Lithium Metal Negative Electrode for Batteries with High Energy Density: Lithium Utilization and Additives

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ABSTRACT

Metallic lithium is considered to be the ultimate negative electrode for a battery with high energy density due to its high theoretical capacity. In the present study, to construct a battery with high energy density using metallic lithium as a negative electrode, charge/discharge tests were performed using cells composed of LiFePO4 and metallic lithium at various lithium utilization values. A relationship was observed between utilization and cycle performance, and the degradation behavior of metallic lithium was evaluated by cross-sectional FE-SEM observations. We also investigated the effects of additives in the electrolyte and found that FEC and VC effectively improved cycle performance.

Keywords: Lithium Metal Negative Electrode, Utilization, Additive, Battery

1. Introduction

Since the early 1960s, lithium metal negative electrodes have been extensively examined due to their high theoretical capacity (3860 mAh g⁻¹) and low redox potential (−3.04 V vs. SHE).¹⁻³ Metallic lithium is considered to be the ultimate negative electrode; however, some limitations need to be overcome for its practical use, such as reactions with electrolytes, inhomogeneous deposition, and low Coulombic efficiency. In the late 2000s, research was conducted on the development of a 500 Wh kg⁻¹-class battery for electric vehicles.⁴ Metallic lithium is considered to be the first candidate for the negative electrode. When a battery cell with 500 Wh kg⁻¹-class is manufactured, it is necessary to use a relatively thin film and to perform charge/discharge at high lithium utilization. In recent years, negative electrode-free batteries have also been suggested,⁵,⁶ but require high lithium utilization. The morphology of deposited/dissolved lithium and the cycle performance of lithium metal negative electrodes are influenced by a number of factors, such as the electrolyte composition, applied current, current collector, separator, and confined pressure.⁷⁻¹⁰ These factors also differ depending on whether a lithium/lithium symmetric cell or full-cell combined with a positive electrode material is used for evaluations. Although these factors have been investigated in detail, limited information is currently available on the effects of lithium utilization on the cycle performance of the cell.¹¹,¹² Therefore, further studies are needed to evaluate the cycle performance of lithium metal negative electrodes at high lithium utilization in order to construct a battery with high energy density.

The effects of lithium utilization on charge/discharge behavior in an electrolyte containing cyclic and linear carbonates have already been reported.¹³ We our research group is currently examining high energy density batteries using a lithium metal negative electrode with transition metal sulfides or FeF3 as the positive electrode.¹³,¹⁴ We previously demonstrated that favorable charge/discharge behavior was observed when the electrolyte containing only cyclic carbonates. This result indicated that the electrolyte has better compatibility with the positive electrode material. To construct the battery with high energy density, as mentioned above, thin metallic lithium must be used at high utilization. Thus, it is important to understand the electrochemical behavior of the lithium metal negative electrode under such severe conditions in the electrolyte containing only cyclic carbonates.

In the present study, we investigated the effects of lithium utilization on the stability of a lithium metal negative electrode in an electrolyte composed of ethylene carbonate and propylene carbonate. The cells evaluated in the present study were constructed using LiFePO4 as a positive electrode, which shows stable cycle performance with a plateau at 3.4 V vs. Li/Li⁺.¹⁵,¹⁶ A cell with different lithium utilization was fabricated by controlling the areal capacity of both LFP and metallic lithium. The effects of additives for the electrolyte were also examined. The results obtained are fundamentally important for the practical use of lithium metal negative electrodes.

2. Experimental

Lithium iron phosphate (LFP) (FE020, MES), acetylene black (AB) (HS-100, Denka), and poly(vinylidene fluoride) (PVdF) (KF7208, Kureha) were mixed with N-methyl-2-pyrrolidone (Kanto Chemical) in a motor to form a slurry. The composition ratio of the electrode was LFP : AB : PVdF = 90 : 5 : 5 in weight. The slurry was coated on carbon-coated aluminum foil and dried in an oven at 120 °C for 12 h. Five types of electrodes with different loading masses of LFP were prepared. The electrodes were 15 mm in diameter. A flat-type cell (Hosen Corp.) was assembled in an Ar-filled glove box with a gas purification system (Miwa MFG, dew point < −80 °C, O2 < 1 ppm) using metallic lithium (Honjo Metal) as a negative electrode and a polypropylene separator. Five thicknesses of lithium metal (50, 100, 200, 300, and 400 μm) were used. In the present study, 1.0 mol dm⁻³ lithium bis(trifluoromethanesulfonyl)amide (LiTFSI)/ethylene carbonate (EC) : propylene carbonate (PC) (1 : 1 vol%) was used as the electrolyte (Mitsubishi Chemical). Fluoroethylene carbonate (FEC, lithium battery grade), vinylene carbonate (VC, lithium battery grade), vinyl ethylene carbonate (VE, lithium battery grade), and vinylidene carbonate (VDC, lithium battery grade) replaced 10 wt% of the FEC in the electrolyte.
carbonate (VEC, lithium battery grade), ethylene sulfite (ES, lithium battery grade), and propylene sulfite (PS, lithium battery grade) were purchased from Kishida Chemical.

Charge/discharge tests were performed at 25 °C using a charge/discharge system (ACD-M01C, Aska Electronic). Cut-off voltages for the discharge and charge processes were set at 2.5 and 4.0 V, respectively. After charge/discharge tests, the lithium metal negative electrode was washed with dimethyl carbonate (DMC). A cross-section of the deposit was observed under a field emission scanning electron microscope (FE-SEM, JSM-6700FV, JEOL) after polishing with ion beams using a cross-section polisher (IB-19520CCP, JEOL). When lithium metal was transferred from the Ar-filled glove box to FE-SEM and the polisher, the transfer vessel used was not exposed to air.

In the present study, lithium utilization was defined as follows:

$$\text{lithium utilization} \ (%)=\frac{\text{areal capacity of } LFP \ (\text{mAh cm}^{-2})}{\text{areal capacity of } \text{Li} \ (\text{mAh cm}^{-2})+\text{areal capacity of } LFP \ (\text{mAh cm}^{-2})} \times 100 \quad (1)$$

### 3. Results and Discussion

Table 1 shows 10 types of cell configurations fabricated to investigate the effects of lithium utilization on the stability of the lithium metal negative electrode toward the charge/discharge cycle. In the present study, 1.0 mol dm$^{-3}$ LiTFSI in EC : PC (1 : 1 vol%), a conventional electrolyte, was selected as the electrolyte to assemble the cell. Figure 1(a) shows changes in the discharge capacity of cells using LFP of 4.3 or 4.4 mAh cm$^{-2}$ and metallic lithium with a different areal capacity (Cell Nos. 1–5 in Table 1). The galvanostatic charge and discharge cycling were conducted at a current density of 1.0 mA cm$^{-2}$, which was calculated from the area of the lithium metal negative electrode. This current density corresponded to an approximately 0.17C rate calculated from the capacity of LFP. The capacity of the cell with high lithium utilization, i.e., using thin metallic lithium as the negative electrode, decayed more rapidly. The lithium that originally existed was gradually consumed during the discharging process. Cells with lower lithium utilization exhibited capacity decay from approximately 100 cycles. Figure 1(c) shows the cumulative discharge capacity of cells. Decay was considered to be caused by the clogging of the separator and depletion of the electrolyte in the cell as the cumulative discharge capacity increased. The cell with lithium utilization of 10% exhibited better cycle performance than the other cells. We are currently investigating why cycle performance did not correspond to the order of utilization, and one of the factors responsible may be the confined pressure in the cell, which changes depending on the thickness of the electrode. Figure 1(b) shows changes in the discharge capacity of cells composed of LFP with different areal capacities and the lithium metal negative electrode of 10.3 mAh cm$^{-2}$, which was the thinnest metallic lithium used in the present study (Cell Nos. 6–10 in Table 1). Galvanostatic charge/discharge cycling was conducted at a current density of 0.2C, which was calculated from the capacity of LFP in each cell. The charge/discharge curves of the cell using LFP with a different areal capacity was shown in Fig. S1. The initial discharge capacity was almost 140 mAh g$^{-1}$, regardless of lithium utilization. The slightly lower capacity of the cell with lithium utilization of 1% was attributed to experimental weighing errors. The capacity of the cell with lithium utilization of 1% exhibited negligible degradation even after 300 cycles, whereas those with lithium utilization of 5, 11, 16, and 30% decayed rapidly after approximately 250, 150, 100, and 30 cycles, respectively. Even when thin metallic lithium was used, more than 300 cycles of charge/discharge was possible when lithium utilization was low. The cumulative discharge capacity of cells was shown in Fig. 1(d). Charge/discharge continued in the cells with lithium utilization of 1 and 5%, even after 200 cycles, due to the smaller cumulative discharge capacity than those of the other cells. In these experiments, the interpretation of the results obtained was slightly complicated because the discharge rate (current density) and amount of metallic lithium changed as the capacity of LFP changed. However, the capacity of the cell with lithium utilization of 30% was restored when the lithium metal negative electrode was replaced by a new one after capacity decay (Fig. S2), clearly indicating that the cause of decay is the metallic lithium negative electrode.

Since cycle performance markedly changed depending on the utilization of lithium, the morphology of lithium after the charge/discharge test was observed by FE-SEM, including cross-sectional observations, as shown in Fig. 2. Cells with lithium utilization of 5 and 30% (Cell Nos. 7 and 10, respectively) were disassembled after 5 and 30 cycles, respectively, and the lithium metal negative electrode was then examined. As shown in Figs. 2(a)–2(d), the surface of lithium was inhomogeneous in both cells after 5 cycles; however, a marked difference was confirmed in cross-sectional images. A thin mossy deposit was detected on the original metallic lithium when lithium utilization was 5%. Contrary thicker deposit (~40 μm thickness) was found when lithium utilization was 30%. Formation of this deposit was attributed to the deposition of the decomposition product of the electrolyte at a higher current density.

### Table 1. Cell configurations to investigate the effects of lithium utilization on the stability of the lithium metal negative electrode.

| Cell No. | Areal capacity of the LFP positive electrode/mAh cm$^{-2}$ | Areal capacity of the lithium metal negative electrode/mAh cm$^{-2}$ | Thickness of the lithium metal negative electrode/μm | Lithium utilization/\(\%\) |
|----------|----------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------|---------------------------|
| 1        | 4.3                                                     | 82.4                                                          | 400                                               | 5                         |
| 2        | 4.4                                                     | 61.8                                                          | 300                                               | 7                         |
| 3        | 4.4                                                     | 41.2                                                          | 200                                               | 10                        |
| 4        | 4.4                                                     | 20.6                                                          | 100                                               | 18                        |
| 5        | 4.3                                                     | 10.3                                                          | 50                                               | 29                        |
| 6        | 0.1                                                     | 10.3                                                          | 50                                               | 1                         |
| 7        | 0.5                                                     | 10.3                                                          | 50                                               | 5                         |
| 8        | 1.3                                                     | 10.3                                                          | 50                                               | 11                        |
| 9        | 2.0                                                     | 10.3                                                          | 50                                               | 16                        |
| 10       | 4.4                                                     | 10.3                                                          | 50                                               | 30                        |
and utilization. After 30 cycles, the mossy deposit was thicker in the cell with lithium utilization of 5%, whereas the original thickness of the lithium metal negative electrode was almost unchanged (Figs. 2(c) and 2(f)). In contrast, in the cell with lithium utilization of 30%, the thickness of the mossy deposit increased and partially extended into the original metallic lithium (Figs. 2(g) and 2(h)). The cell exhibited capacity decay after 30 cycles, as shown in Fig. 1(b), which was considered to be due to the consumption of the original metallic lithium during the discharge reaction. In order to develop a lithium metal negative electrode with high utilization, it is important to suppress mossy deposits during charge and the consumption of metallic lithium during discharge.

Various additives have been proposed to improve the cycle performance of the lithium metal negative electrode, and their chemical structures and amounts have been shown to significantly influence performance. In the present study, typical additives, which are considered to form a film on the negative electrode under a reducing atmosphere, were applied to the electrolyte in the cell with high lithium utilization. Figure 3 shows changes in the discharge capacity and charge/discharge curves of the cell with lithium utilization of 30% when FEC and VC were added to 1.0 mol dm$^{-3}$ LiTFSI in EC : PC (1 : 1 vol%). With both additives, cycle performance was dependent on the amounts added. Comparisons of the effects of FEC and VC revealed that cycle performance...
was favorable when FEC was used as an additive. When VC was added, an increase in overvoltage was confirmed in the charge/discharge curve at 50 cycles, suggesting the formation of a film with higher resistance than with the addition of FEC. VEC, ES, and PS were also examined as additives, and the results obtained indicated that VEC was as effective as VC, while ES and PS did not improve cycle performance (Fig. S3). Figure 4 shows FE-SEM images of the lithium metal negative electrode after the charge/discharge cycle using the electrolyte with 5 wt% of FEC. When the electrolyte containing FEC was used, a black deposit was detected on metallic lithium after disassembling the cell. This deposit was hard, brittle, and easily exfoliated, possibly due to the high content of inorganic components derived from the decomposition of FEC.\textsuperscript{19,21,22}

Figures 4(a) and 4(b) show FE-SEM images of the deposit and the part from which it was exfoliated after 5 charge/discharge cycles, respectively. In cross-sectional images (Fig. 4(c)), the thickness of the deposit was thinner than that obtained in the electrolyte without the additive, suggesting that the decomposition of the electrolyte was suppressed by the film that formed on lithium after the addition of FEC. After 30 cycles, a significant difference was observed between the presence and absence of additives, with the consumption of metallic lithium being negligible in their presence (Fig. 4(d) to 4(f)). These results indicated that the dissolution and deposition of lithium proceeded uniformly due to the film formed by

![Figure 3](image1.png)

**Figure 3.** Discharge capacities against cycle numbers and charge/discharge curves of a LFP/Li cell. The electrolyte was 1.0 mol dm\(^{-3}\) LiTFSA in EC : PC (1 : 1 vol%) containing (a, b) FEC and (c, d) VC. The charge/discharge test was performed at 0.2C rate at 25 °C.

![Figure 4](image2.png)

**Figure 4.** Surface and cross-sectional FE-SEM images of the lithium metal negative electrode after the charge/discharge cycle. Lithium utilization and the number of cycles were as follows: (a, b, c) 30% and 5 cycles, and (d, e, f) 30% and 30 cycles. The electrolyte was 1.0 mol dm\(^{-3}\) LiTFSA in EC : PC (1 : 1 vol%) containing 5 wt% of FEC. The charge/discharge test was performed at 0.2C rate at 25 °C.
the addition of FEC. As shown in Fig. 4(b) and (e), the lithium surface was not heavily roughened at the position from which brittle deposits were exfoliated. Easily exfoliated and thick deposits did not appear to function as a protective film, the so-called solid electrolyte interphase (SEI). If the deposits contained the electrolyte, the electrode/electrolyte interface should be on the lithium. The buried interface between the electrode and film is important for understanding charge/discharge behavior.23-24 The chemical composition of the deposits and the underlying lithium surface will be evaluated by X-ray photoelectron spectroscopy and other methods in the future with changes in the electrolyte and lithium salt.

4. Conclusion

The charge/discharge behavior of a lithium metal negative electrode was investigated with a focus on lithium utilization using a LFP positive electrode. When the charge/discharge test was conducted at a high utilization rate, capacity decay was observed after approximately 30 cycles, regardless of whether the thickness of lithium or capacity of LFP was changed. Cycle performance was improved when additives such as FEC and VC were used in the electrolyte. FE-SEM observations of metallic lithium after cycling showed a difference in the thickness of the deposits on top of lithium that depended on whether FEC was used in the electrolyte. Furthermore, the consumption of metallic lithium was suppressed, which was attributed to the effects of the film formed by the addition of FEC. We are currently investigating the chemical compositions of effective film components, but deposits should be considered in the analysis.

The electrochemical behavior of a lithium metal negative electrode needs to be considered not only in terms of utilization, but also other parameters, such as the electrolyte, lithium salt, type of separator, cell shape, electrolyte volume, confined pressure, current density, and temperature. Although the present results are from our experimental system, they will provide useful information for future research on the practical use of metallic lithium negative electrodes.

Supporting Information

Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00085.

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