. [6,7]. According to the results, the surface area of the powder electrode was about six times larger than that of the foil electrode. Also by the Image analysis with Image-Pro (Media Cybernetics, USA), based on quantitative microscopic theory, the porosity of the powder electrode was 11.8%. The electrolyte used was propylene carbonate (PC) containing 1 M LiClO_4 .

The construction of the beaker cell was performed in a glove box under a dry argon atmosphere at room temperature. The beaker cell was wrapped with parafilm in order to prevent any reaction from occurring between the electrolyte and air. The details of the apparatus and procedures were reported elsewhere in the literature [7].

The electrochemical behaviors of the Li electrodes were analyzed through impedance measurements (Solatron 1255), which were performed at open-circuit potential. The amplitude of the applied alternating potential was $\pm 5 \text{ mV}$, and its frequency was varied from 100 kHz to 0.01 Hz. Discharge/charge cycling was performed using a WBCS3000 cycler (WonATech). Each dissolution and deposition step was performed by passing a charge or discharge of 7.36 C cm^{-2} at 1 mA cm^{-2} , respectively.

A highly efficient digital camera was used to take close-up pictures of the beaker cells, in order to visually examine the amounts of dead lithium and dendrite accumulated on the electrode surface during cycling. The values of the resistance of the surface film (SEI) on the Li electrode were obtained from the diameter of the first semi-circle in the Cole–Cole plot of the impedance results [8]. The amount of electrolyte lost was determined quantitatively by measuring the amount of electrolyte remaining after each cycle. A centrifugal separator (Hanil MF

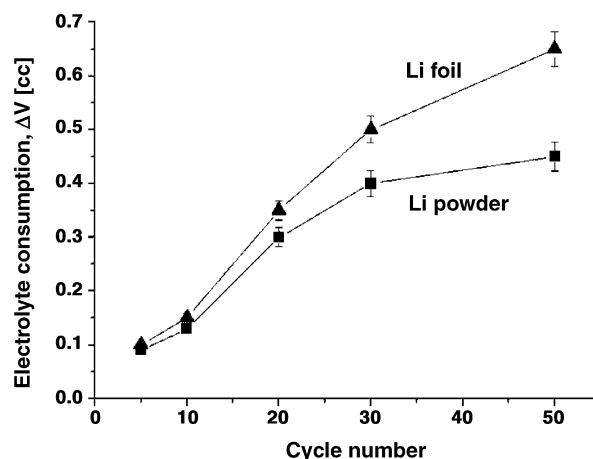


Fig. 2. Electrolyte consumption in the beaker cells using the Li foil and Li powder electrodes during cycling.

600) was used to recover the electrolyte which adhered to the wall of the beaker cell. The amount of electrolyte was measured using a 1 ml masspipet, whose the span size was 0.01 ml.

The electrode was dipped in solvent (PC) for 24 h in order to remove the Li-salt and dead lithium from its surface. After

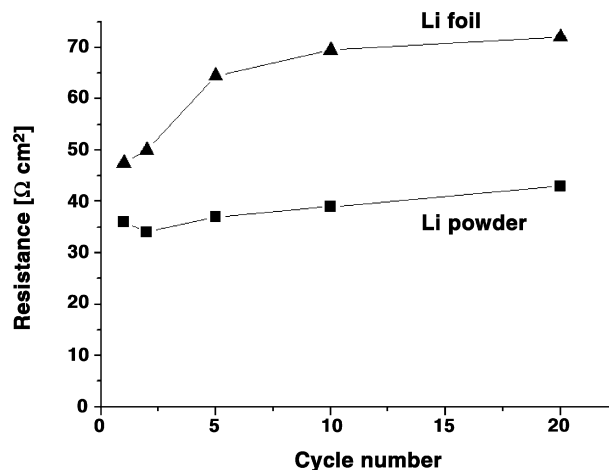


Fig. 3. Change in surface resistance of the Li foil and Li powder electrodes during cycling in PC containing 1 M LiClO_4 .

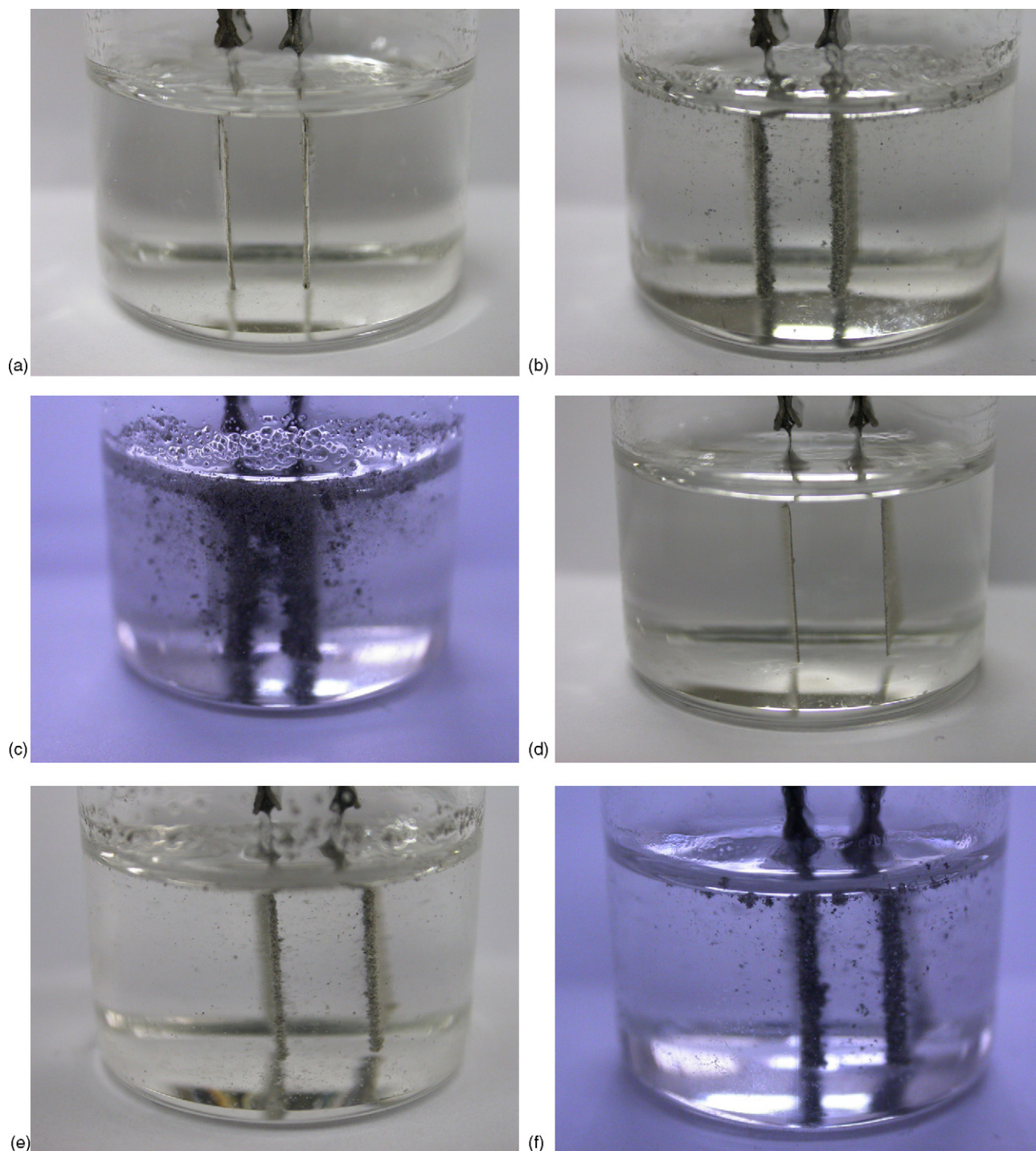


Fig. 4. A picture of the beaker cells using the Li foil electrode (a–c) and Li powder electrode (d–f) after various numbers of cycles.

drying the electrode, the change in thickness of the electrode was measured using an electro-micrometer (Mitutoyo MDC-25S). All these steps were performed in a glove box under a dry argon atmosphere.

3. Results and discussion

The amount of electrolyte lost during cycling was measured quantitatively in both the powder electrode and foil electrode

cells and a comparison of the results is shown in Fig. 2. The consumption of the electrolyte in the powder electrode cell is about 30% less than that in the foil electrode cell after 50 cycles. In particular, the consumption of the electrolyte in the powder electrode cell increased very little after 30 cycles and seemed to eventually level out, while in the case of the foil electrode cell the consumption increased continuously. After 50 cycles, the consumption of the electrolyte in the powder electrode cell was 0.45 cm^3 , while that in the foil electrode cell was 0.65 cm^3 . The

difference in consumption between the foil and powder electrode cells was 0.2 cm^3 after 50 cycles.

The electrolyte consumption in the cells was caused by the reaction between the Li electrode and electrolyte, and resulted in a thick SEI layer being deposited on the Li electrode. Therefore, measuring the surface resistance of the electrode allowed the extent of the reaction to be indirectly estimated. The surface resistances of the Li powder electrode during cycling were measured and compared with those of the Li foil electrode, in order to uphold the results of electrolyte consumption. Fig. 3 shows that the surface resistances of the foil electrode increased from $47.5 \Omega \text{ cm}^2$ to $72 \Omega \text{ cm}^2$, while those of the powder electrode increased from $36 \Omega \text{ cm}^2$ to $43 \Omega \text{ cm}^2$ after 20 cycles. In the case of the powder electrode, there was little difference between the surface film resistances at the 1st and 20th cycles. The small value of the surface resistance even after 20 cycles indicated that the reaction between the Li electrode and electrolyte was restrained and the consumption of electrolyte, therefore, might be small. The impedance changes of the powder electrode were compared with those of the foil electrode as a function of the immersion time [1]. The results indicated that the surface film of the powder electrode was more stable and homogeneous than that of the foil electrode [1].

The change in thickness of the electrodes depends on the mechanism of lithium dissolution and the deposition behaviors during discharge/charge. While only the surface of the bulk foil electrode took part in the dissolution–deposition behaviors, the whole body of the powder electrode participated in the dissolution–deposition behaviors, due to its porous character. The details of these behaviors were reported microscopically elsewhere [9]. In this study, the macro aspects of dissolution and deposition in the Li powder electrode, such as the dimensional changes, were studied.

Fig. 4 shows a series of pictures depicting the changes occurring in the beaker cells during cycling. From 0 to 5 cycles, the state of the beaker cells for the foil and powder electrodes looked almost identical. However, in the case of the foil electrode (Fig. 4c) after 20 cycles, more dead lithium was observed than in the case of powder electrode (Fig. 4f). Also the swelled surface of the foil electrode showed that dendrite formation occurred in large quantities. Similar behaviors were reported for optical cells elsewhere in the literature [4].

The non-uniformity of the surface films on the foil electrode induces a highly non-uniform current distribution of Li dissolution–deposition [10,11]. Lithium ions were not deposited evenly on the surface of the foil electrode, because of its lack of uniformity. In contrast, lithium ions were deposited uniformly on the surface of the powder electrode, because it had more deposition sites than the foil electrode. For these reasons, the surface of the foil electrode became increasingly swelled and contained an increasing amount of dead lithium with increasing cycling.

At each discharge/charge state, the change in thickness of the electrodes was measured quantitatively, and the results are shown in Fig. 5. Each five cell was used for measuring the thickness of the electrodes and the standard deviation of the results was under 5%. In the case of the foil electrodes, a thickness

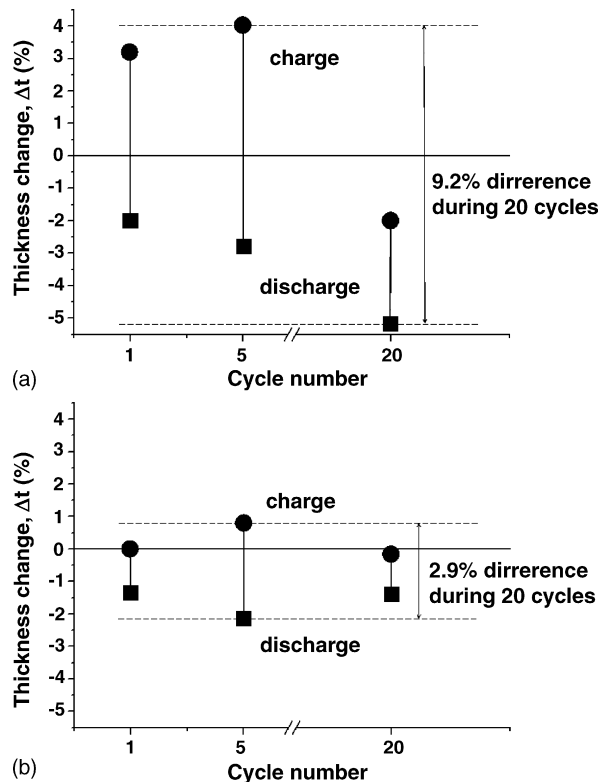


Fig. 5. Thickness changes of the Li foil and Li powder electrodes after various discharge/charge cycles (1st, 5th and 20th cycles). Amplitude of whole variations: (a) 9.2% of the initial dimension and (b) 2.9% of the initial dimension.

change of more than 5% was observed during discharge/charge. Especially after the 20th discharge, the thickness of the foil electrode decreased by 5.2% compared with its initial state. This result, as borne out by the results shown in Fig. 4, was caused by the reduced thickness of the electrode due to the formation of dead lithium. The change in thickness of the powder electrode, on the other hand, was small enough to be considered almost negligible. It was only 1.57% even at the 20th discharge/charge cycle. After 20 cycles, the amplitude of the whole variation in the foil electrode was 9.2% of the initial dimension, while it was only 2.9% in the case of the powder electrode. This indicates that the change in thickness of the powder electrode was 68% less than that of the foil electrode after 20 cycles. In short, lithium dissolution–deposition during cycling occurred only on the surface of the foil electrode, whereas it occurred not only on the surface but also in the porous interior of the powder electrode.

4. Conclusion

Discharge/charge tests were performed using Li symmetric beaker cells. The changes in thickness of the Li electrode and the amount of electrolyte lost in the cell were measured directly during cycling.

The electrolyte loss in the powder electrode cell was much smaller than that in the foil electrode cell and almost stopped after 30 cycles. The electrolyte consumption in the powder electrode cell was 30% less than that in the foil electrode cell after 50 cycles. The surface film resistance of the powder electrode

increased only slightly during the first 20 cycles. This confirmed that the electrolyte consumption was limited in the powder electrode cell and that the SEI of the powder electrode was stable and homogeneous.

The variation in thickness of the powder electrode during discharge/charge was very small, being only 32% of that of the foil electrode after 20 cycles. This limited variation might be due to the porous characters and stable and homogeneous SEI of the powder electrode. The formation of lithium dendrite might also be suppressed in the Li powder electrode cell for various reasons.

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