The growth of dendrites on the electrodes during charge–discharge cycles can lead to short-circuit and potential ignition, which limit the capacity and application of the rechargeable batteries. With the development of in situ electrochemical liquid cell transmission electron microscopy, the growth process of metallic dendrites can be observed in real-time. However, there remains a great challenge to operate the electrochemical liquid cell experiments successfully and repetitively. Herein, the lithium-ion battery electrolyte system and the other electrolyte system of silver nitrate with sodium nitrate aqueous solution are adopted in our experiments to demonstrate the problems in conducting electrochemical liquid cell experiments. Influence factors are summarized, including the tube residual, cleanliness of electrodes, bubbles in the liquid cell, and the stability of the electrochemical system. All these aspects affect the electrochemical liquid cell experiments, and understanding these influencing factors is beneficial to improve the success rate of experiments. This work may offer guidance for the wide application of in situ electrochemical liquid cell transmission electron microscopy in observing the growth of dendrites in batteries.

1. Introduction

The growth of metallic dendrites on the anode during the charge–discharge cycles is a major obstacle for the next-generation electrochemical liquid cell experiments. These dendritic structures are known to be the leading cause of short-circuit and thermal runaway. Therefore, the formation of dendrites in electrochemical cells indicates immediate security issues about next-generation battery development. To deal with the dendritic issues, it is crucial to observe these formed dendrites under different conditions and explore underlying mechanisms.

Multiple methods have been employed to observe the dendrites including spectroscopic techniques such as Raman spectroscopy, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, and transmission electron microscopy (TEM). However, it is difficult to study the structure and chemistry of dendrites at the nanoscale because of the limited spatial resolution. In recent years, there are some researches on the lithium dendrites at cryogenic temperatures by transmission electron microscopy (TEM) but the growth dynamics of dendrites are invisible in the analysis. With the development of micro-electromechanical systems (MEMS) technology in situ liquid cell TEM (LC-TEM), it has become feasible to observe the deposition and dissolution of dendrites in the charge–discharge cycles, and there are a few successful cases on observing metallic dendrites in situ electrochemical liquid cell experiments, such as lithium dendrite and silver dendrite. Compared with the spectroscopic techniques and TEM operated at cryogenic temperatures, LC-TEM allows observing the formation of dendrites in electrochemical reactions, which offers the opportunity to study the growth dynamics of dendrites in real-time at the nanoscale. However, owing to the limited space in TEM liquid cells in contrast to the conventional electrochemistry, there are still many problems in operating the in situ electrochemical liquid cell experiments, making it difficult to be reproduced and widely applied. Analyzing these problems is beneficial to the repeatability of in situ electrochemical liquid cell experiments. Here, experimental challenges of in situ LC-TEM of two electrochemical deposition systems are demonstrated and discussed. The two systems are 1) 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate/diethyl carbonate in a 1:1 volume ratio (1:1 EC/DEC) and 2) 2 mM silver nitrate (AgNO₃) with 50 mM sodium nitrate (NaNO₃). The cyclic voltammogram (CV) shows some common problems in electrochemical deposition-dissolution processes. By adjusting the parameters of experiments, a normal CV can be achieved. The influence factors of tube residual, pretreatment of MEMS device, and stability of electrochemical systems are discussed, and all these aspects affect the success rate of electrochemical liquid cell experiments.

2. Results and Discussions

2.1. Experimental Equipment

The conventional three-electrode electrochemical device is shown in Figure 1a, and the working electrode (WE), reference electrode (RE), and counter electrode (CE) are fixed on a reaction tank. With
the development of MEMS chip for LC-TEM, the function of electrification has been achieved by the miniaturized circuits. In the electrochemical TEM setup, the top chip has three electrodes with a built-in spacer of 500 nm and the WE is on the electron-transparent silicon nitride (Si$_3$N$_4$) membrane window, whereas the bottom chip only has a membrane window and its spacer is 500 nm. Therefore, the two chips are assembled into an electrochemical liquid cell as shown in Figure 1b, and the paired chips can be loaded on a TEM holder (Poseidon Select, Protochips) to observe the electrochemical process in real-time. The bottom chip is embedded in a gasket at the apical groove area of the holder, and the top chip covers the bottom chip and groove area, and finally the Poseidon Select lid compacts the paired chips to form an airtight chamber. Using the chip-based TEM holder, both ex situ and in situ electrochemical experiments can be performed. The ex situ electrochemical liquid cell experiment is displayed as in Figure 1c, and the paired chips are loaded at the tip of the TEM holder while the electrolyte flows through the liquid cell by inlet and outlet tubes. To reduce the noise of electrochemical test in ex situ experiments performed outside of the microscope, the electrochemical station needs to be grounded. The ex situ electrochemical liquid cell experiment eliminates the effect of electron beam and high vacuum environment, and it is a convenient way to study the influencing factors on electrochemical liquid cell experiment. Figure 1d indicates the in situ electrochemical liquid cell experiment inside the microscope, and the dynamic process of the WE can be observed under the electron beam, which provides an understanding of the metallic dendrite formation during the electrochemical process.

### 2.2. Electrochemical Liquid Cell Experiment Using Commercial Lithium Electrolyte

To study the formation of lithium dendrites during the charge-discharge cycles, the 1 M LiPF$_6$ in a 1:1 volume ratio EC/DEC is used as an electrolyte in the experiment. All three electrodes are platinum in an electrochemical liquid cell chip. First, the ex situ electrochemical liquid cell experiment is performed outside of the microscope, and the flow rate of the electrolyte is 3 uL min$^{-1}$. The open-circuit potential (OCP) of the system is shown in Figure 2a, and the potential between RE and WE drops several hundred millivolts (mV) in a few minutes, indicating that the electrochemical system is not stable, which could be caused by bubbles in the electrolyte. When the applied voltage is scanning from $-1.0$ to $-3.2$ V with a scanning rate of $20$ mV s$^{-1}$, there is a sharp increase of current around $-3.0$ V, suggesting the reduction reaction of LiPF$_6$ has taken place on the WE. However, the overload current occurs when the reduction peak is imminent (Figure 2b). To observe the reaction process on the WE and understand the reason for the current overload, then the holder is inserted into the microscope to in situ observe the electrochemical reaction process using the same applied potential conditions. However, the CV is always messy when the potential is applied with an electron beam either on or off as indicated in Figure 2c, indicating that the electron beam has no effect on this process. In the meantime, no significant change can be observed on the WE (Figure 2d). The messy CV and the TEM observation cannot provide the specific reason for the failure of the experiment. In addition, as the commercial lithium electrolyte is a complex system when the reduction of Li$^+$ takes place in the WE, what happens on the CE is not clear. These unsuccessful ex situ and in situ experiments demonstrate the road is hard for electrochemical TEM study of lithium-ion batteries. Bubbles are easily generated in the electrolyte system during the CV process, which could be the cause of current overload and messy curves. Because of the complicated electrolyte system and electrochemical irreversibility, there remains a great challenge to study the lithium dendrites using a commercial chip-based TEM holder. For the purpose of observing the lithium dendrites in electrochemical liquid cell experiments, as will be detailed in Section 2.4.
2.3. Electrochemical Liquid Cell Experiment Using AgNO₃ with NaNO₃ Aqueous Electrolyte

As observing Ag dendrites are normally easier than Li dendrites, then a simple electrolyte system of AgNO₃ with NaNO₃ is selected to further demonstrate the problems in electrochemical liquid cell experiments. In this case, all experiments are carried out ex situ. After several attempts, the electrolyte of 2 mM AgNO₃ with 50 mM NaNO₃ is able to obtain normal CV, and the CV curve is depicted in Figure 3a. It can be seen that both the oxidation and reduction peaks appear in the CV curve. The scanning voltage range is between -500 and 50 mV with a scanning rate of 40 mV s⁻¹, and the flow rate of the electrolyte is 3 μL min⁻¹. After the electrochemical experiments, the top chip is inserted into the microscope for checking. Some dendrites can be found on the WE (Figure 3b), and energy-dispersive X-ray spectroscopy (EDS) mapping confirms that the dendrites are pure Ag (Figure 3c). Furthermore, the electron diffraction pattern obtained from the tip of a dendrite shows the single crystalline feature of [101] zone axis of Ag (Figure 3d). Therefore, by giving attempts of ex situ electrochemical liquid cell experiments before doing in situ directly, some problems may be avoided and the success rate might be improved. Next, on the basis of these two examples, some common issues are summarized and discussed in the following.

2.4. Common Problems in Electrochemical Liquid Cell Experiments

2.4.1. The Tube Residual

Although the tubes are cleaned after liquid flow experiments, residual still exists in tubes. This problem is easily ignored by many researchers. To demonstrate it, the precipitations in flowing electrolytes caused by tube residual are checked after the experiments. Some precipitations appear in the effluent liquid when the electrolyte of AgNO₃ with NaNO₃ aqueous solution flows through the inlet and outlet tubes. The elemental composition of precipitations is analyzed and shown in Figure 4. It can be seen that the precipitations contain chlorine, silver, and carbon elements. The precipitations indicate the AgNO₃ electrolyte reacts with the residual in tubes, and it may cause the instability of the electrochemical experiments. To minimize the effect of tube residual, the tubes are suggested to be cleaned several times by water or ethanol before the start of the next electrochemical liquid cell experiment.
Figure 3. The ex situ electrochemical liquid cell experiment of AgNO₃ with NaNO₃ aqueous electrolyte. a) The CV curves scan between −500 to 50 mV with a scanning rate of 40 mV s⁻¹. b) TEM image of the dendrites. c) The EDS mapping shows the dendrites are pure Ag. d) The electron diffraction pattern of an Ag dendrite (inserted image with a 50 nm scale bar).

Figure 4. The scanning transmission electron microscopy (STEM) image of precipitate (200 nm scale bar) and its corresponding EDS mappings. It shows that the carbon, silver, and chlorine elements exist in the precipitate.
2.4.2. Pretreatment of Chips

The cleanliness of the electrode surface is one of the most important problems in electrochemical experiments. In addition to the ordinary cleaning of electrochemical liquid chips by acetone and methanol, 10% nitric acid solution and deionized water are also used to clean the chips, and the plasma cleaning of chips is the final step of cleaning. Through these procedures, the cleanliness of the chips can be guaranteed.

2.4.3. Bubbles

Another common issue is the formation of bubbles in the liquid cell, which can be prevented by modifying the electrode. For example, when zinc is deposited on the WE through the reduction of aqueous zinc sulfate solution, the water on the CE is oxidized to release oxygen. By depositing zinc on the WE can reduce the formation of oxygen bubbles, the deposition method is vacuum deposition by brass wire.\[34\] Besides, the ultrasound of electrolytes and tubes filled with liquid in advance are both beneficial to prevent the introduction of bubbles. These bubbles may affect the uniform distribution of electrolytes and disconnect the RE from the electrochemical system.

2.4.4. Open Circuit Potential

The OCP of the electrochemical system should be tested before collecting the CV curve. OCP is an index of the stability of an electrochemical system. For a stable system, the OCP generally fluctuates within 5 mV in minutes as shown in Figure 5. There is much greater analytical certainty for the next CV process based on the constant OCP. The long-time flow of electrolytes will improve the stability of the electrochemical system in liquid cell experiments.

By reducing tube residual, thorough cleaning of chips and preventing the introduction of bubbles, the repeatability and success rate of in situ electrochemical liquid cell experiments may be improved.

3. Conclusion

Although a few examples of the observation of dendrite formation by in situ electrochemical LC-TEM have been demonstrated in previous reports, there remains a great challenge to make the electrochemical process in liquid cell repeatable and widely used. By studying the electrochemical process using commercial lithium battery electrolyte and AgNO₃ aqueous solution system in liquid cell, some common issues on electrochemical liquid cell experiments are summarized and discussed. The precipitate from the electrolyte is easily caused by tube residual, and the uncleaned electrodes and the bubbles in the liquid cell could result in the overload of current. Thorough cleaning of tubes and chips is helpful to improve the stability of the electrochemical process, and the bubbles can be avoided by pretreatment of electrolyte and modifications of CE. Furthermore, the OCP serves as an index indicating whether or not the electrochemical system is stable, and the fluctuations of OCP should be within 5 mV in a stable electrochemical system. Taking these factors into account when operating electrochemical liquid cell experiments, the successful CV curves can be obtained as that of the macro-scale conventional electrochemistry. These pitfalls discussed here may offer useful tips for performing in situ electrochemical liquid cell experiments. On this basis, understanding the formation of dendrites in a rechargeable battery system can be better achieved. Hence, future work on the mechanisms of dendrites formation in different electrolyte systems and thereby inhibit the growth of dendrites in batteries is expected.

4. Experimental Section

Electrolyte Preparation: 2 mM AgNO₃ with 50 mM NaNO₃ aqueous solution was used for the deposition of Ag dendrites. Commercial battery
electrolyte of 1 M LiPF₆ in a 1:1 volume ratio EC/DEC was used for the growth of lithium dendrites.

In situ Electrochemical Liquid Cell Experiments: The top chip was ECT-45 PT with three platinum electrodes, and the bottom chip was ECB-39 GF with 500 nm spacer. The chips were purchased from Protochips, Inc. The paired chips were assembled on the Protochips Poseidon holder. The electrochemical workstation was Gamry Reference 600+.

The Characterization of TEM: The TEM image, diffraction pattern, and EDS mappings were all obtained from JEOL JEM-200 F at 200 kV.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

cyclic voltammograms, dendrites, electrochemical liquid cells, transmission electron microscopy

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