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Short communication

The effects of current density and amount of discharge on dendrite formation in the lithium powder anode electrode

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Abstract

A compacted lithium powder anode was used to improve the demerits of dendrite formation of lithium metal. Dendrite formation of lithium metal was restrained to use compacted lithium powder anode under a specific amount of discharge and the current density. In this study, the amount of discharge and the current density which suppress dendrite formation at the surface of a lithium powder electrode were investigated on an experimental basis. Discharge/charge reactions were accomplished on various values of the amount of discharge and current density by using beaker cells. It was analyzed by SEM images whether dendrite was formed or not on the surface of lithium powder electrode. From the various experiments, the relationship between current density and total amount of discharge was deduced as a simple mathematical model. From the model, the critical condition of total amount of discharge for dendrite formation in Li-powder electrode was increased from 0.1 mA cm^{-2} to 1 mA cm^{-2} current density. However, the critical condition of total amount of discharge was decreased over 1 mA cm^{-2}. Using the model, the condition whether dendrite formed or not on the Li-powder anode could be estimated.

Keywords: Lithium secondary battery; Lithium metal battery; Lithium powder electrode; Dendrite formation

1. Introduction

Lithium has a high theoretical specific capacity, which makes it an attractive material for secondary batteries. However, it is difficult to use lithium metal directly as anode material because of dendritic growth on the surface during a charge (deposition). Dendrite formation gives rise to safety problems and deterioration of cycling efficiency, etc. [1,2]. Dendrite formation on the surface of lithium metal and alloys has been studied widely and shown to have a direct relation with current density [3–6]. One of the solutions was suggested by Orsini et al. The large surface area of Li-anode was conceived to suppress dendrite formation [4].

Compacted lithium powder with a 10–20 μm thick LiF surface layer was used as an anode material and showed an improved cycling ability and suppression of dendrite formation [7–9]. The increase in surface area and low value of the internal impedance of the lithium powder cell, which resulted from tight and homogeneous surface layers, are claimed to suppress dendrite formation and to reduce electrolyte depletion during cycling [9,10].

During the deposition process, however, dendrites formed in the lithium powder anode at very high current density. Dendrite formation was suppressed at low current density corresponding to C/10, C/2 and C/1, but dendrites formed at high current density corresponding to 2C and 3C even in lithium powder cells. [11] There has been a report that demonstrated the effect of the total amount of discharge on dendritic growth on a lithium powder anode. According to that report, the total amount of discharge affected the morphology of the lithium powder. Dendrites appeared when the shape of the lithium powder particles changed from spherical to hemispherical during the discharge process. In other words, dendrites appeared if the powder was dissolved by more than 50%, suggesting that the total amount of

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discharge may be another variable affecting dendrite formation in a lithium powder anode [12].

Dendrite formation for bulk lithium and lithium alloys has been well studied [3–6], but that for lithium powder cells is not fully understood. Furthermore, because dendrite formation behavior depended on the charge/discharge rate and the total amount of discharge, the combined effects should be considered. The main purpose of the present research was to observe dendrite formation behavior as a function of current density and total amount of discharge in lithium powder anode cells, and to rationalize the behavior in analogy to solidification behavior in metals. That is, a simple relation between two variables affecting the formation of dendrites was deduced, and a range of these variables in which dendrite formation is suppression was suggested to exist in lithium powder cells.

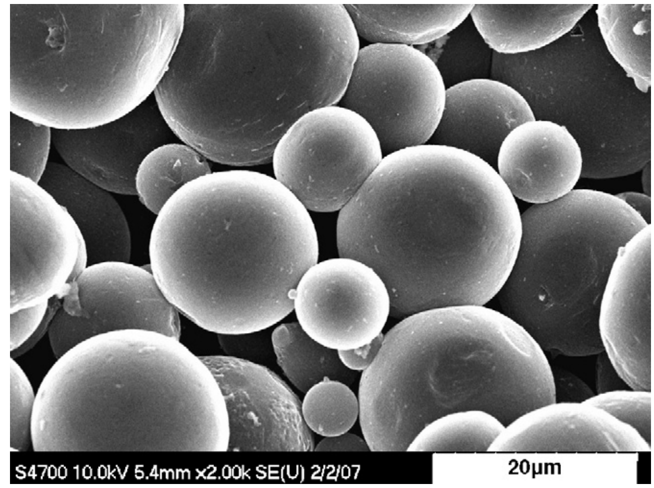

Fig. 1. Pristine compacted Li-powder electrode.

2. Experimental

Lithium powders were made in the laboratory by the droplet emulsion technique (DET) [8]. The surface-modified powders were manufactured by introducing fluorine during the DET process. The formation of the LiF surface film on the powders was examined by XPS [13]. To make an electrode, lithium powder (0.006 g) was compacted to a square (1 cm × 1 cm) by applying pressure of about 15 MPa. The typical microstructure of a compacted lithium powder electrode is shown in Fig. 1. The powder particles are spherical, and the porous characteristics of the lithium powders can be observed in Fig. 1. The porosity of the powder electrode was about 11.8% [10]. The surface area of the powder electrode was measured by the Brunauer–Emmett–Teller (BET) method and directly by linear sweep voltammetry, and was found to be 4.5–6-fold larger than

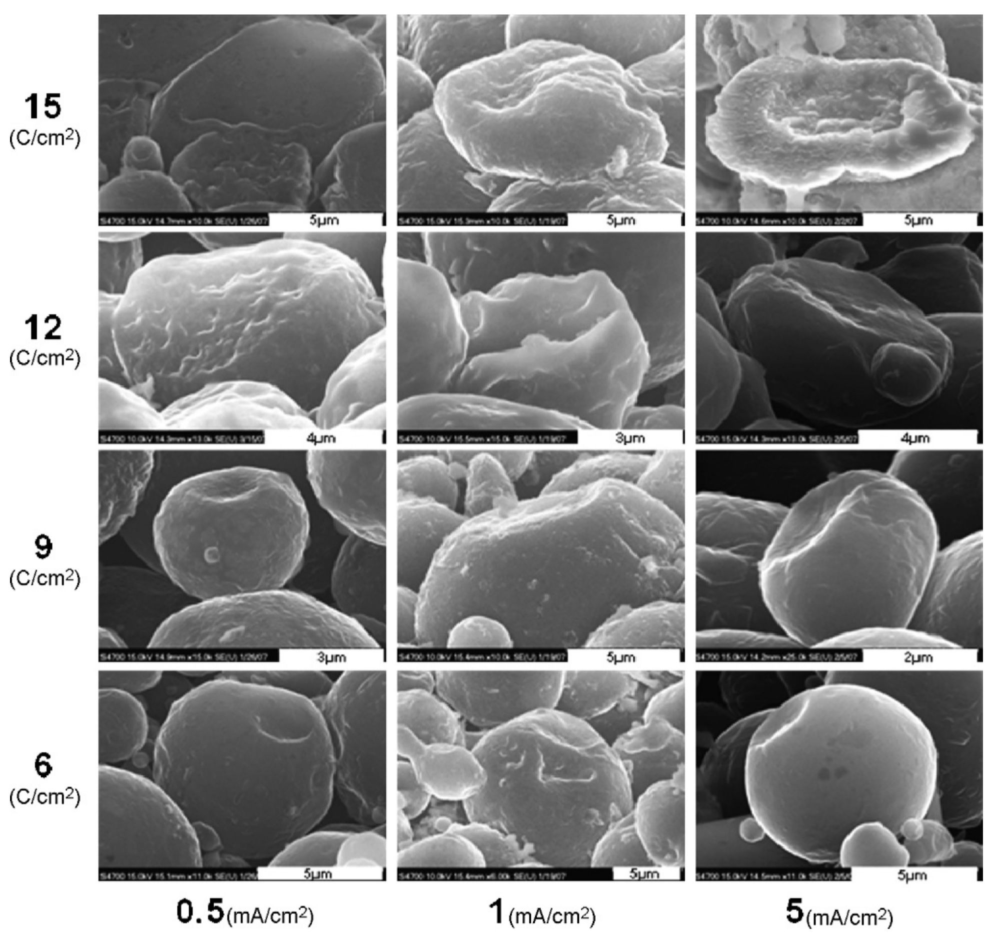

Fig. 2. SEM images of lithium powder anode after dissolution.

that of a bulk film [14,15]. The electrolyte consisted of ethylene carbonate (EC) and dimethyl carbonate (DMC) at a volume ratio of 1:1, and 1 M $LiClO_4$ (Technosemichem, Korea). The beaker cell consisted of a compacted lithium powder working electrode and a lithium foil counter electrode. Charge and discharge cycling was performed using a WBCS3000 (Wonatech) battery tester system. SEM images of the lithium powder electrodes were examined, after only one discharge, and after a cycle of discharge/charge. In this case, discharge is a kind of dissolution process (no deintercalation), and charge is a deposition process (no intercalation). To aid observations, the sample was tilted and fixed at 48°.

3. Results and discussion

3.1. Morphology of a lithium powder electrode after discharge

SEM images of the morphology of a lithium powder anode after the first dissolution (discharge) are shown in Fig. 2 for each current density and total amount of discharge. Although the initial spherical shape of the particles was preserved before dissolution, the shape was distorted after dissolution. The morphology change depended on the total amount of discharge, which affects dendrite formation during the deposition process

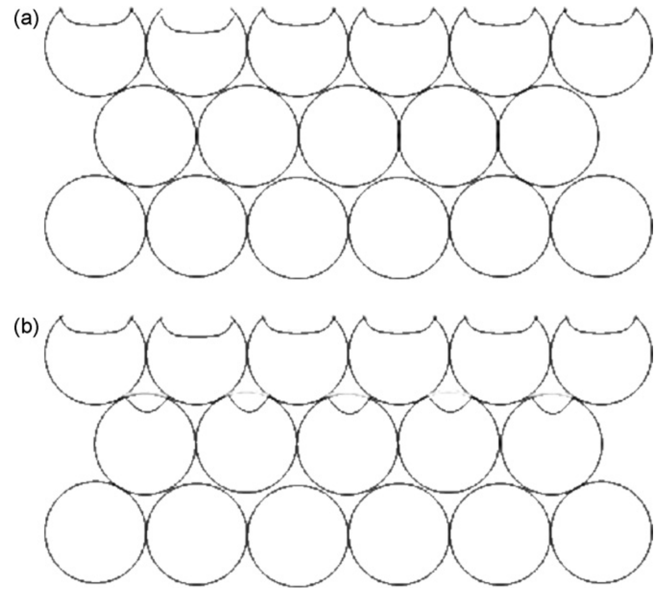

Fig. 3. Illustration of compacted lithium powder layers dissolved at: (a) high current density and (b) low current density.

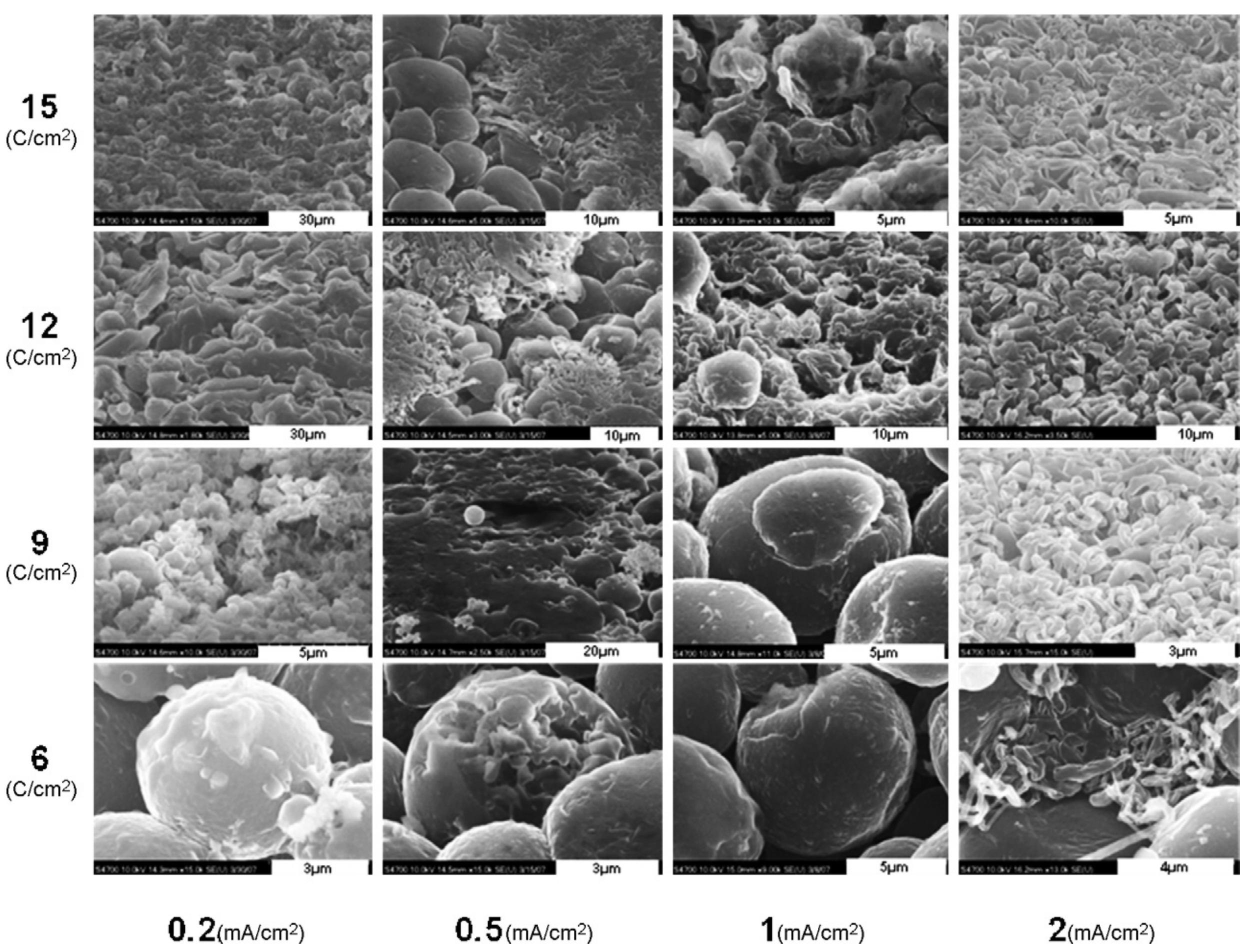

Fig. 4. SEM images of the lithium powder after one cycle of dissolution/deposition.

(charge). When the powder was over 50% dissolved, the particle shape changed to hemispherical, and dendrites were formed at the powder electrode during deposition [12].

The experimental results show that the change of morphology in the lithium powder was unrelated to current density. However, the total amount of discharge affected the morphology of lithium powders during the dissolution process (see Fig. 3). At high current density, the highest (or first) layer of compacted powders was dissolved. However, the other layers (second and deeper) were dissolved at low current density [12]. The morphology change had the same trend for each powder, and they had similar shapes at each total amount of discharge, irrespective of current density during the dissolution process. Comparing each SEM image, the powder particles were observed to become hemispherical at a total amount of discharge of 12C cm^{-2}. Consequently, if the total amount of discharge is the only variable affecting dendrite formation in the powder electrode, we can assume that dendrites will be formed at a total amount of discharge of $\geq$12C cm^{-2}, irrespective of current density. However, current density is another important factor in dendrite formation. To conclude, dendrites are formed only in a specific range of current density and a total amount of discharge of $\geq$12C cm^{-2}.

3.2. Morphology of a lithium powder electrode after discharge/charge

Fig. 4 shows SEM images of the morphology of a lithium powder anode after the first dissolution/deposition process under various conditions of current density and total amount of discharge. From the analysis of these SEM images it was found that after deposition with a current density of 2 mA cm^{-2}, dendrites formed at 6C cm^{-2}, a comparatively small amount of discharge. Dendrites formed with a total amount of discharge of 9C cm^{-2} after deposition with a current density of both 0.2 mA cm^{-2} and 0.5 mA cm^{-2}. Hence, when a powder is deposited at these current densities, dendrites should be formed between total amounts of discharge of 6C cm^{-2} and 9C cm^{-2}. However, at a current density of 1 mA cm^{-2}, dendrite formation was observed at a total amount of discharge of 12C cm^{-2}. In summary, the total amount of discharge needed to guarantee no dendrite formation increased with increasing current rate up to 1 mA cm^{-2}, and then decreased with increasing current density. That is, there is a maximum amount of discharge needed to guarantee no dendrite formation. The trend above 1 mA cm^{-2} (the critical rate for the maximum) could be explained if only a few top layers of the powder participate in the reaction at higher current density (Fig. 3). However, it is difficult to account for the trend observed below the critical rate. It was observed that deposition started at the contact region of powders at low current density, while deposition was initiated at the concave part of the powders at high current density. Further studies are needed to elucidate the details of the process.

3.3. An empirical formula

On the basis of the results presented here, dendrite and non-dendrite areas can be identified in the range of current density and the amount of discharge examined. Fig. 5 shows the curve that divides regions of dendrite formation and no dendrite formation.

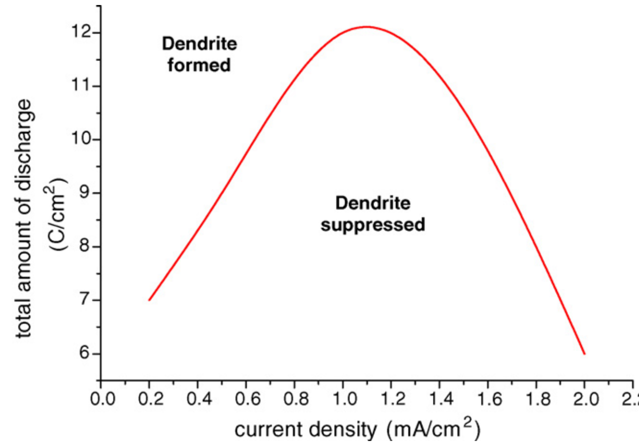

Fig. 5. The line in the figure summarizes our empirical formula. Conditions corresponding to the area under the line suppress.

Through regression methods, the curve can be formulated as:

$$Q = \frac{5.58133}{(1 - 1.0286J + 0.4957J^2)} \qquad (1)$$

Here, J is the current density and Q is the total amount of discharge.

Eq. (1) can be simplified to:

$$\{(J-1)^2 + 1\}Q \approx 11 \qquad (2)$$

When the left-hand side of the equation is smaller than the right-hand side, dendrite formation is not observed on the lithium powder electrode. That is, inequality (3) should be satisfied in order to suppress dendrite formation:

$$\{(J-1)^2 + 1\}Q \prec 11 \qquad (3)$$

4. Conclusion

The combined effects of current density and total amount of discharge on the formation of dendrites on lithium powder electrodes were examined. The lithium powder electrode kept its spherical morphology before dissolution. After the first dissolution and dissolution/deposition process, a change of the electrode morphology was observed by SEM. The SEM images were compared to establish the conditions of dendrite formation. The critical conditions for dendrite formation were investigated. A critical curve was drawn to establish an empirical formula for dendrite formation on a lithium powder electrode.

With increasing current density, the amount of discharge needed to guarantee no dendrite formation increases and then decreases; that is, there is a maximum point in the curve (Fig. 5). The mathematical equation was formulated through regression methods. The optimum conditions needed to guarantee no dendrite formation were a current density of 1 mA cm^{-2} and a total amount of discharge of 12C cm^{-2}.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2007.12.062.

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