

Improvement in lithium cycling efficiency by using additives in lithium metal

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Abstract

The main reason for the reduction in lithium (Li) cycling efficiency at a low-discharge current density is the accumulation of electrochemically inert Li (dead Li) which is isolated from the Li anode. In this work, we investigated the effect of benzene or toluene as additives and their effect of an Li metal sheet with conductive carbon powder on Li-cycling efficiency. Li-cycling efficiency is improved by using the folded Li sheet with benzene adsorbed between the Li layers. This improvement results from the formation of a new film on and in Li. The cycling efficiency of Li with carbon powder is also improved. The improvement is considered as a result from the recombination of dead Li through an electrical path made of carbon powder. © 1997 Published by Elsevier Science S.A.

Keywords. Lithium metal sheet; Additives; Benzene; Toluene; Cycling efficiency; Additives; Dendritic lithium; Dead lithium

1. Introduction

The development of lithium metal (Li) secondary batteries is expected to provide a high energy density power source. Nevertheless, there are some problems to be overcome. These problems are their short cycle life and poor thermal stability which can be clearly observed during low-rate discharge cycles [1,2].

These problems are mainly due to the growth of dendritic Li on the anode. The dendritic Li is isolated from the anode at a low-rate discharge cycle. The isolated Li dendrites then accumulate on the anode during cycling. But as they have no electrochemical contact with the anode, they cannot be used during cycling but they are chemically very active (we will call the isolated Li 'dead Li'). As a result, the Li anode surface area becomes larger, which leads to a poor thermal stability and a short cycle life. We undertook the Li surface area measurements. The surface area after the 6th discharge of a the low-rate discharge cycle is 3 times larger than that for a high-rate discharge cycle [3].

In this work, we investigated the effect of inactive additives on the Li-cycling efficiency by a low-rate discharge cycle.

We prepared a layered Li sheet with additives (benzene and toluene) between the layers. These compounds are expected to have a relatively less reactivity with respect to Li than electrolytes and to be adsorbed on Li leading to suppression of the reaction between the common electrolyte and Li as well as an improvement in the Li deposition morphology [4]. We also attempted to improve the cycling efficiency by mixing conductive carbon powder in the Li sheet to suppress the accumulation of dead Li.

2. Experimental

2.1. Lithium sheet with a layered structure of Li/additive/Li

These additives were used to examine the cycling efficiency of Li in the following three experiments:

1. Li foil without any treatment was cycled with the aromatic additives added to the electrolyte at 0.01 mol/l.
2. Li sheet with a layered structure of Li/additive/Li was prepared in a dry room (RH less than 10%) by coating an Li sheet with additives, and folding, pressing and rolling the sheet. This process was repeated more than ten times as shown in Fig. 1.
3. As comparison, we cycled an Li sheet with a layered structure without any additive.

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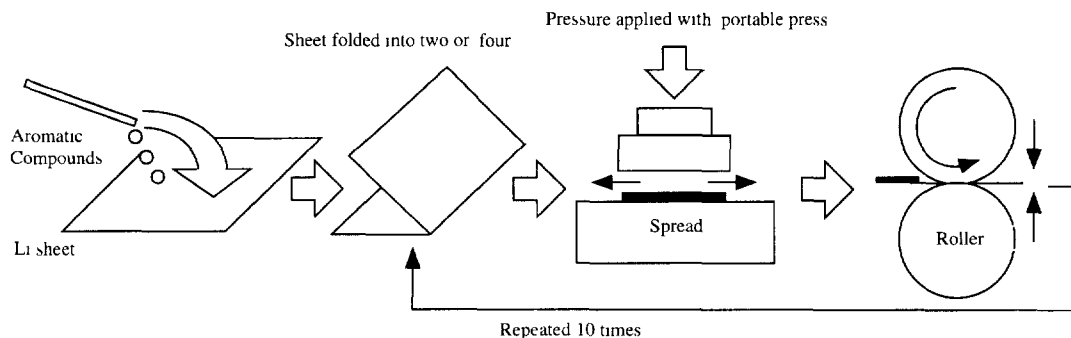


Fig. 1. Preparation of an Li sheet with a layered structure.

2.2. Lithium sheet with carbon powder

To connect the electrical path between the dead Li and the sheet easily and to recycle the dead Li for the charge/discharge cycle, we fabricated the sheet by mixing a conductive carbon powder (Meso Carbon Micro Bees, MCMB, Osaka Gas Corporation) in Li. The sample prepared by this method is similar to the Li sheet with a layered structure. The carbon powder was placed on the Li foil and then folded and pressed. This process was repeated more than ten times. The carbon was mixed at a ratio of 20 vol.%.

2.3. Cell type and cycling conditions

We made coin-type cells (23 mm in diameter and 2 mm thick) using the Li sheets mentioned above (surface area 2.0 cm^2) as a working electrode. The counter electrode was a pure Li sheet (surface area 2.0 cm^2) and the electrolyte consisting of 1.5 M LiAsF_6 in EC (ethylene carbonate)/2MeTHF (2-methyltetrahydrofuran) (1:1). All cells were cycled at a discharge current of 0.2 mA/cm^2 for 18 h and at a charge current of 1.0 mA/cm^2 for 9 h. After 10 cycles, the cells were discharged to -2.0 V at 3.0 mA/cm^2 to obtain the residual lithium content of the anode. This cycling condition is a kind of accretion method which enables to calculate the cycling efficiency. Then, the figure-of-merit (FOM) for the Li cycling efficiency was determined by Eq. (1). It shows the average number of times that an Li atom can be re-used in successive cycles of metal plating and stripping. The cycling efficiency was calculated from the FOM by Eq. (2) [5]

$$\text{FOM} = \frac{\text{accumulated discharge capacity to the end of cycle}}{\text{Li capacity in a cell}} \quad (1)$$

$$\text{FOM} = \frac{nA}{B - C}$$

$$\text{Eff} = \left(1 - \frac{1}{\text{FOM}}\right) \times 100 \quad (2)$$

where Eff is the cycling efficiency (%); n the cycle number (10); A the discharge capacity (7.2 mAh); B the initial Li capacity in the cell (72 mAh), and C the residual Li capacity (mAh).

3. Results and discussion

Table 1 shows the influence of the additives on the Li-cycling efficiency. The cycling efficiency with the additives is approximately 5% greater than that without additives. Table 2 shows the influence of additives on efficiency of the Li sheet with a layered structure of Li/additive/Li. Here, the values are about 10% greater than that for a pure Li sheet without additives.

The cycling efficiency of the Li sheet with a layered structure without additives is also greater than that of a pure Li sheet and is nearly the same as that of the Li sheet with the layered structure. From these results, we confirmed that the

Table 1
Influence of additives on cycling efficiency (added to the electrolyte for 0.01 mol/l)

Additive	Efficiency	FOM
Benzene	91.2	11.4
Toluene	92.6	13.5
No additives	86.5	7.41

Table 2
Influence of additives on cycling efficiency (with layered structure)

Additive	Efficiency (%)	FOM
Benzene	96.2	26.3
Toluene	97.3	37.0
No additives	95.9	24.4

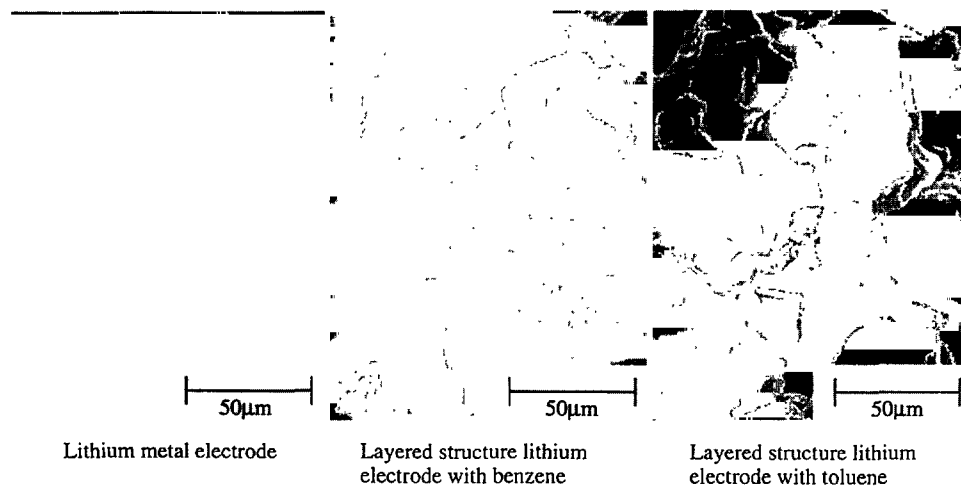


Fig. 2 SEM images of an Li sheet with a layered structure after the 20th charge.

cycling efficiency of the Li sheet is particularly improved by using the layered structure.

Fig. 2 shows scanning electron microscope (SEM) images of the Li sheet surfaces after the 20th charge. We can see that the surface of the sheet is covered with dead Li in all images, however, the surface of Li with the layered structure seems to be smoother than the Li metal surface. The improvement in Li-cycling efficiency with the layered lithium is considered as a result from the formation of a new surface layer by repeated pressing and folding of the foil. Another reason could originate in the surface layers which are embedded in the Li foil by the fabrication process. One possible reason is that a fraction of the layer may appear at the surface of the film after cycling and the boundary between the layer and Li may become an active site for Li deposition. Many active sites may cause uniform Li deposition resulting in a larger FOM.

Fig. 3 shows the cycling efficiency of an Li sheet with carbon powder. The FOM of an Li sheet with carbon powder is five times larger than that of a pure Li sheet.

Fig. 4 shows SEM images of the Li sheets for a low-rate discharge cycle after the 10th charge. The left image is of the Li metal, and the right image is of Li metal with a 20 vol.% carbon powder content. Many Li dendrites can be seen on the Li metal after the 10th charge, and the surface is covered by mossy Li. Dendritic Li can also be seen in the image on the right, but it is thicker than that on the pure Li metal surface and there is no mossy Li.

We believe that the improvement in cycling efficiency is mainly caused by the re-connection of dead Li and the sheet. Another possible reason is a uniform Li deposition at Li-metal powder boundary which is probably an active site for Li deposition.

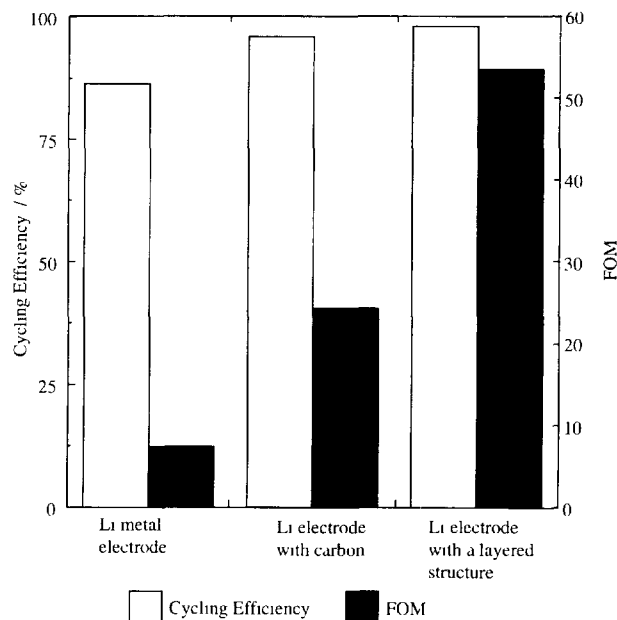


Fig. 3. Cycling efficiency of a pure Li sheet and an Li sheet with carbon.

4. Conclusions

By using a folded Li sheet with benzene adsorbed between the Li layers we obtained an FOM value three times larger than that for a pure Li sheet. This improvement seems to be caused by the formation of a new film on Li surface. The FOM is also improved by using Li with carbon powder. This improvement is considered as a result from the easy re-connection of the dead Li with the sheet via the carbon powder. Another reason for the improvement is believed to be the Li-(surface layer embedded in Li) or Li-carbon powder boundary which is probably an active site for Li deposition.

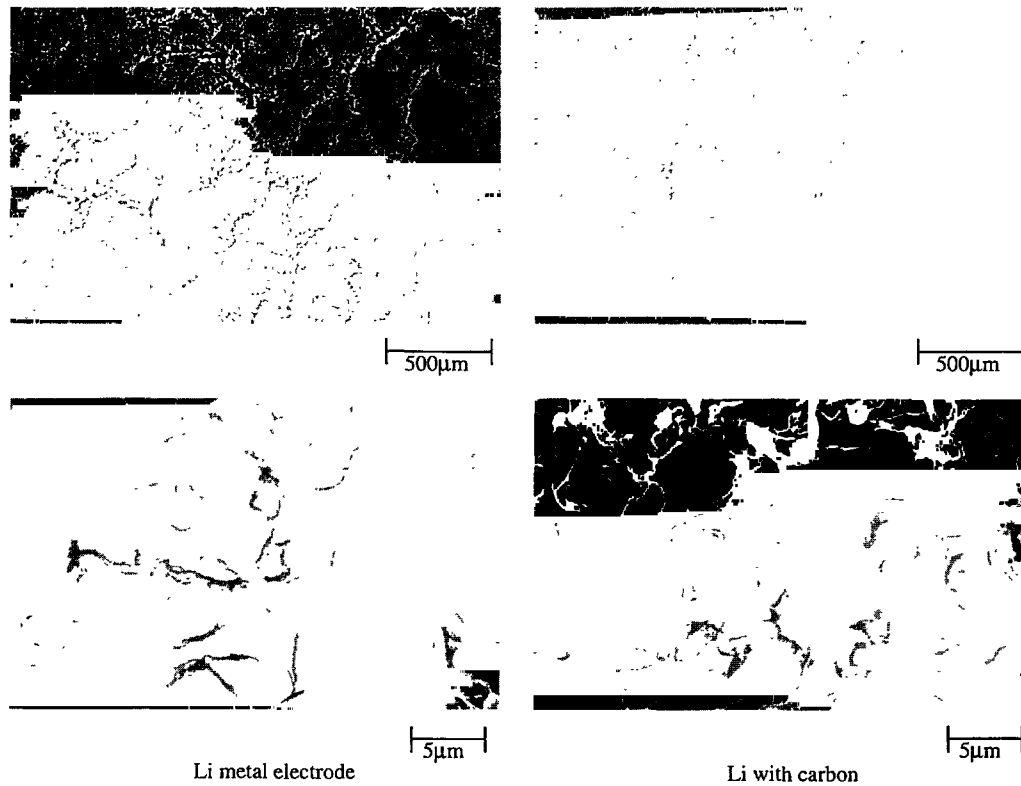


Fig. 4. SEM images of an Li sheet and an Li sheet with carbon powder after the 10th charge.

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