

Probing interfacial electrochemistry by in situ atomic force microscope for battery characterization

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Abstract

Lithium-ion batteries (LIBs) have been widely used in electric vehicles and energy storage industries. An understanding of the reaction processes and degradation mechanism in LIBs is crucial for optimizing their performance. In situ atomic force microscopy (AFM) as a surface-sensitive tool has been applied in the real-time monitoring of the interfacial processes within lithium batteries. Here, we reviewed the recent progress of the application of in situ AFM for battery characterizations, including LIBs, lithium–sulfur batteries, and lithium–oxygen batteries. We summarized advances in the in situ AFM for recording electrode/electrolyte interface, mechanical properties, morphological changes, and surface evolution. Future directions of in situ AFM for the development of lithium batteries were also discussed in this review.

KEYWORDS

electrode/electrolyte interface, in situ atomic force microscopy, lithium batteries, mechanical properties, morphological and surface evolution

1 | INTRODUCTION

Lithium-ion batteries (LIBs) have attracted continuous attention since their inception and have been widely used in electronic devices, electric vehicles, energy storage devices, and beyond.^{1–7} Due to the limited theoretical capacity of LIBs, new lithium battery

systems with high theoretical capacity (such as Li–air batteries^{8–11} and Li–sulfur batteries^{12–15}) have also been extensively studied to meet the increasing energy demand. To develop high-performance batteries with high energy and power density, high Coulombic efficiency, long cycle life, and improved safety, a multiscale and multidimensional understanding of the

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battery materials, interfaces, and processes is of great significance.

The performance of the lithium batteries depends on a variety of interfacial processes and reactions within them, including the morphological and volume changes of electrode caused by ion intercalation/deintercalation, the formation of solid–electrolyte interphase (SEI) and cathode–electrolyte interphase (CEI) initiated by electrolyte decomposition, and the dendrite growth induced by uneven lithium plating and stripping.^{16–19} Therefore, combining advanced in situ characterization techniques to observe the interfacial processes and reactions within LIBs in real time could contribute to better investigation of the battery operation and degradation mechanism,

thus providing directions for optimizing battery performance.

In the past decades, various advanced techniques have been applied to investigate the material properties of LIBs and interfacial processes. Among various in situ characterization techniques (X-ray-based microscopes, electron microscopes, scanning probe microscopes [SPMs], etc.), in situ atomic force microscopy (AFM) is a valuable technique for battery research due to its high spatial resolution, ability to directly image surface morphology and mechanical properties, and versatility in sample preparation and operating conditions. In situ AFM can provide high-resolution morphological, mechanical, and electrical information over a large length scale (nanometers to tens of micrometers) and

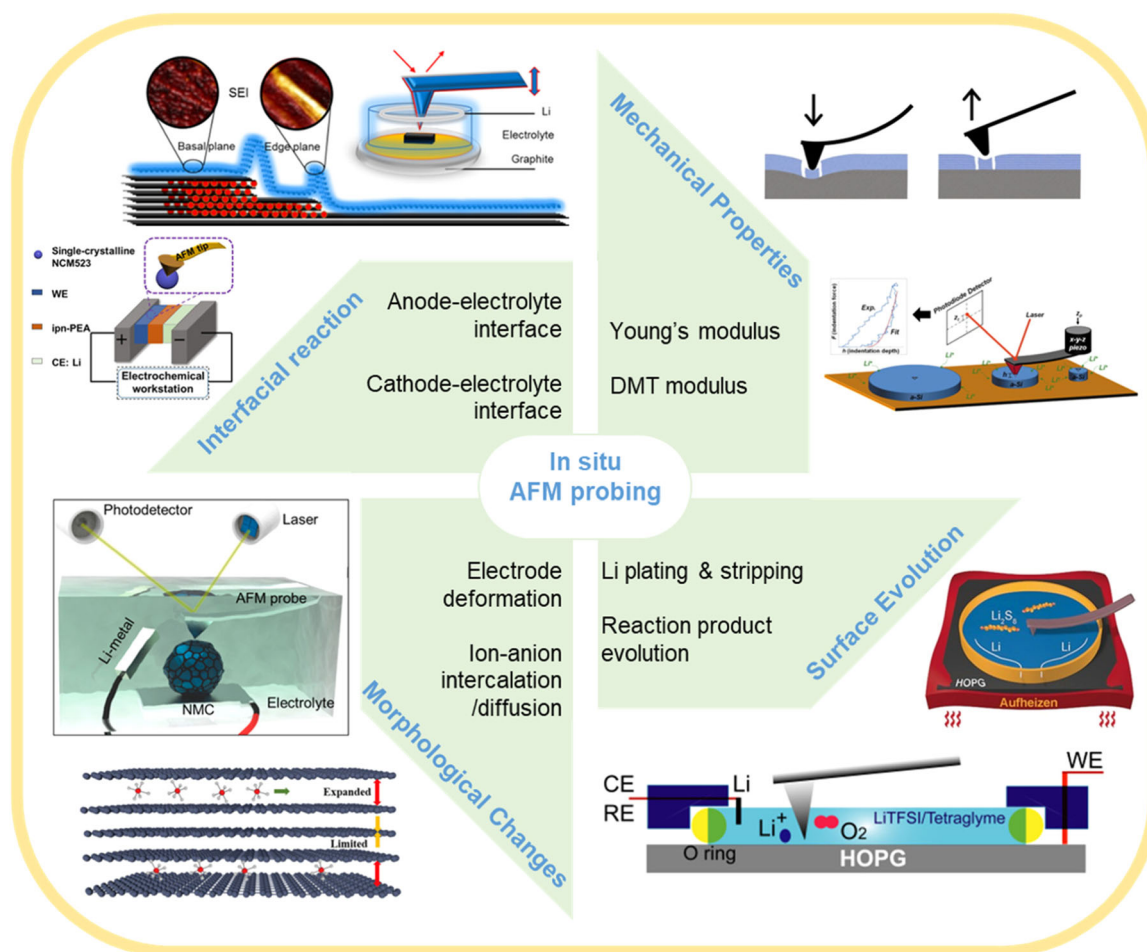


FIGURE 1 Overview of the applications of in situ atomic force microscopy (AFM) for lithium batteries. Anode–electrolyte interface characterization image. Reproduced with permissions.²⁶ Copyright 2020, American Chemical Society. Cathode–electrolyte interface characterization image. Reproduced with permission.²⁷ Copyright 2022, Wiley-VCH GmbH. AFM indentation image. Reproduced with permission.²⁸ Copyright 2020, Elsevier Inc. Silicon electrode image. Reproduced with permission.²⁹ Copyright 2014, Elsevier B.V. Li–S battery characterization image. Reproduced with permission.³⁰ Copyright 2017, Wiley-VCH GmbH. Li–O₂ battery characterization image. Reproduced with permission.³¹ Copyright 2013, American Chemical Society. NMC deformation characterization image. Reproduced with permission.³² Copyright 2020, Elsevier Ltd. Anion intercalation characterization image. Reproduced with permission.³³ Copyright 2020, Tsinghua University Press and Springer-Verlag GmbH Germany, part of Springer Nature. CE, counter electrode; DMT, Derjaguin–Muller–Toporov; HOPG, highly oriented pyrolytic graphite; PES, 1% prop-1-ene-1,3-sultone; RE, reference electrode; WE, working electrode.

high adaptation in different atmospheres, enabling the possibility to monitor the interfacial changes in nanoscale resolution and in real time.^{20–22} Directly imaging of surface morphology and topography during electrochemical reactions can also be achieved by in situ AFM, providing insights into phenomena such as surface roughening, dendrite growth, and phase transformation. In addition, in situ AFM can be used to measure mechanical properties such as adhesion and stiffness, which are important for understanding the mechanical evolution of electrodes. Another advantage of in situ AFM is its versatility in terms of sample preparation and operating conditions. Unlike X-ray diffraction (XRD) or scanning electron microscope, which often require specialized sample preparation and vacuum environments, AFM can be used with a wide range of electrode materials and electrolytes. Moreover, AFM can operate in a variety of gas atmospheres (ambient air, inert gas, or vacuum) as well as in liquid environments,^{23–25} enabling studies of various electrochemical reactions and interfaces.

In this review, we briefly review the applications of the in situ AFM in LIBs and Li–sulfur batteries, as well as in Li–air batteries. We mainly discuss the in situ AFM techniques for investigating electrode–electrolyte interfaces, mechanical properties, morphological changes, and surface evolution (Figure 1). We believe that the in situ AFM would make great contributions to the in-depth understanding of the operation, degradation, and failure mechanism of batteries, promoting the development of lithium batteries.

2 | ELECTRODE–ELECTROLYTE INTERFACES

The properties of the electrode–electrolyte interface play a key role in determining lithium battery performance.^{34,35} For example, the decomposition of the electrolyte leads to the generation of SEI on the anode and CEI on the cathode, whose physical and chemical properties (including morphology, thickness, compactness, and composition) affect the cyclability, capacity, and safety of the battery. The in situ AFM provides a direct visualization for observing the interfacial processes at a high resolution and in real time, contributing to the analysis of the structure and properties of SEI and CEI.

2.1 | Anode–electrolyte interface

SEI is an ionically conductive but electronically insulating layer, which is formed by the reductive decomposition of the electrolyte (lithium salt, solvent, and

additives) during the initial battery formation process and can prevent further electrolyte decomposition and ensure stable interfacial lithium-ion diffusion. The formation of the SEI involves three main steps: electrolyte solvent/anion reduction, reduction product growth, and SEI layer deposition.^{36,37} In situ AFM, as an advanced topographic characterization technique, has been employed to visually observe the formation process of SEI at a nanoscale resolution. For the better resolution of SEI, early in situ AFM studies employed ideal electrodes such as highly oriented pyrolytic graphite (HOPG) and silicon electrodes assembled by chemical vapor deposition, with surface roughness within tens nanometer.^{38,39}

HOPG has been widely used in AFM studies for achieving atomic resolution due to its convenient cleaving procedure, crystalline anisotropy, atomically flat defect-free surface, and highest three-dimensional (3D) ordering.^{20,40} Combining the AFM techniques with cyclic voltammetry (CV) could provide direct evidence and detailed images of SEI formation processes. An early study utilized the in situ electrochemical AFM approach to understanding the SEI live formation (Figure 2A). The HOPG surface with clear edge sites and basal planes exposed was interface-free between the potential range 2.5 and 2.1 V. As the potential decreased to below ~1.5 V, nanoparticles (NPs) gradually accumulated along the edge sites of HOPG, which was attributed to the initial intercalation of solvated lithium ion into the HOPG top graphene layer and ethylene carbonate (EC) reduction. At around 1.0 V, the basal planes of HOPG were engulfed by SEI, which correlated to the significant reduction of carbonate.⁴⁰

To improve the adaptability of SEI, an ideal electrolyte composed of stable solvent and high ion conductivity lithium salts is urgently needed.^{43–46} For instance, the effect of lithium bis(fluorosulfonyl)imide (LiFSI) concentrations to form SEI was studied via the in situ AFM, which revealed that the LiFSI concentration in electrolytes greatly influenced the modulus and thickness of the as-formed SEI layer. The results showed that the SEI layer (~70 nm) formed in 2 M LiFSI/1,2-dimethoxyethane (DME) was thicker than the SEI formed in other electrolyte concentrations. This thickest SEI layer possessed the highest rigid lithium fluoride (LiF) content, which was generated from the FSI[−] decomposition. Such strong SEI enabled fast lithium diffusion and uniform lithium deposition and protected the lithium anode from electrolyte corrosion.⁴⁷ Due to their incombustibility, excellent ionic conductivity, and high electrochemical and good thermal stability, ionic liquids (ILs) are regarded as promising electrolytes for LIBs.^{48,49} In situ AFM was applied to explore the whole SEI generation process (nucleation, growth, and formation) on

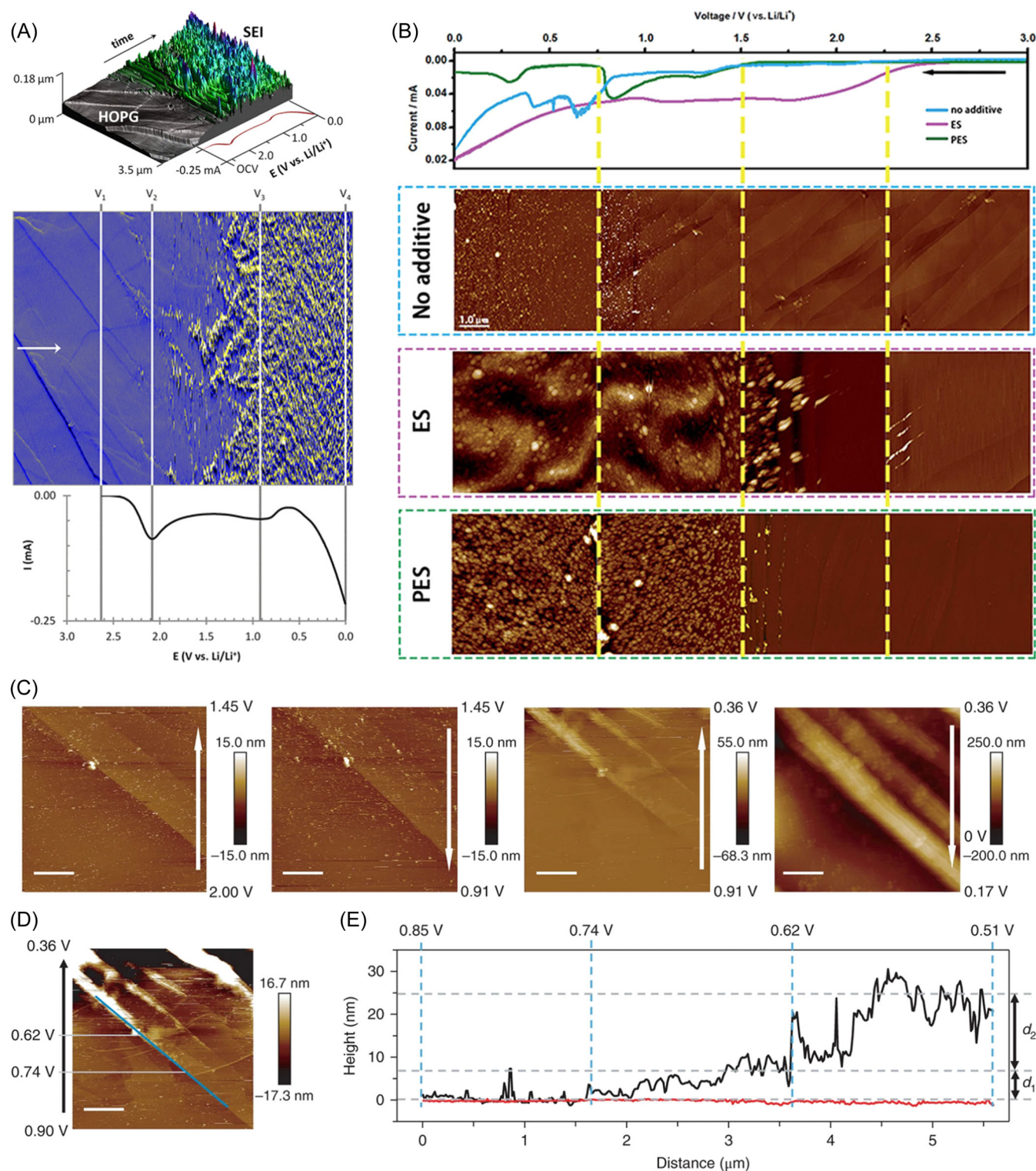


FIGURE 2 (A) Solid-electrolyte interphase (SEI) formation process on a highly oriented pyrolytic graphite (HOPG) surface in 1.5 M LiTFSI /ethylene carbonate (EC) electrolyte during cathodic cyclic voltammetry (CV) scan (scan rate: 5 mV/s). Reproduced with permission.⁴⁰ Copyright 2014, American Chemical Society. (B) Cathodic CV curves (scan rate: 2 mV/s) of the HOPG electrode in 1 M $\text{LiPF}_6/\text{EC}/\text{dimethyl carbonate}$ with no additive, 1% ethylene sulfite (ES) additive, and 1% prop-1-ene-1,3-sultone (PES) additive, and corresponding in situ atomic force microscopy (AFM) images demonstrating the evolution of SEI. Reproduced with permission.⁴¹ Copyright 2018, Royal Society of Chemistry. (C) Topological imaging of HOPG during the CV scan (scale bars, 1 μm). (D) Correlation of morphology and potential during the initial cathodic scan (scale bar, 1 μm). (E) Height distribution of SEI along the blue line in (D). Reproduced with permission.⁴² Copyright 2019, Nature Publishing Group.

HOPG substrate in IL-based electrolytes. The results indicated that different types of anions in the IL electrolyte significantly influenced the SEI structure. In $[\text{BMP}]^+[\text{TFSI}]^-$ -containing LiTFSI, the formed SEI films tended to be loose and rough with a 3D growth mode, while thin and compact SEI films were formed with a two-dimensional growth mode in $[\text{BMP}]^+[\text{FSI}]^-$ -containing LiFSI.⁵⁰

The addition of electrolyte additives is regarded as an effective and simplest method for optimizing SEI properties. In situ electrochemical AFM has been employed to monitor the formation process of SEI under different electrolyte systems (with/without electrolyte additives), contributing to analyzing the effect of electrolyte additives on the microstructure of the SEI layer. Since sulfur-containing species are more easily reduced than other components in the electrolyte, they have been reported to facilitate the formation of a stable SEI layer.^{51,52} Two sulfur-containing additives, ethylene sulfite (ES) and prop-1-ene-1,3-sultone (PES), were investigated in our previous work.⁴¹ The results suggested that both PES and ES facilitated the SEI formation, in which ES possessed a higher reduction potential. It is worth noting that ES can not only be reduced to form SEI earlier than PES but also formed a denser and more stable SEI to better protect the graphite electrode and improve the stability of the battery (Figure 2B).

Combining in situ AFM with other characterization methods, such as XRD, X-ray photoelectron spectroscopy (XPS), scanning electrochemical microscopy (SECM), neutron reflectometry (NR), Raman spectroscopy, and electrochemical quartz crystal microbalance (EQCM), can provide more comprehensive information on SEI formation process, structure, and composition. For instance, ex situ XPS has been combined with in situ AFM to demonstrate the formation of the hard and dense SEI layer composed of LiF in the LiPF_6 /fluoroethylene carbonate/dimethyl carbonate (LiPF_6 /FEC/DMC) electrolyte.⁴⁶ SECM and in situ AFM were combined in one platform for consecutive investigation of the formation and electrochemical properties of SEI, in which a small area was scratched away via AFM and clearly visualized in the SECM mapping, proving the electronically insulating properties owing to the partially removed SEI.⁵³ The combination of in situ NR and in situ AFM precisely monitored the morphology evolution and the heterogeneities of individual SEI features, in which the scattering length density recorded by NR further provided chemical nature and structural evolution information of SEI.⁵⁴ Correlative characterization techniques, including in situ AFM, in situ XPS, and in situ Raman, were conducted on both planar and sandwich model lithium batteries during operation to investigate the electrolyte effect on the device performance. The results show that a dense and flat SEI film can be readily generated in a high-concentration electrolyte, demonstrating

good cycling stability and reversibility. The SEI composition derived from the high-concentration electrolyte was further analyzed, which was composed of LiF, Li_2S , and Li_3N and mainly from the reduction process of FSI^- .⁵⁵

Since EQCM could provide mass change information of electrodes during the discharge/charge process, the combination of EQCM with in situ AFM contributes to a deeper understanding of the complex structure of SEI. Our previous work quantitatively monitored the mass change of interfacial components and recorded real-time topological images of HOPG and SEI height distribution during CV scanning (Figure 2C–E) and confirmed the following distinct stages for SEI formation in 1 M LiPF_6 /EC/DMC electrolyte: formation of LiF (cathodic scan to 1.5 V), Li^+ co-intercalation (cathodic scan to 0.88 V), the initial reduction of EC (cathodic scan to 0.74 V), further reduction of EC (cathodic scan to 0.6 V), the final reduction of EC (cathodic scan to 0 V and then anodic scan to 0.3 V), and lithium alkylcarbonate reoxidation (anodic scan above 0.3 V).⁴²

Besides the graphite anodes, other different types of anodes, such as alloy-type anodes (Si, Sn, SiO, etc.), lithium metal anodes (LMAs), and metal oxide anodes, are widely studied and considered promising LIB anodes.^{56–59}

It was reported that in situ AFM was conducted to investigate the effect of FEC additive on the SEI film formation of the commercial SiO/C anode (Figure 3A–C). According to the recorded potential-dependent morphology AFM images and XPS chemical composition analysis results, it was found that a compact, dense, and stiff SEI layer (mainly composed of LiF) was formed on the SiO/C anode surface with the FEC addition. In contrast, only a thin and scattered SEI layer was formed in the EC-based electrolyte.⁶⁰ The SEI formation at early stages on the Sn anode in the EC-based electrolyte was studied via the in situ AFM. The results revealed that SEI film was formed at ~ 2.8 V and then gradually changed in morphology between the potential of 0.7 and 2.5 V. In the following CV cycles, the SEI was not stable and continuously reformed, which could not effectively protect the Sn anode from electrolyte reduction. The interfacial chemistry of the Sn anode and/or the electrolyte needed further optimization.⁶²

Overlithiated organosulfides can form robust SEI and are regarded as promising candidates for LMA protection for stable lithium metal batteries. In situ techniques, including in situ AFM and in situ Raman, were combined to visualize the interfacial evolution (Figure 3D,E) and chemical transformation during the overlithiation process in sulfurized polyacrylonitrile (SPAN). The results showed that the C–S bond broke and the C–Li bond formed during the overlithiation process. The newly formed nucleophilic C–Li further triggered the electrolyte decomposition and hybrid inorganic–organic SEI formation on the SPAN

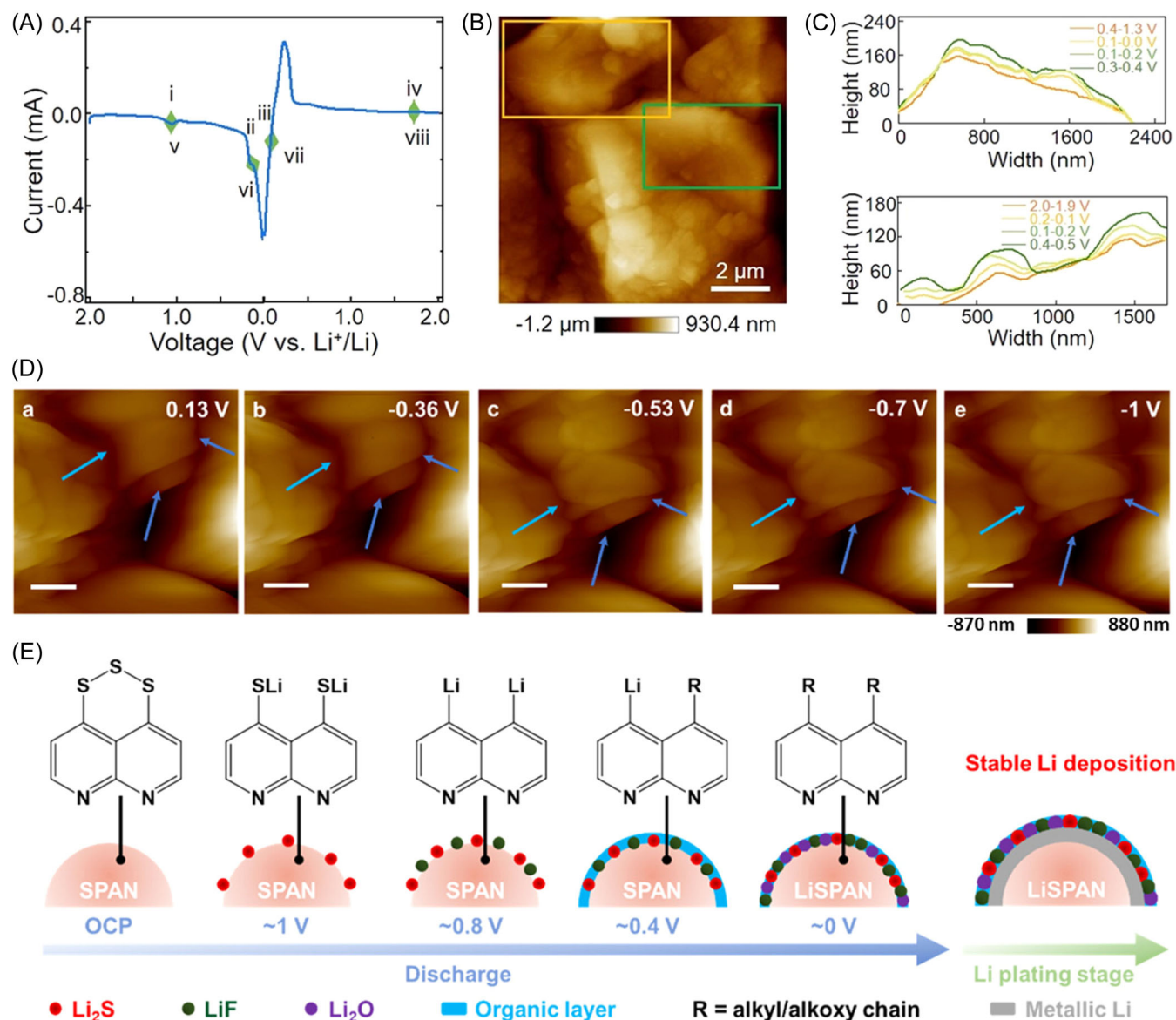


FIGURE 3 (A) Cyclic voltammetry (CV) curve of the SiO/C anode in fluoroethylene carbonate (FEC)-based electrolyte during the in situ atomic force microscopy (AFM) measurement (scan rate: 0.25 mV s⁻¹). (B) AFM image of the anode in the selected area before cycling (orange frame: SiO; green frame: graphite). (C) Line profiles of SiO (top) and graphite (bottom) in selected areas. Reproduced with permission.⁶⁰ Copyright 2021, American Chemical Society. (D) In situ AFM monitoring of sulfurized polyacrylonitrile (SPAN) at the lithium deposition stage. (E) Schematic of the mechanism of SPAN during the overlithiation process. Reproduced with permission.⁶¹ Copyright 2021, American Chemical Society.

surface, which contributes to the construction of stable LMAs.⁶¹

The direct visualization of SEI layer formation on a Li₄Ti₅O₁₂ (LTO) anode was realized via the in situ AFM technique under potential control. It was found that no SEI was formed on the LTO surface in the EC/DME-based electrolyte between the potential range of 2.5 and 1.0 V. Notably, when the potential was decreased to 0 V, an SEI layer was formed. The effect of different electrolyte additives on the SEI formation was also studied in this

work. The results indicated that a dense SEI layer formed with the ES additive and the electrode possessed the smallest polarization with the FEC additive.⁶³ The in situ AFM also provided visual evidence of SEI formation on a Fe₃O₄ anode during the discharge/charge process. The recorded AFM images demonstrated that the as-formed SEI layer in the FEC-based electrolyte was more compact and stable than that as-formed in the EC-based electrolyte. This dense film could efficiently prevent the Fe ion migration and further improve the battery performance.⁶⁴

2.2 | CEI

CEI is generally considered to be a heterogeneous multicomponent film formed due to the decomposition of electrolytes on the cathode surface. However, compared with the extensive study of SEI, the investigation of CEI is comparatively insufficient. The complexity of CEI structure brings great challenges to developing stable CEI layers, so the study of the formation mechanism and properties of CEI plays a key role in improving the capacity, cycle life, and overall safety of batteries.⁶⁵

In situ AFM has been applied to observe the evolution of CEI on LiCoO_2 cathode during electrochemical cycling. The results suggested that CEI films only formed on the edge plane of the LiCoO_2 cathode with loose fibrillar structures, which were unstable and decomposed at low voltage (Figure 4A). This loose structure could not completely coat the edge plane or block further oxidation of the electrolyte or protect the LiCoO_2 from a trace amount of HF in the electrolyte, which was detrimental to the battery cycling and performance. To enhance the stability in high-voltage cycling, a thin layer of Al_2O_3 was coated on the cathode surface, which successfully suppressed the formation of CEI at the LiCoO_2 edge plane and demonstrated significantly improved cycle stability at high voltage.⁶⁶

The surface regulation and dynamic degradation of single-crystalline Ni-rich cathode (SC-NCM) within solid-state lithium batteries (SSLBs) was investigated via the in situ AFM. Unstable and inhomogeneous CEI film with surface defects was observed on SC-NCM electrodes during the cycling process. To solve this issue, the Li_3PO_4 coating layer was introduced to the SC-NCM electrodes to mediate their surface structure and CEI evolution process. First, the cell with Li_3PO_4 -coated SC-NCM electrodes (L-NCM) was held at ~ 4.08 V for 1 h, and some amorphous products were gradually formed on the L-NCM surface. As the charging process proceeded, these amorphous products accumulated and evolved into the planar amorphous film. When the potential increased to 4.2 V, the homogenized film ultimately formed on the L-NCM surface. After cycling, this film became denser and smoother and covered the entire L-NCM surface (Figure 4B–D). Notably, this amorphous LiF-rich CEI well maintained its structure during the subsequent cycling process, which suppressed undesired side reactions and enhanced the interfacial stability, further contributing to the cycle life stability and rate capability enhancing.²⁷

A facile protocol was developed to in situ observe and characterize a single-particle electrode via in situ AFM. It was discovered that the formation of CEI on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particle cathode surface was highly related to the exposed planes. The CEI film with a thickness of 4–5 nm was formed on the (111) surface at ~ 4.78 V and

maintained stable when the potential decreased. In contrast, no detectable CEI film was generated on the (100) surface during the first cycle. This work suggested that the interfacial catalytic activity of electrolyte oxidation is closely related to the facet properties.⁶⁷

The in situ AFM was applied to investigate the CEI changes in high-energy-density lithium- and manganese-rich (LMR) materials. It was found that a dense and uniform passivation CEI film was formed on the LMR material surface at high voltage. Further, XPS characterization confirmed that the CEI was composed of LiF. The as-formed stable LiF-rich CEI film inhibited the electrolyte oxidation, thus suppressing the generation and accumulation of CO_2 on the LMR material surface. The battery (LMR||Li) test demonstrated that the formed CEI film significantly improved the battery rate and cycling performance in the commercial carbonate electrolyte.⁶⁸

3 | MECHANICAL PROPERTIES

The mechanical degradation process of electrode materials plays an important role in limiting the lifetime of advanced LIBs. For instance, the repetitive intercalation and deintercalation of ions during discharge/charge induced the volume expansion and contraction of electrodes under fatigue loading conditions, which leads to electrode fracture/breakage and further affects the battery energy storage capacity and cycle life.^{69,70} Therefore, measuring and understanding the mechanical properties and evolution of electrode materials during the discharge/charge process, such as fracture strength and Young's modulus (YM), is of great significance for achieving long-cycle-life batteries. Due to the convenience of measuring force and displacement using an AFM tip, AFM has been widely applied to study and measure the mechanical properties of electrode materials, such as YM, fracture strength, stiffness, and adhesion.^{71–74} Combining with electrochemical testing, the mechanical behaviors of electrode materials upon the battery cycling process can be investigated via the in situ AFM techniques.

The mechanical changes of the SEI layer at the HOPG and graphite anodes were investigated by in situ AFM. HOPG was first studied as a model system to explore the SEI formation and corresponding mechanical property evolution. Then industry-relevant graphite sheet was further investigated (Figure 5A). It was found that two types of SEI simultaneously formed at the basal and edge planes of graphite; meanwhile, the thickness of SEI in the edge site was bigger than that in the basal plane. The addition of FEC and vinylene carbonate in 1 M LiPF_6/EC /ethylmethyl carbonate (EC/EMC) electrolyte increased YM and reduced

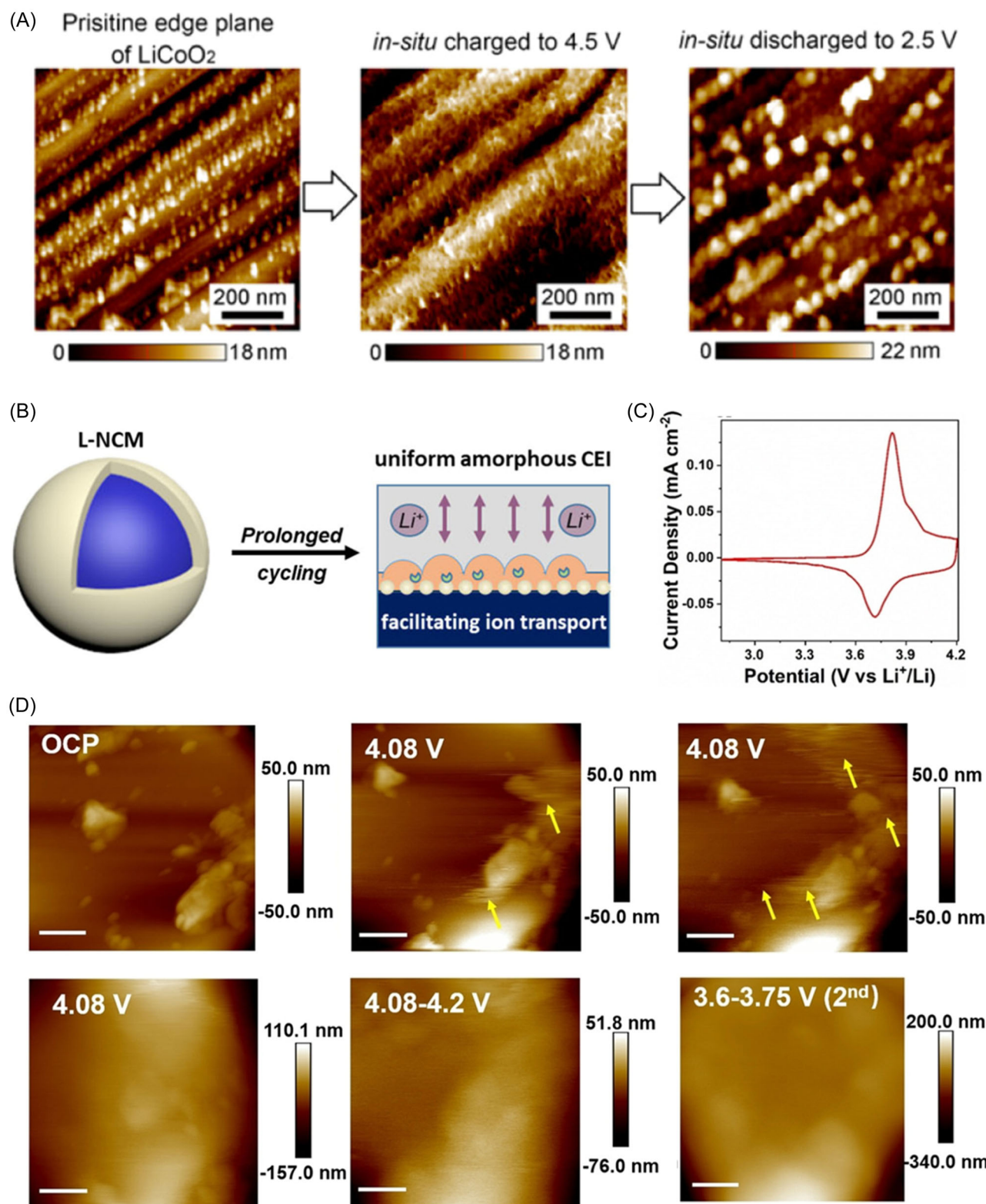


FIGURE 4 (A) In situ atomic force microscopy (AFM) images of the cathode–electrolyte interphase (CEI) film formation and decomposition on the edge plane of LiCoO_2 crystal. Reproduced with permission.⁶⁶ Copyright 2017, American Chemical Society. (B) Schematic illustration of the surface degradation and interfacial regulation mechanism of the Li_3PO_4 -coated single-crystalline $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) (L-NCM) electrodes. (C) The first cycle of cyclic voltammetry (CV) curves (scan rate: 0.1 mV/s) and (D) corresponding in situ AFM images demonstrate the surface evolution of CEI film on the L-NCM cathode electrode in a solid-state lithium battery. Reproduced with permission.²⁷ Copyright 2022, John Wiley and Sons.

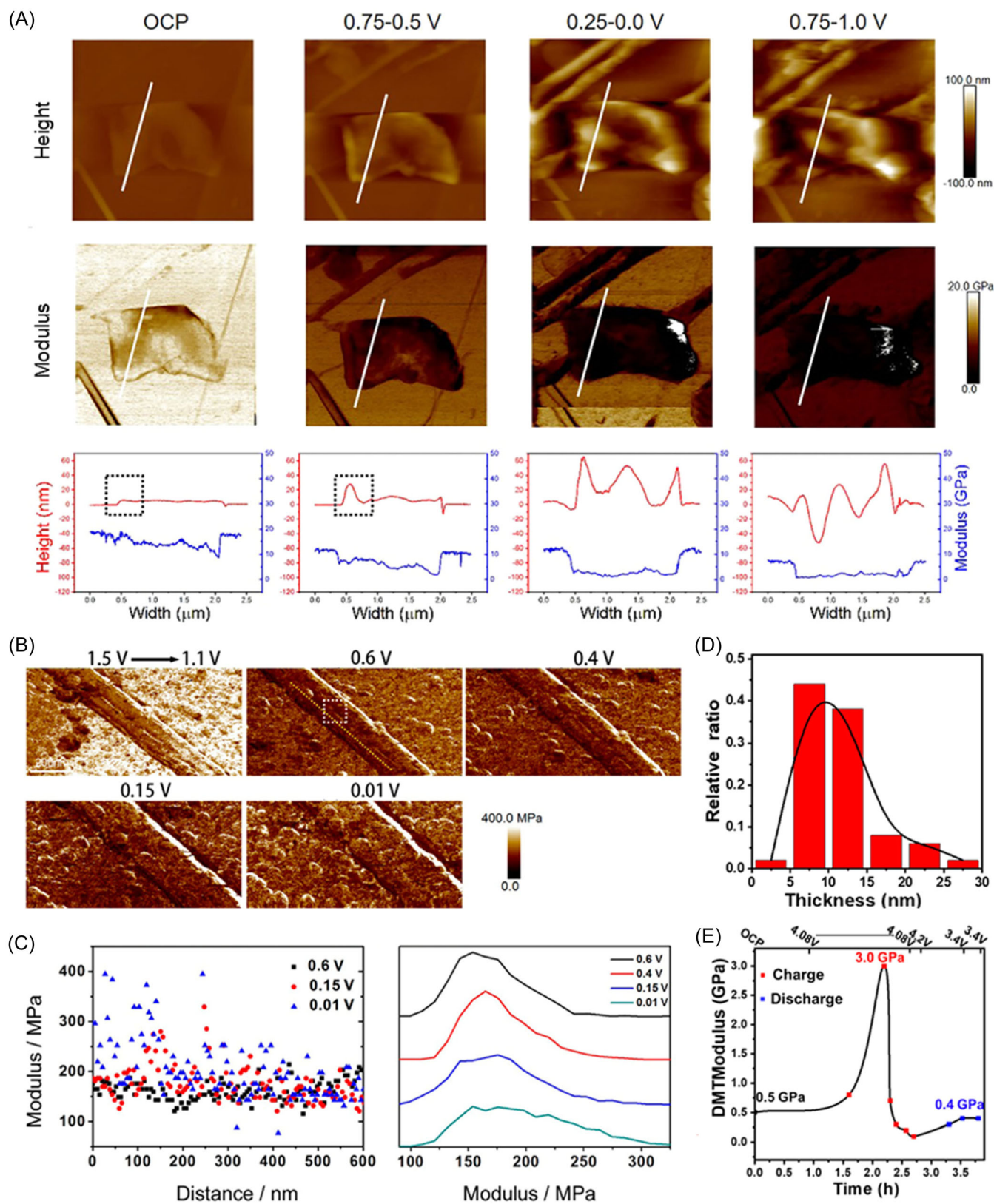


FIGURE 5 (See caption on next page).

SEI thickness and roughness, thus further enhancing the battery performance. Due to its high edge-to-basal ratio, the individual graphite anode showed a lower SEI modulus and more SEI covering, compared to the HOPG. The different material structures (strain behavior, the density of step edges, etc.) of HOPG and graphite further lead to different device performances.²⁶

Due to its natural abundance, high specific capacity, and relatively low working potential, silicon has been considered a promising anode material for LIBs.^{77,78} Huge volume change during cycling and derived mechanical stress bring great troubles to maintaining electrode and SEI structure integrity, which leads to undesirable fast performance degradation.^{79,80} The studies that focused on the interfacial behavior and electrochemical reactions of silicon anode are of great importance for improving battery performance and stability. In situ AFM was used to investigate the SEI growth and mechanical properties of a silicon nanowire electrode, which quantitatively tracked YM and morphology changes during the SEI growth process.⁷⁵ Three distinct stages were observed during the SEI growth process. Figure 5B shows the recorded in situ YM mapping of the Si nanowire. At the initial discharge stage, the YM of the Si nanowire surface was around 700 MPa. When the voltage was reduced to 0.6 V, the YM decreased to ~150 MPa, which was attributed to the newly formed primary SEI film during discharge. The YM and morphology remained unchanged when discharged to 0.4 V. In the second stage (discharged to 0.15 V), a thick and particle-like SEI formed with slightly increased and inhomogeneous YM. In the final stage (further discharged to 0.01 V), the YM became more inhomogeneous. Furthermore, the YM of the selected position was analyzed to study its distribution and trend during the SEI growth process (Figure 5C). During the growth process, the YM increased obviously and became more inhomogeneous. Meanwhile, the statistical mean value and distribution of YM during the growth process showed a slight increase, suggesting the composition evolution of SEI films. The mechanical evolution on the cross-section of micro-sized silicon anode was successfully visualized via the in situ AFM, including initial pulverization, irreversible volumetric changes, the onset of particle crack formation and its patterns, fresh SEI formation

at cracked surfaces, and particle isolations. The results indicated that the upper cutoff voltage could suppress the mechanical failure of the micro-sized silicon anode and subsequently improve capacity retention with a reduced cell impedance.⁸¹

In situ AFM has also been utilized to disclose the mechanical properties and interface evolution of CEI. For instance, the dynamic formation of CEI on $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) electrode in an SSLB was monitored via the in situ AFM.⁷⁶ The average Derjaguin–Muller–Toporov (DMT) modulus of the NCM523 electrode surface was 0.5 GPa at the open-circuit potential (2.85 V). No evident morphology and DMT modulus changes were observed when charged to 4.08 V. Then, the SSLB was held at 4.08 V for 1.2 h, in which some filamentous products first appeared accompanied by the DMT modulus increase to 3 GPa, and then some flocculent products deposited accompanied by DMT modulus decrease to 0.5 GPa. As the charging process proceeded, the products evolved into a flocculent film with a low DMT modulus (0.3 GPa). At the following charging process (to 4.2 V), no significant changes were observed in terms of DMT modulus and morphology. Then, the SSLB discharged to 3.4 V, and the film became denser and smoother with a slight increase in DMT modulus (to 0.4 GPa). Furthermore, the film thickness was measured from the analysis of the recorded AFM images (Figure 5D). The results showed that the film thickness was around 11.18 nm. The DMT modulus evolution of the selected position is demonstrated in Figure 5E. Notably, the DMT modulus was stable during the SSLB cycling process, suggesting the mechanical property of this film turned stable after the first cycle. The real-time visualization of the CEI growth via in situ AFM provides more details and evidence of the interfacial behavior and mechanical properties, further contributing to the development of SSLB.

4 | MORPHOLOGICAL CHANGES

The studies of electrode morphological changes in LIBs, including dimensional changes (height and volume), morphological evolution, and topography changes, play a vital

FIGURE 5 (A) In situ atomic force microscopy (AFM) of an individual graphite sheet on the highly oriented pyrolytic graphite (HOPG) substrate in the electrolyte of ethylene carbonate/ethylmethyl carbonate (EC/EMC). Height and modulus information of four potential steps (open-circuit potential [OCP], 0.75–0.5, 0.25–0.0, and 0.75–1.0 V). Reproduced with permission.²⁶ Copyright 2020, American Chemical Society. (B) The AFM images of Young's modulus mapping of a single silicon nanowire (SiNW) anode in the first discharge process. (C) The distribution of Young's modulus along the location marked with a dashed yellow line (left), and the statistic values of Young's modulus of the area marked with a dashed white box (right). Reproduced with permission.⁷⁵ Copyright 2014, American Chemical Society. In situ AFM of the $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523) electrode surface during charge and discharge. (D) The Gauss statistic distribution histograms of the film thickness and (E) quantitatively measured average Derjaguin–Muller–Toporov (DMT) modulus of the selected position during charge/discharge. Reproduced with permission.⁷⁶ Copyright 2020, American Chemical Society. OCP, open-circuit potential.

role in a deep understanding of the battery mechanism. In this section, we mainly discussed the morphological changes for different types of anodes and cathodes of LIBs, which were obtained through in situ AFM.

Due to their high theoretical capacity, alloy anode materials that can be alloyed with lithium ions, such as Si and Sn, are considered promising LIBs anode. However, the volume changes (expansion/contraction) of alloy anodes during the lithiation/delithiation process led to electrode structural degradation, further degrading the battery performance. Therefore, investigating the morphological changes of alloy anodes is of great importance for

developing effective methods to stabilize the alloy anodes.^{82–86}

For instance, in situ AFM was applied to quantitatively and qualitatively monitor the morphological evolution of different nanosized amorphous Si (a-Si) nanopillars (height: 100 nm; diameters: 100–1000 nm) during the lithiation and delithiation processes (Figure 6A,B). The nanopillars with a diameter of 100 nm had a volume expansion smaller than 200%. The nanopillars with a diameter bigger than 100 nm all reached a large volume expansion of around 300%. All the nanopillars were roughened with no crack after five cycles. As the cycling process proceeded, the nanopillars with a

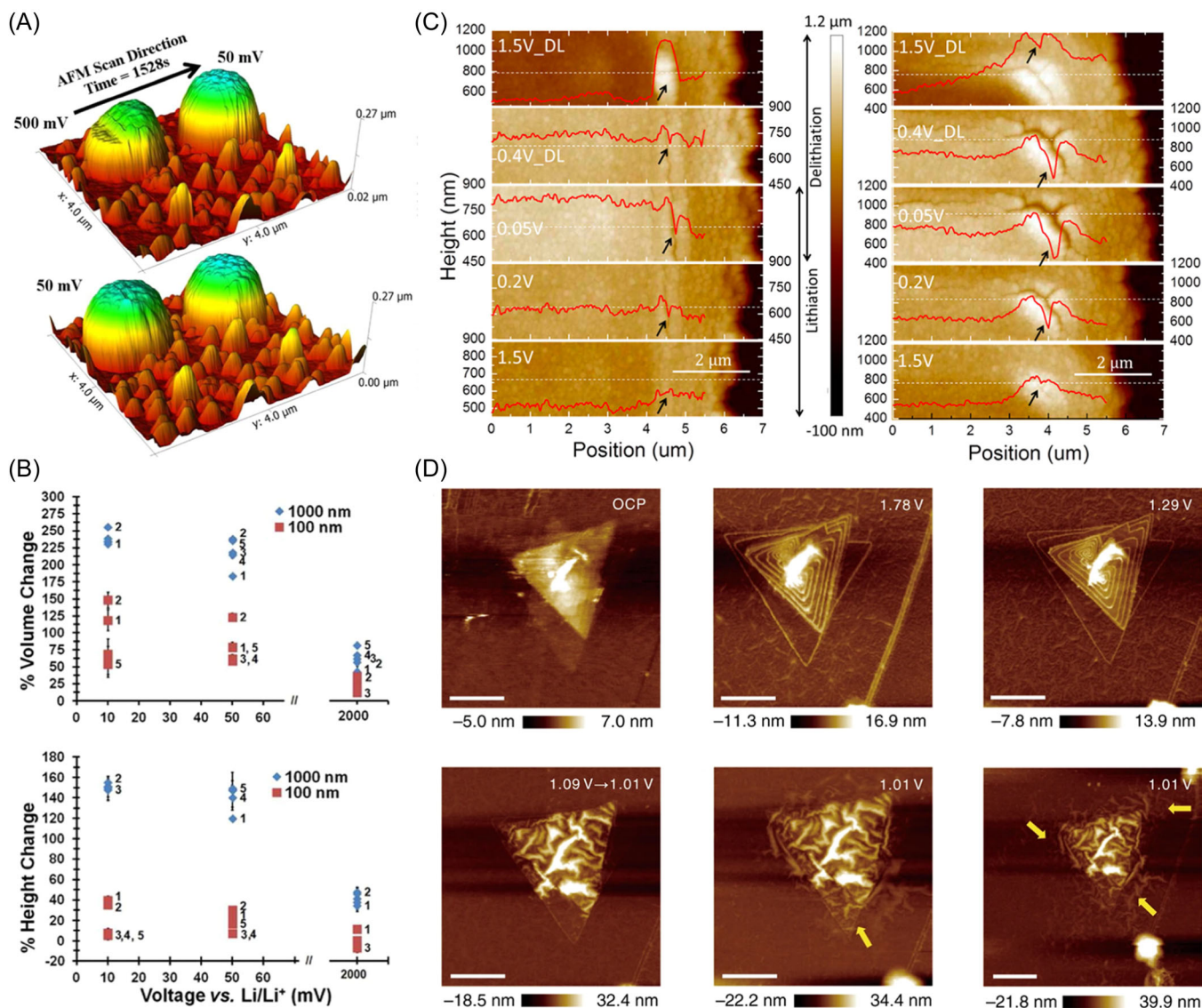


FIGURE 6 In situ atomic force microscopy (AFM) of lithiation and delithiation of amorphous Si (a-Si) nanopillars: (A) AFM images of the growth of the a-Si nanopillars (100 and 1000 nm) during the electrochemical cycling (scan rate: 1 mV/s). (B) Height and volume changes of five cycles. Reproduced with permission.⁸⁷ Copyright 2013, American Chemical Society. (C) Crack evolution of a patterned a-Si electrode at the edge (left) and corner (right) during the third cycle. Reproduced with permission.⁸⁸ Copyright 2016, American Chemical Society. (D) In situ AFM images of the interfacial morphologies evolution on a multilayer triangular molybdenum disulfide (MoS₂) electrode. Reproduced with permission.⁸⁹ Copyright 2019, Nature Publishing Group.

diameter of 100 and 200 nm were kept intact, while the nanopillars with a diameter of 300 nm cracked after 27 cycles. This real-time qualitative examination of the morphological (height and volume) changes of the a-Si nanopillars motivates future studies to quantify the structural integrity changes of Si nanopillars.⁸⁷ In situ AFM has also been utilized to observe the influence of volume expansion/contraction of Si electrodes in the mechanical degradation of SEI (Figure 6C). It was found that the SEI was tensed when the Si electrode expanded, which induced crack formation in the surface layer. Then, the cracks were not fully filled in at the low potential and further reopened and closed in the next cycles. This work directly monitored the SEI fracture process, which contributes to the chemical-mechanical degradation studies and capacity fade predictions of LIBs.⁸⁸

In addition to the Si materials, molybdenum disulfide (MoS_2) is also considered a promising LIBs anode material due to its high theoretical specific capacity. However, the SEI of the MoS_2 anode is unstable; therefore, the study of the structural evolution of the MoS_2 anode is crucial for battery performance improvement. It was reported that in situ AFM has been employed to monitor the dynamic lithiation/delithiation and SEI film formation on the large-area ultra-flat monolayer MoS_2 electrode. As shown in Figure 6D, the triangular MoS_2 had a layer spacing of ~ 0.7 nm at open circuit potential. When the potential decreased to 1.29 V, the electrode/electrolyte interface remained unchanged. Notably, when the potential decreased from 1.09 to 1.01 V, the triangular MoS_2 suddenly wrinkled, indicating the flexibility of the MoS_2 anode. As the lithiation proceeded, the bottom side of the triangular MoS_2 also wrinkled and then spread from the defect sites to the surrounding places. However, during the following discharging process, the as-formed wrinkles did not completely return to the original flat shape and the volume expansion was irreversible either. This work revealed the influence of surface defects on reaction kinetics, which contributes to a deeper understanding of structure-reactivity relationships.⁸⁹

The morphological evolution and dynamic mechanism (dynamic pathway and degradation mechanism) of the lithium and lithium-indium alloy anodes in the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -based all-solid-state Li metal batteries were investigated via the in situ AFM techniques (Figure 7A). Due to the low ionic migration barrier and fast ionic diffusion coefficient of the lithium-indium alloy anode, a homogeneous SEI shell was formed on this alloy anode, which further induced the uniform growth of Li_xIn lamellae during the lithiation process. Furthermore, the volume and surface area of the wrinkling structure were quantitatively analyzed, which suggested the breathing phenomena of the cycling behavior during the

lithium-indium dealloying/alloying processes, enabling favorable inner lithium accommodation.⁹⁰

Besides the real-time monitoring of lithium-ion intercalation behavior in LIBs, the real-time observation of intercalation/deintercalation processes in dual ion batteries (DIBs) was also achieved via the in situ AFM (Figure 7B,C). Through measuring the distance changes between graphene layers during the intercalation process, it was found that PF_6^- intercalated in one of every three graphite layers with a speed of $\sim 2 \mu\text{m}\cdot\text{min}^{-1}$. At high voltages, the graphite wrinkled and suffered structural damage with electrolyte decomposed on its surface, leading to the cycling performance degradation of DIBs.³³

5 | SURFACE EVOLUTION

In situ AFM has also been applied to directly visualize the surface evolution of electrodes with high spatial resolution, such as the dendrite formation during lithium anode plating and stripping processes,^{91–94} and the deposition and dissolution/decomposition of intermediates/reaction products on the cathode surface of the lithium-sulfur batteries^{30,95–98} and lithium-oxygen batteries.^{31,99–102}

The ununiform lithium stripping and plating upon cycling induced the dendrite formation on the lithium anodes, which reduced the battery performance and even potentially caused the short circuit, further leading to safety problems. Therefore, studying the dendrite formation process on the lithium anode surface is crucial for improving battery design and safety. In situ AFM measurements have been conducted to directly visualize the lithium stripping and plating process on the pristine lithium anode and lithium polyacrylic acid (LiPAA) SEI layer-modified lithium anode (Figure 8A). The SEI on the pristine lithium anode surface was not stable and was destroyed by the dynamic lithium stripping/plating behavior, further causing the side reactions and dendrite formation. Notably, after applying a smart LiPAA SEI with good stability and high bonding ability, the uneven stripping/plating behavior was markedly reduced, and the side reactions were greatly reduced with significantly improved battery safety.⁹² In situ AFM has also been reported to provide insights into the lithium nitrate-regulated lithium stripping/plating process in gel polymer electrolyte (GPE)-based lithium metal batteries at the nanoscale. Amorphous nitride SEI was formed due to the addition of lithium nitrate, which facilitated lithium-ion diffusion, stabilized a compatible interface, and regulated the lithium nucleation/growth. The deposited lithium was compact. The lithium dissolution exhibited good reversibility, ensuring the cycling performance of

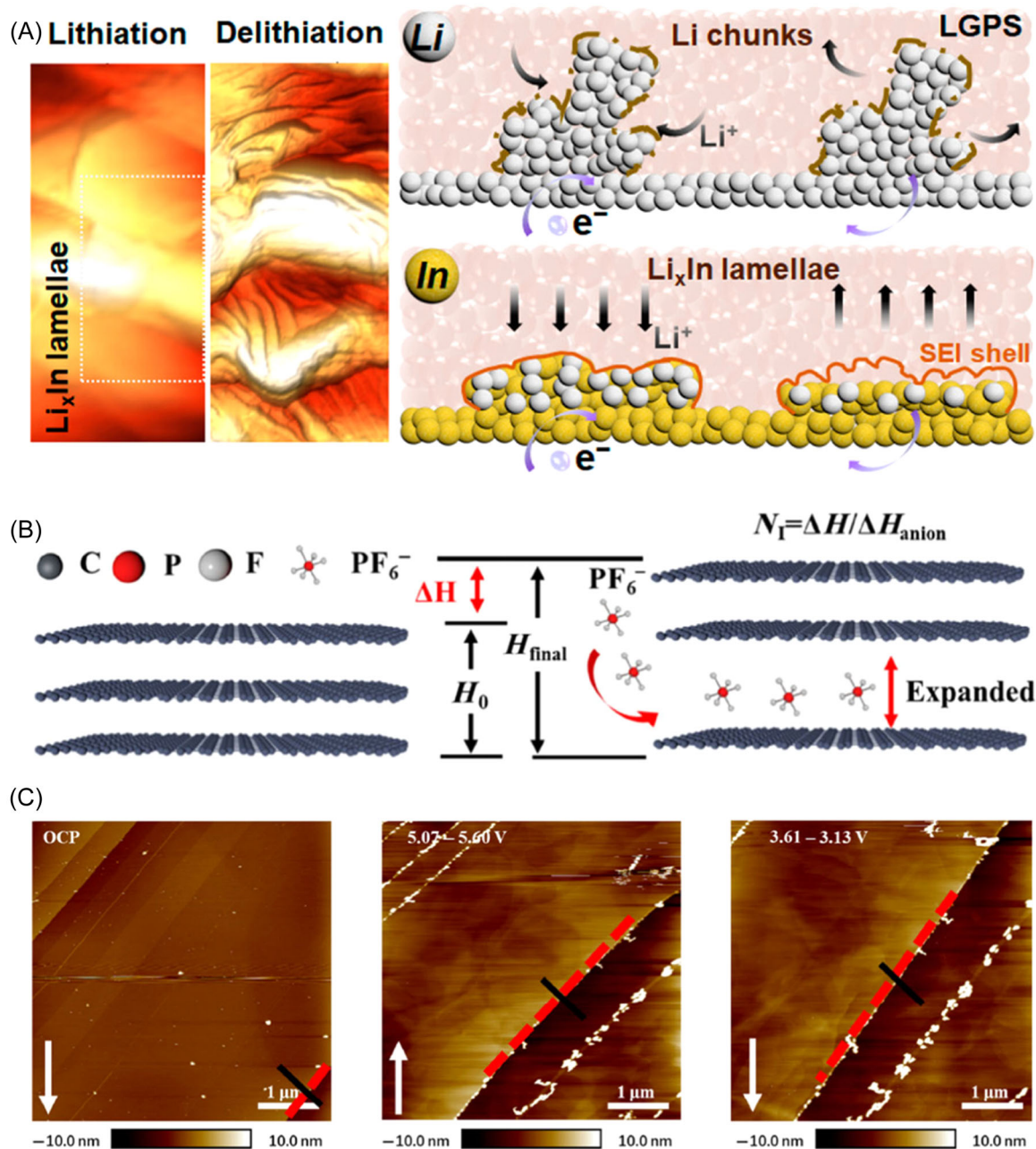


FIGURE 7 (A) Atomic force microscopy (AFM) images of Li_xIn lamellae at lithiation and delithiation states and schematic of the interfacial mechanism of lithium electrode (top) and indium electrode (bottom). Reproduced with permission.⁹⁰ Copyright 2021, American Chemical Society. (B) Description of parameters related to the PF_6^- anion intercalation process of highly oriented pyrolytic graphite (HOPG) in carbonate electrolyte. (C) In situ AFM images of HOPG anode in carbonate electrolyte at different voltages. Reproduced with permission.³³ Copyright 2020, Tsinghua University Press and Springer-Verlag GmbH Germany, part of Springer Nature. LGPS, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$.

lithium metal batteries.⁹³ In situ AFM was also applied in the monitoring of initial lithium deposition in FEC-based and EC-based electrolytes on graphite anodes for understanding the lithium dendrites growth evolution processes at the nanoscale. The results showed that a denser and harder LiF -rich SEI layer was formed in the FEC-based electrolyte, which sufficiently impeded the lithium ion reduction and deposition on the anode

surface and suppressed dendrite growth.¹⁰³ The dynamic Li plating/stripping behaviors upon cycling at the gel polymer electrolytes/lithium metal electrode interface in the quasi-solid-state lithium metal batteries were monitored by in situ AFM. Uneven lithium deposition with cavity-shaped defects and partial dissolution was observed at the lithium metal and gel polymer electrolyte interface. Furthermore, the addition of LiNO_3 induced

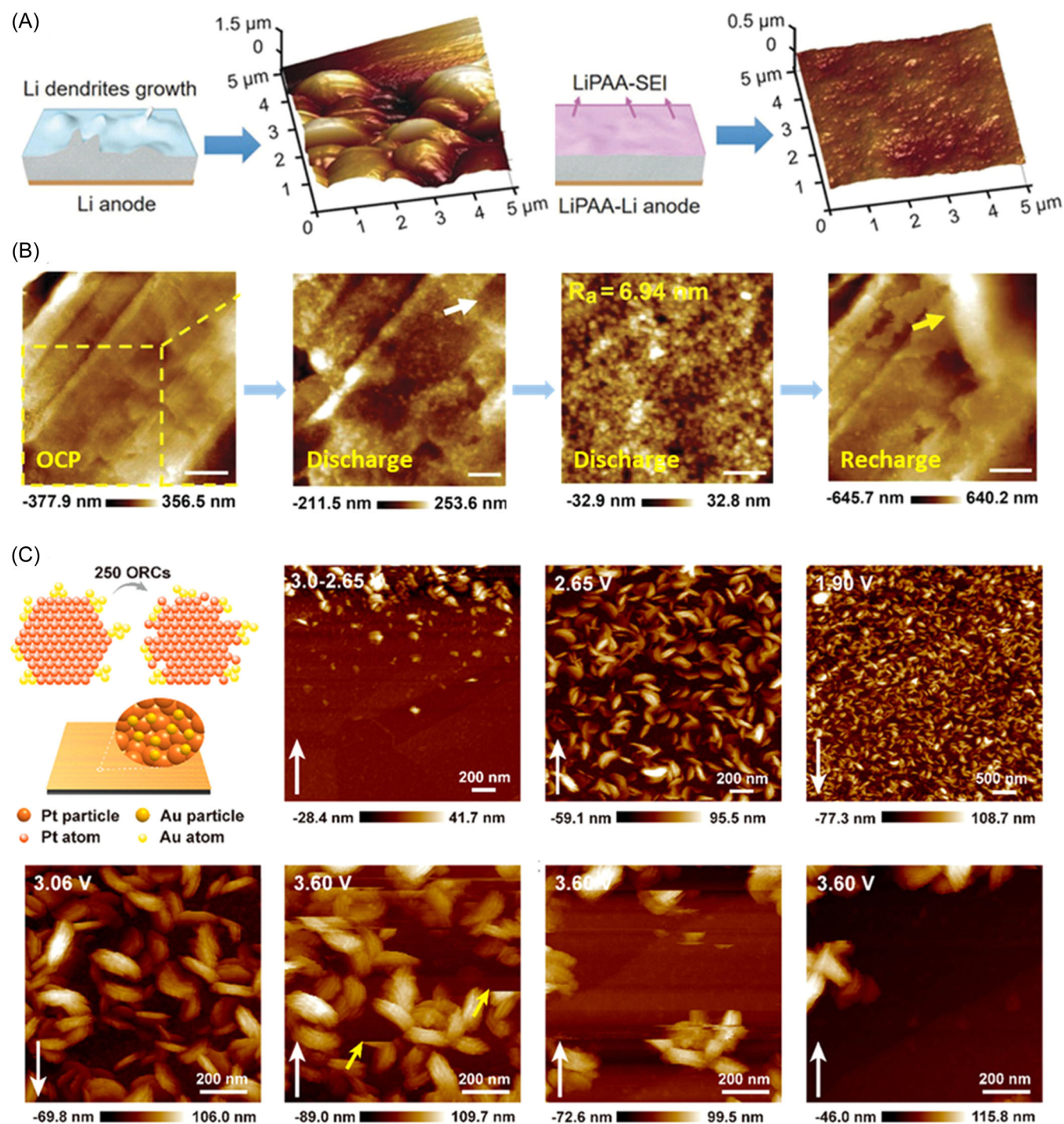


FIGURE 8 (A) Schematic and atomic force microscopy (AFM) images of pristine Li anode (left) and lithium polyacrylic acid-Li (LiPAA-Li) anode (right) after the lithium stripping process. Reproduced with permission.⁹² Copyright 2017, John Wiley and Sons. (B) In situ AFM monitoring of the Li anode surface evolution in a quasi-solid-state lithium-sulfur (QSSLs) cell containing 5 wt% LiNO_3 . Reproduced with permission.⁹⁶ Copyright 2022, John Wiley and Sons. (C) In situ AFM images on the Pt/Au nanoparticle electrode surface upon the discharge/charge process in a Li-O₂ model cell. Reproduced with permission.¹⁰⁰ Copyright 2021, American Chemical Society. OCP, open-circuit potential; SEI, solid-electrolyte interphase.

the formation of SEI film and homogeneous lithium deposition/dissolution. It also demonstrated good reversibility of lithium metal upon the lithium plating/stripping process.⁹³

The back and forward diffusion of polysulfide between the anode and cathode of lithium-sulfur batteries is called the shuttle effect, which can lead to severe corrosion of the lithium anode and irreversible

capacity loss of batteries. Thus, direct characterization of the deposition and dissolution processes of the lithium sulfide intermediates is of great significance in understanding polysulfide shuttle mechanisms and facilitating its improvement. For instance, in situ AFM was utilized to monitor dynamic processes and interfacial properties on the additive-mediated lithium anode surface at the nanoscale. After adding lithium nitrate to the electrolyte, two SEI formation stages were detected. First, loose NPs (~102 nm) were formed at the OCP. Then, dense NPs (~74 nm) were formed during the discharge process, caused by the synergistic effect of lithium nitrate and lithium polysulfides (Figure 8B). The as-formed dense SEI film can not only prevent the erosion of lithium polysulfides but also homogenize the lithium deposition behavior, thereby improving the electrochemical performance of lithium-sulfur batteries.⁹⁶ The investigation of the interfacial behavior at a high temperature (60°C) in lithium-sulfur batteries, including the dynamic evolution of insoluble Li_2S and Li_2S_2 , was realized via the in situ AFM. An in situ-formed functional film was detected after Li_2S nucleation upon discharge at 60°C. This as-formed film reduced the lithium-ion transport distance between the higher order sulfides and lower order sulfides, promoted the oxidation of Li_2S_2 and Li_2S upon the charge, and facilitated the interfacial morphology maintenance after cycling, which provides insights into the benign interface conservation and the performance optimization of lithium-sulfur batteries.³⁰

For lithium-oxygen batteries, the sluggish decomposition of discharge products (Li_2O_2) led to large overpotential and poor cycling stability. The side reactions and instability of the aprotic electrolyte further degraded the battery performance. Monitoring the generation and decomposition of reaction products during the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is crucial for understanding the correlations between the products' morphology and catalytic activity. In situ AFM has been applied to record the dynamic surface evolution of the Pt NP electrode in lithium-oxygen batteries (Figure 8C). The pristine platinum NPs promoted the nucleation and growth of Li_2O_2 nanosheets with reduced overpotential. As the cycling proceeded, the platinum particle size gradually increased and induced cracks on the electrode surface. Meanwhile, the morphology of Li_2O_2 evolved into a larger toroidal structure with degraded reversibility and capacity. After modifying the Pt electrode with a certain amount of gold NPs, the stability of the electrode increased. No obvious particle accumulation and cracks were observed on this gold-modified Pt electrode after 250 cycles, indicating that gold inhibited the morphological evolution of platinum and improved the stability of

platinum without catalytic activity degradation.¹⁰⁰ In situ AFM has also been employed to record the real-time images of surface evolution on a gold electrode in the lithium-oxygen batteries, which revealed the correlations between ORR and OER catalytic activity and the nanostructure of the gold electrode. The results indicated that nanoporous gold facilitated the nucleation and growth of Li_2O_2 discharge products, while the densely packed gold NPs promoted the full decomposition of Li_2O_2 . These observations shed light on the mechanism of nanostructure catalyst-based lithium-oxygen batteries and provide strategies for improving lithium-oxygen batteries.¹⁰¹

6 | SUMMARY AND OUTLOOK

Developing advanced high spatial and temporal resolution in situ characterization techniques is crucial for understanding the operation, degradation, and failure mechanism of lithium-based batteries. In this paper, we reviewed the application of in situ AFM in LIBs, lithium-sulfur batteries, and lithium-oxygen batteries, including the studies of electrode-electrolyte interfaces, mechanical properties, morphological changes, and surface evolution, which contributes to the electrode and electrolyte optimization and battery performance improvement. Future perspectives of the in situ atomic force techniques in battery characterization are demonstrated as follows:

- (1) *Developing in situ electrical properties characterization:* In addition to the as-mentioned progress of in situ AFM, other SPM techniques are also considered promising methods to explore the interfacial process and operation mechanism of lithium-based batteries. For example, electrochemical strain microscopy can measure the localized, electrochemically induced volumetric strain, which provides real space mapping of lithium-ion diffusion and contributes to understanding the role of grain defects/orientation in lithium-ion transport.^{104–106} Scanning ion conductance microscopy can simultaneously and fast scan the topography and map the variation in electrochemical activity.^{107,108} Kelvin probe force microscopy could obtain a high-resolution mapping of electrochemical surface potentials.^{109–111} Due to the advantages and limitations of each SPM technique, it is significant that various SPM methods can be combined to investigate the materials, interfaces, and processes of lithium-based batteries.
- (2) *Integration of multidimensional characterization:* Considering the complicated physical-chemical

reactions in battery systems, the other future direction is combining other advanced characterization methods to acquire the real-time composition changes during the electrochemical process of lithium batteries, such as XRD, XPS, and Raman, which is beneficial for systematically understanding the underlying mechanism of batteries and guiding its design and performance improvement. These developed novel in situ SPM techniques could also be applied beyond the lithium system, such as sodium-ion batteries, potassium-ion batteries, and magnesium-ion batteries, providing a useful tool to realize the development of high-performance battery systems and meet the increasing energy demand.

- (3) *Operando characterization under various operation conditions*: AFM observation on real electrodes should be further carried out to reveal the practical reaction mechanism. Besides, multi-functional in situ cells should be designed to enable the testing under different operation conditions of LIBs (such as under high/low temperatures, under different working gas and liquid, electrolyte and gas circulation systems, and electrical and mechanical abuse conditions).
- (4) *Advanced electrode manufacturing techniques*: Micro- and nanofabrication technologies (such as photoetching, electron beam evaporation, and 3D printing) should be further introduced to develop various electrode structures that simulate the reaction process in different battery systems. Besides, interface pretreatment techniques (such as ion beam etching and plasma etching) should also be widely employed to create an optimized interface for AFM characterizations.
- (5) *Artificial intelligence-assisted AFM analysis*: Advanced computational and algorithmic techniques should be introduced for high-fidelity AFM characterization and analysis. Meanwhile, the characterization data from AFM observation should be used in machine-learning models for a better understanding of the reaction mechanism.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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