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Advances in sealed liquid cells for in-situ TEM (electrochemial investigation of lithium-ion battery

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Abstract

Lithium-ion battery (LIB) technology is currently the most important and promising energy storage technology that has captured the portable electronic market, invaded the power tool equipment market, and penetrated the electric vehicle market. The ever-growing demand for its energy capacity necessitates the understanding of (de)lithiation mechanism on a nanoscale, and thus the development of platforms enabling in-situ electrochemical TEM characterization. Sealed liquid cell (SLC) device has been widely recognized as the most desirable platform, since it allows the introduction of commercial volatile electrolytes into TEM. However, a comprehensive review summarizing the current development of SLCs for in-situ TEM LIB research is missing and in urgent need for its benign development. This review article aims to fill this gap. © 2014 Elsevier Ltd. All rights reserved.

Contents

1.	Intro	duction	197
	1.1.	Importance of lithium ion batteries (LIBs)	197
	1.2.	Challenges in current LIB research	197
	1.3.	Importance of developing platforms enabling in-situ electrochemical TEM characterization for LIBs	197
	1.4.	Scope and goal of this article	198
2.	Platf	orms with an open-cell configuration for in-situ TEM electrochemical characterization of LIBs	198
	2.1.	Platforms using no electrolyte with an open cell configuration for in-situ TEM electrochemical	
		characterization of LIBs	198

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	2.2.	Platforms	s using r	non-vo	latile	(soli	d or	nor	I-VO	latil	le li	qui	d) (eleo	ctro	olyt	es \	wit	h ai	n op	ben	ce	ll c	onf	igu	rati	ion	
		for in-situ	л ТЕМ е	lectro	chem	ical d	hara	acte	riza	tion	n of	LIE	ß.															 . 198
3.	Plat	forms with	a seale	d-cell	config	gurat	ion f	for i	n-si	tu T	ΈM	ele	ectr	och	nem	ica	l cł	nara	acte	eriz	atio	n o	of L	IBs				 . 200
	3.1.	Different	configu	iratior	s of S	LCs o	desig	gned	for	' in-	situ	TE	EM e	elec	tro	che	emi	cal	cha	arad	ter	iza	tio	n of	f LI	Bs		 . 200
	3.2.	Application	ons of S	LCs fo	r in-s	itu T	EM e	elect	roc	hem	nica	l cł	nara	acte	eriz	atio	on d	of L	IBs									 . 203
4.	Sum	mary and f	uture re	esearc	h dire	ctior	ns																					 . 207
Ack	nowl	edgments .																										 . 208
Ref	erend																											 . 208

1. Introduction

1.1. Importance of lithium ion batteries (LIBs)

Modern society requires tremendous amount of energy, but the dependence on fossil fuel has caused serious environmental problems including global warming and air pollution. Since renewable energy sources such as solar and wind power are often intermittent, dramatic advances in electrical energy conversion and storage technologies to balance energy supply with demand is a pressing worldwide imperative, especially for electrification of transportations [1-4]. The electrochemical approach to store and restore electrical energy is the most attractive way because the conversion between electrical and chemical energy shares the common carrier: electrons [5]. Fuel cells and batteries are two such electrochemical storage devices that enable chemical-electrical energy conversions in a single or reversible way, respectively. Specifically, batteries are the main contenders for managing renewable resources and to favor the deployment of electric cars [5].

Among present battery technologies, Li-ion battery (LIB) technology is the most advanced and appealing one [6,7] that occupy the energy storage market for all mobile devices such as phones, computers, tablets, organizers, etcetera. LIB technology exceeds any other competing technologies in energy density (210 Wh kg^{-g}; 650 Wh l^{-h}), by at least a factor of 2.5 [5]. With its attractive performances, long life cycle and high rate capability, LIB technology has captured the portable electronic market, invaded the power tool equipment market, and penetrated the electric vehicle market [5].

1.2. Challenges in current LIB research

The substantial improvement in the charge capacity of LIB cells results in as much as a 50% improvement in cell specific energy, particularly due to the improvement on the anode side[1]. However, great challenges exist in extending cell lifetime, particularly with the newer high-capacity anodes and cathodes, such as alloy or conversion anodes including Si, Sn, Fe_2O_3 , etcetera. The large volume changes during cycling often results to large capacity loss after the first cycle and shorter cycling lifetimes [8], which is economically unbearable because any cost savings from improving the specific energy of a battery module is lost if its lifetime decreases. Therefore, fundamental understanding and studies in mechanisms that control battery performance and reliability, such as reactions at the electrode/ electrolyte interface, structural and mechanical changes in the

electrodes, and chemical changes in the electrolyte, are indeed necessary.

1.3. Importance of developing platforms enabling in-situ electrochemical TEM characterization for LIBs

The large volume expansion of new high-capacity anodes and cathodes during initial reaction with Li [8] often leads to various mechanical failure modes, including plasticity, cracking, spallation, loss of electrical contact of the anode particle with the current collector, and ultimately the degradation of LIBs after electrochemical cycling. Advances in OD [9], 1D [10] and 2D [11-26] material fabrication technologies have enabled various forms of nanoscale materials, which can be used as nanostructured anodes to accommodate the large volume changes during cycling. For example, silicon nanowire anodes were reported to retain high capacity during several charge-discharge cycles in spite of an initial volume change of 400% [27], while bulk silicon loses more than 80% of its capacity in less than 10 cycles due to pulverization [28]. Moreover, nanoscale anodes/ cathodes also reduce cell impedance and increase power capabilities [29]. The use of nanoscale materials in LIBs introduces challenges for structural and electrochemical characterization, as their small physical dimension (nm to 10's of nm) and size-dependent properties require utilization of probes with nm or better spatial resolution [30]. Although traditional electrochemical tests (e.g. charge-discharge cycling, cyclic voltammetry, electrochemical impedance spectroscopy), are de rigeuer(required by etiquette) for characterizing battery performance, insight into mechanisms at the atomic to nanoscale is of critical importance, and characterization methods that provide mechanistic information of charge/discharge dynamics of individual grains and particles are most illuminating and desirable [31]. Transmission electron microscopy (TEM) investigations excel in providing structural and compositional information with nanoscale spatial resolution and subsecond temporal resolution. To provide the atomic to nanometer resolution and to examine mechanisms of charge storage or degradation at the single particle level instead of averaging over an ensemble of particles, new platforms enabling high-resolution imaging and simultaneous electrochemical characterization inside TEM, that is, in-situ TEM characterization, are in urgent need for LIB research and development. Unlike ex-situ studies, which involve unexpected reactions due to the removal of the particles from their native and reactive environment [31], in-situ TEM electrochemical characterization will mimic the true environment in a commercial LIB cell. Conventional TEM is not

compatible with studies of electrochemical energy storage processes, but the development of TEM holders and liquid cell platforms encapsulating thin liquid layers promise in-situ imaging and spectroscopy of electrochemical processes [32,33] (e.g. electrodeposition [34] and dendrite growth [35]) on the nanoscale [36-38], by incorporating electrodes [34,39] in a liquid environment. The in-situ liquid TEM has allowed quantitative analysis of processes (e.g. nanoparticle growth from solution[40-42]), and direct observation of beam sensitive systems (including macromolecular complexes [43,44], soft materials[45,46]) and of processes that span from the electrochemical deposition of metals[34,35], to growth of different nanostructures [40,41,47-50]. Now it gains growing attention for LIB research.

Apart from nanostructured anodes/cathodes, the development of platforms enabling in-situ TEM electrochemical characterization is also required by various other aspects of LIB research. For example, one of the most well-known reactions at the electrode/electrolyte interface is the formation of the solid-electrolyte interphase (SEI), which is a reaction product of mixed composition formed on highvoltage anodes (e.g. Li metal or graphite-lithium intercalation compounds) or cathodes, by electrochemical reduction or oxidation of the electrolyte^[51], respectively. The study of the SEI layer requires the use of commonly used LIB electrolytes (volatile carbonate-based solution), the ability to monitor the changes in SEI layer with cycling, time or temperature, and probes having sufficient spatial resolution to detect a reaction product layer of a few nm thick. All of these requirements make ex-situ characterization inappropriate for the study of SEI, since the SEI layer is highly sensitive to moisture, air, and other kinds of contaminations [52]. The importance and critical need to develop platforms enabling in-situ TEM electrochemical characterization of LIBs are thus obvious. Furthermore, the detailed understanding in dendritic growth of lithium metal on the electrode also requires such in-situ TEM platforms, because the dendritic growth of lithium metal on the electrode can lead to short-circuit and thus battery failure [52].

The platforms developed for in-situ TEM electrochemical characterization of LIBs so far can be classified into two categories: 1) platforms with an open-cell configuration; and 2) platforms with a sealed liquid cell (SLC) configuration. SLCs are micro-electromechanical systems (MEMS)-based platforms enabling the usage of carbon-based volatile electrolytes, which are widely used in commercial LIBs.

1.4. Scope and goal of this article

Although SLC has been widely recognized by the community as the most desired tool for in situ TEM study of LIBs, there have been no efforts to summarize the current developments in this field. This review aims to summarize the current research fronts and serve as guidance for future development of SLCs for in situ TEM studies of LIBs. This review is organized into four sections. The first section presents the background information, followed by the second section introducing the platforms with an open-cell configuration. SLCs are discussed in detail in the third section, including the different designing features of SLCs developed to date, and their applications in LIB research. The final section serves as a summarization of the whole article and points out the future research directions of SLCs for in-situ TEM electrochemical characterization of LIBs.

2. Platforms with an open-cell configuration for in-situ TEM electrochemical characterization of LIBs

Tremendous progress has been made towards in-situ direct observation of structural and chemical evolution of electrodes for LIBs [53-55]. Platforms that enable in-situ TEM electrochemical characterization were first designed with an open-cell configuration, thus forbidding the usage of carbon-based volatile electrolytes in commercial LIBs. These early-stage platforms enabled in-situ TEM electrochemical characterization of changes that do not directly depend on the nature of the electrolytes. These changes occur in LIB cathode and anode materials during lithiation and de-lithiation, and are primarily a function of the Li content of the anode or cathode (e.g. the phase changes that occur in conversion anode materials or certain cathode materials, such as $LiMn_2O_4$ [56]). Three different types of these early-stage platforms have been developed [30]: platforms that use no electrolytes, platforms that use solid electrolytes, and platforms that use non-volatile liquid electrolytes. The following Sections (2.1 and 2.2) will discuss about these three early-stage platforms briefly in a separate manner.

2.1. Platforms using no electrolyte with an open cell configuration for in-situ TEM electrochemical characterization of LIBs

Anode or cathode reactions with solid Li in the absence of electrolytes are not strictly electrochemical in nature, because there is no separation of the oxidation and reduction processes. However, these reactions may reveal information during solid-state reactions or solid-state diffusions of Li, which are issues of interest for LIB electrochemistry. For example, J.P. Sullivan et. al. [30] studied the lithiation mechanism of multiwall carbon nanotubes to investigate the solid-state reactions of electro-active materials with Li. The solid-state reaction was initiated by placing Li metal in contact with an individual carbon nanotube, by using a nano-manipulator inside the TEM [57]. An immediate reaction involving Li diffusion into the carbon nanotube was observed, and the diffusion was found to be slow enough that a Li particle diffused only tens of nm within a few minutes [30].

2.2. Platforms using non-volatile (solid or non-volatile liquid) electrolytes with an open cell configuration for in-situ TEM electrochemical characterization of LIBs

In order to investigate true electrochemical reactions inside a TEM, it is necessary to separate the oxidation and reduction processes through the use of an electrolyte [30]. Therefore the platforms that use solid electrolytes or non-volatile liquid electrolytes are of most interest. The fundamental designing

concept of the open cell is schematically illustrated in Fig. 1 (a) for ionic liquid and Fig. 1 (b) for solid electrolyte (e.g. Li₂O) [32,33]. To date, the majority of in-situ TEM electrochemical analyses on LIBs were based on the use of solid electrolytes or non-volatile liquid electrolytes to accommodate the in-situ cells in high vacuum TEM environments [58-62], and have made significant progresses in understanding electrochemical reactions in LIBS. For example, crack propagation in microsized particles [58,63], preferential volume expansion along [110] direction of Si anode [64], and ledgemediated-migration of sharp phase boundary at the amorphous/crystalline interface [65] were elucidated based on dynamic atomic rearrangements.

Many researches have been done on open cells using solid electrolytes. For example, using the naturally-grown Li_2O layer on Li as the solid electrolyte, HRTEM observation of electrochemical lithiation in FePO₄, in-situ study of lithiation process of single-crystal Si nanowire and lithiation/delithiation of amorphous Si nanospheres were performed by Yujie Zhu [66], Huang [62,65] and McDowell [67], respectively. Other solid electrolytes have also been adopted for open cells, such as LiAlSiO_x in a solid-state open-cell microbattery [68] and a 90 μ m thick glass ceramic sheet of composition $Li_{1+x+y}Al_{y}$. Ti_{2-y}Si_xP_{3-x}O₁₂ [69] used to directly observe the battery reaction near the electrode/electrolyte interface in a TEM.

lonic liquids can be used as an electrolyte in high vacuum environments because of their high salt solubility and extremely low vapor pressure [70]. Their high electrochemical stability, low flammability, and low vapor pressure have been widely investigated by using them as LIB electrolytes [70] inside a TEM without encapsulation [30]. The ionic liquids can be introduced into the TEM by spin coating, drop casting, or dipping [30]. The ionic liquid has sufficient surface tension to bridge small openings, enabling its use without substrate support in an open-cell configuration, which is a desirable feature to minimize the sample thickness for high resolution TEM imaging [30]. For example, an ionic liquidbased electrolyte was used to observe in-situ lithiation of a single SnO₂ nanowire anode during electrochemical charging by Huang [33] and Wang [71]. One drop of ionic liquid-based electrolyte was shown to be enough [59] for studying the electrochemical and structure properties of hollow carbon nanofibers coated with amorphous Si on both the exterior and interior surfaces as an anode. Real time and atomic-scale observations of battery charging and discharging processes can also be performed by using room-temperature ionic liquid electrolytes [62]. J.P. Sullivan et al. [30] developed an open cell to utilize ionic liquid electrolytes including 1,2-Dimethyl-3-propylimidazolium (DMPI) with bis(trifluoromethylsulfonyl)imide (TFSI) and Li-TFSI salt, and 1-butyl-3methylimidazolium (BMI) with hexafluorophosphate (PF6) and LiPF6 salt.

However, three typical deficiencies are associated with the open-cell configuration using solid electrolytes or nonvolatile liquid electrolytes. Firstly, for the open cell, the electrolyte is only in point contact with the electrode, which may inadvertently modify the diffusion patterns of Li ions in the electrode, and therefore, what has been obtained is not necessarily representative of the case where the electrode is fully immersed in the liquid electrolyte in a real battery. Secondly, for the case of using Li₂O as the electrolyte, a large overpotential is normally applied to drive the Li ions into the electrode, which may change the kinetics and phase behaviors of solid-state electrode lithiation. Thirdly, the use of the ionic liquid or Li₂O electrolyte excludes some of the fundamental processes which only occur in real electrolytes and the battery operating conditions, such as the interaction between electrolyte and electrode and the SEI layer formation. Therefore, these early-stage platforms (platforms with an open-cell configuration and avoiding volatile electrolytes hereafter) will be eventually replaced by SLCs, which enable the introduction



Fig. 1 [86]: (a) Schematic drawing showing the experimental setup of the open-cell approach using ionic liquid as electrolyte; (b) Schematic drawing showing the setup of the open cell approach using Li metal as lithium source and Li_2O as solid electrolyte.

3. Platforms with a sealed-cell configuration for in-situ TEM electrochemical characterization of LIBs

The high vacuum of TEM sample chambers, typically 10⁻⁵ Torr or better[72], forbids the introduction of volatile electrolytes into TEM chamber for electrochemical study. However, typical commercially available Li-ion batteries usually use carbonate-based liquids as electrolytes, such as diethyl carbonate (DEC), dimethyl carbonate (DMC) mixed with ethylene carbonate (EC), etcetera. To enable in-situ TEM characterization of electrochemical reactions in real lithium ion batteries, sealing those volatile liquids inside a sufficiently narrow channel for electron transmission is a wise option. The platforms that enable in-situ electrochemical characterization with any types of electrolytes and a sealedcell configuration are classified as sealed liquid cells (SLC), which enable the potential use of volatile carbon-based electrolytes for LIB research. Actually the concept of sealed-cell configuration is not recently invented. In 1991, Nan Yao [73] used two pole pieces to seal gas and maintained high gas pressure in the sample region, for studying supported metal catalysts during catalytic process in a TEM column. A good summary of nanoscale in-situ TEM studies of gas-solid interactions can be found in the relevant review article [74]. For SLCs, however, liquid is sealed in the cell instead of gas. One of the first TEM SCLs was created by F.M. Ross et al. [34,75] to study Cu electro-deposition during TEM imaging. This SLC platform sealed the aqueous electrolyte by assembling two silicon chips with thin silicon nitride membranes in a face-to-face configuration. This flip-chip approach allows imaging chemical reactions in liquids with high spatial resolution [34,37,38,41,76] with different membranes of silicon nitride, silicon dioxide, or polymer, such that it has been adopted in various studies, including cell imaging [77-79] and nanoparticle synthesis [38] in solutions. For example, electrochemical deposition of polycrystalline Au [76], anisotropic electrodeposition of nickel nanograins [80], and electrochemical growth of single crystal lead dendrites through nucleation, aggregation, alignment, and attachment of randomly oriented small grains [81] were imaged by using electrochemical SLCs.

To date, large progress has been made on fabrication and testing of the design features (including sealing, assembly, alignment, etc.) of SLCs [30], which opens the opportunity to address key questions on the electrode – electrolyte interfaces in native liquid environments, for example, Kyong Wook Noh et al. [82] captured cyclic formation and dissolution of solid-electrolyte interphase at a Sn electrode in commercial liquid. Due to the reduced length scale of the electrodes, limited electrolyte volume, low current measurements [83], high vapor pressure of commercial electrolytes, and low contrast of lithium during TEM imaging through the membrane window, the application of SLCs as in-situ electrochemical TEM cells for LIB research is still a great challenge and very limited. The following sections will discuss in detail about the design features and application of different SLCs that have been reported to date for LIB research.

3.1. Different configurations of SLCs designed for in-situ TEM electrochemical characterization of LIBs

To ignite the electrochemical reactions on electrodes in SLCs, either the electron beam of TEM or external electrical current is utilized. To use electron beam as the excitation agent, high-energy imaging electrons (300 kV) are needed to irradiate the solution, generating radicals and solvated electrons by primary and secondary scattering. For the case of a simple salt dissolved in an aqueous solution, the electron beam essentially acted as a reducing agent, where the created radicals, such as the aqueous electrons, induced the reduction of metallic cations to grow metallic nanoparticles from solution [84]. In more complex solutions, such as Li battery electrolytes, the solvated electrons, and other radical species induced by the electron-beam would interact through secondary chemical reactions with the salt and solvent. The time evolution with increasing cumulative dose caused an electron-beam induced breakdown of the electrolytes, which was applied to perform in situ investigation on the degradation of various electrolytes [85]. Following the mainstream of SLC designs, the two silicon nitride (SiN_x) membranes supported on Si chips enclosed the liquid sample and performed as an electron transparent viewing area, as in Fig. 2.

To use external electrical current as excitation agent, electrodes need to be patterned and fabricated onto the Si chips in SLCs. Different numbers, materials and designs of electrodes have been used for various SLCs. Two 120 nmthick gold electrodes were used in the SLC designed and fabricated at the Marvell Nanofabrication Laboratory of the University of California at Berkeley [52], which enabled the observation of SEI formation, Li dendrite growth, and Li – Au reaction on the electrodes. The gold electrodes were deposited on the bottom chips with a face-to-face distance of 20 μ m, as shown in Fig. 3 (a). The SLCs used 200 μ m thick silicon wafers as bottom and top chips, onto which 35 nm thick low-stress silicon nitride films (25 $\mu m~\times~6~\mu m)$ were evaporated as viewing windows through photolithographic patterning and etching. The bottom and top chips were sealed by 150 nm thick sputtered indium spacer. The commercial electrolyte for lithium ion batteries, that is, 1 M lithium hexafluorophosphase LiPF6 dissolved in 1:1 (v/v)ethylene carbonate (EC) and diethyl carbonate (DEC), was



Fig. 2 [85]: Schematic of the windowed-cell used in the fluid stage. Spacers separating the chips in combination with the membrane bulging due to the pressure differential with the microscope vacuum determine the total fluid path length.

Assembled Cell



С

In situ

Observation

Left Electrode

(LE)

a. SEI Formation

Fig. 3 [52]: A scheme of in situ TEM observation of the electrochemical reaction using an electrochemical liquid cell: (a) A top microchip patterned with 150 nm thick metallic indium was covered and stuck onto bottom microchip with 120 nm thick gold electrode deposited on it, which is the assembled liquid cell for TEM visualization when embedded in a TEM holder; (b) Cyclic voltammetry with a different voltage range applied to the electrochemical liquid cell TEM holder; (c) Real time electro-de – electrolyte interface reaction with commercial LiPF6/EC/DEC electrolyte loaded in the liquid cell.

loaded into the reservoirs with a syringe, and then flew into the viewing window by capillary force. The cell and the reservoirs were then covered by Cu foil and sealed by epoxy. The dimensions of a biasing cell were $\sim 3 \text{ mm} \times 3 \text{ mm}$ square and $\sim 400 \,\mu\text{m}$ thick. Both of the working and counter electrodes were extended to two gold pads in two reservoirs, with gold wires bonded onto each gold pad and connected to the two copper electric pads at the tip of electrochemical holder, as shown in Fig. 3 (a). An electric bias was applied by an electrochemical workstation connected to the electric pads through copper wires, such that the detailed electrochemical reactions were monitored in situ by application of a cyclic voltammetry (Fig. 3 (b)).

а

Electrochemical

Liquid Cell TEM

Top Chip

Bottom Chip

The configuration of electrodes can be totally different. such as the SLC created by Megan E. Holtz et al. [31] and shown in Fig. 4 (a) and (b). The three patterned electrodes on the top chip were optimized for electrochemical cycling and imaging. Instead of using traditional high-atomicnumber electrode materials such as Pt and gold, which obscure imaging, they used a carbon working electrode to scatter electrons weakly. Moreover, they chose titanium as adhesion layer material under the platinum reference and counter electrodes instead of chromium, to avoid the rapid diffusion of chromium into electrodes in traditional siliconprocessing methods. The adoption of the carbon working electrode enabled imaging with little loss in spatial resolution and contrast, which was dominated by scattering in the liquid only [31]. The holder they used was a Protochips Poseidon.

J.P. Sullivan et. al. [30] designed a total of twenty different electrode configurations for the bottom chip, ranging from 4 electrodes up to 10 electrodes, and one set of the designs are shown in Fig. 5. They created a SLC with multiple electrical and insulating layers, using micro-electromechanical systems (MEMS) fabrication processes.

The silicon nitride windows were controlled to be less than 20 nm thick to reduce electron absorption during TEM imaging. This approach required the nitride windows to be small so that the alignment of the top and bottom chips is more complicated. They designed raised alignment features to promote precise X-Y alignment and buried electrical interconnects, as shown in Fig. 6.

Observe Window

Right Electrode

b. Li-Au Reaction

c. Li Dendrite Growth

Not only the electrode patterns can be modified, new materials can also be deposited onto existing electrodes to serve as real anode or cathode. Meng Gu et al. [86] designed a SLC for in situ TEM studies to observe the structural evolution of a single Si nanowire upon lithiation/delithiation with controlled battery operating conditions. The conceptual setup for implementation of the in situ SLC is schematically illustrated in Fig. 7. The working electrode was a single Si nanowire, while the counter electrode was a small piece of Li metal loaded on a separate Pt electrode in an Ar-filled glove box to avoid over oxidation. The biasing chip has six Pt electrodes extending from the SiN_x window to the edge of the chip, allowing the connection of the electrode to the outside circuit, as shown in Fig. 8 (a). A single or multiple Si nanowires were mounted on one of the Pt electrodes by focused ion beam (FIB) manipulation and Pt deposition welding and extend to the electrontransparent SiNx (50 nm thick) membrane region to enable imaging, as illustrated in Fig. 8 (b) and (c). The electrolyte used was Lithium perchlorate in ethylene carbonate (EC)dimethyl carbonate (DMC), with a weight ratio of the components as follows: 8.67 wt% of LiClO₄; 32.36 wt% of EC; 58.97 wt% of DMC (the EC/DMC mixture solvent was prepared first, and LiClO₄ salt dried at 110 °C in vacuum for overnight was added to the solvent). A droplet of the prepared electrolyte was applied to the top surface of the SiN_x membrane (fully immersing all of the Pt electrodes, Li metal, and Si NWs), and a blank chip with a SiN_{x}



Fig. 4 [31]: Schematic of the in situ electrochemistry TEM holder and electrochemical data. (a) Cross-sectional view of the holder, with silicon nitride membranes encapsulating a fluid layer. The working electrode (WE), made of carbon, lies in the viewing window, with LiFePO₄ (LFP) nanoparticles deposited on top. The platinum counter electrode (CE) is coated with an excess of activated carbon (AC). In EFTEM mode, energies are selected by a slit to be imaged. (b) Schematic of the top chip, with three patterned electrodes: a carbon WE on the viewing membrane, Pt reference electrode (RE), which is not used in the battery experiment, and Pt CE. The connection leads are covered by SU8, and the contact pads to the holder do not contact the liquid so as to minimize electrochemical activity outside the viewing window.



Fig. 5 [30]: Optical microscope image (upper left) and scanning electron microscope (SEM) images of the bottom chip showing one of the twenty electrode configurations.

membrane facing down was placed over the biasing chip to seal the liquid electrolyte. The viewing window dimensions were $50 \ \mu m \ \times \ 50 \ \mu m$ and the normal thickness of liquid layer was $500-1000 \ nm$ (it may change because the



Fig. 6 [30]: Schematic of the electrochemical platform for TEM imaging. The ridge and trench structures are reversed in this schematic for clarity of the figure. In the fabricated structure, the electrodes are buried beneath silicon nitride and silicon dioxide up to the region immediately surrounding the silicon nitride window.



Fig. 7 [86]: Schematic drawing showing the setup of the liquid cell battery.

membrane will bulge outward in TEM column due to the pressure differences). The whole device was implanted on a biasing in situ TEM liquid holder (Hummingbird Scientific, Lacey, WA, USA), and the liquid electrochemical cell was connected to an electrochemical testing station (Bio-Logic, Knoxville, TN) fitted with the ultralow current capability. therefore allowing the test of the single nanowire battery in both potentiostatic and galvanostatic modes. Two types of Si nanowires (Si NWs) were used for this study, that is, asgrown crystalline Si NWs and crystalline Si NWs with halfside Cu coating. The coated thin Cu layer served dual functions: (1) to provide mechanical support to the Si NW during cycling, therefore potentially extending the lifetime of the NWs in Li-ion batteries; (2) to increase the electrical conductivity of the Si NWs that can again potentially enhance the performance of these NWs in Li-ion batteries.

Although the majority of SLCs adopted microelectromechanical systems (MEMS)-based techniques, using SiN_x membranes as viewing windows, some other materials have also been utilized to replace SiN_x, such as graphene [87]. The in situ graphene-sealed liquid cell (G-SLC) [36,87] was designed to investigate the lithiation dynamics of Si nanoparticles (NPs) in LIBs, unveiling atomic-level phenomena in liquid environments, as two graphene sheets can trap liquid even inside a high-vacuum TEM chamber. Si NPs were immersed in the liquid electrolyte, as schematically represented in Fig. 9. The liquid electrolyte (1 M of lithium



Fig. 8 [86]: (a) SEM image of the inner side of the biasing chip; (b) Magnified view of the region labeled by the orange rectangle; (c) SEM image showing the welded Si NW electrode onto the Pt contact. Note that the Li location is labeled by the light blue color object in panel (a).



Fig. 9 [87]: Schematic illustration of a G-SLC. Si NPs are immersed in the liquid electrolyte, while the volume expansion of each Si NP is monitored in real-time.

hexafluorophosphate ($LiPF_6$) in solvent mixture consisting of ethylene carbonates (EC), dimethyl carbonates (DMC), and diethyl carbonates (DEC) in a 1:1:1 volumetric ratio) containing Si NPs was first dropped on a CVD-grown graphene sheet. Then the second graphene sheet was transferred onto the first one followed by suction of the liquid electrolyte. After the suction process, the graphene sheets became sealed through van der Waals interaction through the spots where the electrolyte was removed, but a small amount of the liquid electrolyte still remained trapped between the two graphene sheets. The chemical lithiation of Si NPs were initiated and facilitated by electron beam bombardment in TEM column, and visualized in real time. Novel phenomena during lithiation of Si NPs, such as preferential lithiation onset along certain crystal orientations followed by isotropic Li diffusion in the inner regions of Si NPs, were revealed.



Fig. 10 [31]: In situ charging and discharging of the cathode material LiFePO₄ in 0.5 M Li₂SO₄ aqueous electrolyte: the 5 eV spectroscopic EFTEM images of charging and discharging at indicated times. Scale bar is 400 nm. Bright regions are delithiated FePO₄ and dark regions are LiFePO₄. There are more bright regions of FePO₄ at the end of charge cycles and less during the discharges. White arrows point toward "bright" charged particles, and black arrows point toward "dark" discharged particles.

3.2. Applications of SLCs for in-situ TEM electrochemical characterization of LIBs

To track the lithiation process and elucidate the lithiation mechanism, the following techniques can be used: morphological imaging, electron diffraction [88,89], energy-dispersive X-ray (EDX) and electron energy loss spectroscopy (EELS). Morphological imaging cannot give chemical information [31], and diffraction spots are guickly obscured in thicker liquid films. Moreover, lithium scatters electrons so weakly that elastic imaging is challenging and EDX signal for lithium has a much too low energy for detection. EELS offers chemical fingerprints (core-loss EELS) and electronic structure information (valence EELS), but EELS of Li in liquid will be degraded by multiple scattering events in thick liquids [90] and the lithium K-edge $(\sim$ 54 eV) cannot be distinguished from many transition metal (e.g. Fe [91]) edges and the superimposed bulk plasmon of the thick liquid films, which makes the majority of Li-edge spectroscopy to be ex-situ [86] and core-loss EELS of the lithium practically impossible in a liquid cell. Therefore, valence EELS is the best way to interrogate electronic structure and detect the state of lithiation of battery electrodes in SLCs, because valence EELS provides strong signals due to large scattering cross sections and low background from the liquid (the electronic structure shift usually occurs at energies below \sim 6-7 eV where the electrolyte is transparent and stable [31]). The spatial resolution of valence EELS is ultimately limited by the delocalization of the low-energy excitations [92], multiple scattering in the liquid environment and low-dose imaging conditions, to be on the nanometer scale. Megan E. Holtz et. al. [31] successfully observed the lithiation state by valence energy-filtered TEM (EFTEM) in thicker liquid layers than commonly allowed by core-level spectroscopy [90], probing the low-energy regime at \sim 1-10 eV. They employed ab initio theory to calculate optical gaps of the relevant solvated species, taking solution effects into account with a hybrid function [93] including a nonlinear description of the polarization response of the surrounding liquid. By combining electrochemistry in the TEM with valence spectroscopic imaging and theory, they identified the lithiation state of both the electrode and electrolyte during in situ operation. Their work demonstrated the unique ability of an in situ TEM SLC to observe the Li de/insertion dynamics and degradation of LiFePO₄ cathode in real time. The real-time evolution of individual grains and nanoparticles of LiFePO₄ (cathode) [31] was studied in the native environment of a battery in a liquid cell TEM (as mentioned above). Particles (lithium-rich/poor) were observed to delithiate one at a time in a mosaic fashion, with different delithiation mechanisms in neighboring particles. Core-shell structures and anisotropic growth in different particles within the same agglomerate on the electrode were directly imaged along with the phase transformations, thanks to the in-situ SLC design. Although they used Li₂SO₄ aqueous electrolyte due to its high abundance, less viscosity, low weight, and nontoxicity [94], volatile electrolytes could be used in their SLCs. They imaged at 5 eV with a 5 eV wide energy window [31] to track the state of lithiation (Fig. 10). There were clear differences between the charged (Fig. 10, right) and the discharged state (Fig. 10, left) in both the particles and the solution in the 5 eV spectroscopic images. Particles showed more bright regions (corresponding to delithiated FePO₄) in the charged state. The cluster of particles was brighter in the charged image as marked by black arrows, especially around the edges of the cluster. The brightest



Fig. 11 [52]: (A-J) Time evolution of the growth and dissolution of Li–Au alloy and lithium dendrite; (K) the corresponding applied electric potential and measured electric current from frame A to frame J; (L) plot of Li–Au layer thickness and area as a function of time; (M) dimension and area evolution of the lithium dendrite tip as a function of time during cyclic voltammetry in the voltage range of 0 to -3 V at scan rate of 0.1 V/s.

particles may correspond to completely delithiated FePO₄, whereas the overall slight increase in intensity in the particles may indicate partially delithiated particles. On discharge, these bright regions of FePO₄ disappeared, transitioning back to LiFePO₄.

The electrochemical lithiation of Au electrode, dendritic growth of crystalline lithium, and the subsequent stripping of lithium and thinning of Li - Au layer under the applied cyclic voltammetry was observed by Zeng et al. [52], using

commercial LiPF₆/EC/DEC electrolyte, which proved that real electrolyte of LIBS can be used in electrochemical SLCs [52]. Fig. 11 (A) – (J) shows the sequential images representing the early stage of electrolyte decomposition, lithiation of gold electrode, and the subsequent growth and dissolution of lithium dendrites. Fig. 11 (k) shows the corresponding applied electrical potential and measured electrical current from frame (A) to frame (J). The thickness of Li–Au alloy did not change drastically at the later



Fig. 12 [85]: e^- beam induced breakdown of different electrolytes upon irradiation. (a - e) Cropped BF STEM images showing the time evolution of five different electrolytes at serial exposure times. (f) Frames from a data set probing the stability of the solvent EC/DMC for the same dose conditions as above over 7 min of continuous irradiation. (g) TEM images of an irradiated area of the LiAsF6 in DMC mixture after separating and washing the Si chips for performing postmortem analysis. Low-magnification (left) and high-resolution TEM and consequent fast Fourier transform of the irradiated area shows the presence of LiF nanocrystals.

stage, as shown in Fig. 11 (L). During stripping, the dissolution of plated lithium starts from the tip and the kink points as a reverse process of plating (Fig. 11 (M)). The formation of SEI layer on the other side of the electrode was also captured for better understanding of correlation between cyclic stability and the passivating film formed during the charge-discharge process in real LIBs. The drawback in their design was a lack of lithium metal source inside the SLC to supply the consumed lithium ions, such that the Li ion concentration in the electrolyte changed during the reaction. Adding a lithium metal source and an additional reference electrode into the SLC is necessary for direct comparison between the electrochemical processes inside a TEM column and that in real LIBs.

SLCs have also been used to study the stabilities of different electrolytes commonly used for Li-ion and $Li - O_2$ battery [95,96]. Five different electrolytes [85], including $LiAsF_6$ salt dissolved in three different organic solvents: (1) 1,3-dioxolane (DOL), (2) dimethyl carbonate (DMC), (3) a mixture of DMC and ethylene carbonate (EC) and LiTf in dimethyl sulfoxide (DMSO), LiPF₆ in EC/DMC were studied. Fig. 12 shows six different time series of bright-field (BF) STEM images corresponding to the five electrolyte solutions and the EC/DMC solvent alone. To ensure that the observed lack of degradation products when imaging the LiTf:DMSO mixture was not a result of improper focus, the edge of the window was recorded as a reference. Fig. 12 shows that apart from LiTf in DMSO, all the other salt containing solutions tested showed some evidence of degradation. It is worth to note that the degradations of the electrolytes were triggered by the imaging electrons (300 kV), instead of extra electrodes. This work shows that the electronbeam in the STEM can be used as an effective tool for evaluating stability and degradation in battery electrolytes by allowing direct visualization of the reductive decomposition of the electrolyte components, instead of post-mortem analysis (chromatography) [97,98]. This in situ approach can potentially be used for more rapid identification of next-generation electrolytes.

The lithiation and delithiation process of fully submerged electrodes is another important application of SLCs. For example, the de/lithiation process of Si NW electrodes during electrochemical testing were observed [86] by using in-situ SLC platform and real electrolyte (as mentioned previously). The structural evolution of the Si NW upon lithiation is illustrated in Fig. 13 (a)–(c). The pristine Cu-Si NW has an overall diameter of \sim 100 nm as revealed by the dark contrast in Fig. 13 (a). The width of the Cu coating on the Si NW was measured to be \sim 80 nm. The lithiation of the Si nanowire immersed in the liquid electrolyte progressed in the core-shell fashion. The total diameter of the wire changed from 100 to 298 nm at 1658 s (Fig. 13 (b)) and to 391 nm at 2462 s (Fig. 13 (c)). The diameter as a function of lithiation time is plotted in Fig. 13 (d). The increase of the diameter was guicker at the beginning of the lithiation and slowed down with the progression of the lithiation process. The lithiation behavior observed by the in situ SLC was also compared with that obtained based on the open-cell configuration in their study. For the case of SLC, the Si NW was fully immersed in the liquid electrolyte so that the insertion of lithium ions into Si was from all possible directions at the same time. The lithiation of the single nanowire proceeded in a core-shell mode with a uniform shell thickness along the axial direction of the whole nanowire, providing a global view of the response of the whole single NW with lithium insertion. However, for the open-cell configuration the lithium ion source was only in contact with the end of the Si nanowire, leading to the sequential lithiation process of the nanowire in only one direction.



Fig. 13 [86]: In situ liquid-cell TEM observation of the lithiation of the Cu-coated Si (Cu-Si) NW. (a) TEM image showing the pristine state of the Cu-Si NW at 0 s; (b) core-shell formation of the Cu-Si NW during lithiation at 1658 s; (c) TEM image of the Cu-Si NW at 2462 s; (d) plotted width changes of the NW as a function of time. Note that, in all images from a to c, the Pt contact region is labeled by the black lines in the left of the image. The inset in panel c illustrating the cross sectional image after anisotropic swelling of the Si nanowire upon lithium insertion with maximum volume expansion along the $\langle 110 \rangle$ direction.

Apart from Si NW electrodes, Si nanoparticles (NPs) as electrode material were also studied by using G-SLC [36,87], which showed that the very first lithiation at the Si-electrolyte interface had the strong orientation dependence favoring the <110> directions, but then the Li diffusion occurred isotropically after passing the initial stage regardless of the NP size. This indicated that the ratelimiting diffusion barrier is at Si-electrolyte interfaces instead of within Si or at the interfaces between lithiated and unlithiated regions. The orientation-dependent initial lithiation phenomenon was evidenced by HRTEM images as well as electron diffraction analyses, as shown in Fig. 14. For the representative three Si nanoparticles (whose original diameters are 34, 83, and 103 nm), their morphological and dimensional changes along <110>, <111>, and <100> directions were monitored. The selected-area electron diffraction patterns (the left ones in Fig. 14 (a-c)) indicated that all of the three Si nanoparticles were single-crystalline with <110> zone axes. The lithiation progressed predominantly along <110> directions, leading to the anisotropic volume expansion along the same crystal orientations, as indicated by the white arrows in Fig. 14 (a-c).

Based on the above discussions, the major research achievements to date in applications of SLCs for in-situ TEM electrochemical characterization of LIBs are highlighted as following:

1) The stabilities and degradation mechanisms of commercial electrolytes commonly used for Li-ion and $\text{Li}-\text{O}_2$

battery were studied [85], providing reference for future choices on electrolytes.

- 2) The lithiation and delithiation process of fully submerged electrodes, such as Si NW electrodes [86,99], Sn electrodes [82] and Si nanoparticles (NPs)[87], during electrochemical testing were observed by using in-situ SLC platform and real electrolyte.
- The electrochemical lithiation process, such as dendritic growth of crystalline lithium [31], stripping of lithium [31], SEI layer formation [100,101], etcetera, were observed in real time with nanoscale resolution during electrochemical charge and discharge [31] using commercial electrolyte [52].

4. Summary and future research directions

In this article, the current development and research fronts of SLCs in in-situ TEM electrochemical characterization of LIBs have been discussed in detail. In sum, the open-cell approach provides important information about the composition, phase transformation, and atomic resolution structural changes of the electrode, allowing higher spatial resolution than the case of using SLC [65], while artifacts [86], especially for the lithium diffusion pattern, may be produced by the open-cell configuration. On the other hand, SLC allows any form of liquid electrolyte relevant to real battery and full emersion of the electrodes, enabling the study of the real electrolyte – electrode interaction, including SEI formation and growth kinetics. SLC offers global



Fig. 14 [87]: Morphological and dimensional changes of Si NPs analyzed by GLC-TEM during the course of lithiation: (a-c) Time series bright-field TEM images of the Si NPs with initial diameters of 34, 83, and 103 nm, respectively. The white arrows indicate the Si <110> directions. The SA-EDPs in (a-c) indicate crystalline nature of the pristine Si NPs and their crystallographic orientations along <110> zone axes. The scale bars in (a-c) are 20 nm.

dynamic structural evolution of the whole anode, which is essential for understanding the behavior of the materials in the electrode [86]. Therefore, SLC provides indispensable complementary information to the open-cell approach.

However, TEM characterization of lithium through a liquid is challenging because lithium is a weak elastic scatterer and multiple scattering from the liquid could dominate the signal, resulting to a poor spatial resolution and contrast. Consequently, the spatial resolution and contrast needs to be enhanced. The future research direction is to improve SLC designs for better spatial resolution, which can be realized by decreasing the thickness of the liquid layer, redesigning the electrode configuration, utilizing alternative viewing window materials, employing different electrolytes, controlling electron dose, optimizing spacer thickness etcetera. With an improved spatial resolution, various new research frontiers, including defect structure within SEI layer during (de)lithiation process, can be explored by using SLCs in TEM, rendering it the most promising technique for in-situ electrochemical characterization of LIBs.

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209

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