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Short communication

The effect of internal resistance on dendritic growth on lithium metal electrodes in the lithium secondary batteries

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Abstract

In a lithium secondary battery, the effect of the current rate affect on dendritic growth has been established. In the present, a series of experiments was conducted at a constant current rate, but at various the cell internal resistances. Different temperatures at −5 °C, 15 °C, and 35 °C were applied to change the internal resistance. The present experiment found that as the resistance was varied, the voltage gradient also varied and accordingly to maintain a constant current rate, and that the Sand's time was measured differently at such varying voltage gradients. That voltage was also decreased together with the resistance to apply a constant current density results from Ohm's law. It was found that even if the current density remains constant, the size of the area where dendrites are generated will vary in accordance with the theory of solidification.

Keywords: Lithium secondary battery; Lithium metal battery; Dendrite formation; Lithium deposition; Voltage gradient

1. Introduction

One of the most important properties of batteries is their capacity. For this it possesses, metallic lithium is a good candidate for the anode in a secondary battery because very high theoretical specific capacity. However, the growth of dendrite affects the cycleability of this type of the electrode [1,2]. Dendrite is generated from the repetitive deposition and dissolution of lithium during charging and discharging, and the cycle is shortened due to this dendritic growth [3]. The commercial use of lithium secondary batteries has been restrained due to this problem. The current rate was one of the major causes of dendritic growth [4]. In the theory of solidification, the growth rate and temperature gradient are the factors that determine dendrite and planar [5]. However, in Li deposition, only the current rate is determined. If we regard the current rate a factor that determines the growth rate, Li deposition will also have an additional condition such as temperature gradient for determining dendritic growth. In addition to the current rate, voltage gradient may be another factor that affects dendritic growth. However, it is not easy to change the voltage gradient while maintaining a constant current rate. Accordingly, we tried to change the internal resistance while maintaining a constant current rate, and through Ohm's law, so as to change the voltage gradients.

2. Experiments

Both the electrode and counter electrode were made with a lithium foil. The lithium foil was 0.15 mm thick. The separator was made of Teflon, which has a groove 0.5 mm wide, 1 cm long, and 1 mm thick. The configuration of the standard coin cell (CR 2032: diameter 20 mm, height 3.22 mm) was used in the experiments. The electrolyte used was 1 M $LiPF_6$ in the volume ratio of 1:1:1 for ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (from Techno Semichem), respectively. Coin cells were assembled in an Ar gas-filled glove box.

The resistance of the electrolyte varied with the temperature. In general, electrolyte resistance decreases as the temperature of the electrolyte increases [6]. The internal resistance of the cell, therefore, changes with temperature and was measured by an impedance analyzer (SI 1280B, Solartron). The experiment was conducted at different temperatures of −5 °C, 15 °C, and 35 °C, and regulated by the thermostat. The temperature was kept constant when the coin cell's impedance and Sand's time

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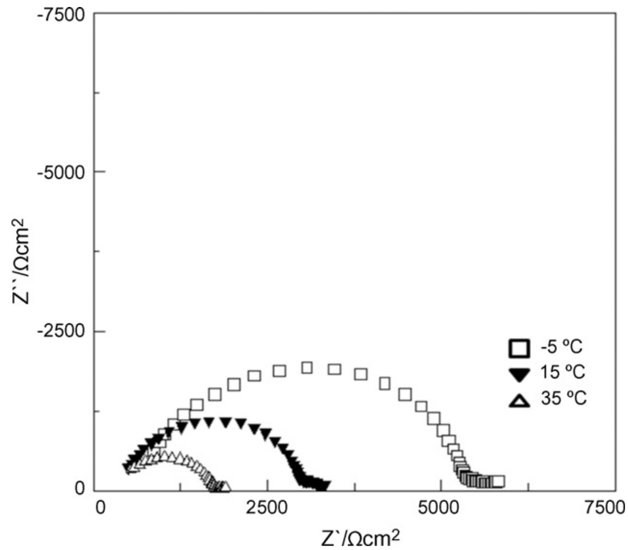

Fig. 1. The impedance of the coin cell at different temperature −5 °C, 15 °C, and 35 °C.

were measured. The impedance analyzer was employed to measure alternating current impedance spectra, with a frequency range from 100 mHz to 100 kHz and an alternating current voltage oscillation of 5 mV. After a 3 h aging process, dc current with a constant current rate of 1 mA cm^{-2} flowed for 30 min through the cell using lithium/lithium. The current density of 1 mA cm^{-2} was calculated based on area of the groove.

3. Results and discussion

3.1. Estimate of Sand's time

3.1.1. The internal resistance at different temperatures

The internal resistance was changed by changing the temperature (Fig. 1). The internals resistances are calculated as difference between the final and initial points of the impedance arcs. They account for the Li/electrolyte interfaces and neglect solution resistance. The internal resistance was considerably larger than that of general coin cells, mainly due to the presence of the separator. The thickness of the separator used in this experiment was 1 mm, which was much thicker than separators in common use today. Moreover, because the material was Teflon, which is difficult for Li ions to move through, and the reactive area was 0.5 mm^2, which was a part of the Teflon, the resistance showed a considerably high trend. Fig. 1 shows a graph which shows that the internal resistance decreases as the temperature increases, demonstrating that the resistance can be controlled by temperature.

3.1.2. The Sand's time at different temperatures

Fig. 2 measures the Sand's time, which is the time elapsed until a short occurs when discharging takes place at different temperatures. The slope of the voltage changed abruptly at the Sand's time, which is defined as the time when dendrite growth reaches the counter electrode [4]. Fig. 3 is the average of Sand's time at different temperature. As can be seen from this figure, the lower the temperature, the higher the Sand's time. Therefore, we can see that a high resistance adversely affects the growth and the growth rate is low, whereas a low resistance enhances the growth and the resulting growth rate is high. Further more, as the resistance varies as a function of temperature, the voltage gradients required for achieving a constant current rate varies. The voltage gradient equals d*V*/d*x*, and because d*x* is the distance between the electrodes, which is identical to 1 mm for all cases, the voltages gradient only depends on d*V* which is

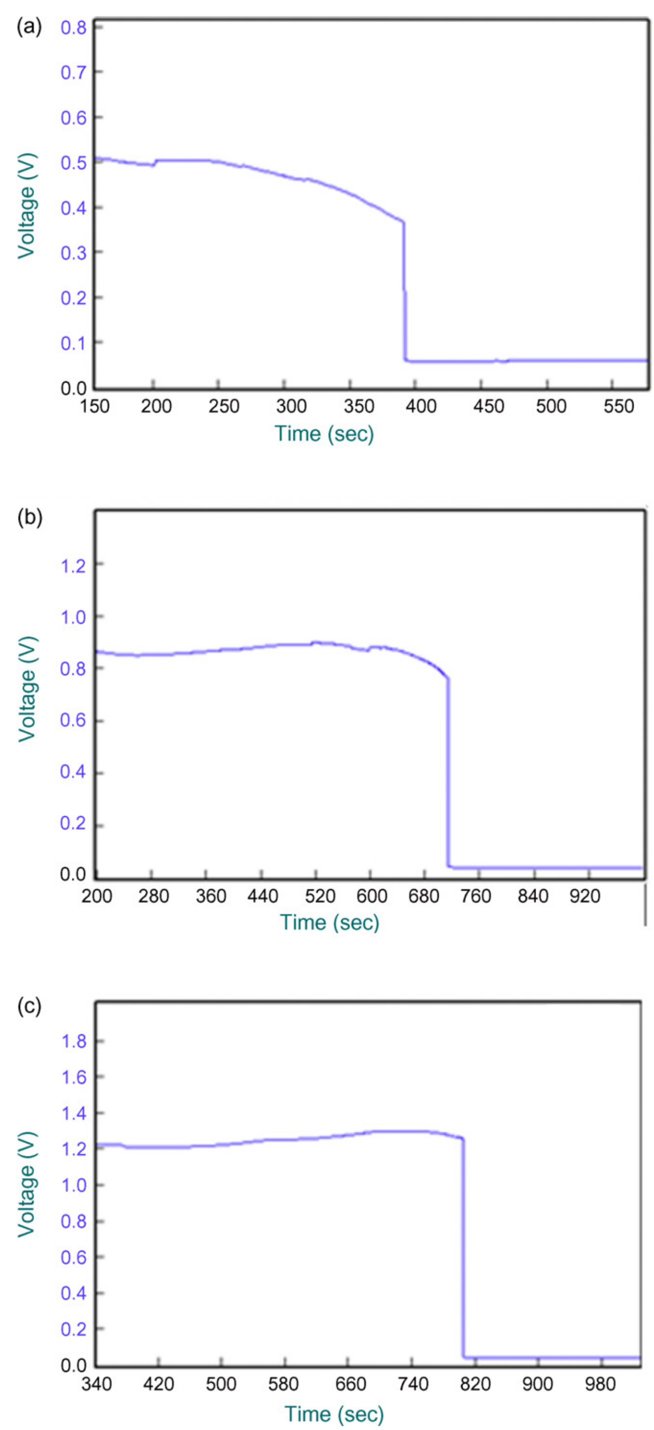

Fig. 2. The Sand's time of coin cell at different temperatures (a) 35 °C, (b) 15 °C, and (c) −5 °C.

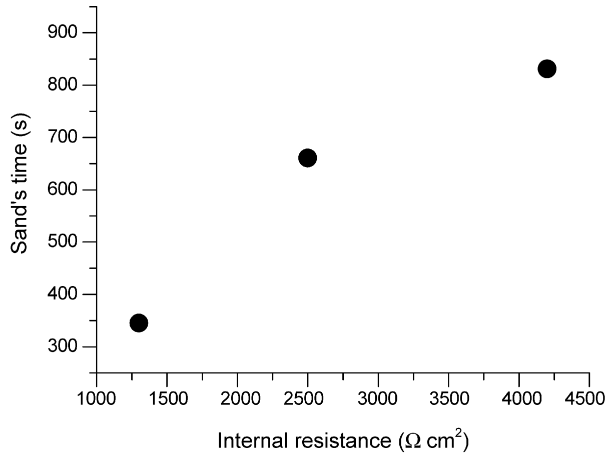

Fig. 3. The graph of the average time of Sand's time and the internal resistance at discharging 1 mA cm^{-2}.

the difference in the voltage between the electrode and counter electrode.

3.2. The relationship of voltage gradient and current rate

3.2.1. The voltage gradients of the lithium metal electrode

The graph in Fig. 4 shows the relationship between the voltage gradient required to maintain a constant current rate until a short occurs in the cell and the resistance of the cell. As the current rate is kept at 1 mA cm^{-2} for all cases, if the resistance is different, the voltage gradient must change to maintain a constant current rate. In other words, the higher the resistance, the higher the voltage gradient, and the lower the resistance, the lower the voltage gradient, respectively.

3.2.2. The critical current rate

We can determine the dendritic growth by calculating the critical current rate given by [7]

$$\tau = \pi D\left(\frac{C_0 e}{2Jt_a}\right)^2, \quad \text{with } t_a = \frac{\mu_a}{\mu_a+\mu_c} \tag{1}$$

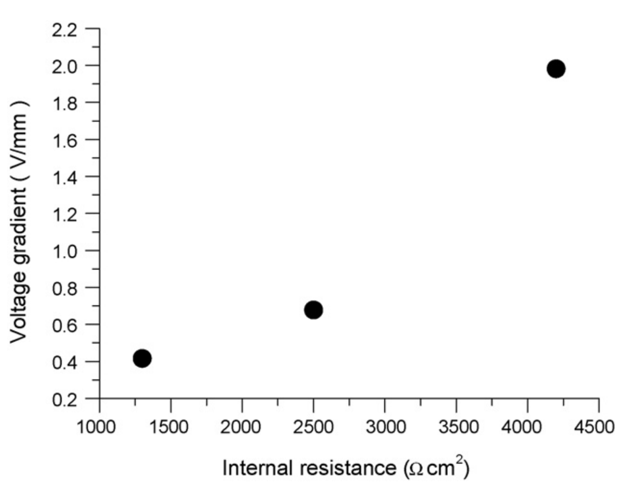

Fig. 4. The plot of internal resistance and voltage gradient at different temperatures.

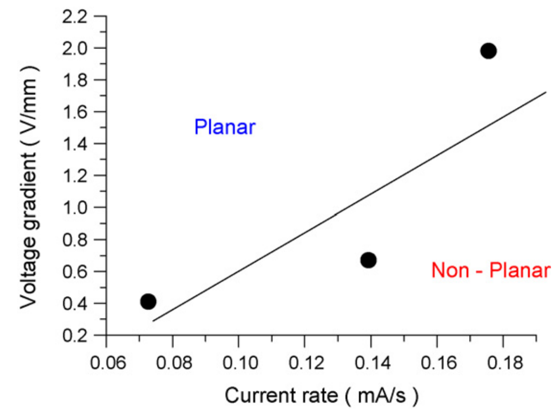

Fig. 5. The area of dendrite/non-dendrite in lithium deposition analogous to theory of solidification.

Eq. (1) is a formula for calculating the Sand's time τ. The equation depends on the diffusion constant D, the initial concentration C_0, elementary charge e, the current density J, and the mobilities μ_a and μ_c.

$$J^* = \frac{2C_0 eD}{t_a L} \tag{2}$$

Eq. (2) is a formula for calculating the electrical density J^* at which the dendrite formation is initiated [7]. Here, L is the distance between the electrodes, which is the thickness of the separator, i.e., 1 mm.

$$J^* = \frac{8\tau J^2 t_a}{\pi C_0 eL} \tag{3}$$

Eq. (3) substituting Eq. (1) in Eq. (2). By substituting the experimentally determined Sand's time into Eq. (1), Eq. (3) can be made to fit the experimental value.

As a result, J^* = 0.0727 mA cm^{-2} at 35 °C, J^* = 0.1393 mA cm^{-2} at 15 °C, and J^* = 0.1756 mA cm^{-2} at −5 °C.

3.2.3. The area of dendritic growths

Fig. 5 shows a graph based on the critical current rate and voltage gradients. It has a characteristic that is similar to the planar/non-planar areas in the theory of solidification. In the theory of solidification, the planar/non-planar areas are divided by the temperature gradient and growth rate. Likewise, in the case of the lithium deposition, the planar/non-planar areas shown in the graph are determined by the voltage gradient and current rate.

4. Conclusions

The purpose of the present experiment was to investigate the influence of the voltage gradient on the dendritic growth. To change the voltage gradient, the resistance was changed, and to change the resistance, the temperature was changed. As a result, it was found that as the resistance increased, the dendrite grew more slowly. In order to hold the current rate constant one has to vary the voltage gradient. The latter depends on the cell resistance, which in turn is a function of the temperature. Thus, variation of cell temperature and keeping the current rate constant allows us to identify the area of intense dendritic growth in (current rate)/(voltage gradient) coordinates. In lithium deposition, the voltage gradient and charge rate in the charge/discharge process are analogous to the temperature gradient and growth rate during solidification. We have now improved our understanding regarding the conditions of dendritic growth and thanks to these results the latter can be predicted in a better way.

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References

[1] J.-I. Yamaki, S.-I. Tobishima, K. Hayashi, K. Saito, Y. Nemoto, M. Arakawa, J. Power Source 74 (1998) 219–227.
[2] P.C. Howlett, D.R. MacFarlane, A.F. Hollenkamp, J. Power Source 114 (2003) 277–284.
[3] W.S. Kim, W.Y. Yoon, Electrochem. Acta 50 (2004) 541–545.
[4] M. Rosso, T. Gobron, C. Brissot, J.N. Chazalviel, S. Lascaud, J. Power Source 97–98 (2001) 804–806.
[5] W. Kurz, D.J. Fisher, Fundamentals of Solidification, 3rd ed., Lausanne, (1989), pp. 133–161.
[6] B. Klassen, R. Aroca, M. Nazri, G.A. Nazri, J. Phys. Chem. B 102 (1998) 4795–4801.
[7] C. Brissot, M. Rosso, J.N. Chazalviel, S. Lascaud, J. Power Source 81–82 (2001) 925–929.