Electrochemical Properties and Deposition/Dissolution Behavior of Li Metal Negative Electrode in VS₄/Li Battery

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ABSTRACT

In order to develop high-energy batteries, it is important to understand the charge/discharge characteristics of the Li-metal negative electrode when operating with high Li utilization; these characteristics determine the practical capacity of the negative electrode. In this study, electrochemical properties and deposition/dissolution behavior of Li metal negative electrodes in a VS₄/Li battery with high Li utilization and current density were investigated. The potentials of the positive and negative electrodes were measured separately using a three-electrode cell. During discharge (Li dissolution) at the negative electrode, a semi-quantitative correlation was observed between the Coulombic efficiency and the capacity at which the slope of the potential curve increased sharply. The Coulombic efficiency of the negative electrode improved when vinylene carbonate (VC) or fluorooxyethylene carbonate (FEC) was added to the electrolyte. Granular particles were found to be deposited on the entire surface of the charged negative electrodes. The average particle size followed the order FEC > LiClO₄ > LiNO₃ > Li₂SO₄, which determines the practical capacity of the negative electrode, also exerting a significant influence on the cycle performance.

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1. Introduction

Batteries containing a sulfur-based positive electrode and a Li metal negative electrode (S/Li battery) are extensively investigated as a promising candidate for next-generation batteries. ¹–⁴ Li,S and Li metal have very high theoretical capacities of 1770 and 3860 mAh g⁻¹, respectively. Hence, batteries containing Li,S and Li are expected to have extremely high energy densities. In fact, development of S/Li batteries with an energy density of over 300 Wh kg⁻¹ and even 500 Wh kg⁻¹ is underway.

However, the practical application of S as a positive electrode material is hindered by two major obstacles: low electrical conductivity and dissolution of polysulfide anions into organic electrolytes. To address these problems, use of transition metal polysulfide materials such as Li₂S-Cu, Li₂-FeSₓ, MoS₂, and TiSₓ has been proposed. ⁵–¹⁷ Formation of S-metal bonds improves the electronic conductivity of the electrode and suppresses the dissolution of the anions into the electrolyte. Furthermore, these metal polysulfide electrodes function in carbonate-based electrolytes, which are commonly used in Li-ion batteries and provide high ionic conductivity and effective negative electrode passivation, whereas conventional S electrodes are incompatible with carbonate-based electrolytes. ¹,¹⁴,¹¹,¹³,¹⁸ Earlier, we had reported that the vanadium sulfide (VS₄) electrode exhibits a high initial capacity of above 700 mAh g⁻¹,¹⁹ and we found that the cyclability of the electrode can be improved by amorphizing the VS₄ active material. ²⁰ We are currently examining a 300 Wh kg⁻¹ class battery using a VS₄ positive electrode and a Li metal negative electrode. ²¹

A number of factors, such as electrolyte composition, current collector, separator, confined pressure, and applied current, affect the cycle performance of Li metal electrodes. ²₂–²⁴ Utilization of Li, which determines the practical capacity of the negative electrode, also exerts a significant influence on the cycle performance. ²⁶,²⁷ We previously reported that the use of 30% Li severely degrades the cycle performance of the Li negative electrode, using LiFePO₄ as a stable counter electrode to evaluate the Li electrode. ²⁸ However, it is essential to utilize ≥30% Li to obtain batteries with energy density of over 300 Wh kg⁻¹. In addition, because a high-energy battery has high areal capacity, its charging/discharging at a high current density becomes inevitable. Furthermore, it has been reported that positive electrode materials affect the deposition/dissolution morphology and polarization of the Li negative electrode during charging/discharging through the dissolution of elements present in the positive electrode and the decomposition products of the electrolyte. ²⁹ Therefore, it is important to understand the charge/discharge characteristics of the Li electrode when operating with high Li utilization and high current density with full-cell configuration for developing VS₄/Li batteries.

In this study, we aimed to investigate the charge/discharge characteristics of a Li metal negative electrode in a VS₄/Li battery with high Li utilization and high current density. VS₄/Li full-cells were fabricated using a thin Li negative electrode and a VS₄ positive electrode with sufficient areal capacity. To examine the electrochemical properties of the Li electrode during charge/discharge, the potentials of the positive and negative electrodes were measured separately using a three-electrode cell. The cycle performance was evaluated using electrolytes of different solvents and additives. Furthermore, the surface and cross-sectional morphologies of Li deposition/dissolution at the negative electrode were observed using scanning electron microscopy (SEM). Finally, the correlation between the capacity reversibility and morphology was discussed.
2. Experimental

To improve the charge/discharge properties of the active material, amorphous VS₄ (a-VS₄) was synthesized using crystalline VS₄ (c-VS₄) as the starting material via mechanical milling at room temperature.⁵⁰ c-VS₄ was prepared from VS₃ (99%, Kojundo Chemical Laboratory) and S (99.9%, Wako Pure Chemical), as reported previously.⁵¹ c-VS₄ powder and zirconia balls were placed in a zirconia pot in Ar atmosphere, set in a planetary ball mill apparatus (FRITSCH, Pulverisette 7), and treated at a rotation speed of 270 rpm for 40 h to obtain a-VS₄.

The positive electrode was fabricated using a mixture of 85 wt% a-VS₄ powder, 11 wt% Ketjenblack, and 4 wt% natural polymer-based binder on an Al current collector. An electrode of diameter 14 mm was punched out and used to fabricate a test cell. Next, 50-μm-thick Li metal press-bonded on a Ni current collector (Honjo Metal) was used as the negative electrode (diameter = 15 mm). A three-electrode cell (stainless steel housing) with a Li reference electrode and a polypropylene membrane (Celgard 3501) were used as the electrochemical test cell and separator, respectively. The cells were assembled in an Ar-filled glove box. The VS₄ loading was 6.7 mg cm⁻². The initial capacity per electrode area was determined to be 4.7 mAh cm⁻² from the initial discharge capacity of the positive electrode (approximately 700 mAh g⁻¹), affording Li utilization of 46% for the negative electrode (i.e., the areal capacity ratio of the positive/negative electrodes was 0.46/1). The electrolytes used comprised 1 mol dm⁻³ lithium bis(trifluoromethanesulfonyl)amide (LiTFSAm) solutions with ethylene carbonate/diethyl carbonate (EC/DMC; 1/1 v/v), EC/ethylmethyl carbonate (EC/EMC; 1/1), and EC/polypropylene carbonate (EC/PC; 1/1) as the solvents and vinylene carbonate (VC) or fluoroethylene carbonate (FEC) as the additive at 5 vol%. VC and FEC are typical additives used to improve the cycle performance of Li negative electrodes.²³,⁴⁰ The LiTFSAm solutions with EC/DMC, EC/EMC, and EC/PC were purchased from Mitsubishi Chemical, and VC and FEC were obtained from Kishida Chemical.

The charge/discharge characteristics were evaluated using a potentiostat/galvanostat (Solartron 1287). The cell voltage (V(cell)) and charge/discharge tests using a three-electrode cell. As a cycle test, the cells were charged/discharged 100 times with a cell voltage range of 1.5–2.6 V and a current density of 1.6 mA cm⁻², which correspond to a current-rate of 0.2 C with a specific capacity of 1195 mAh g⁻¹ as 1 C for VS₄. Note that the capacity value with mAh g⁻¹ units represents the capacity per weight of the VS₄ active material.

To confirm the effect of the VS₄ positive electrode on the Li negative electrode, a charge/discharge test using a Li/Cu half-cell also was performed. A Li/Cu two-electrode cell (stainless steel housing) was assembled using a Cu foil (diameter = 16.3 mm) as the counter electrode and the same Li electrode, separator, and LiTFSAm solution as described above. The Li/Cu cell was charged/discharged 100 times at 1.6 mA cm⁻². The discharge cutoff was the capacity of 8.3 mAh (corresponding to 46% Li utilization) or a voltage of –2.0 V and the charge cutoff was +2.0 V. All electrochemical measurements were performed at 25°C.

The surface and cross-sectional morphologies of the negative electrodes after the initial charge/discharge were observed using two types of scanning electron microscopes. For surface observation, the JSM-6510A scanning electron microscope (JEOL) was used at an accelerating voltage of 10 kV. The cross-sectional morphology and composition of the electrodes were investigated using the SU-8230 scanning electron microscope (5 kV, HITACHI) and energy-dispersive X-ray spectroscopy (EDX; OXFORD INSTRUMENT, X-MaxN, 10 kV), respectively. The samples for the cross-sectional SEM and EDX were prepared using Ar-ion milling (Gatan, Ion, liquid-nitrogen cooled). All samples for SEM were observed without exposure to the atmosphere.

3. Results and Discussion

Figure 1a shows typical changes in V(cell) and Pₑ during the charge/discharge (3rd cycle) of VS₄/Li cells, in which EC/PC was used as the solvent. A discharge capacity of >600 mAh g⁻¹ per VS₄ weight was observed. Because both the negative and reference electrodes comprise Li metals, their V(cell) and Pₑ were almost equal, except during the late stages of discharge.

Figure 1b shows the change in Pₑ during the same charge/discharge cycle as depicted in Fig. 1a. During charging (Li-deposition process), the absolute value of Pₑ, which shows the polarization of the Li negative electrode, decreased rapidly at the beginning of the charge and then became almost constant. The former could be attributed to the decrease in reaction resistance due to the increase in the Li-deposition area by nucleation, while the latter could reflect the deposition of Li over the entire electrode and the deposition area becomes almost constant. During the discharge (Li dissolution), Pₑ increased gradually from the beginning to the middle of the discharge, while it increased sharply at the late stage of discharge. This potential change during discharge can be understood as follows: During the dissolution of the Li deposited in the previous charging cycle, the reaction environment did not change suddenly; therefore, Pₑ also changed slowly (dissolution 1 in Fig. 1b). When bulk Li begins to dissolve after the soluble portion of the deposited Li is dissolved completely, the reaction resistance increases and Pₑ increases sharply (dissolution 2). Resistance in dissolution 2 increases because of the possible formation of a high-resistivity film on the surface of bulk Li, and the reaction is limited to a narrow region because the bulk Li surface is covered by the residue that did not dissolve during dissolution 1. According to this model, the
capacities at dissolutions 1 and 2 are due to reversible and irreversible Li deposition/dissolution, respectively. Therefore, the ratio of the capacity of dissolution 1 to the total capacity, i.e., the normalized capacity value at the end point of dissolution 1, almost closely corresponds to the Coulombic efficiency of the negative electrode.

Figure 2 shows $P_N$ plotted against the normalized capacity during discharge at the 2nd, 3rd, and 4th cycles using EC/PC, VC-added EC/PC (EC/PC + VC), and FEC-added EC/PC (EC/PC + FEC). In all cycles, the increase in $P_N$ at the late stage of discharge when VC or FEC was added was delayed compared to that without the addition. The above interpretation of dissolutions 1 and 2 suggests that the Coulombic efficiency of the Li negative electrode with the additive is higher than that without the additive. In addition, EC/PC + FEC showed a lower $P_N$ than the other two over the entire discharge region. This indicates that the addition of FEC reduced the reaction resistance of Li dissolution at the negative electrode. Here, no significant difference was observed in the discharge curves of the 1st cycle with and without additives. Generally, a slightly soluble film composed of constituents such as LiO$_2$, Li$_2$CO$_3$, and LiOH, is formed on the surface of pristine Li electrodes (the so-called native film). In the 1st discharge, because the polarization was large during the dissolution of Li through the native film, it is considered that the difference in polarization resulting from the use of the additives was difficult to observe.

Figure 3a shows the $V_{Cel}$, $P_P$, and $P_N$ curves during the cycle test using EC/PC. After 30 cycles, the discharge capacity decreased significantly. At the end of the discharge in the capacity-reduced cycles, $P_N$ greatly increased (>0.2 V) and $P_P$ became much higher than the cut-off $V_{Cel}$ of 1.5 V. That is, the end of the discharge is controlled by $P_N$. Because the large increase in $P_N$ indicates the depletion of active Li in the negative electrode, degradation of the negative electrode is the major reason for the decrease in the capacity. The degradation of the negative electrode from this relatively early cycle is largely due to the charge/discharge at high Li utilization.

The $V_{Cel}$, $P_P$, and $P_N$ curves during the cycle test with EC/PC + VC and EC/PC + FEC are shown in Figs. 3b and 3c, respectively. In both cases, no significant increase in $P_N$ was observed up to 100 cycles, and $P_P$ reached almost 1.5 V at the discharge end. This result indicates that Li in the negative electrodes remained active even after the cycle test. This improvement in the cyclability of the Li electrode is attributed to the increase in the Coulomb efficiency by the addition of VC or FEC. This result is consistent with the tendency expected from the shapes of the $P_N$ curves shown in Fig. 2. In addition, the absence of an increase in $P_N$

![Figure 2](image)

**Figure 2.** $P_N$ plotted against the normalized capacity during discharging at the 2nd, 3rd, 4th cycles, using EC/PC, VC-added EC/PC (EC/PC + VC) and FEC-added EC/PC (EC/PC + FEC).

![Figure 3](image)

**Figure 3.** $V_{Cel}$, $P_P$, and $P_N$ curves during the cycle test using (a) EC/PC, (b) EC/PC + VC, and (c) EC/PC + FEC.
Although the capacity decreased synchronously with the increase in the negative electrode, the capacity change can be calculated mainly by the degradation of the negative electrode. Even with the additive, the decrease in the former and the increase in the latter were well synchronized without the additive. Even with the additive, the decrease in the capacity can be attributed mainly to the degradation of the negative electrode. Figure 4c shows the result when EC/PC was used as the solvent. Although the capacity decreased synchronously with the increase in \( P_N \) without the additive, no increase in \( P_N \) was observed for up to 100 cycles with the additives. This result indicates that the Coulombic efficiency of the Li electrode was significantly improved by the addition of VC or FEC. It also indicates that the capacity decrease in the case of EC/PC with the additives is mainly due to the degradation of the positive electrode. Furthermore, the value of \( P_N \) in EC/PC + FEC was lower than that in EC/PC or EC/PC + VC, indicating that the addition of FEC decreased the reaction resistance of Li dissolution at the negative electrode. These results show that EC/PC + FEC is best suited for improving the performance of the negative electrode. The discharge capacities at the 2nd cycle with EC/PC, EC/PC + VC, and EC/PC + FEC were 625, 539, and 689 mAh g\(^{-1}\), respectively. The initial capacity of the VS\(_4\) positive electrode was the highest when EC/PC + FEC was used. In addition, EC/PC + FEC had a higher capacity to up to 50 cycles than the other two (EC/PC and EC/PC + VC). EC/PC + FEC was also the optimum choice for the VS\(_4\) positive electrode. The solvents and additives are stable at the positive electrode potential (1.5–2.6 V), but are reduced at the negative electrode potential (~0 V). Decomposition products at the negative electrode can adversely affect the cyclability of the positive electrode. It is possible that the addition of FEC led to the formation of a stable film on the surface of the positive electrode, thereby suppressing the formation of decomposition products and the resulting effect on the positive electrode. Here, because VS\(_4\) is initialized to Li\(_x\)VS\(_4\) with a structural change during the 1st discharge, the 2nd discharge capacity value is a more suitable index for comparing the initial Li-release capability of the positive electrode.

A comparison of the changes in \( P_N \) showed that the cyclability of the negative electrode is better in EC/PC-based electrolytes than in EC/DMC- and EC/EMC-based electrolytes (Figs. 4a, 4b, and 4c). A previous study on the effects of electrolytes on Li electrodes has reported that cyclic carbonate solvents (PC and EC) lead to better uniformity of deposited Li film and higher Coulombic efficiency than linear carbonate solvents (DMC and EMC). It is suggested that the difference in the molecular structure affected the decomposition behavior of the solvents on the surface of the Li electrode, resulting in a difference in the deposition/dissolution morphology and the reversibility of Li.

Assuming that the capacity decrease with cycling was caused only by the negative electrode, the capacity change can be calculated from the Coulombic efficiency of the negative electrode. In the absence of the additive, this assumption can be applied as a rough approximation because the capacity reduction was greatly dominated by Li depletion of the negative electrode. The curves shown in Fig. 5a are the capacity changes calculated with different Coulombic efficiencies, using the values of the initial capacity and Li utilization for charge/discharge with EC/EMC (6.4 mAh and 41 %, respectively) and EC/PC (6.9 mAh and 44 %, respectively). The Coulombic efficiencies were estimated to be 0.85 and 0.94 by comparing the measured values of the discharge capacity in EC/EMC and EC/PC, respectively (triangle and square symbols, respectively, in Fig. 5a). Figure 5b shows \( P_N \) (normalized at maximum \( P_N \) during each cycle) plotted against the normalized capacity during the 4th to 12th and 4th to 20th discharges with EC/EMC and EC/PC, respectively. The \( P_N \) for EC/EMC and EC/PC increased sharply around the estimated efficiencies of 0.85 and 0.94, respectively. This result indicates that the deposition/dissolution model described above, in which the normalized capacity at the end point of dissolution 1 corresponds to the Coulombic efficiency of the negative electrode, is semi-quantitatively appropriate. In the case of EC/PC + VC and EC/PC + FEC, the above calculation is not directly applicable because Li was not depleted in the negative electrode during the cycle and the positive electrode degradation had a large effect on the capacity decrease. However, the Coulombic efficiency of the positive electrode is limited by the Coulombic efficiency of the negative electrode.

**Figure 4.** Discharge capacity and \( P_N \) at the discharge-end during the cycle test, using (a) EC/DMC, (b) EC/EMC, and (c) EC/PC as the solvents.
Figure 5. (a) Capacity changes calculated with different Coulombic efficiencies, using the values of initial capacity and Li utilization for the charge/discharge with EC/EMC (6.4 mAh and 41%) and EC/PC (6.9 mAh and 44%), along with the measured values of the discharge capacity (triangle and square symbols). (b) $P_N$ (normalized at maximum $P_N$ during each cycle) plotted against the normalized capacity during the 4th to 12th and 4th to 20th discharges with EC capacity (triangle and square symbols). (c) Calculated capacity retention at Li utilization of 50% for the Coulombic efficiency of 0.95, 0.98, and 0.99. (d) The discharge capacity change measured during the cycle test in the Li/Cu half-cell using EC/PC (circle symbol), along with the capacity change calculated when the Coulombic efficiency was 0.94 (solid line).

efficiency of those with a higher cyclability of the negative electrode than EC/PC was estimated to be greater than 0.94. Figure 5c shows the calculated capacity retention at Li utilization of 50% for the Coulombic efficiencies of 0.95, 0.98, and 0.99. The Coulombic efficiency of 0.99 is required to achieve a negative electrode cyclability of more than 100 cycles. The Coulombic efficiency of the negative electrode at high Li utilization should be further increased for the practical application of Li electrode in high-energy batteries.

Figure 5d shows the change in the discharge capacity measured during the cycle test in a Li/Cu half-cell using EC/PC (circle symbol). The measured capacity change was in good agreement with the calculated capacity change when the Coulombic efficiency was 0.94 (solid line). Hence, there is no significant difference in the Coulombic efficiency of the Li electrode of the VS$_4$/Li full-cell and the Li/Cu half-cell, suggesting that the VS$_4$ positive electrode did not exert any major effect on the cyclability of the Li negative electrode. Here, for charge/discharge by the half-cell, because Li metal is deposited/dissolved on both the Li electrode and the Cu counter electrode, the amount of Li inactivated per cycle was calculated as follows: (charge or discharge capacity) \times (1 - efficiency value) \times 2.

To investigate the effect of the additives on the dissolution/deposition behavior of Li, the surface and cross-sectional morphologies of the Li negative electrodes charged/discharged using EC/ PC, EC/PC + VC, and EC/PC + FEC were observed by SEM. In the surface SEM, the samples were observed at a tilt angle of 45° to facilitate the viewing of the three-dimensional morphology. Figures 6a, 6b, and 6c show low-magnification SEM images of the Li electrode surface after the 1st discharge (1st dissolution), 1st charge (1st deposition), and 2nd discharge (2nd dissolution), respectively. A pitted morphology (10–50 µm pitch) due to nonuniform dissolution was observed in all electrodes after the 1st discharge. After the 1st charge, the entire electrode was covered with deposits, and after the 2nd discharge, it was covered with finer deposits. Macroscopic dissolution/deposition morphology was common for all the three samples.

Figures 7a, 7b, and 7c show high-magnification SEM images of the Li electrode surface after the 1st discharge, 1st charge, and 2nd charge, respectively. After the 1st discharge, a fine fibrous insoluble residue was observed on the uneven morphology of all electrodes. After the 1st charge, granular particles deposited on the entire surface of the electrodes were observed. The average particle size followed the order EC/PC + FEC > EC/PC + VC > EC/PC. Some cord-shaped deposits were also observed in EC/PC and EC/PC + VC. After the 2nd discharge, very fine fibrous residues covering the entire electrode were observed. While almost exclusively fibrous residues were observed in EC/PC + VC and EC/PC + FEC, some cord-shaped residues were also observed in EC/PC. Similar residues have been observed in previous studies, in which the residues were found to contain inactivated Li comprising.
both chemically formed Li compound and electrically insulated Li metal.26,29-31,44-46 Thus, the amount of the residues is considered to be the dominant factor in determining the Coulombic efficiency of the Li electrode. This result suggests that the efficiency is lower for EC/PC with a mixture of fibrous and cord-shaped residues and high for EC/PC + VC and EC/PC + FEC without cord-shaped residues. This result can also explain the improvement in the cyclability of the negative electrode by the addition of VC or FEC (Fig. 4c).

It must be noted here that the Li electrode in EC/PC + FEC, which has a large particle size, has a smaller surface area than those in EC/PC and EC/PC + VC (Fig. 7b). This result could mean that the area of the reaction interface decreases when FEC is added. The smaller the reaction interface, the larger the reaction resistance. In contrast, FEC addition decreases the resistance of Li dissolution (Figs. 2 and 4c). Hence, it can be suggested that the change in resistance due to the addition of FEC is caused by other factors such as the resistance of the surface film (i.e., the solid electrolyte interphase; SEI) of the Li electrode.

Figures 8a and 8b show cross-sectional SEM images and EDX composition maps of the Li negative electrode after the 3rd discharge using EC/PC and EC/PC + FEC, respectively. C, O, F, and S were detected in the residue area. Because these are the constituent elements of the electrolyte, a significant portion of the residue was decomposed by the side reaction between the electrolyte and the Li electrode (S could be derived from both the electrolyte and the VS4 positive electrode). Because the products must contain Li compounds, suppressing the side reaction is important for further increasing the Coulomb efficiency of the Li electrode. In EC/PC + FEC, the intensity of F was higher than that in EC/PC. Because FEC containing F has a higher reduction potential than EC and PC, FEC was preferentially decomposed and F was incorporated into the product. Previous studies on FEC addition have reported that SEI-containing LiF is formed on the surface of the Li electrode, thereby reducing the resistance of Li deposition/dissolution reaction.40-42,47 It can be suggested that this F-containing component is responsible for improving the Coulombic efficiency by the addition of FEC. Furthermore, the presence of this component in the SEI of the Li electrode may reduce the reaction resistance of Li dissolution when PC/EC + FEC is used.

4. Conclusions

The electrochemical properties and deposition/dissolution behavior of Li metal negative electrodes in VS4/Li batteries with high Li utilization and current density were investigated. The potential
change of the negative electrode during charging/discharging was understood to reflect the physical processes during Li deposition/dissolution. The Coulombic efficiency estimated from the capacity at which the slope of the negative electrode potential curve sharply increases during discharge and that estimated from the capacity decreases during the cycle test were semi-quantitatively consistent.

EC/PC + FEC was the most suitable choice for improving the cyclability of both the negative and positive electrodes. The Coulombic efficiency of the negative electrode using EC/PC was estimated to be approximately 0.94, and those using EC/PC + VC and EC/PC + FEC were >0.94. The average size of the particles deposited during charging followed the order EC/PC + FEC > EC/PC.

**Figure 7.** High-magnification SEM images (tilt 45°) of the Li electrode surface after (a) the 1st discharge, (b) 1st charge, and (c) 2nd discharge.

**Figure 8.** Cross-sectional SEM images of the Li negative electrode after the 3rd discharge using (a) EC/PC and (b) EC/PC + FEC.
PC + VC > EC/PC. A mixture of fine fibrous and cord-shaped residues was observed on the discharged negative electrode using EC/PC, while almost exclusively fibrous residues were observed on the electrode using EC/PC + FEC. The improvement in Coulombic efficiency with the addition of FEC can be attributed to the reduction in the amount of the cord-shaped residue. A significant portion of the residue comprised the product of the side reaction between the electrolyte and the Li electrode. Hence, suppressing the side reaction is important for further increasing the Coulombic efficiency of the negative electrode. A detailed study on residue formation and the chemical and physical structures of residues is under progress.

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