



Specific surface-area measurement of lithium anode in rechargeable lithium cells

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Abstract

This paper reports the first successful measurement of the specific surface-area of a lithium metal anode by employing the BET method under optimum experimental conditions. The test cell used here is an AA-size cylindrical cell with a lithium anode and an amorphous- V_2O_5 - P_2O_5 cathode. The experimental results clearly reveal that the lithium surface-area increases after a low-rate discharge cycle. For example, the specific surface-area of a lithium at a low-rate discharge current density of 0.2 mA cm^{-2} is $26 \text{ m}^2 \text{ g}^{-1}$ which is twice that at a high-rate discharge current of 3 mA cm^{-2} . The influence of the discharge depth on the lithium surface-area is also examined. The surface-area measurement method described here will be useful in terms of finding a way to improve both the cycle life and safety of rechargeable, lithium-metal cells. © 1998 Elsevier Science S.A.

Keywords: Lithium anode; Lithium cell; Safety; Rechargeable cell

1. Introduction

The development of rechargeable cells with lithium (Li) metal anodes is expected to provide power sources with high specific energy. Nevertheless, there are certain problems that need to be overcome, namely, short cycle life and poor thermal stability. These problems are clearly observed during low-rate discharge cycles, such as below a rate of 0.1 C (10-h discharge rate) [1,2]. They are assumed to arise from an increase in the surface-area of the lithium anodes, which is mainly due to the accumulation of dead lithium on the anode [3,4]. The dead lithium is not in electrical contact with the anode but has high chemical activity [1–4]. The increase in the lithium surface-area is assumed by many researchers to reduce the safety of the lithium cell [1–4]. These assumptions have yet to be proved, however, since the surface area of a lithium anode has not yet been measured experimentally. Observations using a scanning electron microscope (SEM) reveal that the lithium surface becomes rougher with an increase in the number of charge–discharge cycles [5,6]. Nevertheless, SEM observations do not provide quantitative evaluation

of the surface-area. To find a way of improving both the cycle life and the safety of rechargeable lithium cells, it is very important to measure the surface-area of a lithium anode in a cell.

In our previous work, we reported the possibility of measuring the surface-area of lithium by using the BET method [7]. This paper reports the first successful measurement of the specific surface-area of a lithium anode by employing the BET method under the optimum experimental conditions proposed here. We have also examined the influence of the discharge current or depth-of-discharge on the lithium surface-area. The test cell comprised an AA-type cylindrical cell with a lithium metal anode and an amorphous V_2O_5 - P_2O_5 cathode [8].

2. Experimental

2.1. Experimental equipment

The specific surface-area of the lithium anode was measured with an AccuSorb 2100-01 instrument (Shimadzu). Fig. 1 shows the setup for measuring the surface-area with this apparatus. The morphology of the cycled lithium was studied with an JSM-3SCFS (JOEL) scanning electron microscope.

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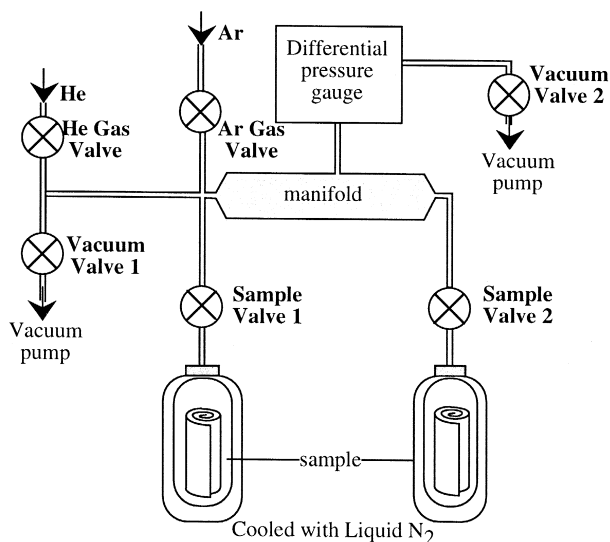


Fig. 1. Schematic drawing of specific surface-area measurement system.

2.2. Experimental cell

Tests were performed on an AA-type cylindrical cell with a lithium metal anode and an amorphous (a-) $V_2O_5-P_2O_5$ cathode (Li/a- $V_2O_5-P_2O_5$ cell) [3], as shown in Fig. 2. These cells include an anode sheet, a cathode sheet and a separator sheet that are spirally wound together. The anode is a lithium metal sheet which is $150 \mu\text{m}$ thick, 4.87 cm wide, and 28.0 cm long. The cathode mixture consists of a- $V_2O_5-P_2O_5$ (95:5 in molar ratio) as the main active material; a conductive carbon and polymer binder is printed on the metal substrate [8]. The cathode sheet is of the same size as the lithium anode sheet. The electrodes are separated with a polypropylene separator (25 μm thick). The electrolyte solution is a mixture of ethylene carbonate (EC) and 2-methyltetrahydrofuran (2MeTHF) with dissolved LiAsF_6 . The EC and 2MeTHF are mixed in a volume ratio of 1 to 1, and LiAsF_6 is added to obtain a concentration of 1.5 mol dm^{-3} .

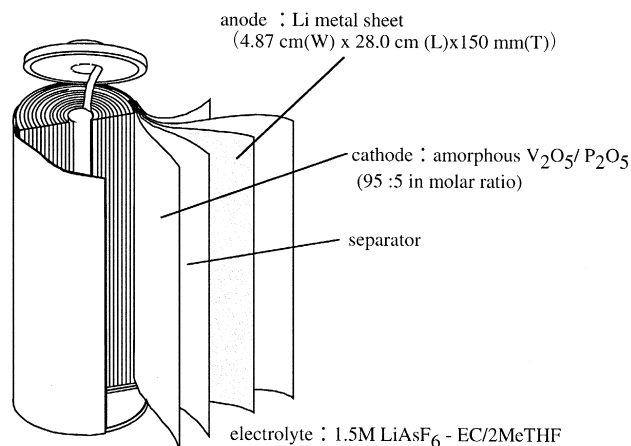


Fig. 2. Structure of AA-size lithium cell.

2.3. Determination of optimum experimental conditions

As no previous work has been reported on lithium surface-area measurement by the BET method, it was first necessary to determine the optimum experimental conditions.

The BET method is generally used to measure surface-area by calculating the amount of gas adsorbed on a sample. In this study, the amount of gas adsorption is measured by detecting the difference between (i) the pressure when the manifold shown in Fig. 2 is filled with argon gas, and (ii) the equilibrium pressure after the sample valve is opened. The sample must have a sufficiently large surface area to satisfy the marginal sensitivity of this pressure gauge, which is 1×10^{-3} Torr. To measure the lithium surface-area successfully, the following experimental conditions had to be optimized: (i) the adsorption gas; (ii) the optimum adsorption gas pressure; and (iii) the size of the lithium sheet sample. To determine these experimental conditions, the surface area of a commercially available lithium sheet (Honjyo-Metal) was measured as received.

(i) Adsorption gas— N_2 is generally used as the adsorption gas for the BET method measurements because it has a high adsorption power and is inexpensive. Lithium reacts with N_2 gas, however, to form Li_3N ; thus, argon (Ar) was used as the adsorption gas, since it does not react with lithium.

(ii) Optimum adsorption gas pressure—The following conditions were adopted for the gas pressure. The Ar-gas induced pressure was raised in 50 Torr steps in the 200–700 Torr range. At least an hour was necessary for the pressure of the measuring system to reach equilibrium.

(iii) Sample size—After considering both marginal sensitivity and the results of the surface-area measurement for

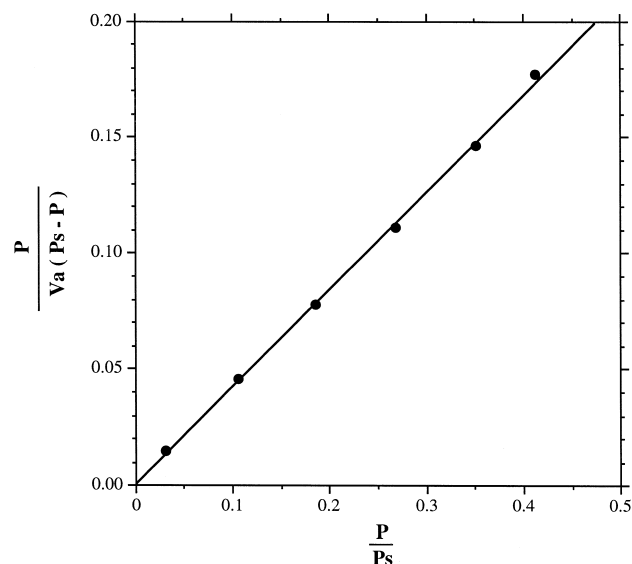


Fig. 3. BET plot of commercially available lithium sheets as received.

TiO₂ powder, a standard sample for AccuSorb 2100-01, it was decided that two lithium sheets for an AA size cell should be used as the sample to be measured in each experimental run. Each lithium sheet was 4.87 cm wide, 28.0 cm long, and 150 μm thick, as mentioned in Section 2.2. When only one lithium sheet was used, the measurements failed.

The BET plot of two lithium anode sheets as received is shown in Fig. 3. This BET plot shows a linear relationship, which agrees very well with the BET equation [9]. The specific surface-area of a lithium sheet before cycling was 1.0 m² g⁻¹, as calculated from the slope of the tangent and the intercept value following the BET equation.

These results show that the lithium surface-area can be measured by using Ar gas as the adsorption gas, and by optimizing both the equilibrium pressure and the size of the sample. In addition, it should be noted that the equilibrium pressure must be adjusted when different charge–discharge cycling conditions are used.

3. Results and discussion

3.1. Influence of discharge current density on the cycle life and thermal stability of the lithium metal cell

The influence of the discharge current density on the cycle life and the thermal stability of the lithium metal cell is described below.

First, the charge–discharge cycle test results are outlined. Fig. 4 shows the cycling profile of an AA-size Li/a-V₂O₅–P₂O₅ cell. The charge–discharge tests were

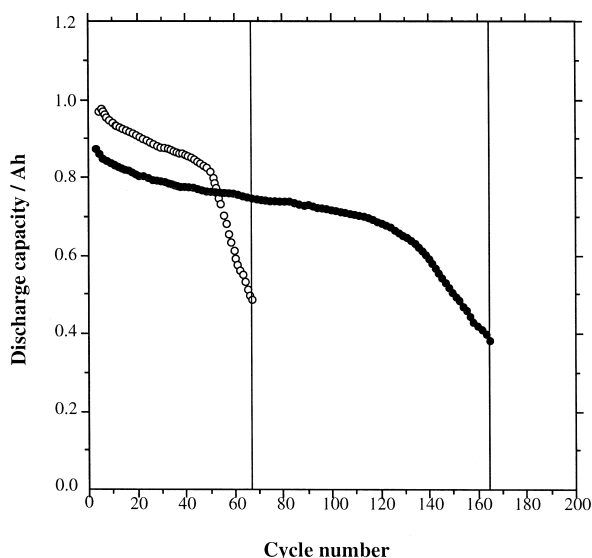


Fig. 4. Influence of discharge current density on cycle life of an AA Li/a-V₂O₅–P₂O₅ cell cycled galvanostatically between 1.5 and 3.3 V with a charge current density of 1.0 mA cm⁻²; ○: discharge current density, 0.5 mA cm⁻²; ●: discharge current density, 5.0 mA cm⁻².

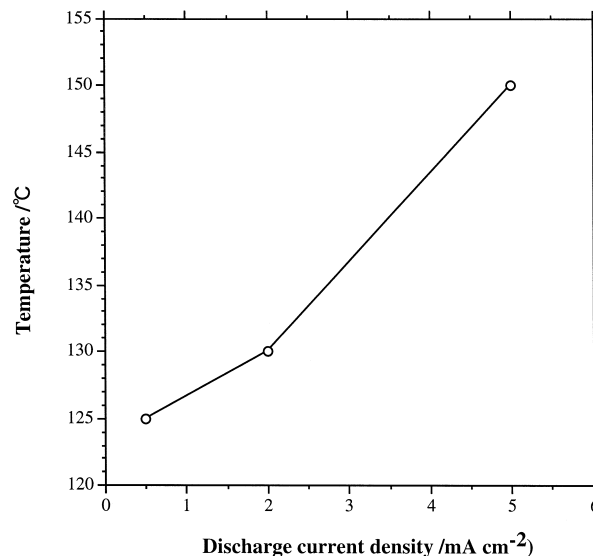


Fig. 5. Relationship between the discharge current density and the thermal stability temperature limit of an AA Li/a-V₂O₅–P₂O₅ cell cycled to EOL between 1.5 and 3.3 V with a charge current density of 1.0 mA cm⁻².

carried out galvanostatically between a 1.5 V discharge cut-off and a 3.3 V charge cut-off. In Fig. 4, the open circles plot the profile at a low discharge rate of 0.5 mA cm⁻², and the filled circles show the profile at a high discharge rate of 5.0 mA cm⁻². The charge rate for all the cells has a constant value of 1.0 mA cm⁻². The end of life (EOL) was defined as the cycle number at which the discharge capacity is half its initial value. At a low discharge of 0.5 mA cm⁻², the EOL of the AA cell is at about 60 cycles, and at a high discharge of 5.0 mA cm⁻², it occurs at about 160 cycles. From these results, shown in Fig. 4, it is clear that the cycle life at a low discharge rate is considerably shorter than that obtained at a high discharge rate. Similar results have been reported for the Li/Li_xMnO₂ or Li/Li_xMoS₂ system [1,2].

Next, the influence of the discharge current on the thermal stability (safety) is described. A heating test in an incubator is an effective way of evaluating the temperature limit of thermal stability, which is defined as the maximum temperature at which the cell does not catch fire [1–3]. The temperature limit is one of the fundamental properties for determining cell safety [1–3]. The heating test is carried out as follows. The incubator temperature is raised from room temperature at a rate of 5°C min⁻¹. The incubator temperature is held at a constant level once it has reached the target value. The target temperature is varied in 5°C step until the thermal stability temperature limit is determined. Fig. 5 shows the influence of the discharge current density on the thermal stability temperature limit for the AA Li/a-V₂O₅–P₂O₅ cell. The thermal stability temperature limit becomes higher as the current density increased. From the results shown in Fig. 5, it is clear that a lithium metal cell cycled at a low discharge rate has poor thermal

stability. Similar results have been reported for the Li/Li_xMnO₂ and Li/Li_xMoS₂ cell systems [1,2].

3.2. Influence of depth-of-discharge on lithium surface-area

The influence of the depth-of-discharge (DOD) on the lithium surface-area was examined. Tests were performed on four AA-size Li/a-V₂O₅-P₂O₅ cells, which were discharged at 3.0 mA cm⁻² for 0, 20, 40 and 60 min, respectively. After discharge, each cell was disassembled and the lithium anode sheets were removed carefully from the cells in a dry air atmosphere (relative humidity below 1%). Next, the lithium anode sheets were immersed in 2MeTHF for more than 12 h to wash off the electrolyte solution. It has been reported that the reaction rate of 2MeTHF toward lithium is very slow [10]. The lithium sheets were then thoroughly dried in a vacuum and weighed. The specific surface-area was measured at least five times for each measurement. BET plots of the lithium sheets after discharge at 3 mA cm⁻² are given in Fig. 6. The relationship between the discharge time and the specific lithium surface-area is given in Fig. 7. The specific surface-area increases with discharge time. The specific surface-area of the lithium anode in the cell before discharge is 0.8 m² g⁻¹, which is the data point for 0 min in

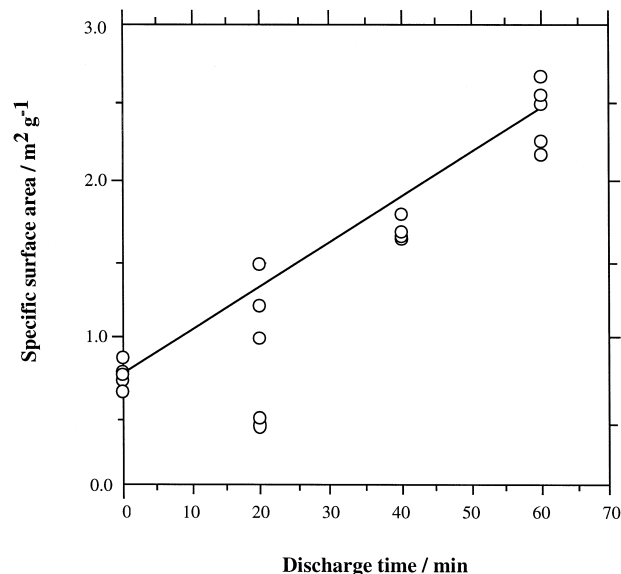


Fig. 7. Change in specific surface-area of lithium in an AA Li/a-V₂O₅-P₂O₅ cell with increase in discharge time at a discharge current density of 3.0 mA cm⁻².

Fig. 7. It is smaller than the specific surface-area (1.0 m² g⁻¹) of the commercially available lithium sheet as received, as mentioned in Section 2.3. We suggest that the

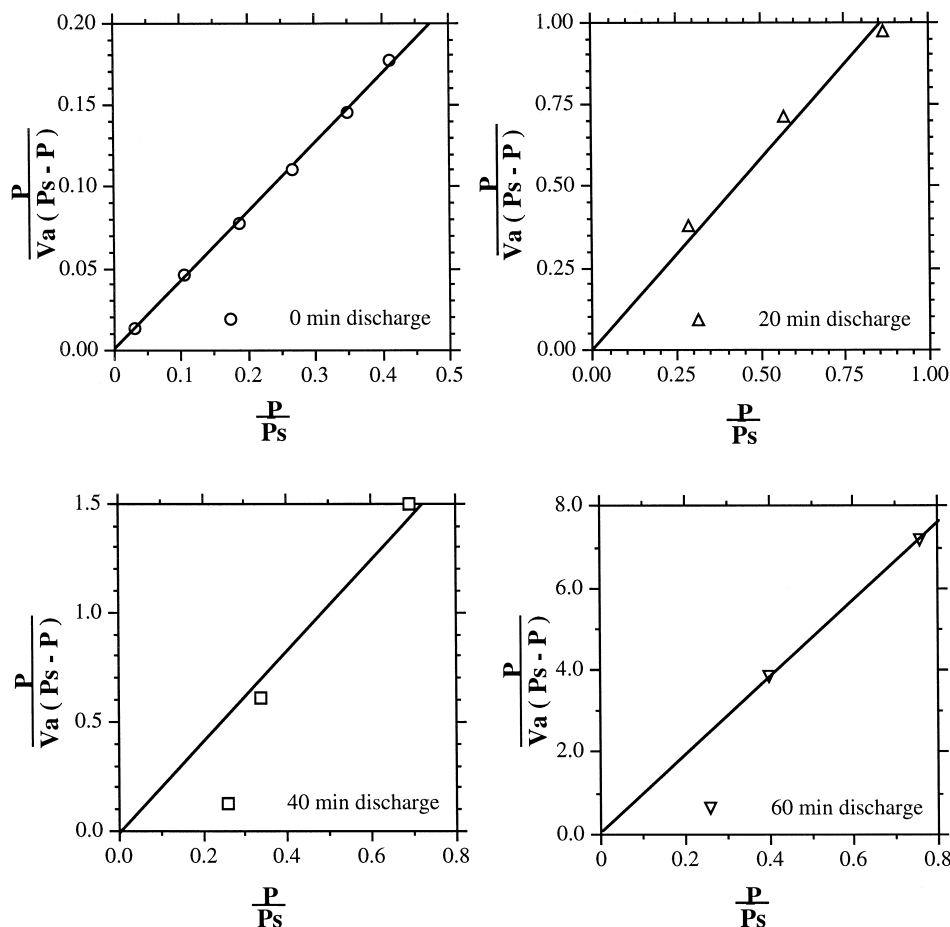


Fig. 6. BET plots of lithium sheets after discharge at 3.0 mA cm⁻². ○: 0 min; △: 20 min; □: 40 min; ▽: 60 min.

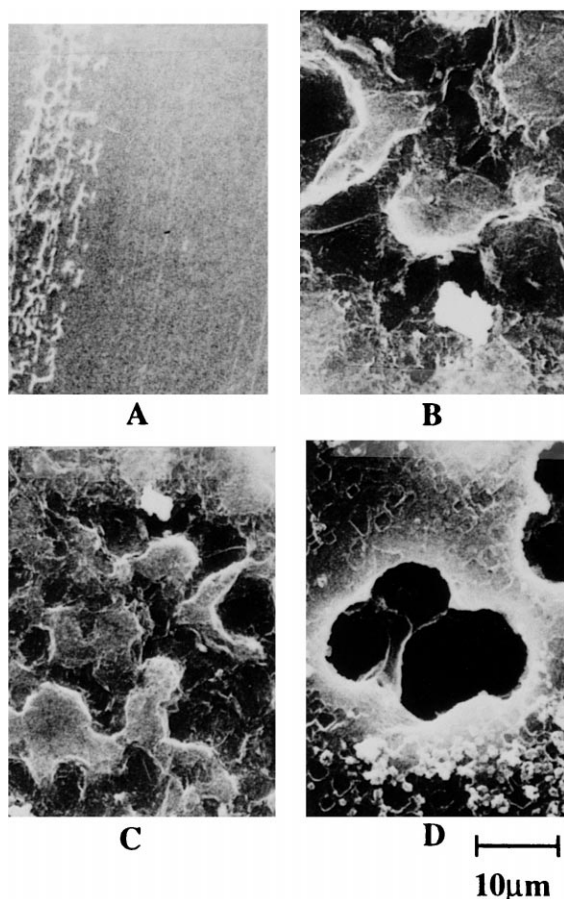


Fig. 8. Electron micrographs of the lithium surface after discharge at 3.0 mA cm^{-2} , A: 0 min, B: 20 min, C: 40 min and D: 60 min discharge.

reason for this difference in the surface areas of uncycled lithium sheets is that products are formed on the surface of the lithium anode as a result of the reaction between lithium and the electrolyte [11,12]. This is because the commercially available lithium sheet is not in contact with the electrolyte solution before the surface-area measurement.

Fig. 8 shows electron micrographs of a lithium anode surface. The roughness of the lithium surface increased with discharge time. These SEM observations support the surface-area measurement.

3.3. Influence of discharge current on lithium surface-area

The influence of the discharge current on the specific surface-area of a lithium anode was investigated. The AA-size Li/a- V_2O_5 - P_2O_5 cells were cycled galvanostatically with different discharge current densities between 1.5 V discharge cut-off and 3.3 V charge cut-off voltages. The cells were cycled at a high rate of 3 mA cm^{-2} and at a low rate of 0.2 mA cm^{-2} . The charge rate was constant at 1.0 mA cm^{-2} for all the cells. After the sixth discharge, the cells were disassembled, and the lithium surface area was measured. BET plots of the lithium anode sheets after

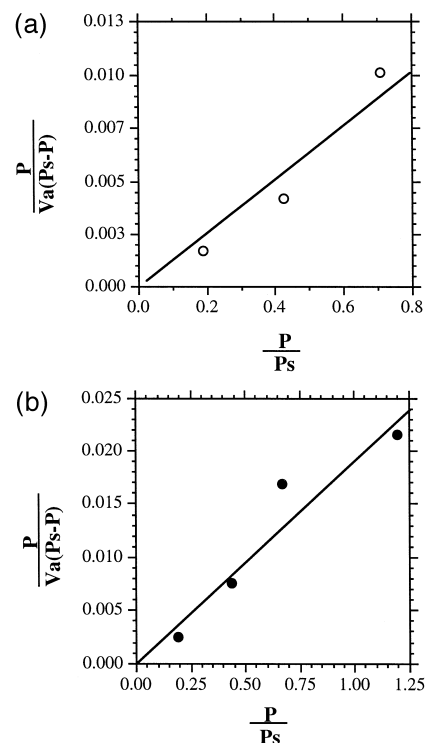


Fig. 9. BET plots of lithium anode of AA Li/a- V_2O_5 - P_2O_5 cells after the sixth cycle between 1.5 and 3.3 V with a charge current density of 1.0 mA cm^{-2} ; \circ : discharge current density, 0.2 mA cm^{-2} ; \bullet : discharge current density, 3.0 mA cm^{-2} .

the sixth discharge for different discharge current densities are presented in Fig. 9. Table 1 lists the specific lithium surface-area after the sixth discharge with different discharge current densities. The specific surface-area for a low discharge rate of 0.2 mA cm^{-2} is $26 \text{ m}^2 \text{ g}^{-1}$, and for a high discharge rate of 3.0 mA cm^{-2} , it is $13 \text{ m}^2 \text{ g}^{-1}$. It is clear that the surface-area for low-rate discharge cycles is double that for high-rate discharge cycles. In addition, the surface area increases with cycling. The surface-area after the sixth discharge at a low discharge rate is 30 times larger than that before cycling ($1 \text{ m}^2 \text{ g}^{-1}$).

Electron micrographs of the lithium anode surface after the fifth discharge are given in Fig. 10. It is found that, after low-rate discharge cycles, the surface of the anode is covered with dead lithium, and has a rougher appearance than the surface after the high-rate discharge cycles. It is

Table 1

Relationship between specific surface-area of lithium and discharge current density after the sixth discharge cycle

Charge-discharge condition	Specific surface area ($\text{m}^2 \text{ g}^{-1}$)
Discharge, 0.2 mA cm^{-2} Charge, 1.0 mA cm^{-2}	25.8
Discharge, 3.0 mA cm^{-2} Charge, 1.0 mA cm^{-2}	13.2
Without cycling	0.862

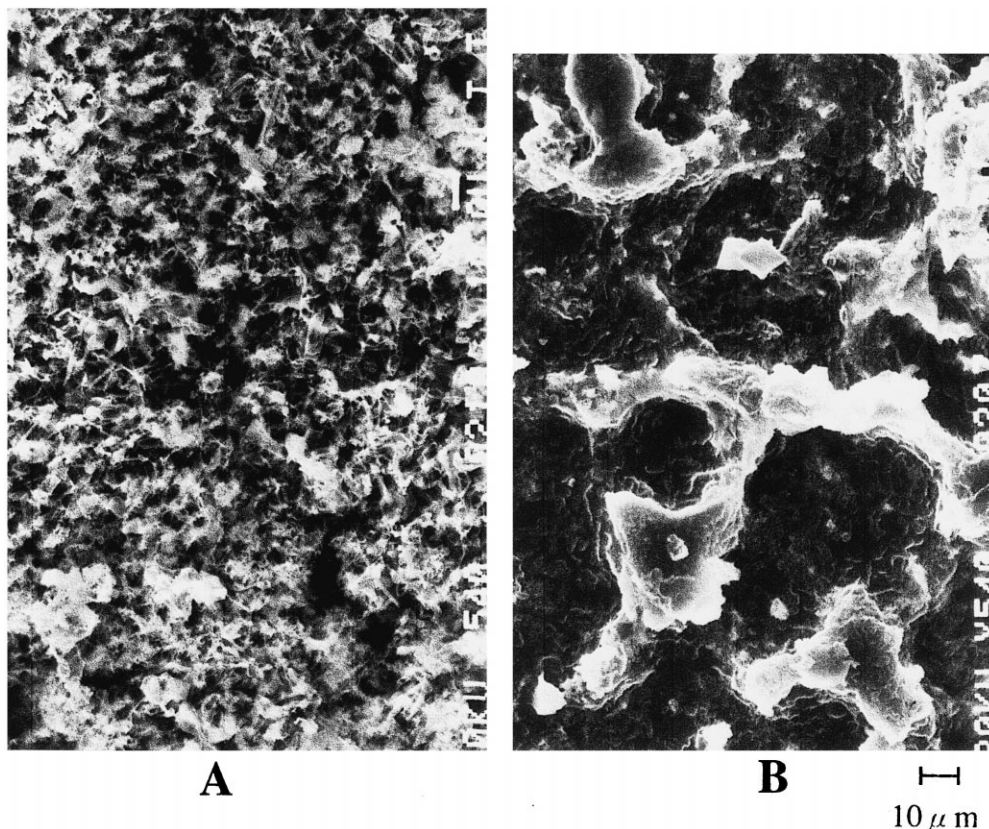


Fig. 10. Electron micrographs of the lithium surface of a AA Li/a- V_2O_5 - P_2O_5 cell after the fifth cycle between 1.5 and 3.3 V with a charge current density of 1.0 mA cm^{-2} ; A: discharge current density, 0.2 mA cm^{-2} ; B: discharge current density, 3.0 mA cm^{-2} .

considered that the main reason for the increase in the lithium surface area is the accumulation of dead lithium on the anode surface. A considerable amount of dead lithium may accumulate on the anode during low-rate discharge cycles.

4. Conclusion

The specific surface-area measurement of a lithium anode has been determined by employing the BET method for AA-type cylindrical cells with a lithium metal anode and an a- V_2O_5 - P_2O_5 cathode. Three main results have been obtained.

(1) The specific surface-area of lithium can be measured by the BET method under the following conditions: (a) by using Ar gas as the adsorption gas, (c) by optimizing the Ar gas pressure, and (c) by using an adequately sized sample lithium sheet.

(2) The specific lithium surface-area increases simply with an increase in discharge time; after a 60-min discharge, the value was 3.0 mA cm^{-2} , i.e., three times larger than that before discharge.

(3) The surface-area of lithium at a low discharge current is experimentally proved to be larger than that at a high discharge current. The surface-area of lithium after

the sixth discharge at a discharge current density of 0.2 mA cm^{-2} is double that at a discharge current density of 3.0 mA cm^{-2} .

We believe the method described here for measuring lithium surface-area will be very useful given the search for a way to improve the cycle life and the safety of lithium metal cells.

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