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ARTICLE

Unveiling the Mechanisms of Lithium Dendrite Suppression by Cationic Polymer Film Induced Solid-Electrolyte Interphase Modification

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It is crucial to suppress lithium dendrite formation in lithium metal batteries. Formation of good solid-electrolyte interphase (SEI) has been considered to be effective in limiting lithium dendrite growth. However, how SEI may be modified during lithium deposition is hard to resolve due to challenges in *in-situ* investigation of the SEI with fine details. We report an *in-situ* study that uncovers the lithium dendrite suppression mechanism arising from SEI modifications by a poly(diallyldimethylammonium chloride) (PDDA) cationic polymer film, using electrochemical liquid cell transmission electron microscopy (TEM). Lithium nanogranules are obtained in the presence of the polymer film. Chemical mapping of the deposits provides remarkable details of SEI on individual nanogranules. It shows that lithium fluorides are uniformly distributed within the inner SEI layer of individual lithium nanogranules, arising from the instantaneous reaction of the deposited lithium with PF_6^- ions accumulated by the cationic polymer film, thus the dendritic growth of lithium is prohibited. The ability to directly measure SEI chemistry at the nanoscale down to the individual nanograins *in-situ* and unveil its correlation with lithium deposition behavior opens future opportunities to explore unsolved mechanisms in batteries.

Introduction

Lithium metal anodes have more than ten times higher theoretical specific capacity than graphite anodes currently used in lithium ion batteries. However, dendritic growth of lithium metal results in shortened cycle life of devices utilizing these anodes and can cause serious safety issues. Thus, the exploration of effective means to limit the lithium dendrite formation is significant for developing next generation high energy batteries.[1] Many studies have shown that polymer films coated on the lithium anode can successfully suppress the growth of lithium dendrites.[2] For instance, improved performance has been achieved in lithium metal batteries with polymer film coated electrodes.[3-8] The suppression of dendrite growth is often attributed to the mechanical properties of the polymer films[3-5] or the improved physicochemical properties of the solid-electrolyte interphase (SEI) formed on lithium metal by electrolyte decomposition.[6-8] It is well known that SEI plays a critical role in allowing the lithium anode to function in batteries.[1] However, since SEI and lithium metal are sensitive to air exposure and may be damaged by post processing, it has been a great challenge to directly study the SEI on lithium experimentally.[9] So far, it is unclear how SEI is modified (e.g., by a polymer film) at the nanoscale and thus suppress the lithium dendrite formation.

A variety of methods[10-15] have been used to investigate SEI including the spectroscopic techniques such as x-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy, etc. Characterizations with the spectroscopic methods have contributed to the understanding of SEI chemistry.[9, 15] However, due to the limited spatial resolution, it is hard to resolve the structure and chemistry of SEI at the nanoscale.[10-12] In contrast, transmission electron microscopy (TEM) is powerful in providing spatially resolved information. For example, TEM operated at cryogenic temperature (Cryo-EM) has recently used to study SEI and an unprecedented level of information on the structures of SEI has been achieved.[13, 14] However, damage to SEI during post processing of the sample is a major concern. In order to reveal the modifications of SEI fine structure induced changes in the growth behavior of lithium, *in-situ* TEM studies of the dynamic electrochemical deposition of lithium can be the most effective approach.

We investigate the mechanisms of lithium dendrite suppression by a poly(diallyldimethylammonium chloride) (PDDA) cationic polymer film through direct measurement of SEI using *in-situ* electrochemical liquid cell TEM. PDDA is an attractive high charge density cationic polyelectrolyte,[16-18] which is

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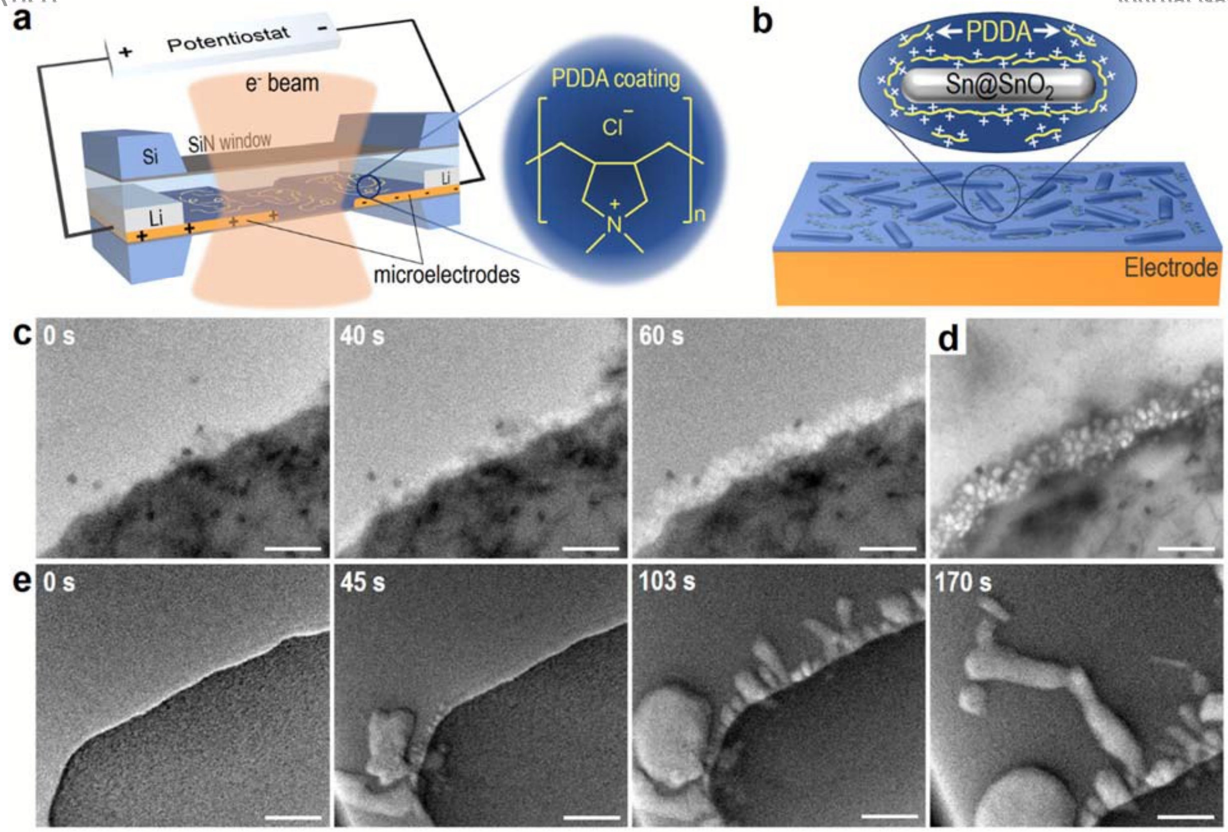

Fig. 1. *In-situ* electrochemical liquid cell transmission electron microscopy (TEM) investigation of the cationic polymer film effects on the electrochemical deposition of lithium. (a) A schematic design of the *in-situ* liquid TEM experiment with a cationic polymer coating. The chemical structure of the cationic polymer, poly(diallyldimethylammonium chloride) (PDDA), is also shown. (b) A schematic drawing of Sn@SnO_2 nanostructure-assisted cationic polymer coating for the *in-situ* liquid TEM experiment. (c) Sequential TEM images of *in-situ* lithium metal plating in the presence of the Sn@SnO_2 nanostructure-assisted cationic polymer coating layer (Video S1). (d) A TEM image obtained after the *in-situ* liquid TEM experiment corresponding to (c). (e) Sequential TEM images of *in-situ* lithium dendritic growth in an electrochemical liquid cell without the polymer film (Video S3). All scale bars are 1 µm.

multifunctional in battery applications including as a polymer electrolyte.[18-23] PDDA polymer electrolyte has shown high Li-ion conductivity, chemical and thermal stabilities.[17] It has been reported that the PDDA film on the anode can improve the performance of lithium metal batteries,[17, 19] however the underlying mechanisms are still unsolved. We consider that the beneficial results are unlikely derived from the mechanical suppression of lithium dendrites by the polymer film itself, since the PDDA film may not offer better mechanical properties than a typical separator.[24-27] In this work, we directly compare the dynamic electrochemical deposition of lithium in liquid TEM cells and characterize their SEIs under conditions with and without the PDDA cationic polymer film. Changes in the lithium growth behavior due to the polymer density variations are also studied. Importantly, direct mapping of the chemical distribution within the SEI is accomplished using scanning TEM (STEM) energy-dispersive x-ray spectroscopy (EDS) without using destructive techniques or low temperature experiments.[13, 14] Our *in-situ* experiment results are also supported by coin cell battery experiments, which validate the nanoscale *in-situ* approach.[28] This study allows to unveil the mechanisms of lithium dendrite suppression by a polymer film through modifications of SEI chemistry. It demonstrates significant advances in the investigation of spatially resolved SEI chemistry with *in-situ* experiments. The results expand our knowledge on the lithium dendrite suppression and controlling of lithium SEI chemistry, which is essential for future lithium battery development.

Results and discussion

In-situ lithium growth under a cationic polymer film

A schematic design of the *in-situ* electrochemical liquid cell TEM setup is shown in Fig. 1a. A Li/Li symmetric cell is constructed by attaching lithium flakes onto the Ti electrodes and using 1M $LiPF_6$ in propylene carbonate (PC) as electrolyte. The top and bottom Si/SiN chips are sealed using an ultraviolet-curing adhesive, which is much more effective in trapping liquid electrolytes in the electrochemical liquid TEM cell than some previously reported methods.[29, 30] A sweep-step function (linear sweep potential followed by constant potential bias at the ending potential) is applied to the device for *in-situ* lithium plating in the electrochemical liquid TEM cell. Reaction dynamics are recorded using a charge-coupled device (CCD) at two frames per second. Details of the design and fabrication of

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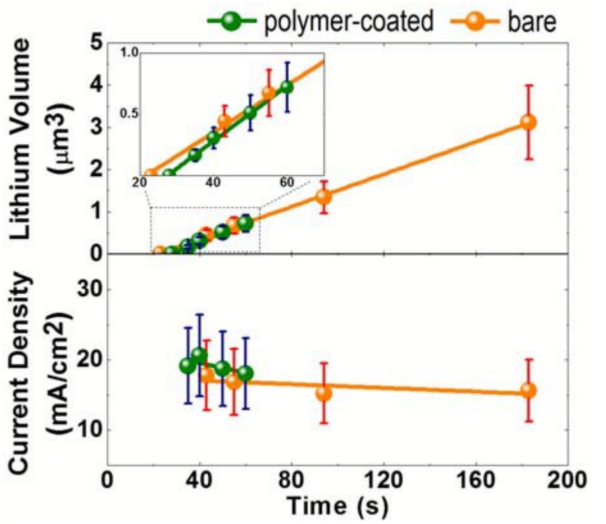

Fig. 2. Lithium volume changes and current density profiles as a function of time (calculated based on the *in-situ* TEM Videos S1 and S3). Measurement errors are indicated on the plot. Linear regression lines are also drawn on the plot.

the electrochemical liquid TEM cell are elaborated in Experimental section.

It is challenging to coat the PDDA film in the thin electrochemical liquid TEM cell with controlled polymer density (a chemical structure of PDDA is shown in Fig. 1a). Here we introduce a unique method. By taking advantage of the fact that PDDA is also widely used as surfactant in colloidal nanocrystal synthesis,[31, 32] we prepare a dilute solution of PDDA with Sn@SnO_2 nanostructures (Sn nanowires/nanoparticles with a thin layer of surface oxide). The PDDA chains adhere to the surface of Sn@SnO_2 nanostructures by electrostatic attraction, while some remain free in the solvent (see details in ESI and Fig. S1). The solution is loaded through a reservoir of the electrochemical liquid cell and is drawn into the cell by capillary force (Fig. S2). After the solvent evaporated, the electrodes of the electrochemical liquid cell are coated with the PDDA polymer film (see a schematic drawing in Fig. 1b and optical microscope images in Fig. S3). The cationic polymer area density can be controlled by varying the area density of Sn@SnO_2 nanostructures on the electrodes. It is known that Sn and SnO_2 experience large volume changes when they react with lithium ions in lithium-ion batteries.[33] Here, the Sn@SnO_2 nanostructures remain inert without participating in reactions during lithium deposition (Fig. S4). This is likely due to their high contact resistance with the electrodes in the cell. According to previous studies,[34, 35] heating or welding is necessary in order to make sufficient electrical contact between the nanoparticles and electrodes in electrochemical liquid TEM cells. The effectiveness of the Sn@SnO_2 nanostructure-assisted PDDA coating method is further discussed in ESI.

A representative *in-situ* liquid TEM lithium electrodeposition in the presence of the Sn@SnO_2 nanostructure-assisted cationic polymer film is shown in Fig. 1c (also see Video S1). After the application of the linear sweep potential, the lithium begins to deposit at the edge of the electrode, where a higher electric field is expected. The bright contrast of lithium is attributed to the lower scattering cross-section of electrons in lithium metal than in Ti, Sn, or lithium compounds. Lithium nanogranules with an average size of 200 nm are plated on the electrode without any protruding dendrites (Fig. 1d). More results on lithium nanogranular growth with the cationic polymer coating can be found in Fig. S5. As control experiments, the growth of lithium nanogranules without electron beam irradiation (Fig. S6) or without the assistance of Sn@SnO_2 nanostructures is also demonstrated (Fig. S7, Video S2). Further details of the control experiments are provided in ESI.

We compare *in-situ* lithium plating without the polymer film to these results. Similar to what has been observed in previous studies,[36, 37] lithium is irregularly plated on the electrode, which promotes dendritic growth (Fig. 1e, Video S3). As shown in Fig. 1e, the morphology of individual dendritic grain varies, likely due to the nanoscale inhomogeneity of the local environments.[38] The trajectory of lithium volume changes and the estimated current densities with time show similar trends in both cases, with and without the cationic polymer coating, as shown in Fig. 2. This shows that the cationic polymer film changes the lithium growth behavior and morphology.

We investigate the nucleation and growth dynamics of individual lithium nanogranules to understand the mechanisms of their growth in the presence of the cationic polymer film. Sequential TEM images show the growth of several lithium nanogranules (Fig. 3a, Video S4). It is hard to distinguish SEI at the initial state (at 0 s) due to the low contrast and limited spatial resolution under the imaging conditions (e.g., thick liquid cells, low dose imaging, etc.). However, dark regions can be identified on the electrode after a potential has been applied for 11–17 seconds. Since the subsequent lithium deposition appears to be brighter and the dimensions of dark regions are consistent with the lithium nanogranules, we consider the dark regions correspond to SEI on lithium. Interestingly, the deposition of thick SEI layers (more than 100 nm) is observed as soon as lithium is deposited (Fig. 3a), or even before lithium growth can be clearly identified (Fig. S9a). This implies that reactions with the electrolyte occur instantaneously when lithium is deposited, which leads to the rapid formation of SEI. This behavior can also be recognized in a plot of how the lithium nanogranule size changes with time (Fig. 3b, Fig. S9b). In addition to the fast development of SEI at the early stages, another distinct feature is that the lithium nanogranules stop growing after they reach critical sizes (about 150–450 nm). In the meantime, the SEI becomes darker, suggesting that its density has increased. Our observations suggest that the chemistry of SEI likely plays a major role in lithium nanogranular growth and the inhibition of dendrite formation, as discussed later in the manuscript.

We next examine the final sizes and stability of lithium nanogranules grown under different densities of the cationic polymer coating (Fig. 3c). Since the ratio of PDDA to Sn@SnO_2 nanostructures in the solution is fixed, the area density of the polymer coating can be estimated by that of Sn@SnO_2 nanostructures in the film (see detailed measurements in ESI and Table S1). The size distributions of the lithium nanogranules

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are obtained from a set of *in-situ* TEM experiments where the cationic polymer density varies (Fig. S10 and Table S1; see ESI for more details on the discussions of the nanogranule size measurements.). The results show distinct trends. First, higher cationic polymer densities result in smaller lithium nanogranules. Second, the size distribution of nanogranules becomes narrower as the cationic polymer density increases. In the case of a very low density of cationic polymer (e.g., Case I in Fig. S10 with the estimated polymer density of 0.3 mg/m^2), there is a large size distribution of lithium nanogranules, suggesting that the lithium nanogranules become unstable and are prone to form dendrites.

Chemical imaging of SEI on lithium nanogranules

We further analyze the SEI on lithium nanogranules non-destructively using STEM-EDS by taking full advantages of the *in-situ* TEM experiments. The lithium nanogranules grown in a liquid TEM cell from the *in-situ* experiments are characterized without being exposed to air (see more detailed sample preparation in Experimental section and ESI). A representative high-angle annular dark field (HAADF) STEM image shows many dark round lithium nanogranules in the field of view (Fig. 4a). Lithium appears dark in the HAADF STEM image because of its low atomic mass featuring a low scattering cross-section. We focus on chemical mapping of the distribution of carbon (C), oxygen (O), fluorine (F), and phosphorus (P) within the SEI layer relative to their distribution in the electrolyte residue in the liquid cell. Elemental maps of the titanium (Ti) electrode, tin (Sn) from the Sn@SnO_2 nanostructures, nitrogen (N) from SiN membrane and PDDA, and chlorine (Cl) from anion residue of PDDA are also obtained (Fig. S13). An enlarged view of a region with a lithium nanogranule clearly shows the elemental distributions of C, O, F and P within the SEI layer and the electrolyte residue (Fig. 4b). It is notable that F is highly concentrated at the surface of lithium nanogranule and uniformly distributed encircling the nanogranule. In contrast, P is concentrated only in certain regions around the lithium nanogranule. C and O are more broadly distributed both in the SEI layer and the surrounding electrolyte residue. The EDS quantifications show 41 at% F and 8 at% P in the whole area of Fig. 4a, among the total amount of C, O, F, and P (at% represents the percentage in atomic ratio; see more Table S2). The F and P compositions in areas with only the electrolyte residue are significantly lower, e.g., 4 at% F and 2 at% P (Fig. S14 and Table S3). As comparison, there are 7 at% F and 1 at% P, among the total amount of C, O, F, and P, in the fresh electrolyte (1M $LiPF_6$ in PC). This suggests that fluorine and phosphorus are accumulated within the SEI layer during the growth of lithium nanogranules underneath the cationic polymer film.

EDS line-scan profiles across the SEI layer of a representative lithium nanogranule show more details of the elemental

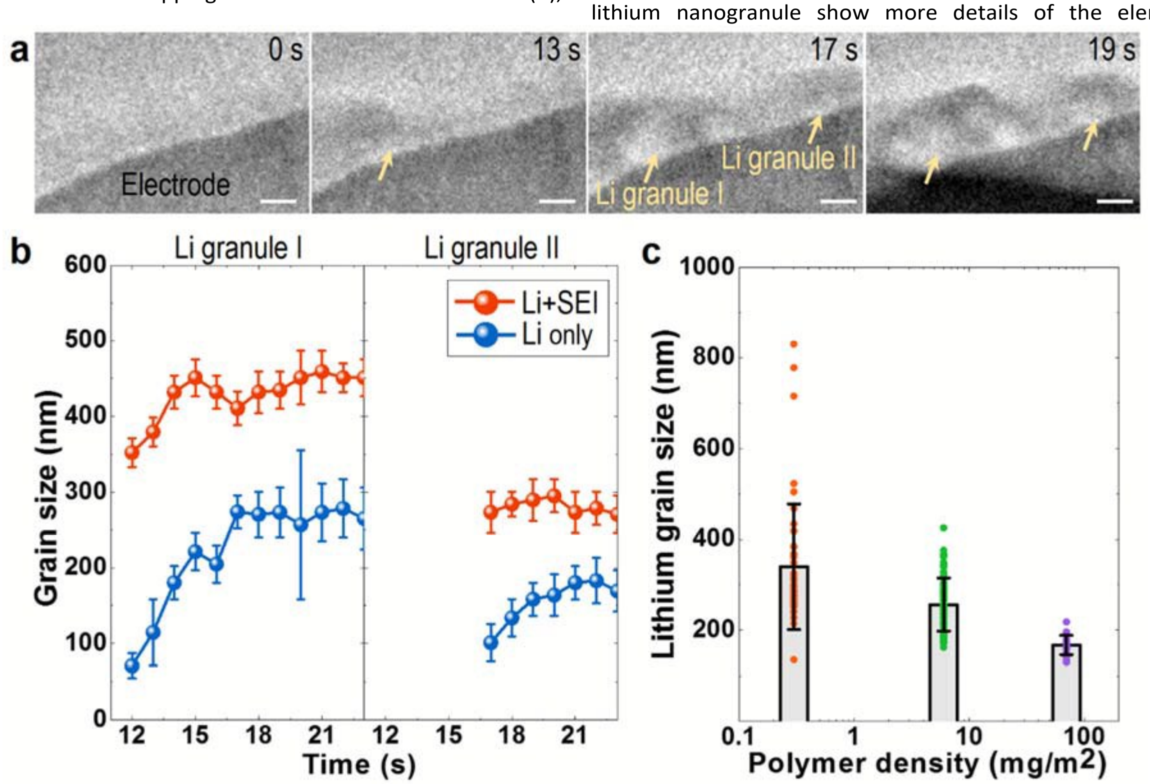

Fig. 3. *In-situ* observations of lithium nanogranular growth in the presence of the PDDA cationic polymer coating. (a) Sequential TEM images showing the growth behaviors of lithium and solid electrolyte interphase (SEI) layers. Scale bars are 200 nm. (b) Size evolution of representative lithium nanogranules during lithium deposition. Measurement errors are indicated. Details of the measurement are shown in Fig. S8. (c) Size distribution of lithium nanogranules as a function of the cationic polymer area density. Data were obtained from a set of *in-situ* TEM experiments where the cationic polymer area density varies. The diameter of each lithium nanogranule is shown as solid dots. Columns and error bars indicate the average diameter and the standard deviation of lithium nanogranules in each sample.

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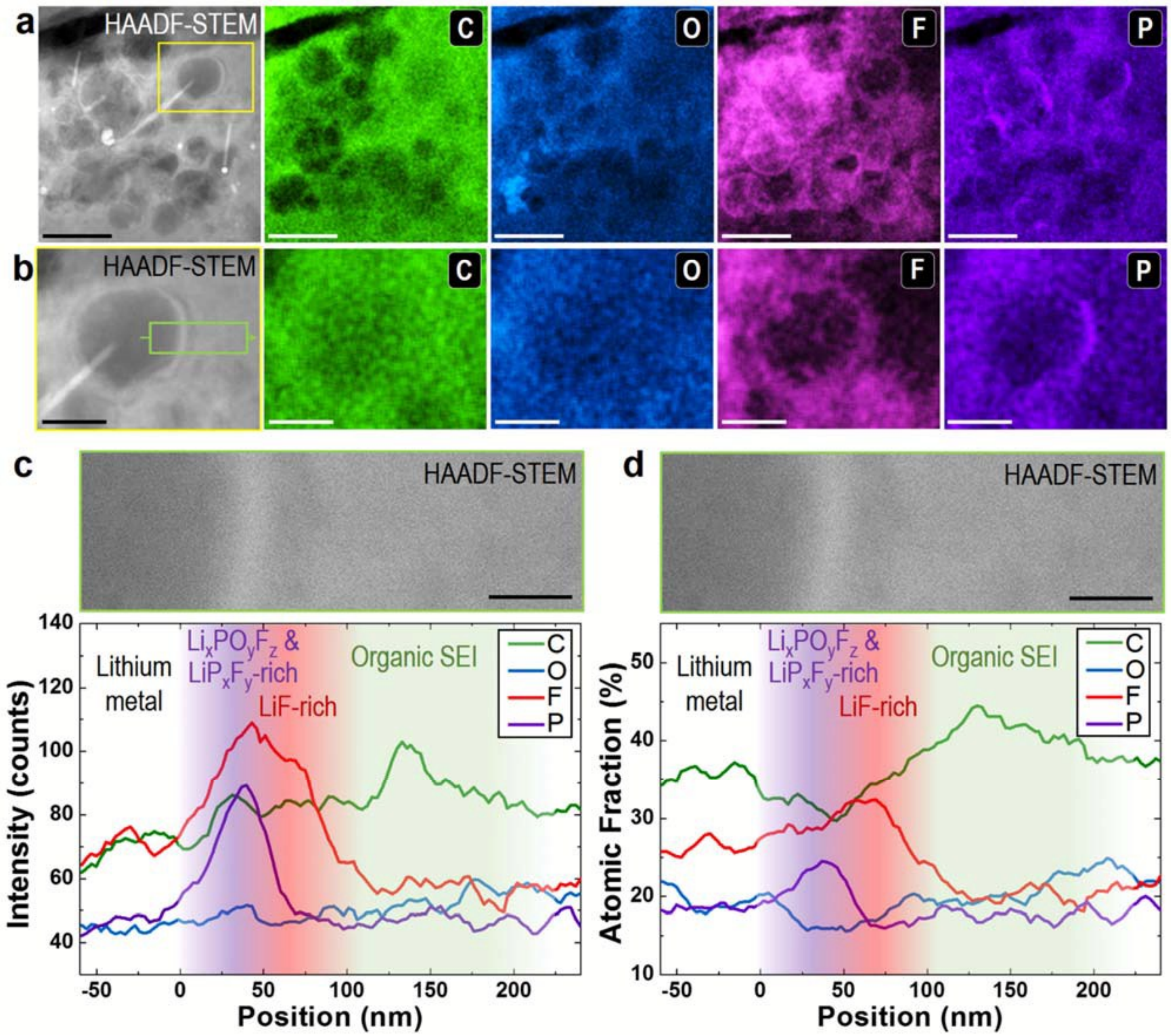

Fig. 4. Scanning TEM (STEM) energy-dispersive x-ray spectroscopy (EDS) analysis of SEI on lithium nanogranules in the presence of PDDA cationic polymer coating. (a) A high-angle annular dark-field (HAADF) STEM image and EDS elemental maps of lithium nanogranules and their SEI layers. Scale bars are 500 nm. (b) A magnified HAADF-STEM image and corresponding EDS elemental maps of a representative lithium nanogranule. The corresponding area is marked with a yellow box in the HAADF-STEM image in (a). Scale bars are 200 nm. (c, d) EDS line-scan profiles of the lithium nanogranule surface corresponding to the marked region in (b), where both intensity (c) and atomic fraction (d) are obtained. Each point was integrated with a window of 100 pixels × 3 pixels (96.8 nm perpendicular and 2.9 nm parallel to the scanning line) to enhance EDS signals. The corresponding HAADF-STEM image is shown above each profile for better understanding. Scale bars are 50 nm.

distribution within the SEI. The EDS line-scan profiles are collected from an area of 96.8 nm × 300 nm, as highlighted in Fig. 4b. Each point in the line-scan profile is integrated within a window of 100 pixels × 3 pixels (96.8 nm perpendicular and 2.9 nm parallel to the scanning line) to enhance the signals. Both intensity profiles and calculated atomic fraction profiles for each element (i.e., C, O, F and P) are provided (Fig. 4c,d). We find that both phosphorus and fluorine signals are the most intense near the lithium nanogranule surface. Phosphorus is concentrated in the 0–50 nm inner layer and fluorine is more broadly distributed in the 0–100 nm layer of the SEI. The distribution of phosphorus may vary in 0–100 nm range depending on lithium nanogranules. A slightly higher concentration of carbon and oxygen is found 100–200 nm above the nanogranule surface. This is consistent with the previous reports that SEIs consist of an inorganic inner layer (e.g., LiF, LiP_xF_y, $Li_xPO_yF_z$, Li_2O, Li_2CO_3, etc.) and an organic outer layer.[39] Our EDS line-scan profiles reveal the spatial distributions of these compounds. For instance, LiF is 50–100 nm-thick within the inner layer. 50 nm-thick LiP_xF_y and $Li_xPO_yF_z$ reside within the inner layer of SEI concentrated at some positions. We consider the uniform distribution of LiF within the inner layer of SEI to be the key factor in the suppression of lithium dendrite growth; more will be discussed later. To the

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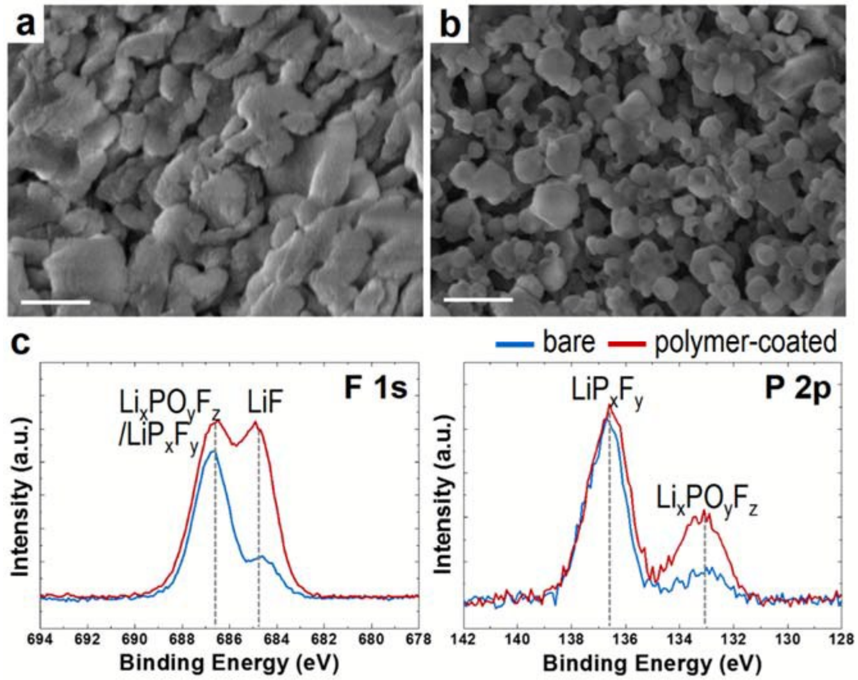

Fig. 5. Lithium metal with SEI electrochemically plated onto Cu foil in Li/Cu coin cells. A current density of 10 mA/cm^2 and a capacity of 1 mAh/cm^2 were used. (a, b) Scanning electron microscopy (SEM) images of electrochemically plated lithium (a) without and (b) with the cationic polymer coating on the Cu foil. Scale bars are 500 nm. (c) X-ray photoelectron spectroscopy (XPS) analysis of the plated lithium surface corresponding to the SEI. High-resolution XPS spectra of F 1s and P 2p peaks without (blue) and with (red) the cationic polymer film on the Cu foil.

best of our knowledge, such detailed chemical distribution within the SEI on the individual lithium nanograins coupled with *in-situ* experiments has not previously been achieved.

Lithium nanogranular growth in coin cell batteries

Lithium plating experiments are also performed using lithium battery coin cells to compare with the above *in-situ* TEM experiments that used electrochemical nanobattery cells. Two types of Li/Cu coin cells are built, one with the PDDA cationic polymer film drop-casted on the Cu foil current collector and the other without the polymer film. The battery coin cells are discharged to a capacity of 1 mAh/cm^2 (Fig. S15). A high current density of 10 mA/cm^2 is used to match what was observed in the *in-situ* liquid TEM experiments. After the discharge, the coin cells are disassembled inside an Ar-filled glove box and the electrodes are transferred for scanning electron microscopy (SEM) imaging and XPS measurements.

The SEM images of the lithium plated on the Cu foil with and without the cationic polymer film show distinctly different morphologies (Fig. 5a,b). Without the polymer film, much larger lithium grains (in micrometers) can be found (Fig. 5a), while the lithium grown under the cationic polymer film shows nanogranular morphology (Fig. 5b). These are consistent with our *in-situ* liquid TEM experiment results (see more results in Fig. S16).

The XPS spectra also show the influence of the cationic polymer film on lithium plating. Specifically, the surface chemistry of the plated lithium changes in the presence of the cationic polymer film coating on the electrode. XPS F 1s and P 2p spectra for the plated lithium with and without cationic polymer film are shown in Fig. 5c. Additional spectra of C 1s, N 1s, O 1s, and Li 1s can be found in Fig. S17. The peak at ~686.7 eV in the F 1s spectra corresponds to LiP_xF_y/$Li_xPO_yF_z$, and the peak at ~684.8 eV is attributed to LiF.[40, 41] It is clear that the concentration of LiF on the coated surface is significantly higher than that on the bare Cu foil. The P 2p spectra show that the concentration of another fluorinated lithium compound ($Li_xPO_yF_z$) also slightly increases in the polymer coated cell. These XPS results reflect the average distribution of different fluorinated compounds on the surface of the plated lithium (400 µm × 400 µm spot size). These results support our *in-situ* TEM observations that fluorine and phosphorus accumulate under the cationic polymer film. The coin cell experimental results are further discussed in ESI.

It is worth noting that lithium nanogranular growth was also obtained on the cycled lithium metal anode in coin cells previously.[42] Electrolyte with high concentration of fluorinated lithium salt (10 M lithium bis(fluorosulfonyl)imide (LiFSI) in ethylene carbonate/dimethyl carbonate (EC/DMC)) was used, which led to high ratio of LiF on the lithium anode measured by XPS.[42]

Mechanisms of lithium dendrite suppression by a cationic polymer film

Our systematic *in-situ* experimental results with complementary *ex-situ* experiments reveal the mechanisms of lithium dendrite suppression by a cationic polymer film, which is not limited to PDDA. As shown in the schematic in Fig. 6, the cationic polymer can trap PF_6^- ions from the electrolyte through

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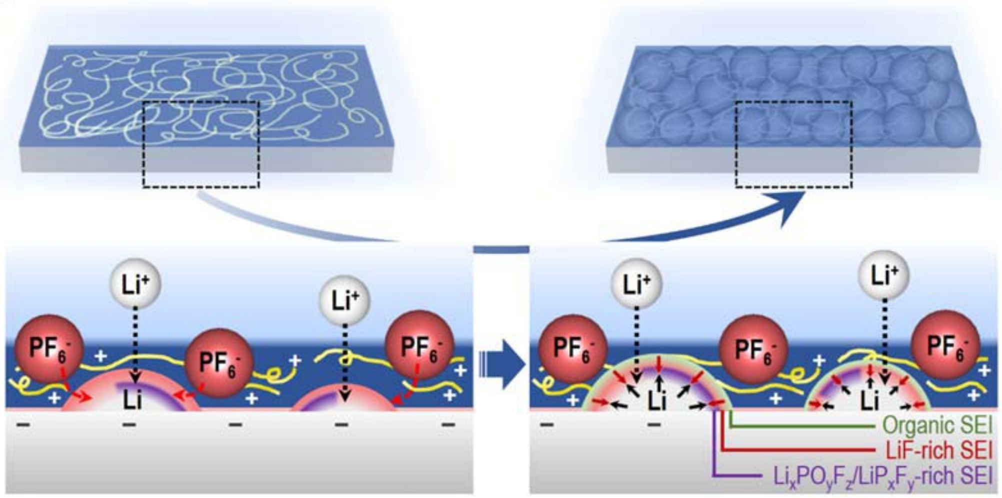

Fig. 6. A Schematic drawing of electrochemical growth mechanisms of lithium metal and the formation of SEI with a cationic polymer film on the electrode.

electrostatic attractions.[43, 44] Thus, the electrode surface is surrounded by the electrolyte with abundant PF_6^- ions. As soon as lithium is deposited on the electrode surface through the reduction of Li^+ ions that permeated the polymer film, PF_6^- ions react with the lithium. It leads to the rapid formation of 50–100 nm thick LiF-rich SEI layer surrounding the lithium deposits. Fluorophosphates, such as LiP_xF_y, and $Li_xPO_yF_z$, can be also obtained almost at the same time. Possible chemical reactions are suggested in Equation (1)–(5)[45, 46] as below.

$$LiPF_6 + 2Li \rightarrow 3LiF + PF_3 \quad (1)$$
$$LiPF_6 \rightleftharpoons LiF + PF_5 \quad (2)$$
$$PF_5 + 2xLi \rightarrow xLiF + Li_xPF_{5-x} \quad (3)$$
$$PF_5 + H_2O \rightarrow POF_3 + 2HF \quad (4)$$
$$POF_3 + 2xLi \rightarrow xLiF + Li_xPOF_{3-x} \quad (5)$$

We consider the instantaneous formation of LiF-rich SEI on an individual lithium nanogranule suppresses its rapid growth and promotes the nucleation of new lithium nanogranules. Thus, a layer of deposits with lithium nanogranules is achieved on the electrode during lithium plating. The formation of lithium nanogranules is not dependent on the specific electrode, since similar morphology of lithium has been achieved on the cycled lithium metal anodes,[42, 47] as well as on Cu electrodes (Fig. 5) in coin cells.

Although the lithium nanogranular growth arising from LiF-rich SEI is consistent with the previous claims that LiF is effective in suppressing lithium dendritic growth,[10, 42, 47-51] the pathways of lithium dendrite suppression by the nanogranular growth of lithium have not been unveiled before. Previous studies were not able to elucidate the mechanisms of lithium nanogranular growth associated with LiF-rich SEI,[42, 47] which is largely due to the lack of ability to resolve spatial distribution of SEI chemistry on individual lithium nanogranules and the dynamic lithium plating. Especially, it has not been possible to reveal the nanogranular growth of lithium induced by a cationic polymer film without the high resolution *in-situ* imaging technology.

This work provides additional insights into the LiF-rich SEI in controlling the growth of lithium. For instance, since the interfacial area is minimized in the nanogranular morphology of lithium, it implies the significance of high interfacial energy between Li and LiF for controlling the growth of lithium[50]. Moreover, since the sizes of Li nanogranules decrease with the increase of cationic polymer density (higher PF_6^- anion concentration) (Fig. 3c), we postulate that a dense SEI or mechanically strong LiF-rich SEI (i.e. high bulk modulus[50]) may limit the Li-ion diffusion and reduce the growth of individual lithium nanogranules.

It is remarkable that LiF-rich SEI on lithium nanogranules has been achieved in the conventional electrolyte without introducing extra fluorine sources (e.g. adding fluoroethylene carbonate (FEC) or LiF additives[10, 48]). It demonstrates the great advantages of applying a cationic polymer film on the anode. The effectiveness of PDDA cationic polymer film in lithium dendrite suppression is expected to be applicable to other systems. First, PF_6^- anions can be trapped by other cationic polymers due to electrostatic interactions. Second, since PC solvent has higher reduction potential than most of other carbonates,[52, 53] LiF-rich SEI on lithium nanograins is also expected in other electrolytes. For example, PC may be replaced by various solvents, such as diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), etc. Considering the high reduction potential of PF_6^- anion,[53] LiF-rich SEI can be achieved with $LiPF_6$ salt in solvents other than carbonates as well. Other lithium salts containing fluorine, such as lithium bis(trifluoromethanesulfonimide) (LiTFSI), can also have similar effects given its high reduction potential.[53]

Lastly, our results show that several inorganic compounds, e.g., fluorophosphates and fluorides, are distributed layer-by-layer within the SEI on individual nanogranules (Fig. 4c,d). The different chemical/electrochemical reaction rates for each compound formation may have contributed to the layer-by-layer growth of different SEI compounds. The concentration variations of fluorophosphates within the SEI may have resulted from the self-agglomeration of the compound nanoparticles.[54] Unveiling of the layer-by-layer distribution of compounds within the SEI expands our knowledge of SEI structure.[55]

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Conclusions

In conclusion, this study demonstrates the unique capability of resolving the spatial distribution of SEI chemistry by *in-situ* electrochemical liquid cell TEM. This capability allows to uncover the mechanisms of lithium dendrite suppression by a cationic polymer film. We found that lithium nanogranules are formed when PDDA cationic polymer film is applied on the electrode. This results from the cationic polymer film trapping of PF_6^- ions and thus the SEI chemistry on individual Li nanogranules being modified by forming a LiF-rich inner layer. The uniformly distributed LiF-rich SEI on individual lithium nanogranules assists the nucleation of new lithium nanogranules while suppressing the rapid growth of the existing nanogranules. Similar results are expected in other systems with different cationic polymers or electrolytes. This work sheds light on strategies for lithium dendrite suppression, for instance, a unique way to achieve LiF-rich SEI without supplying extra fluorine in the electrolyte.

Experimental

Materials and synthesis

Poly(diallyldimethylammonium chloride) (PDDA) solution (20 wt% in H_2O, average Mw: 200,000-350,000), $SnCl_4$ (99.995%), $NaBH_4$ (≥96%), 1M lithium hexafluorophosphate in propylene carbonate (1M $LiPF_6$ in PC) electrolyte, and lithium metal were purchased from Sigma Aldrich. The previously reported recipe was slightly modified for the synthesis of the Sn@SnO_2 nanostructure-assisted PDDA coating solution.[32] 0.5 mL PDDA and 0.1 g $NaBH_4$, a reducing agent, were dissolved in 60 ml deionized water. 0.09 g $SnCl_4$ solution diluted in 30 ml deionized water was added dropwise to the stirred PDDA+$NaBH_4$ solution. The synthesized gray solid products were washed with deionized water and ethanol lastly. The resulting products were dispersed in ethanol and thoroughly ultrasonicated to generate free-PDDAs, separated from the surface of Sn@SnO_2 nanostructures, for the better coating on the electrodes in the liquid TEM cells.

In-situ liquid TEM experiments

Fabrication details of the electrodes-deposited liquid cells for the *in-situ* liquid TEM experiments are described in our earlier papers.[29, 30] Titanium electrodes were deposited instead of the earlier gold electrodes considering the larger electrochemical stability window of titanium in lithium-based batteries.[56, 57] UV-curing adhesives were used to seal the bottom/top chips after the TEM viewing-window alignment, which are chemically stable with the liquid electrolyte and firmly cured within 30 seconds of UV-light exposure. The synthesized Sn@SnO_2 nanostructure-assisted PDDA coating solution was loaded through the reservoir of the assembled electrochemical liquid TEM cell and dried overnight for the investigation of lithium growth under the cationic polymer film. The solution flows through the gap between the top and bottom chips by capillary force. Lithium flakes were attached onto both Ti electrodes exposed in the reservoirs of the assembled chips to construct the Li/Li symmetric cell. The liquid electrolyte (1M $LiPF_6$ in PC) was loaded through the reservoirs by a pipette and the reservoirs were sealed by the UV-curing adhesive. Electrically conducting wires connected to the Ti electrodes and protruding from the liquid TEM cell were pasted onto the cables at the tip of the customized TEM holder by a silver conductive paint. The cables from the other side of the TEM holder were connected to a potentiostat (CH Instruments). For the *in-situ* TEM-voltammetry measurements, a linear sweep potential was applied to the electrode up to ±4–6 V at 0.1 V/s sweep rate, considering the higher resistance of the electrode-deposited liquid TEM cells than the typical coin-type battery cells, and the ending potential was constantly applied to continue the reaction. Voltage and current profiles are shown in Fig. S11 and further discussed in ESI. Electron beam with very low electron dose rate of ~0.2–0.5 $e^-/Å^2s$ was used during the *in-situ* TEM experiments to avoid unexpected electron beam-induced reactions. The *in-situ* TEM lithium plating reactions were recorded at two frames per second using a charge-coupled device (CCD) installed in the TEM. For the STEM-EDS analysis, low but slightly higher dose rate TEM electron beam (~1 $e^-/Å^2s$) was steadily radiated to the liquid electrolyte for more than 20 minutes to make protection layer on the *in-situ* grown lithium by the e-beam polymerization of the liquid electrolyte.[58] Then, the liquid TEM cell was carefully separated to perform the STEM-EDS experiments in order to achieve enhanced EDS signals. The top and bottom SiN membranes remained on the both sides of the *in-situ* grown lithium after the cell separation, making double protection layers with the polymerized electrolyte. The *in-situ* liquid TEM experiment was performed with JEOL JEM-2100 200 kV LaB_6 TEM instrument and the following STEM-EDS experiment was performed with FEI ThemIS 300 kV field-emission TEM instrument equipped with Bruker SuperX EDS detectors.

Lithium plating in coin-type cells and characterization

Half inch copper foil was washed with 1.0 M hydrochloric acid solution for 10 minutes, then rinsed with water (3 times), followed by an ethanol wash (3 times), and dried under vacuum for 12 hours at room temperature. To construct the Li/Cu coin cell with the cationic polymer film, approximately 50 μl of 2 wt% PDDA in ethanol solution was drop-casted onto the copper foil and dried under vacuum for 3 days at room temperature. CR2032 coin-type cells were assembled with the PDDA coated copper foil (or a bare copper foil as a control experiment), lithium foil, Celgard 3501 separator, and 1M $LiPF_6$ in PC electrolyte in the Ar-filled glove box (less than 0.1 ppm of O_2 and 0.0 ppm of H_2O). Electrochemical tests were performed using a battery cycler (VMP3; Bio-Logic Science Instruments). The cells were discharged at 10 mA/cm^2 current density to a capacity of 1 mAh/cm^2. For SEM and XPS experiments of the lithium plated onto the copper foil, the discharged cells were opened in the Ar-filled glove box and the lithium-plated copper foil was washed with dimethyl carbonate solvent to remove $LiPF_6$ residue. For the SEM experiment, the sample was transferred in

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the air-sealing bag to the SEM room to minimize the air-exposure. SEM images of the lithium on the copper foil were acquired at an acceleration voltage of 3 kV (Gemini Supra 55-VP; Zeiss). For the XPS experiment, the samples were loaded onto the transfer holder in the glove box and vacuum pump to ensure the samples were not exposed to air. XPS spectra were obtained with Al K-alpha x-ray source, 400 µm × 400 µm spot size, 0.1 eV step size, and 50 ms dwell time (K-Alpha Plus; Thermo Scientific).

Conflicts of interest

There are no conflicts to declare.

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Broader Context

for

"Unveiling the Mechanisms of Lithium Dendrite Suppression by Cationic Polymer Film Induced Solid-Electrolyte Interphase Modification" (EE-ART-02-2020-000518)

Dendritic growth of lithium metal is a primary concern for the development of high energy lithium metal batteries. It is known that solid-electrolyte interphase (SEI) plays a vital role in controlling the lithium growth. There have been reports that polymer film coating on the lithium metal anode can improve the battery performance, likely resulting from the modification of SEI. However, how SEI is modified at the nanoscale and thus suppresses the lithium dendrite formation are unclear. This is due to challenges in directly characterizing the SEI, since SEI is sensitive to air exposure and may be damaged by post processing. Here, through *in-situ* liquid cell transmission electron microscopy with nanoscale chemical imaging of SEI, our study revealed the mechanisms of lithium dendrite suppression induced by a poly(diallyldimethylammonium chloride) (PDDA) cationic polymer film. We found that the rapid formation of 50-100 nm-thick LiF-rich SEI layer leads to the growth of lithium nanogranules. This work suggests a unique approach to obtain LiF-rich SEI without supplying extra fluorine in the electrolyte. The capability of *in-situ* nanoscale chemical imaging of SEI provides the opportunities to explore the fundamental mechanisms behind the performance of batteries.