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In situ characterization of electrochemical processes in one dimensional nanomaterials for energy storages devices

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ABSTRACT

One dimensional (1D) nanomaterials, which show tremendous potential in constructing high performance energy storage device, have gained considerable research interests. However the electrochemical reaction mechanism is still elusive. The most challenging issue in energy storage is developing insightful operando probes for the electrochemical processes. Notably, the in situ characterization of 1D nanomaterials is crucial to investigate the structural changes and uncover the intrinsic reasons for the capacity fading. Therefore numerous in situ characterization methods have been developed, such as in situ electron microscopy, X-ray detection techniques, spectroscopic techniques, nuclear magnetic resonance techniques, etc. Recent developments on *in situ* characterization technologies are summarized in this review. Different energy storage devices are involved, including Li-ion batteries, Na-ion batteries, supercapacitors, Li-air batteries and Li-S batteries. A new type of energy storage device, single nanowire device, has been also emphasized in this article. The reported highlights and developments are further discussed in details according to their reaction mechanisms. Through in situ characterization, no completely reversible volume expansion and phase transformation were observed during the lithiation and delithiation process. More structural/morphological damage and different electrochemical mechanisms were caused by the replace of lithium ions with sodium ions. The electron/hole doping of electric double layer capacitive materials and oxidation state of pseudocapacitive materials were focused. The growth and decomposition process of Li₂O₂ and polysulfide were also observed. The optimization mechanisms, including coating and doping of high conductivity materials, were proved to increase the electric/ion conductivity and reduce the cracks. The above mentioned results indicated that 1D nanomaterials with continuous ion/electron channels and short diffusion distance for electrolyte ions showed superior structural stability. Finally, the challenges and perspectives of the in situ characterization of 1D nanomaterials during electrochemical processes are emphasized as the conclusion.

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1. Introduction

Owing to the ever-dwindling fossil fuel and its serious pollution in the 21st century, the demand for electric energy obtained from renewable energy sources (e.g., solar and wind power) grows fast. Unfortunately, the energy from fluctuant resources is usually intermittent, which limits the efficient utilization of renewable energy. Energy storage devices, which can shift electric energy from peak to off-peak periods, are highly desired to be developed and utilized [1]. Among these devices, lithium-ion batteries (LIBs) have been widely applied in mobile phone and other portable devices, and in recent decades they have dominated the portable electronic markets due to their high energy density, good cyclability, and safe operating condition [2]. However, the rare lithium (Li) sources, low power density, and limited specific capacity need to be addressed for the application of LIBs in wider areas including electrical vehicles and power grids [3]. Recently, sodium-ion batteries (SIBs) have shown prime significance regarding the limited Li sources [4]. Meanwhile, sodium (Na) with natural abundance, non-toxicity, suitable redox potential, and similar intercalation chemistry to Li, holds promise to be a wise complement or substitution of Li in energy storage devices. Therefore, intensive researches on room temperature SIBs have arisen in recent years [5]. With respect to power density, supercapacitors, also known as electrochemical capacitors or ultracapacitors, have emerged as promising candidates in energy storage field due to their high power density, pulse power supply, long cycle life, simple principle, and high dynamic of charge propagation [6,7]. In such cases, supercapacitors show great potential to offer an exciting approach to meet the increasing power demands. Furthermore, the combination of supercapacitors and LIBs is believed to be a favorable trade-off among power density, energy density, cycle life, and efficiency [8,9]. Until recently, in addition to the aforementioned energy storage devices, to go beyond the horizon of LIBs, two new types of batteries, Li–air and Li–sulfur (Li–S) batteries with high theoretical specific capacities are considered as alternative options. Moving from traditional cathode to sulfur and oxygen has many merits beside high capacity such as low cost, safe operating voltage, and nontoxicity [10,11]. As a result, with a goal of pursuing next-generation energy storage devices, researchers have dedicated themselves to the long-term development of rechargeable Li–air and Li–S battery.

Apparently energy storage devices are indeed sophisticated systems associated with electrode structure, efficient electrolyte, packaging technology, etc. Optimized electrode structures through some physical and chemical strategies are proven to be effective on enhancing the performance of the energy storage devices. One dimensional (1D) nanomaterials possess unique properties, such as the high surface and volume ratio, the short diffusion length, and the completely different properties between the axial and radial directions [12–15]. Therefore, 1D nanomaterials are believed to provide better opportunity for improving the performance of electrochemical energy storage among currently existed electrode materials of different energy storage devices. Recently, various 1D nanomaterials have been applied in the electrochemical storage devices [16–24]. Compared with the energy storage devices based on bulk materials, the electrochemical performance of 1D nanomaterials are improved obviously due to their accommodation ability of electrochemical strain, faster charge transport, and better conducting pathways [13,25,26].

Up to now, there still exist numerous challenges in constructing 1D nanomaterial-based high performance energy storage devices. Among them, the in-depth investigation on the aforesaid energy storage devices is the principal task of researchers involved in the development of next-generation inexpensive, reliable, and robust energy storage systems. Before 2009, the characterization of 1D nanomaterials electrode was mainly focused on the ex situ probing, such as X-ray diffraction (XRD), [27-29] transmission electronic microscopy (TEM), [30,31] X-ray photoelectron spectroscopy (XPS), [32,33] etc. The physical or chemical changes of electrodes after cycling, being detected by ex situ methods had been revealed. But the real-time electrochemical processes and the capacity fading mechanisms of the 1D nanomaterials electrode remained unclear. While it should not be neglected that, these energy devices are sophisticated systems in which various physical and chemical processes involved, for instance, structural degradation, phase transition, and electrolyte decomposition, etc. For these reasons, it is necessary to note that the ex situ characterization methods can not realize the clear observation of electrochemical processes. This critical problem largely restricts the development and optimization of high-performance electrode. In situ, an expression in Latin means in position, and in modern materials technology refers to real-time observation on materials in their original position. This allows in situ characterization to be most effective method to observe the dynamic electrochemical processes. In other words, these in situ investigations can provide deeper and more direct insights into the materials' degradation and phase transformation mechanisms during charge and discharge. The 1D nanomaterials play an important role in the characterization since the breakthroughs of in situ characterization technologies. With the unique 1D structure geometry, the 1D nanomaterials have the ability to connect with macro or micro scale systems and reduce the difficulty for constructing a monitor device [14]. Meanwhile, the freestanding 1D nanomaterials can guarantee the investigation of high-resolution structural evolution of active materials without the influence of non-active materials during batteries' operations. On reviewing the current literatures, it is evidenced that the 1D nanomaterials are suitable platforms

for in situ characterization of the electrochemical processes. There have been a few reviews that summarized the characterization of electrochemical processes by in situ TEM and the development of in situ characterization technologies in LIBs [34-40]. Whereas a review dedicating to in situ characterization of 1D nanomaterials and covering comprehensive application fields including LIBs, SIBs, supercapacitors, Li-air and Li-S batteries, to the best of our knowledge, has never been reported. Numerous in situ characterization methods are used to investigate the electrochemical processes of the 1D nanomaterials, such as in situ TEM, XRD, scanning electron microscope (SEM), nuclear magnetic resonance (NMR), etc. Every in situ characterization method exhibits its unique characterization principle and also shares complementary benefits from each other. The principle and characteristics of common characterization methods used for observing the electrochemical process of 1D nanomaterials were summarized in Table 1.

This presented review intends to be an update and mainly focuses on 1D nanomaterials based on our research interests and comprehensive understanding. Herein, we summarize the recent advances in the characterization of 1D nanomaterials electrode by *in situ* characterization techniques in different energy storage devices. This review is divided into the following sections. In the Sections 2–6, some new discoveries of 1D nanomaterials during the electrochemical processes are reviewed, including these discoveries in LIBs, SIBs, supercapacitors, Li–air and Li–S batteries, new single nanowire (NW) based nanobattery. The development of *in situ* characterization technologies in a variety of energy storage devices will be reviewed below.

2. In situ characterization of lithium-ion batteries

The LIBs have been widely applied in the portable electronic, electric vehicle due to their higher energy density than other

Table 1

Principle and characteristics of different characterization technologies.

Characterization technologies	Characterization principle	Characterization characteristics
In situ TEM	The electrons which are transmitted through the thin sam- ples or nano batteries are detected to obtain the ultrahigh resolution image of electrode materials during the electro- chemical process.	 a) Observe the morphological changes. b) Distinguish the lithiation and delithiation phase (Combine with selected area electron diffraction (SAED)). c) Distinguish the distribution of elements and content (Combine with electron energy loss spectroscopy (EELS), energy dispersive spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS)). d) Measure the mechanical properties (Combine with atomic force microscopy cantilever).
In situ SEM	When an electron beam is focused on the sample, the sec- ondary or backscattered electrons are emitted from sample and detected to obtain the high resolution image.	 a) Observe the morphological changes. (The resolution is lower than TEM). b) Distinguish the distribution of elements and content (Combine with EDS or WDS). c) Measure the mechanical property (Combine with a microelectromechanical force sensor).
In situ XRD	The interference enhancement and disappearance of X-ray produced a diffraction pattern when X-ray is scattered by the crystallographic structure.	 a) Monitor the crystallographic structural changes and stability during charge/discharge or cycling process.
In situ X-ray absorption spec- troscopy (XAS)	When X-ray past through a sample, the intensity of incident X-ray was reduced due to scattered X-ray, fluorescence X-ray or photoelectrons.	a) Distinguish the species and content of elements.b) Measure the oxidation state of elements.c) Detect the information about the molecular structure (especially for
In situ X-ray absorption near- edge structure (XANES) In situ extended X-ray absorp- tion fine structure (EXAFS)	XANES is in the region between 10 eV up to 50 eV above the edge X-ray absorption spectrum. EXAFS starts approximately from 50 eV and continues up to 1000 eV above the edge.	amorphous materials).
In situ Raman	The frequency of irradiation monochromatic light change after it hits a sample due to the inelastic scattering between the light and sample. The shifts of frequency correspond to the vibrational modes of Raman-active molecules.	 a) Determine the structural changes of electrodes or nanodevice dur- ing cycling.
In situ infrared spectroscopy	The sample absorbs infrared light when the vibrational fre- quencies of groups are consistent with that of infrared light.	a) Determine the species of the ions in electrolyte during cycling.
In situ NMR	The nucleus resonate at a strong magnetic field and absorb the specific frequency radio frequency radiation	a) Observe the local electronic environment around the nucleus.

energy storage devices, such as supercapacitors, Ni–MH batteries, and lead acid batteries [41]. The 1D nanomaterials can allow the continuous electron conduction, shorten the diffusion distance of Li⁺ ions, and accommodate Li-induced stress. Thus, many electrodes of high energy density, high power density, and long-life-time LIBs are constructed by 1D nanomaterials [42]. A wealth of mechanistic studies, supported by *in situ* characterization technologies, have rationalized the better structure design and performance enhancement. On the basis of such knowledge, the development of *in situ* characterization technologies in LIBs is reviewed in four parts which are divided by different electrochemical mechanisms.

2.1. In situ characterization of conversion and alloying reaction mechanism

2.1.1. SnO₂

The first research work on *in situ* characterization of 1D nanomaterials in LIBs was *in situ* TEM observation of SnO₂, achieved by Huang et al. in 2010 [43]. Due to the high reversible capacity and robust chemical stability, SnO₂ is a promising anode material of LIBs [44–46]. The reaction front which propagated progressively along the NW was observed (Fig. 1a and b). The single crystal SnO₂ was converted into amorphous Li₂O, Sn and Li_xSn. The dislocation cloud was found to be the precursor of the electrochemical driven solid-state amorphization. There were no fractures or cracks along the NW. This study proved the high structural stability of the 1D nanomaterials. This concept was further developed by Nie et al., they used an aberration-corrected scanning TEM to realize an atomic scale resolution observation of SnO₂ NW [47]. Owing to

high-resolution TEM, the Burgers vector of the dislocations was determined to be [$\overline{111}$]. Also, the Li ions were discovered to diffuse along the [001] direction in the {020} planes of SnO₂ NW preferentially and the lithiated stripes passing through the SnO₂ NW as the reaction front, leaving the Sn and Li_xSn nanoparticles in the Li₂O matrix.

Actually in commercial batteries, the electrode is immersed in the electrolyte, which is different from the nanobatteries in TEM. This geometry is called as the "flooding geometry". Different from the end-contacted geometry, the SnO_2 NW was lithiated more quickly in liquid electrolyte (Fig. 1c), because some strips which acted as multiple reaction front were generated. All stripes inclined 61° with respect to the side surface of the NW. A high-resolution TEM confirmed that the stripes were parallel to the (020) plane [48]. After lithiation, the surface of SnO_2 NW became rough, the Li_xSn which possessed a spherical morphology was discovered to be embedded in the amorphous Li_vO matrix (Fig. 1d) [49].

An intriguing and important study on Sn particle formation and dendrite growth was also represented by *in situ* TEM characterization. The large spherical Sn nanoparticles with sizes of 20– 200 nm grew instantaneously on the single-crystalline SnO₂ NW at large current density [50]. The Li fiber nucleated from the SnO₂ NW tip and extended along the SnO₂ NW's axis, which was attributed to the strong electric field enhancement effect induced by the sharp NW's tip [51]. These investigations are helpful to explain the reason of short circuit and improve the cycling stability.

In an effort to reduce the capacity loss which was caused by the aforesaid lithiation-induced strain, the lithiation processes of SnO_2 NW with different coating materials were investigated. Due to the fast electronic conduction and confinement of the coating, the



Fig. 1. (a) Schematic of the end-contact geometry nanobattery setup for anode study and the lithiation process of the anode. (b) The TEM micrograph of the migration of a high density of dislocations at the reaction front. (c) The schematic drawing of the conceptual design of the miniaturized battery using an ionic liquid-based electrolyte. (d) The TEM imaging, EDS chemical composition analyses of the NWs following the initial charging of \sim 14 h. (a) Reprinted with permission from Ref. [34]. Copyright 2012 WILEY-VCH Verbg GmbH&Co. KGaA, Weinheim. (b) Reprinted with permission from Ref. [43]. Copyright 2010 AAAS. (c and d) Reprinted with permission from Ref. [49]. Copyright 2011 American Chemical Society.



Fig. 2. (a) Schematic illustration explaining the leapfrog cracking and nanoamorphization lithiation mechanism of ZnO NW. (b) TEM image of the crack on the ZnO NW at the early stage of lithiation. (c) Tensile stress–strain curve of the bulk ZnO without Li (circles), with Li at the concentration ratio of 1 Li/(ZnO)₈ (squares), and 2Li/(ZnO)₈ (triangles). (d) Tensile stress–strain curve of the bulk SnO₂ without Li (circles), with Li at the concentration ratio of 1 Li/(SnO₂)₈ (squares), and 2 Li/(SnO₂)₈ (triangles). Reprinted the permission from Ref. [54], Copyright 2011 American Chemical Society.

lithiation rate of coated SnO_2 NW increased about 2–10 times. The radial expansion was suppressed than that of uncoated one [52]. These results confirmed that the coating strategy is an effective method for improving the cycling performance of electrode.

2.1.2. ZnO

ZnO is another representative anode material undergoing conversion reaction and alloying reaction mechanism during cycling [53]. However, strange phenomenon which was different from SnO₂ NW was found: the reaction front did not move continuously in ZnO NW [54]. Instead, the leapfrog cracking occurred before the reaction front. With further lithiation, these leapfrogs subdivided the ZnO NW into different nanoglass domains and left many glass–glass interfaces (GGI) (Fig. 2a and b). These occurrences of leapfrogs caused the decrease of the strength of ZnO (Fig. 2c and d) [34,54].

2.1.3. SiO₂

Similarly, SiO₂ possessing high theoretical specific capacity of 1965 mAh/g during conversion and alloying processes, has also attracted a great deal of research interests [55]. Especially, SiO₂ is also used as surface passivation of high-capacity electrodes in order to reduce the capacity fading despite the passivation

mechanism remains unclear at present [56]. Zhang et al. assembled the single SiO₂@SiC NW microbattery in TEM [57]. The lithiation products of SiO₂ were Li–Si–O glass, LiSiO₄ and Li₂O. During the lithiation process, the tensile tress in the convex surface facilitated lithiation. After lithiation, the electronic conduction of SiO₂ was enhanced. The *in situ* characterization method combined with the theoretical studies allow an exquisite control and exact probing into the mechanism of surface passivation by SiO₂ coating on the high-capacity materials, a scenario that, in most instances, is not realized in conventional *ex situ* techniques.

2.2. In situ characterization of alloying reaction mechanism

2.2.1. Si&Ge

Among numerous alloying electrode materials, silicon (Si) and germanium (Ge) possessing high theoretical capacity with \sim 4200 mAh/g and \sim 1600 mAh/g respectively, attract considerable research interests [58–60]. In order to reveal the reason for capacity fading, *in situ* characterization technologies were implemented to characterize the evolution processes of Si/Ge.

The lithiation processes of Si and Ge follow a similar process: from crystalline M to amorphous Li_xM , then crystalline $Li_{15}M_4$ (M=Si and Ge) [61]. But the volume changes during lithiation



Fig. 3. (a) Morphology evolution of the Si NW during lithiation in the solid cell. (b) The TEM imaging of lithiated NW viewed along [110]_{si} direction. (c) The TEM imaging of lithiated NW viewed along [111]_{si} direction. (d) High-resolution TEM image showing the lithiation process in crystalline Si through lateral ledge flow at the ACI. (a–c) Reprinted the permission from Ref. [29]. Copyright 2011 American Chemical Society. (d) Reprinted the permission from Ref. [34]. Copyright 2012 Nature Publishing Group.

processes of Si and Ge are quite different. The volume expansion of Si NW was anisotropic (Fig. 3a–c), [62] oppositely, the volume expansion of Ge NW was isotropic [63]. The reason for the difference was attributed by the orientation dependence of interfacial mobility [34]. In order to find out the intrinsic reason of anisotropic interfacial mobility, Liu et al. observed the migration of the Si atom by an atomic scale high resolution TEM [34]. An amorphous Li_xSi alloy/crystalline Si interface (ACI) was observed (Fig. 3d). The ACI migrated through the ledge mechanism which involved the lateral movement of ledges on the {111} atomic planes. The amorphous Li_xSi alloy was produced by layer-by-layer peeling of {111} atomic planes. High density ledges were associated with the {112} and {110} ACIs, but low in {111} ACIs. So the {110} and {112} ACIs moved at least an order of magnitude faster than the {111} ACIs and produced a large number of amorphous lithiation products, leading to the orientation dependence of interfacial mobility.

Except for the anisotropic and isotropic expansion, other unique lithiation phenomena of Si and Ge NW were observed by in situ TEM. The transformation from amorphous Li_xSi to crystalline Li₁₅Si₄ with a deep lithiation process was found to be a spontaneous process without obvious large-scale atomic migration or phase separation [64]. An appealing class of actual situation that represents the real environment is accomplished by the introduction of liquid electrolyte into Si NW under in situ TEM [65]. The difference between the open-cell geometry and flooding geometry was that Li ions could insert into Si from all possible directions at the same time. The flooding geometry showed tremendous potential for the study of the solid electrolyte interphase (SEI), which have severe influences on the electrochemical performance. For the real LIBs, how single Si NW interacts with surrounding nanowires is decisive. Inspired by this speculation, a simulation environment in which two Si NWs existed at the same time was established under in situ TEM [66]. Li ions transported from two Si NWs' interface. After delithiation process, the shear strength of the joint of two NWs was about \sim 200 MPa, indicating that the strong interfacial bonds generated. The Si NWs showed potential in forming self-assembled network, which could provide more robust battery performance. Apart from aforesaid studies, some work concerning physical evolutions of Si NW are also worth mentioning. Liu et al. measured the growth rate of the amorphous Li_xSi on the surface of the crystalline Si NW [67]. The self-limiting lithiation process was observed. Through the theoretical calculation, the intrinsic reason for self-limiting lithiation of the Si NW was attributed to the retardation effect of the lithiation-induced stress. Recently, Wang et al. observed the different damage tolerance of pristine and lithiated Si NW by *in situ* TEM. The brittle fracture of pristine Si NW occurred contrast to the lithiated NW (with the Li-to-Si molar ratio > 1.5) showed the ductile tensile deformation. Molecular dynamics simulations proved the mechanism of brittle-to-ductile transition [68].

In the aspect of Ge NWs, Li ion was observed to insert into the amorphous regions of Ge NWs preferentially [69]. Interestingly, Ge NW was converted into a nanoporous network consisting of interconnected amorphous Ge after delithiation process. The porous structure of Ge which facilitated stress relaxation was maintained. The findings so far illustrated the potential of Ge NWs for applications in long-lifetime anode of LIBs [63]. When the Ge NW was bent, the volume expansion became asymmetrical. The lithiation process was enhanced at the tensile side and suppressed at the other side. The mechanical motion induced by lithiation stress may have an important influence on the electrochemical performance of Ge NW [70].

After disclosing the intrinsic properties of Si and Ge NWs, some optimizing strategies for increasing the conductivity, reducing the cracks and huge volume expansion of the NW electrode were implemented by in situ TEM. The lithiation process of carbon nanofiber (CNF)/amorphous-Si (a-Si) core-shell structure was investigated by Wang et al. [71]. The a-Si/CNF core/shell structure showed no large-scale morphological changes during the charging and discharging, which was different from the pure Si NW. The capacity fading of this composite material was slow, indicating that the Si coating on the conductive substrates was an effective strategy to improve the electrochemical properties. Lu et al. investigated the Sn nanoparticles/Si composite NW. They found that the incorporation of Sn particle increased the lithiation rate. Many pores generated after delithiation process due to the fast lithiation/ delithiation. But the formation rate of pores can be slowed down when the amorphous Si was applied to the Si NW. The Sn nanoparticles and amorphous Si show their potential in improving the rate and cycling performance of the Si electrode [72]. Liu et al. investigated the optimization mechanism of phosphorus doping and carbon coating. The charging rates of C-coated and P-doped Si NW exhibited 2 orders of magnitude faster than that of pristine Si NW [73]. Meanwhile, the Si NW did not fracture during the (de) lithiation process after optimization. This result indicated that rapid charge/discharge and long-life batteries based on Si anode could be realized by the conductive material coating and heteroatom doping. Similar phenomenon was also observed in the metal-coating Si NW. With a single sidewall coating, the volume expansion and morphological changes were affected and the conductivity of Si NW increased, which led to the improvement of coulombic efficiency and rate capability [74]. The inert material coating is another choice for controlling the volume expansion of Si NW. The expansion of Si NW showed less radial expansion and axial contraction after coating thick semi-inert TiO₂ layer on the Si NW [75]. The alucone coating and Al₂O₃ coating Si NW showed a V-shaped and H-shaped lithiation front, respectively. The different lithiation front can be attributed to the difference between the bulk lithiation rate of the coatings and Li surface diffusivity [76]. Another similar example about the volume expansion of Ge NW was realized by ultrathin Si shell depositing on the Ge NW by Liu et al. They found that the surface insertion of Li ions was suppressed in the Ge NW/ultrathin Si core/shell nanostructure. The Si coating created an effective chemical potential barrier for Li ion's

diffusion and reaction at the NW's surface, allowing only axial volume expansion rather than anisotropy volume expansion [77].

Apart from the studies focusing on 1D nanowires previously mentioned, Si nanorod (NR) was also investigated by *in situ* TEM. The lithiation process of amorphous Si NR was found to be controlled by surface diffusion. The small diameter NR (\sim 26 nm) did not fracture and showed a high capacity for accommodating the huge Li-induced stress than thick NR [78].

As previously mentioned in the text, with the help of 1D NW which was easy to be contacted with Li metal or cathode, other Si nanostructures loaded on 1D architecture can also be readily characterized. Based on this idea, the lithiation processes of Si nanoparticles [79–81], mesoporous Si sponge [82], Si nanospheres [83], yolk–shell Si nanoparticles [84] were also observed. During these lithiation processes, the NW was first lithiated and the Li ions were transferred from the Si NW to the specific Si nanostructure being investigated. The Si NW acted as the source of Li ions during the investigation of other Si nanostructures. These investigations indicated that the observational difficulty of the electrochemical processes of non-1D nanomaterials can be reduced through the introduction of the 1D nanomaterials which can be connect with macro or micro scale systems easily.

Besides the *in situ* TEM, other *in situ* characterization technologies were used to investigate the electrochemical processes of Si and Ge. The phase transformation of lithiated Si at different



Fig. 4. (a) Schematics of the *in situ* cell in ⁷Li NMR instrument based on SiNWs electrode. (b) Picture of an *in situ* cell prepared for XRD instrument and SEM image of SiNWs which grow on SS-mesh. (c) SEM images of lithiated Si NW in the *in situ* SEM. (a) Reprinted the permission from Ref. [85]. Copyright 2014 Nature Publishing Group. (b) Reprinted the permission from Ref. [86]. Copyright 2012 American Institute of Physics. (c) Reprinted the permission from Ref. [88]. Copyright 2012 American Chemical Society.

discharge conditions were examined by in situ NMR, as shown in Fig. 4a [85]. A new c-Li_{3.75+ δ}Si over-lithiated phase generated during a slow cycling below 30 mV. The different charging and discharging mechanisms were found to be depended on different cut off voltages and cycling rates. These similar phenomena were also observed in the lithiation process of Ge NW [69]. Another work involving in situ XRD characterization for Si NWs was accomplished by Misra et al. In this work, the lithiation process of Si NWs on the stainless steel (SS-mesh) was investigated (Fig. 4b). They found that the metastable Li₁₅Si₄ phase was avoided by increasing the Si NWs' growth temperature, leading to the improvement of cycling performance of Si NWs [86]. It should be also noted that the mechanical property of lithiated NW was also crucial for constructing long-life batteries. Boles et al. measured the tensile strength and Young's modulus of the Si NW by in situ SEM [87]. The elastic modulus and ultimate tensile strength of alloyed Si NW decreased rapidly after lithiation process indicated that formed amorphous Si layer changed the mechanical properties. They also observed the plastic deformation of lithiated Si NW (Fig. 4c) [88].

2.2.2. Al

As other potential anode materials of LIBs, some metal can alloy with multiple Li ion and exhibit a relative high theoretical capacity [89]. Whereas the huge volume expansion of metal causes the pulverization and the loss of electrical contact during the electrochemical processes. Surface passivation is put forwarded as a common optimizing strategy to improve the cycling performance of metal in spite of the unclear mechanism. To this point, Huang and his colleagues investigated the lithiation process of the Al NW coated with Al₂O₃ layer by in situ TEM technology [90]. The Al/Al₂O₃ NW was found to convert to isolated Al nanoparticles/Li-Al-O glass tube after lithiation process. Impressively, the Li-Al-O glass tube with adequate mechanical strength survived the huge volume expansion and acted as the ion conduction pathway, preventing the losing contact of Al metal with the current collector. On the basis of the experiment carried out, the atom layer deposition (ALD) technology showed tremendous potential in applications for fabricating high-performance commercial batteries.

2.2.3. ZnSb₃

Binary anode electrodes usually have a better electrochemical stability due to the synergistic effects, such as Si/Ge and Sb/Bi [91,92]. But an arduous puzzle that cannot be neglected is the different lithiation processes between binary materials and single component materials. For instance, a new crystalline–crystalline phase transition mechanism in ZnSb₃ NW was observed. The hexagonal ZnSb transferred into cubic LiZnSb instead of the Li₃Sb and LiZn after lithiation firstly. Apparently, more comprehensive theories and detailed studies are needed to explain the lithiation process concerning about crystalline electrode [93].

2.3. In situ characterization of conversion reaction mechanism

Anode materials involving in conversion reaction, whereby multi-electron reaction mechanism occurs during lithiation/delithiation processes, usually exhibit high theoretical capacity [94]. Unfortunately, the unavoidable issues, for instance, the huge volume change, the large voltage hysteresis, and the low coulombic efficiency observed in the first cycle associated with the high irreversible capacity severely affect the performance of the whole battery [95,96]. Consequently, the direct characterization of lithiation processes and their mechanisms are regarded as a vital prerequisite to better regulating and enhancing the performance [97].

2.3.1. RuO₂

Due to the high electrical conductivity and high theoretical specific capacity of 806 mAh/g, RuO_2 attracts researchers' broad attention [98,99]. The lithiation process of RuO_2 was investigated by Gregorczyk et al. [100]. The RuO_2 was converted to the mixed phase of Ru/Li_2O after lithiation, with obvious volume expansion of 95% and passing through intermediate phase of Li_xRuO_2 (Fig. 5a–d). The Ru/Li_2O was converted into the amorphous RuO_2 after 1st delithiation, leaving some unreacted Ru nanoparticles. The cracks during the electrochemical process and incomplete reversible electrochemical reaction were the intrinsic reasons for capacity fading.

2.3.2. CuO

Facilely prepared CuO is also a promising anode of LIBs with theoretical specific capacity of 670 mAh/g [101]. The conversion mechanism of CuO NW was investigated by Wang et al. through *in situ* TEM (Fig. 5e). CuO NW was converted to Cu and Li₂O after 1st lithiation process (Fig. 5f). The diameter of NW after delithiation was still 30% larger than that of pristine CuO NW (Fig. 5g), accompanied by the formation of Cu₂O (Fig. 5h) [102]. The generation of low-capacity Cu₂O caused the rapid capacity fading during the 1st cycle.

2.3.3. Metal sulfides

The sulfides have shown good electrochemical performance in LIBs and SIBs [103,104]. McDowell et al. studied the structural and morphological transformations of transition-metal sulfides when they reacted with Li [105]. Cu₂S experienced a different lithiation process compared with Co_3S_4 and FeS_2 . Due to the high ionic mobility of Cu ions, Cu was extruded out of the metal sulfides nanocrystal, rather than forming the nanoscale mixture of Li₂S and metal nanoparticle. It is indicated that different metal sulfides exhibit their own distinctive electrochemical performance. In order to find out the mechanism of carbon coating, a reported result focusing on the lithiation process of Co_9S_8 /carbon nanotube (CNT) investigated by in situ TEM has represented some interesting phenomena [106]. The Co₉S₈ confined in CNT showed a smaller volume expansion without obvious deformation. For open CNT, the thin graphite layer emerged from the CNT due to the force induced by expansion of Co₉S₈ and continued to protect the active materials.

2.3.4. Fe₃O₄

Fe₃O₄ is believed to be a high-capacity, low-toxicity, and lowcost electrode material [107]. An et al. constructed the hierarchical porous Fe₃O₄/VO_x/graphene NWs by a facile phase separation process from the FeVO₄ · 1.1H₂O@graphene NWs [108]. Under *in situ* XRD measurement, the peaks of Fe₃O₄ shifted to lower angle and then disappeared with the insertion of Li ion. It is indicated that the Fe₃O₄ in hierarchical porous NWs was converted into amorphous state. Similarly, in order to increase the conductivity and enhance cycling performance of Fe₃O₄, the Fe₃O₄/CNF composite was constructed. Though *in situ* TEM and EELS, Fe₃O₄ nanoparticles on the CNF was converted to Fe and Li₂O after first lithiation process, and then converted to FeO after delithiation process [109].

2.4. In situ characterization of intercalation reaction mechanism

The intercalation reaction has facilitated the commercialization of LIBs because the high reversibility and high energy efficiency can be realized through this reaction. For intercalation reaction materials, the crystal structures of the electrode materials remain stable when Li ion intercalate/deintercalate into the host lattices [110]. Therefore the volume change occurring during intercalation



Fig. 5. (a) TEM image of the reaction front of the RuO₂ during lithiation in the solid cell. (b) The polycrystalline network of Ru/Li₂O after the lithiation reaction. (c) Electron diffraction patterns of the NWs during the 1st lithiation. (d) Electron diffraction patterns of the NWs after a full lithiation. (e) TEM image of the reaction front of the CuO during the 1st lithiation process. (f) HRTEM image of the CuO NW after 1st lithiation. (g) Magnified TEM image of the CuO NW after the 1st Li-extraction. (h) HRTEM image taken from the framed area in (g). (a–d) Reprinted the permission from Ref. [100]. Copyright 2013 American Chemical Society. (e–g) Reprinted the permission from Ref. [102]. Copyright 2012 Royal Society of Chemistry.

reaction processes can hardly be detected. In contrast, the phase transformation is quite obvious during the electrochemical processes. Recently, some papers based on *in situ* characterization were reported, including the transition metal oxides, carbonaceous materials, and Li-containing metal oxides, and the main findings are discussed as below.

2.4.1. Negative electrode materials

2.4.1.1. Carbonaceous materials. Carbonaceous materials were used as the negative electrode of LIBs since 1985 [111]. Recently, the capacity of nanocarbon (e.g. graphene, CNTs) was found to be higher than that of graphite because of their abundant active sites and unique physical property [112,113]. A Li-induced embrittlement of CNT was observed by in situ TEM [114]. There were two reasons for this embrittlement: the extra stretch and the weakness of carbon-carbon bond, which was induced by the intertubular Li ion and the electron transferred from Li to the antibonding π orbital. But not all of the carbon materials embrittled due to the insertion of Li ion, for example, the lithiated graphene nanoribbon show the robust mechanical property attributed to a weak coupling between the interlayer and interlayer deformations in graphene [115,116]. Comparison between a variety of carbon materials leads to the conclusion that the fracture mechanism is geometrical configuration dependent.

2.4.1.2. TiO_2 . TiO_2 is one fascinating alternative anode to carbonaceous materials in rechargeable LIBs, as it exhibits superior safety, low cost, chemical stability, and non-toxicity [117]. A new electrochemical reaction mechanism (Fig. 6a) was observed in the lithiation process of amorphous TiO_2 nanotube, the nano-islands $Li_2Ti_2O_4$ crystal (Fig. 6b) with cubic structure, which was converted from amorphous Li_xTiO_2 , was formed during the further lithiation [118]. The reaction mechanism was determined to be Li_xTiO_2+2 $(1-x)Li^+ + 2(1-x)e^- \rightarrow Li_2Ti_2O_4$. The size of the crystalline islands was ~5 nm. This phase transformation was associated with the local inhomogeneity in Li distribution. With respect of crystal TiO_2 , *in situ* TEM measurement on rutile TiO₂ has been also conducted. It is demonstrated that the intermediate (monoclinic) phase Li_xTiO_2 ($x \sim 0.5$) was indeed formed, then was converted to rock-salt phase with continuous lithiation process [119]. Other 1D nanostructured layered TiO₂ (B) NRs were investigated by *in situ* XRD and XAS. A completely monophasic insertion mechanism occurred during the lithiation process. An anisotropic lattice expansion was shown in XRD with the expansion of a/b direction and the constriction of *c* direction. The Ti–O coordination shells will be elongated significantly once more than 0.4 Li⁺ was inserted. The above *in situ* results have externalized the electrochemical reaction mechanism of TiO₂ at different phases [120].

2.4.2. Positive electrode materials

2.4.2.1. $LiMn_2O_4$. In respect to cathode materials for LIBs, spinel $LiMn_2O_4$ will be emphasized on account of its low cost and high safety [121]. The local phase transformation of $LiMn_2O_4$ NW during the lithiation and delithiation processes was observed by Lee et al. (Fig. 6c and d) [122]. The cubic, orthorhombic and tetragonal phases appeared alternately and the orthorhombic phase was an intermediate phase of the tetragonal transition. Takayanagi and his colleagues investigated the high-rate lithiation process of $LiMn_2O_4$ NW [123]. Li-rich and Li-poor phase with different orientations were separated by transition region. In particular, the $LiMn_2O_4$ NW did not fracture with continuous orientation phase during the charge and discharge processes. Through these *in situ* researches, $LiMn_2O_4$ NWs have been clearly verified to be a potential candidate as the cathode of high-rate LIBs.

2.4.2.2. MnO_2 . MnO_2 is another versatile manganese oxide that should be mentioned. MnO_2 has been used as the cathode and anode of LIBs with high capacity, especially for α -MnO₂ consisted of 2 × 2 tunnels which are stabilized by cations, such as K⁺, NH⁺₄ [124,125]. The lithiation process of α -MnO₂ NW was investigated by *in situ* TEM [126]. During the lithiation process, the different expansion behaviors of NW along the [100] and [010] directions



Fig. 6. (a) The schematic graph of various stages of the lithiation process in amorphous TiO_2 nanotubes. (b) Bright field TEM image of an individual amorphous TiO_2 nanotube after lithiation. Several dark contrast particles are detected in the lithiated TiO_2 nanotubes (marked by white dotted circles in (b)). (c) TEM image and the transmission electron diffraction (TED) pattern of a single LiMn₂O₄ NW that contacts ionic liquid electrolyte (right side). The characterization area is marked by a red circle. (d) Schematic illustration of Li concentration and corresponding phase change in a Li_xMn₂O₄ NW during discharge. (a and b) Reprinted the permission from Ref. [118]. Copyright 2014 American Chemical Society. (c and d) Reprinted the permission from Ref. [122]. Copyright 2013 American Chemical Society.

indicated that the asymmetric expansion of NW's tetragonal unit cell, resulting in a new tetragonal–orthorhombic–tetragonal symmetric transition. The intrinsic reason for asymmetric expansion confirmed by density functional theory was the preferential and sequential Li⁺ filling at 8 h sites. K_{0.25}MnO₂ NWs, whose crystal structure is similar to α -MnO₂ NWs, were also investigated by *in situ* XRD [127]. The lattice parameters of *a* and *c* showed an expansion after lithiation and shrinkage after delithiation. There was a deviation from linearity in the relationship between the account of Li ion insertion and the lattice parameter *c*. This result suggested the presence of lattice distortion due to the Jahn–Teller distortion, which was quantitatively analyzed by comparing the variation of the strain along the [121] and [130] directions (Fig. 7a).

2.4.2.3. Vanadium oxides. Due to the unique layered structure and rich chemical valences of vanadium, some vanadium oxides (e. g., V_2O_5 , V_3O_7 , V_6O_{13} , Li V_3O_8) have high theoretical capacity [128–133]. But the crystal structure will disorder during the Li intercalation/deintercalation, which result in rapid capacity fading [134]. The details of lithiation processes and key factors of optimizing strategies are important for reducing the capacity fading. To do so, Strelcov et al. conducted *in situ* SEM characterization to observe the lithiation process of V_2O_5 NW (Fig. 7b) [135]. Although the detection of crystal structure was limited by the low resolution

of SEM, the morphology change of V₂O₅ NW within a larger length scale than TEM was observed. After the V₂O₅ was converted to ω-V₂O₅, no obvious large-scale amorphization or fracture was found. This phenomenon attested the low stress of intercalation reaction and the high structural stability of V₂O₅ NWs. In order to increase the conductance and structural stability of vanadium oxides, the carbon incorporation is widely used for improving the electrochemical performance of active materials [136]. Graphene nanosheets were incorporated on V2O5 nanobelts by sol-gel method [137]. The capacity of graphene-modified V₂O₅ nanobelts approached to the theoretical value. The valence state of V₂O₅ nanobelts in hybrid material was investigated by in operando X-ray absorption near-edge spectroscopy. During the charge and discharge processes, the intensity and peak position of pre-edge and edge showed a major change and exhibited a linear increase/decrease, corresponding to the reversible change of the valence state of vanadium. In other words, these reversible changes of the valence state clearly explained the reason for the high reversible capacity.

2.4.2.4. MoO_3 . MoO_3 is another typical layered material with rich chemical valences of Mo element [138,139]. The Na ion pre-intercalated MoO_3 nanobelts were synthesized by second hydro-thermal reaction between MoO_3 nanobelt and NaCl [140]. The



Fig. 7. (a) Variation of 130 and 121 reflections of cryptomelane which show the variation of Jahn–Teller distortion-induced strain during the charge and discharge processes. (b) Schematic diagram of the single-V₂O₅ nanobelt battery. (c) *In situ* XRD pattern of Na–Mo–O electrode and the charge/discharge profiles during the initial 9 cycles. (d) Schematic diagram of the WO₃ NW's nanobattery in the *in situ* TEM and *in situ* TEM images of WO₃ during the lithiation process. (a) Reprinted the permission from Ref. [127]. Copyright 2013 American Chemical Society. (b) Reprinted the permission from Ref. [135]. Copyright 2015 Royal Society of Chemistry. (c) Reprinted the permission from Ref. [140]. Copyright 2015 Elsevier Ltd. (d) Reprinted the permission from Ref. [142]. Copyright 2015 WILEY-VCH Verbg GmbH&Co. KGaA, Weinheim.

evolution processes of Na–Mo–O and pristine MoO₃ crystal structure after 10 cycles were investigated by *in situ* XRD (Fig. 7c). The difference in XRD patterns between Na–Mo–O and pristine MoO₃ showed the pillar effect of Na⁺ ion in the Mo–O layered structure. The collapse of the layered structure was postponed. So Na–Mo–O with better stability of the crystal structure exhibited enhanced cycling performance than that of pristine MoO₃.

2.4.2.5. WO₃. As a common material for electrochromic devices, WO₃ has captured intensive research interests due to excellent energy-saving effect of WO₃-based electrochromic windows [141]. While in battery research, the lithiation mechanism of WO₃ NW was investigated under *in situ* TEM by Qi et al. [142]. The WO₃ was lithiated to disordered and near-amorphous Li_xWO₃, rather than W and Li₂O. This result proved the chemical stability of WO₃ in the rapid and deep lithiation reaction (Fig. 7d).

The (de)lithiation processes of 1D nanomaterials had been investigated by above *in situ* characterization technologies. The microstructural and morphological changes of the electrode were observed clearly. But there are still many differences between the real batteries and the prototype batteries used in the *in situ* characterization technologies, such as the extensive usage of solid electrolyte rather than the commercial liquid electrolyte in TEM and the demand of the special appliance in other *in situ* characterization technologies. More tests close to the actual situation are expected to be implemented in future.

A summary of the main progress of *in situ* characterization with 1D nanostructure in LIBs discussed in this section, together with their reported phenomena and results, can be found in Table 2.

3. In situ characterization of sodium-ion batteries

The SIBs are emerging as ideal alternative electrochemical storage devices to LIBs, having captured much attention due to the abundant sodium sources and their lower price [145–147].

Nevertheless, the ionic radius of Na ion is larger than that of Li ion, resulting in sluggish electrochemical reaction kinetics. Consequently, the larger structure damage and volume expansion during the circulation process make contribution to a more serious capacity fading issue within SIB [148]. More importantly, in most of the cases, lithiation processes are so entirely and substantially different from sodiation processes that even some mature strategies or techniques quite suitable for LIBs can hardly be directly employed well in SIBs. In response to the limitations, hence the real-time in situ observation of sodiation processes was expected to provide intrinsic probes and pave the way for rational design of high-performance SIBs [149]. Among numerous nanomaterials, 1D nanomaterials are perfect candidates for long-life and high-rate SIBs due to short ion diffusion distance and enough space between individual NW [148,150,151]. The comprehensive understanding of morphological and microstructural changes of 1D nanomaterials during sodiation and desodiation processes are essential for the improving of the electrochemical performance of SIBs. Next, some 1D nanomaterials which were observed by in situ characterization technologies will be summarized.

3.1. Negative electrode materials

3.1.1. Carbonaceous materials

In general, inexpensive carbonaceous materials often receive considerable considerations as battery electrodes [152–154]. The 1D hard carbon materials, owing to their large interlayer distance and good structural stability, show great potential as the anode of SIBs, [155,156]. especially the 1D hollow structure which can accommodate the volume expansion [157]. The hollow core–shell crystalline-carbon/disordered-carbon (c-C/d-C) CNF was sodiated under TEM measurement (Fig. 8a) [158]. The disordered-C showed a higher storage capacity of Na or K ions. Some longitudinal cracks which may cause the capacity fading formed near the interface between c-C and d-C. Such investigation provides mechanistic insights into different sodiation and potassiation processes in c-C

Table 2

Main progress of in situ characterization with 1D nanostructure in LIBs.

Materials	Characterization technologies	Main phenomena and results	Ref.
SnO ₂ NW	In situ TEM	High density of dislocations and large in-plane misfit stresses were found.	[43]
		The Burgers vector of dislocations was $[11]$ and Li ⁺ preferred to diffuse along [001] direction.	[47]
		Sn nanoparticles (20–200 nm) were generated during the lithiation process at high current density of 20 A/cm ² .	[50]
		Lithium dendrite nucleated at the tip of lithiated SnO_2 NW due to the strong electric field.	[51]
	Flooding mode of in situ TEM	All lithiation stripes inclined 61° with respect to the side surface of the NW and were parallel to (020) plane.	[48]
		The spherical Li _x Sn was dispersed in the Li _y O matrix.	[49]
C, Cu or Al coating SnO ₂ NW	In situ TEM	The radial expansion was suppressed and lithiation rate increased by 10 times compared with that of uncoated NW.	[52]
ZnO NW	In situ TEM	The leapfrog cracking occurred before the reaction front and resulted in many glass-glass interfaces.	[54]
SiO ₂ /SiC NW	In situ TEM	The lithiation products of SiO ₂ were Li–Si–O glass, LiSiO ₄ and Li ₂ O. After lithiation process, SiO ₂ changed from brittle material to a material which can	[57]
C: NIMA	In site TEM	accommodate large deformation.	[(2)]
31 1977	III SILU TEIVI	The anisotopic swening depended on the unreferred systal orientations resinced in the dumbert-shaped cross section.	[02]
		An antoppious L ₂ SI and/(Tystame SI merate ingrated in organ the ledge mechanism, righ density ledges were associated with the {112} and {110} ACIs resulted in the origination density ledges of interface ingrated in organism.	[34]
		The self-lithizing narges of Si NW leaving the Si core surrounding with Li Si shell	[67]
		A brittle-to-ductile transition when the Li-to-Si molar ratio is ~ 15	[68]
		The axial tensile strength decreased from 3.6 to 0.72 GPa affer lithiation process	[143]
		Two Si NWs were welded together after lithiation and delithiation process.	[66]
	Flooding mode of in situ TEM	Anisotropic expansion and dumbbell shaped cross section was observed.	[65]
	In situ SEM	The elastic modulus and ultimate tensile strength of alloyed Si NW decreased rapidly after lithiation process. The plastic deformation of lithiated Si NW was found.	[87,88]
	In situ XRD	The metastable $Li_{15}Si_4$ phase was avoided by increasing the Si NW's growth temperature.	[86]
	In situ NMR	Different lithiation and delithiation processes of Si NWs which depend on the different discharge rates and cut off voltages were observed.	[85]
Si NR	In situ TEM	The lithiation process of amorphous Si NR was found to be controlled by surface diffusion. The thinner NR did not fracture.	[78]
a-Si/CNF	In situ TEM	No spallation, cracking, phase separation and large-scale atomic motion were observed during the lithiation process.	[71]
P-doped and C-coated Si NW	In situ TEM	After carbon coating and phosphorus doping, the lithiation rate increased by 1 order of magnitude. The amorphous lithium Si (the lithiation products of intrinsic Si NW) transforms to crystalline Li ₁₅ Si ₄ after a full lithiation process.	[73]
Cu coated Si NW	In situ TEM	The Cu coating suppressed the volume expansion of Si NW and the Cu layer always kept connected with Si.	[74]
Ge NW	In situ TEM	The volume expansion of Ge NW was isotropic. The Ge NW was converted into a nanoporous network consisting of interconnected amorphous Ge after delithiation process.	[63]
	In situ XRD In situ XAS	The Li ions were inserted into the amorphous regions of Ge NW preferentially.	[69]
Ultrathin Si shell/Ge NW	In situ TEM	The surface insertion of Li ions was suppressed in the Ge NW/ultrathin Si core/shell nanostructure. The lithiation and volume expansion only generated in the axial direction.	[77]
Al NW with Al ₂ O ₃ surface lay- ers	In situ TEM	The Al NW pulverized into Al nanoparticles. A Li–Al–O glass tube which formed by the lithiation of Al ₂ O ₃ surface layers improved the mechanical strength and ion conduction after lithiation process.	[90]
ZnSb ₃ NW	In situ TEM	The phase transition from h-LiZnSb to cubic c-Li ₂ ZnSb was observed.	[93]
RuO ₂ NW	In situ TEM	The RuO ₂ was converted to the mixed phase of Ru/Li ₂ O after lithiation, passing through intermediate phase of Li _x RuO ₂ . The Ru/Li ₂ O was converted into the amorphous RuO ₂ after 1st delithiation.	[100]
CuO NW	In situ TEM	CuO NW was converted to Cu and Li ₂ O. Cu ₂ O formed after 1st delithiation process.	[102]
Cu ₂ S, Co ₃ S ₄ or FeS ₂ /carbon tuber	In situ TEM	The metal sulfide was converted to metal and Li ₂ S matrix. Cu metal was extruded from the crystal due to the high ionic mobility.	[105]
Co ₉ S ₈ /CNT	In situ TEM	The volume expansion of Co ₉ S ₈ in CNT was suppressed. Thin graphite layer was emerged from the CNT and continued to protect the metal sulfide.	[106]
Fe ₃ O ₄ /VO _x /graphene NWs	In situ XRD	The peaks of Fe ₃ O ₄ shifted to lower angel and then disappeared with the insertion of Li ion, indicated that the Fe ₃ O ₄ in hierarchical porous NWs was converted into amorphous state.	[108]
CNT	In situ TEM	A Li-induced embrittlement of CNT was observed.	[114]
Graphene nanoribbon	In situ TEM	The lithiation and delithiation processes occurred at the surfaces of graphene nanoribbon and the lithiated graphene nanoribbon showed great flexibility.	[115]
Amorphous TiO ₂ nanotube	In situ TEM	The nano-islands $L_1_2T_2O_4$ crystal with cubic structure during the further lithiation.	[118]
Rutile TiO ₂ NW	In situ TEM	The intermediate (monoclinic) phase $L_x TiO_2$ ($x \sim 0.5$) was formed, then converted to rock-salt phase.	[119]
TiO_2 (B) NRs	In situ XRD	An anisotropic lattice expansion and elongate Ti–O coordination shells were observed.	[120]
LIWIN ₂ O ₄ NW	in situ TEM	ine cubic, orthornombic and tetragonal phase appeared alternately. Li-rich and Li-poor phase with different orientations were separated by transition	[122,123
MnO ₂ NW	In situ TEM	A new tetragonal–orthorhombic–tetragonal symmetric transition and asymmetric expansion of NW's tetragonal unit cell along the [100]/[010] was	[126]
-			

		observed.	
K _{0.25} MnO ₂ NWs	In situ XRD	There was a deviation from linearity in the relationship between the account of Li ion insertion and the lattice parameter, indicating the Jahn-Teller	[127]
		distortion.	
V205 NW	In situ SEM	No obvious large-scale amorphization or fracture of vanadium oxide was found.	[135]
V ₂ O ₅ NRs	In situ XRD	During the lithiation process, ε -V ₂ 0 ₅ was transformed to σ -V ₂ 0 ₅ . After the initial four cycles, some Li ⁺ ions were trapped in the V ₂ 0 ₅ framework.	[144]
	In situ XANES		
V ₂ O ₅ nanobelts/graphene	In situ XANES	The valence state of vanadium changed reversibly during the electrochemical process.	[137]
composite			
Na ion pre-intercalated MoO ₃	In situ XRD	The Na–Mo–O showed more stable crystal structure than pristine MoO ₃ .	[140]
nanobelts			
WO ₃ NW	In situ TEM	The WO ₃ was lithiated to disordered and near-amorphous Li _x WO ₃ .	[142]

and d-C and simultaneously verifies the application potential of hollow CNF in both Na-ion battery and K-ion battery.

3.1.2. SnO₂

Metal oxides constitute a rather broad category of promising materials exploited as LIB electrode due to their high theoretical capacity. In terms of their application as SIB electrode, some metal oxide nanomaterials showed low reversible capacity or limited cycle life [159]. Taking SnO₂ as an interesting example, compared with the lithiation process of SnO₂ NW, the sodiation speed appeared to be ~20 times slower [160]. After the Sn and Na₂O generated, the sodiation process of Sn occurred in two steps: first, the crystalline Sn nanoparticles were initially sodiated via a two-phase mechanism with a migrating phase boundary to form an amorphous Na_xSn alloy ($x \sim 0.5$), and then further sodiated to several Narich amorphous phase. Second, Na-rich amorphous phase was converted to crystallized Na₁₅Sn₄ (x=3.75) which was dispersed in Na₂O matrix via a single-phase mechanism. The difference between the sodiation process and lithiation process was the pores generated after the extraction of Na ions, resulting in a structure of Sn particles confined in a hollow matrix of Na₂O (Fig. 8b-d). The damage of electrode materials after desodiation was greater compared with that of the electrode after delithiation process. It was also reflected in the calculated ideal tensile strength: the tensile strength of sodiated SnO₂ was only 75% of lithiated SnO₂.

3.1.3. CuO

CuO is a promising anode material with high capacity of > 600 mAh/g in SIBs [161]. An exemplary study must be worth mentioning is investigation of CuO NW by Liu et al. [162]. Except for the Cu and Na₂O, the new phase NaCuO (Fig. 8e and f) and Na₆Cu₂O₆ (Fig. 8g and h) formed after the intercalation of sodium ions which was different from the results obtained by *ex situ* XRD [163]. This difference was attributed to the high vacuum in TEM and instability of NaCuO in air. The different reaction mechanisms between lithiation [102] and sodiation processes indicated that the different electrochemical performance of the same electrode in LIBs and SIBs may not only depend on the sluggish reaction kinetics of sodiation process, but also depend on the different diffusion pathways of alkaline ions and the formation of intermediate phase.

3.1.4. NaTi₃O₇

The insertion-host metal oxide anode was also investigated by *in situ* characterization methods to determine structure evolution during (de)sodiation process. Such as NaTi₃O₇, a new intercalation anode of SIBs, was investigated by *in situ* XRD. A two-phase electrochemical process between Na₂Ti₃O₇ and Na₄Ti₃O₇ was observed [164].

3.1.5. Metal sulfides

Numerous examples have appeared in recent literatures concerning about metal sulfides in SIBs [165]. The sodiation of transition metal sulfides was also investigated by *in situ* TEM, such as Co_9S_8 [166]. The Co_9S_8 -filled CNT with an open end showed axial elongation and a small radial swelling, but the closed CNT showed contrary results. The layer distance of CNT increased from 0.34 to 0.38 nm due to the Na⁺-ion insertion. Co nanograins which dispersed in Na₂S matrix were generated after sodiation. The rapid sodiation of Co_9S_8 -filled CNT was realized under high charge voltage, resulting in a drastic swelling and fracturing (Fig. 9a). These findings directly provide evidence for the capacity loss at a high current density during the charge and discharge.

3.1.6. Sb/Ge/TiN

On several instances, metal or metalloids can alloy with a large



Fig. 8. (a) *In situ* TEM image of hollow coaxial a-C/c-C CNF before and after sodiation process. (b-d) *In situ* TEM image of pristine SnO₂ NW, sodiated SnO₂ NW, and desodiated SnO₂ NW, respectively. (e–f) *In situ* TEM image of single CuO NW during the sodiation process at 2280 s and corresponding SAED of the new phase NaCuO. (g–h) *In situ* TEM image of single CuO NW during the sodiation process at 11,280 s and corresponding SAED of the new phase Na₂Cu₂O₆. (a) Reprinted the permission from Ref. [158]. Copyright 2014 American Chemical Society. (b–d) Reprinted the permission from Ref. [160]. Copyright 2013 American Chemical Society. (e–h) Reprinted the permission from Ref. [162]. Copyright 2015 Royal Society of Chemistry.

number of Na, resulting in a much higher capacity, such as the metal and metalloid in group 14 and 15 [167–169]. Recently, the sodiation of Sb thin film on the Ge/TiN core–shell NW was investigated by *in situ* TEM [170]. During the discharge, the volume of Sb film expanded about 260% which was less than the theoretical value due to the failure of the Sb to be fully sodiated. Some time-dependent bucklings and localized separations from the supporting NW due to the stress-relaxation were observed after desodiation (Fig. 9b). This result provided a direct evidence of the huge sodiation stress during electrochemical process.

3.2. Positive electrode materials

3.2.1. K₃V₂(PO₄)₃/C

In addition to *in situ* characterization of anodes in SIBs, the intercalation cathodes were also studied to determine the lattice stability of cathodes [171]. Especially in determining the electrochemical processes of new cathode materials, the *in situ* technologies would exert great importance. $K_3V_2(PO_4)_3/C$ bundled NWs were synthesized using a facile organic acid-assisted method [172]. Through *in situ* XRD, the intensity and position of peak shifted during the charge and discharge reversibly, corresponding to the (de)insertion of K⁺/Na⁺ and the expansion/extraction of the lattice distance (Fig. 9c and d). The vanadium phosphate showed excellent stability which allows the deinsertion of K⁺ ion and insertion of Na⁺ ion without collapse of crystal structure.

In general, it is imperative to note that despite considerable *in situ* researches have been conducted to corroborate the various differences between sodiation processes and lithiation processes existing in many kinds of electrodes. There is still a big gap between the achieved investigation and the increasing demand of SIBs with high electrochemical performance. With the further

development of SIBs, the *in situ* characterization will definitely act as an irreplaceable important tool for observing new phenomena in sodiation processes and improving the electrochemical performance of SIBs.

4. In situ characterization of supercapacitors

Electrochemical capacitors, also called supercapacitors, are expected to complement or replace batteries in electrical energy storage and harvesting applications because of their higher power density compared with the batteries [173]. There are generally two types of supercapacitors: electrochemical double layer capacitors (EDLC) that store energy by ion absorption and pseudocapacitors by fast surface redox reaction [174]. Carbonaceous materials, conducting polymers, and metal oxides, sulfide, nitride are common materials for supercapacitors [175–177]. Due to high specific surface area of the nanostructures, the energy density and power density of these materials were improved effectively after nanocrystallization [178]. Among various nanostructures, the 1D nanostructure provides the short ionic diffusion distance along the radial direction and direct electron pathways along the 1D direction, resulting in higher utilization of electrodes at higher current density and higher transport speed of electrolyte ions [42].

Whereas as the most recent researches reveal that, some issues still exist in the supercapacitors, such as the lower energy density and faster self-discharge compared with LIBs [179,180]. All of these issues restrict the commercialization of supercapacitors. The *in situ* characterization technologies bring the direct evidence of the structure and phase change of the electrode, and achievements will be given below regarding the 1D nanomaterials-based supercapacitors.



Fig. 9. (a) *In situ* TEM image of fractured Co_9S_8 filled CNT after a fast sodiation process. (b) *In situ* TEM image of Sb/TiN NW at the desodiated state with a void separation within the Sb film. (c–d) *In situ* XRD pattern of $K_3V_2(PO_4)_3/C$ bundled NWs at $23-27^\circ$ and $30-34^\circ$ during the first two charge–discharge processes. (a) Reprinted the permission from Ref. [166]. Copyright 2014 American Chemical Society. (b) Reprinted the permission from Ref. [170]. Copyright 2015 American Chemical Society. (c and d) Reprinted the permission from Ref. [172]. Copyright 2015 WILEY-VCH Verbg GmbH&Co. KGaA, Weinheim.

4.1. Electronic double layer capacitor materials

4.1.1. Carbonaceous materials

The carbonaceous materials are suitable for the EDLC due to their low price, high surface area, high electronic conductivity, and controllable porosity [8]. But these materials store energy by physical absorption of the ions in electrolyte whereby every atom can only absorb 0.17–0.20 e⁻ in EDLC, resulting in the low energy density. The ionic liquid (IL) keeps stable at higher operating voltage which is helpful for constructing high energy density supercapacitors [181].

The Raman spectroscopy is an effective method for detecting the structural variation of carbonaceous materials. In the aspect of CNTs, the radial breathing modes (RBMs) at 150–300 cm⁻¹ and the high-energy mode (HEM) at ~1600 cm⁻¹ are related to the electrochemical doping level of CNTs [182,183]. So the *in situ* Raman spectroscopy was used to detect the electrochemical reaction mechanism of CNTs in the aqueous or nonaqueous electrolyte. Ruch et al. tested the single-walled carbon nanotubes (SWCNTs) in Et₄NBF₄/acetonitrile (AN) electrolyte [184]. The electrochemical reaction of SWCNTs was regarded as the electrochemical doping process and observed by *in situ* Raman. There was a strong upshift in the D or G⁺ peaks because of the doping of holes (Fig. 10a and b). This meant that the C–C bonds and the corresponding phonon modes were stiffened. For radial breathing modes (RBMs), the main RBMs band upshifted no matter the hole and electron doping. The intensity attenuation of the RBMs band is determined by the property of the CNT.

Except for the Raman spectroscopy, the infrared spectroscopy which has capability of detecting the organic groups of nonaqueous electrolyte ions is also used in the *in situ* observation of the electrochemical processes of EDLC materials. Rickey et al. investigated the ionic liquid dynamics in CNFs and KOH-activated CNFs by *in situ* infrared spectroelectrochemical test (Fig. 10c). The 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide (EMIm-TFSI) IL was chosen as electrolyte [185]. When the applied voltage was more than 1 V, the concentration of the anion was larger than the concentration of cation in pore of CNFs (Fig. 10d). But the anion concentration decreased and cation concentration increased due to the ionophilicity of CNFs after KOH activation. The investigation provided the direct evidence of a relationship between the electrochemical performance and the surface treatment.

4.2. Pseudocapacitor materials

In common circumstances, the valence state of pseudocapacitor materials varies with the different applied potentials during electrochemical processes. These processes depend on the surface of the rapid redox reaction and capacity fading often occurs due to some irreversible change of oxidation state. Therefore, the monitoring of the valence state is of great importance to explore the



Fig. 10. (a) *In situ* Raman spectra of SWCNTs electrode during the electrochemical doping process in 1 M Et_4NBF_4/AN . (b) The variation of total doping level of per carbon atom and positions of the D and G⁺ peak with different applied potentials upon electrochemical charging in 1 M Et_4NBF_4/AN . (c) Schematic of the *in situ* infrared spectroelectrochemical test with the FTIR spectrometer. (d) Schematic of ion adsorption within the nanopores of CNF at 2 V. (a and b) Reprinted the permission from Ref. [184]. Copyright 2009 Elsevier. (c and d) Reprinted the permission from Ref. [185]. Copyright 2014 American Chemical Society.

fading mechanism. The *in situ* XAS and EXAFS spectra are commonly applied in the analysis of the valence state. Briefly, the XAS is usually used for detecting the species, the content, and the coordination environment of the specific elements. There is a linear relationship between the absorption threshold energy and the oxidation state of the transition metals. While more specifically, the EXAFS spectrum is usually used for obtaining information of the radial distance distribution and local symmetry around the absorbing ions. It provides a powerful tool to investigate the amorphous materials.

4.2.1. MnO₂

MnO₂, with merits of high theoretical capacity, low cost, and low toxicity, is regarded as a promising material for pseudocapacitor [186]. Chang et al. synthesized the MnO₂ nanofibers/graphite substrate composite electrode to investigate the valence change of the electrode during the charging and discharging [187]. They determined the changing oxidation state of MnO₂ under different potentials by XAS (Fig. 11a). When the applied potential cycled from 0 to 1 V, the oxidation state of the MnO₂ increased from +3.23 to +3.95, and then back to +3.27. This indicated that the electrochemical reaction between the MnO₂ and alkali metal cations was not fully reversible. Nam et al. electrodeposited the manganese oxide nanowhiskers on the carbon paper as the electrode [188]. Under in situ XANES measurement, the irreversible capacity increased when the potential range expanded from 0-0.8 V to -0.3-1 V vs. saturated calomel electrode (SCE). Furthermore, from in situ Mn K-edge XANES spectra and Fourier transformed (FT) magnitude of it, the formation of the divalent and tervalent Mn oxide and the dissolution of Mn species may be the reason of the source of irreversible capacity. The electrochemical process of MnO₂/carbon composite was also investigated by Chang et al. [189]. The MnO₂/acid-functionalized CNTs (MnO₂-C/CNTs) and MnO₂/amine-functionalized CNTs (MnO₂-N/CNTs) composite

materials were separately prepared as the electrode. At a low scan rate, the MnO₂-N/CNTs showed more reversible redox reaction, corresponding to the result that the oxidation state of Mn in MnO₂-N/CNTs could restore to the original state after a complete cycle by *in situ* XAS. In contrast, MnO₂-C/CNTs showed a higher capacity at a high scan rate which can be attributed to its high surface area.

Due to the low stability of aqueous electrolyte at high voltage, the IL exhibits unique potential for improving the energy density of supercapacitors [189]. Lee et al. electrodeposited the manganese oxide nanowhiskers on the nickel substrate and used the 1-ethyl-3-methylimidazolium-thiocyanate (EMI-SCN) IL as the electrolyte [190]. From the EXAFS spectra, they thought the SCN⁻ anions in the IL could reversibly insert/desert into/from the tunnels in MnO₂ and participant the redox reaction. Whereas, the anions of other ILs, such as the BF⁻, PF⁻, and nTf⁻ could not insert into the MnO₂ oppositely. Such experiment findings attest the vital role of suitable anion in IL for the construction of the high-energy supercapacitors. Deng et al. investigated α-MnO2 NWs/Ni foam electrode coupled with LiClO₄-OZO quasi-IL as electrolyte by in situ XAS [191]. The reversible peaks position change of Mn K-edge XANES spectra of electrode was observed (Fig. 11b). They found the $Li(OZO)_n^+$ cations inserted into the tunnels of MnO₂ during the electrochemical process, resulting in the large electron transfer, corresponding to the ultrahigh energy density. Recently, Liu and his colleagues used the *in situ* Raman to disclose a more complex process of the non-stoichiometrical α -Mn_{0.98}O₂ [192]. A new mechanism was proposed: after the alkali metal ion deintercalated from the materials, the Mn²⁺ began to act as working ions and deintercalated from the Mn₃O₄ with the increasing of potential. Except for the MnO₂, other metal oxides such as RuO₂ [193] and Mn–Fe mixed oxide [194] were also investigated by the in situ XAS.



Fig. 11. (a) Schematic diagram of the manganese oxide for *in situ* XAS study. (b) *In situ* Mn K-edge XANES spectra of α -MnO₂ NWs/Ni foam electrode in the electrolyte of LiClO₄-OZO. (c–d) *In situ* XRD patterns of the LiCoMoO₄ NWs during the electrochemical process in LiOH and KOH, respectively. (a) Reprinted the permission from Ref. [187]. Copyright 2007 Elsevier. (b) Reprinted the permission from Ref. [191]. Copyright 2011 Royal Society of Chemistry. (c and d) Reprinted the permission from Ref. [196]. Copyright 2015 WILEY-VCH Verbg GmbH&Co. KGaA, Weinheim.

4.2.2. Li2Co2MoO4

Recently, the insertion-type capacitors attracted so much attention due to their high capacity with the intercalation of electrolyte ion into the bulk phase [195]. Similar to battery materials, the understanding of the crystal structure variation mechanisms during the electrochemical processes is essential for obtaining excellent electrochemical properties. An intriguing example of ion insertion phenomenon described above was observed in the investigation of a new Na⁺ superionic conductor (NASICON) type material Li₂Co₂MoO₄. The capacity of Li₂Co₂MoO₄ NRs in Li-based electrolyte is higher than those realized in Na-based and K-based electrolyte attributed to the intercalation of Li ions. This result was further proved by *in situ* XRD. The peak intensity at 21° and 45° were enhanced at the potential window of 0–1.6 V, which was different from the results obtained in KOH (Fig. 11c–d) [196].

5. In situ characterization of Li-air and Li-S batteries

As the demand of other high energy density secondary batteries increases rapidly, Li–air and Li–S, whose theoretical energy density is 3458 Wh/kg and 2510 Wh/kg, respectively, have been speculated as promising energy storage devices [197,198]. As a matter of fact, important advances have been made recently, but significant challenges remain, which are evidenced from the increasing amount of publications on Li–air and Li–S batteries in recent years. Very briefly, the most serious and fundamental issues are: poor cyclability and sluggish kinetic performance for Li–air batteries [199]; shuttle mechanism and self-discharge for Li–S batteries [197]. Moreover, the low electric conductivity of Li₂O₂, Li₂S, and S also restrict the rate performance and cycling performance of the above batteries. Considering these formidable challenges, *in situ* characterization methods are herein envisioned to elaborate some certain scientific issues of Li–air and Li–S batteries and verify the rationality of the optimization strategy.

5.1. In situ characterization of Li-air battery

Due to a large amount of catalytic active sites and 1D electronic pathways, 1D nanomaterials could be utilized as the catalyst for Liair batteries [17,200]. Some intrinsic reasons of the excellent catalytic performance of 1D nanomaterials were investigated by the *in situ* characterization methods.

5.1.1. Pt/MnO₂

The *in situ* XRD which can examine the discharged products and analyze the reaction processes was used to investigate the electrochemical processes of Li–air battery based on Pt/MnO₂ NRs [201]. The growth and decomposition of Li₂O₂ during the charge and discharge processes were analyzed quantificationally by *in situ* XRD with the Si added in the electrode as a reference component. With 5 wt. % Pt adding, the MnO₂ NRs showed best catalytic performance for electrochemical oxidation of Li₂O₂ without side reactions (Fig. 12a). Additionally, other characterization technologies such as infrared spectroscopy [202], Raman [203], XPS, [204] and differential electrochemical mass spectrometry (DEMS) [205] were



Fig. 12. (a) *In situ* XRD patterns of the discharge products using the 5 wt. % Pt/MnO₂ as the cathode in Li–air battery. (b) TEM image of a LiAlSiO_x solid electrolyte coated Si NW contacting with the individual Li₂O₂/CNT. Inset: schematic diagram of *in situ* TEM microbattery. (c) Schematic diagram of all-solid-state Li–O₂ battery in the environmental SEM. (d) *In situ* Raman spectrum of 1D S chain/CNT electrode during initial cycle. (a) Reprinted the permission from Ref. [201]. Copyright 2015 Elsevier. (b) Reprinted the permission from Ref. [207]. Copyright 2013 American Chemical Society. (c) Reprinted the permission from Ref. [208]. Copyright 2015 American Chemical Society. (d) Reprinted the permission from Ref. [21]. Copyright 2014 American Chemical Society.

also used for the investigation of other non-1D electrode materials in Li–air batteries. These technologies show tremendous potential for the characterization of 1D nanomaterials in the Li–air batteries.

5.1.2. CNTs

The use of in situ characterization methods is also manifested to be of effectivity for the investigation of some key electrochemical processes of Li-air battery, such as the electrochemical oxidation of Li₂O₂. The Li₂O₂ was the discharge product which was generated by oxygen reduction reaction (ORR) between the molecular O_2 and Li^+ ions ($O_2 + Li^+ + 2e^- = Li_2O_2$). Questions are that the low conductivity of Li₂O₂ and high overpotential associated with the oxidation of Li₂O₂ inhibit the electrochemical kinetics and reduce the energy efficiency [206]. Therefore, the electrochemical oxidation of Li₂O₂ plays a decisive role in the electrochemical processes of Li-air batteries. Zhong et al. investigated this process by in situ TEM. The microbattery consisted of CNT-supported Li₂O₂ particle as positive electrode and single Si NW as negative electrode (Fig. 12b) [190]. The Li_2O_2 was oxidized preferentially at the interface of CNT/Li₂O₂ due to electron-transport-limited mechanism at high overpotentials, which was caused by the low conductivity of Li₂O₂ and fast electronic conduction of CNTs. Moreover, the electrochemical oxidation of Li₂O₂ was also limited by the low diffusion of Li⁺ ion. The oxidation of Li₂O₂ was found to occur only when the Li₂O₂ contacted with the electrolyte physically. In order to facilitate the electrochemical oxidation of Li₂O₂, the contact area between Li₂O₂ and electrode or electrolyte should be maximized. It is clearly proven that the high surface area and high

electronic conductivity of electrode are desirable for the high performance Li–air battery [207]. The environmental SEM which allows a small count of O_2 in the chamber was also introduced to investigate the growth and deposition of Li₂ O_2 (Fig. 12c) [208]. Some phenomena were observed during the charge and discharge: (1) The Li₂ O_2 particle could grow on another Li₂ O_2 particle, resulting in the generating of larger discharge product. The electrochemical oxidation of Li₂ O_2 began from the surface of Li₂ O_2 particle due to the high electronic conductivity on the surface and large bare surface of Li₂ O_2 . (2) Some bead-like products which may be related to the formation of by-product Li₂CO₃ limited the electron transportation and the cyclability. This indicated that the carbon-free electrode will be a good choice for improving cycling performance of Li–air batteries.

5.2. In situ characterization of Li-S battery

In respect of Li–S batteries, due to the encapsulating or trapping effect and continuous electrical conduction of 1D carbon nanomaterials, the electrochemical performance of the 1D carbon nanostructure-based sulfur cathode can be improved because of the restricted shuttle effect of polysulfide and improved conductivity of sulfur composite materials [209,210].

5.2.1. S-CNT composite

The lithiation mechanism of S confined in CNT was confirmed by *in situ* TEM [211]. The huge volume expansion without any fractures and the high electrical conductivity of CNT as well as Li₂S/S interface ensured the high capacity and the structure stability of S/CNT electrode. The direct transformation of S into Li₂S without any formation of polysulfide which was different from the lithiation processes of S in liquid electrolyte was detected. The difference was contributed to the special form of all-solid-state battery and high vacuum in TEM, indicating that this direct transformation of S may not be generalized. The 1D sulfur was also used as a model for the characterization of the electrochemical reaction in Li–S batteries. The S chain was isolated inside the CNTs. The characterization of the electrochemical (de)lithiation processes of 1D S chain was realized by *in situ* Raman (Fig. 12d). The characteristic Raman peak of long S chains disappeared after discharge below 1.45 V corresponding to the breaking of ordered S chains. Only partial peaks restored after delithiation. These results attested that the transformation from long S chains to short S chains is irreversible [212].

Compared with the research on LIBs which was obtained by *in situ* characterization methods, fewer publications have been reported in the fields of Li–air and Li–S batteries. How to obtain the high capacity/long-lifetime Li–air and Li–S batteries is still a challenge. More advanced 1D nanomaterials and the real-time characterization of the optimization mechanism will be urgently desired to turn up towards exciting new understandings on Li–air and Li–S batteries.

A summary of the most relevant papers of *in situ* characterization with 1D nanostructure in SIBs, supercapacitors, Li–air and Li–S batteries, together with their reported phenomena and results, can be found in Table 3.

6. *In situ* characterization of single nanowire electrochemical device

Compared with the traditional coin battery, the single NW devices have been exploited and demonstrated to be a powerful diagnostic tool without the influence of inactive materials. The single NW devices can also be tested by a variety of characterization methods. Combined with *ex situ* technology, the conductance change of the Si NW [215] and the LiMn₂O₄ NW [216] during the electrochemical processes was observed. Moreover, when the single NW device combines with *in situ* technology, this design provides a unique platform for *in situ* probing of direct correlation of 1D nanomaterials' electrical transport, structure and electrochemistry without disturbing the batteries' components.

All-solid-state single NW electrochemical device was assembled by Mai et al. [217]. The device contained just one vanadium oxide NW as cathode (Fig. 13a) or Si NW as anode (Fig. 13b). The conductance of vanadium oxide NW restored to previous scale with shallow discharge and charge, indicated that structure change of vanadium oxide NW was reversible. But after a deep discharge, the conductance of NW was difficult to recover after charge, indicating that the structure of V_2O_5 was destroyed with too many Li ions intercalated into the layers of the vanadium oxide. The conductance change of Si NW during the electrochemical process showed a different trend. The Si NW's conductance decreased monotonously.

The Raman mapping of Si NW became not uniform and the corresponding Raman spectra showed clear red shifts and broadening, indicating that the crystalline Si lost its order and became metastable amorphous Li_xSi alloy which was consistent with the *in situ* or *ex situ* characterization results of the Si [34,215]. Except for the vanadium oxide NW, the MnO₂ is another promising cathode material for LIBs. Subramanian et al. assembled the single β -MnO₂ NW on-chip microelectrode LIB combined with electrolyte and Li wire [218]. The lithiation phase Li_xMnO₂ was observed by TEM combined with EELS. The conductivity of Li_xMnO₂ NW was

two or three orders lower than that of the pristine state due to the increase of lattice disorder within the material. These results indicated that the decreased conductivity and structural degradation of electrode materials caused the fading of electrochemical storage device. Similar devices were also assembled to investigate the electrochemical process of the MoS₂ [219–221]. Recently, in order to observe the different electrochemical reaction processes of LIBs and SIBs, Xu et al. designed and constructed the single H₂V₃O₈ NW device with multicontacts (Fig. 13c and d) to investigate the transport properties of Li and Na ions in lavered materials [222]. The conductivity of NW decreased during the intercalation/deintercalation of Li⁺/Na⁺ processes. But the conductivity degradation of H₂V₃O₈ NW during the sodiation process was more serious than that in lithiation process due to the larger size of Na⁺ ions and the greater energy barrier. This work provides a direct evidence for large size effects of Na⁺ ions during cycling.

Another aspect deserving emphasis is that, the merits of 1D nanomaterials can facilitate the construction of 1D nanobatteries for efficient in situ characterizations. A 3D all-solid-state coaxial Li ion nanobattery was constructed by Ruzmetov et al. [223]. The LiCoO₂ as the cathode material was deposited on the Si NW substrate which was coated by Ti/Pt/Ti collect layer. LiPON and Si were used as the solid electrolyte and anode of the nanobattery, respectively. With the thickness of LiPON reduced to nanometer regime, the increased electric field led to large electronic current which caused the rapid discharge. The rapid self-discharge can not be avoided until the thickness of electrolyte increased to 180 nm. The void formed at the electrode/electrolyte interface during the electrochemical process, which may result in the capacity loss. The simultaneous characterization of electrode and electrolyte during the electrochemical process was realized by the unique coaxial design. The rapid self-discharge and Li-induced stress were evidenced to be the critical challenges of the 1D nanobatteries.

In a word, this kind of method for the construction of single NW device, without the influence of conductive additives or binder, hence, offers a new strategy for *in situ* probing the electrochemical processes and can be universally applied in various electrode materials. The ability to realize the investigation of Li or Na storage mechanism has been recognized to lay scientific foundation for long-term development of energy storage device. Furthermore, these works act as the power source of micro/nano self-driven device and provide an effective direction for micro/ nano integration.

7. Conclusions and perspective

This review summarizes the recent discoveries of 1D nanomaterials during the electrochemical processes by in situ characterizations. With the development of in situ TEM, SEM, XRD, NMR, XAS and Raman characterizations, many electrode materials of different energy storage devices were investigated. Some general phenomena such as phase transformation and huge volume expansion were observed. While some new mechanisms, such as the new lithiation/sodiation mechanism and certain unique intermediate phases were demonstrated. It can be concluded that mechanical degradation, crystal structure damage, and conductivity decrease are the main reasons for the capacity fading. Besides, the coating layer, size, and geometry are closely related to the performance of electrode materials. The abundant information throughput gained from the in situ studies is valuable for the optimization of electrode. These results are helpful for the development of basic guidelines for the rational design of high-performance electrochemical storage device.

However, there still exists insufficiency and challenges in the field of the *in situ* characterization of 1D nanomaterials:

Main progress of *in situ* characterization with 1D nanostructure in other advanced energy storage devices.

Materials	Characterization technologies	Main phenomena and results	Ref.
	teennoiogies		
Hollow core-shell	In situ TEM	The disordered-C showed a higher storage capacity. Some longitudinal cracks formed near the interface between c-C and d-C.	[158]
c-C/d-C CNF			[100]
SnO ₂ NW		The sociation speed appeared to be ~20 times slower than that of infinition process. Many pores generated after the extraction of Na ⁺ .	[160]
	In situ TEM	The new phases of NaCuO and Na ₆ Cu ₂ O ₆ formed after the intercalation of sodium ion.	[162]
MnO ₂ NW	In situ TEM	Na _{0.5} MnO ₂ and Mn ₂ O ₃ were the sodiation products with the tunnel degradation of α -MnO ₂ .	[213]
Co ₉ S ₈ -filled CNT	In situ TEM	Co nanograins which dispersed in a Na ₂ S matrix were generated. Drastic swelling and fracture were observed at high current density.	[166]
Sb/Ge/TiN core-shell NW	In situ TEM	Some time-dependent bucklings and localized separations from the supported NW were observed after desodiation.	[170]
Zn ₄ Sb ₃ NW	In situ TEM	The sodiation speed of Zn_4Sb_3 NW exceeds 295 nm s ⁻¹ . The Zn_4Sb_3 NW showed no cracking or facture with 81% reversible volume expansion. The layered NaZnSb was	[214]
		formed after the first sociation and desociation processes.	[170]
dled NWs	in situ XRD	The intensity and position of peak changed slightly during the charge and discharge.	[1/2]
CNTs	In situ Raman	A strong upshift in the D or G^+ peaks was observed because of the hole doping. The main RBMs band upshifted no matter the hole and electron doping.	[184]
CNF	In situ infrared	The anion concentration decreased and cation concentration increased after KOH activation.	[185]
	spectroscopy		
MnO ₂	In situ XAS	The oxidation state of the MnO ₂ increased from $+3.23$ to $+3.95$, and then back to $+3.27$.	[187]
		The formation of the divalent and tervalent Mn oxide and the dissolution of Mn species were observed when the potential range expanded from 0–0.8 V to $-0.3-1$ V vs.	[188]
		The oxidation state of Mn in MnO ₂ -N/CNT could restore to the original state after a complete cycle	[189]
		The SCN ^{$-$} anions in the IL could reversibly insert/desert into/from the tunnels in MnO ₂ and participate the redox reaction	[190]
		$H(0,20)^+$ cations inserted into the tunnels of MO ₀ during the electrochemical process	[101]
	In situ Raman	$h_{\rm cos}$ at the stabilized in the transfer of the particular protocost in the stabilized from the Mn_0, with the increasing of potential	[107]
Li-Co-MoO NRs	In situ XRD	The park interstities at 21° and 45° were enhanced at the potential window of 0 to 16V in 10H which was different from the results obtained in KOH	[106]
Dt/MnO. NRs	In situ XRD	The growth and decomposition of i.e. during the charge and discharge processes were an alwaed quantificationally 5 wt $^{\circ}$ Dr/MnO, showed here catalytic performance	[201]
r ywno ₂ wrs	III SILU XKD	without the side reaction.	[201]
CNT	In situ TEM	The Li_2O_2 was oxidized preferentially at the interface of CNT/ Li_2O_2 . The oxidation of Li_2O_2 occurred only when the Li_2O_2 contacted with the electrolyte physically.	[207]
		The Li ₂ O ₂ particle could grow on another Li ₂ O ₂ particle. The electrochemical oxidation of Li ₂ O ₂ began from the surface of Li ₂ O ₂ particle. Some bead-like products limited	[208]
		the electron transportation and the cyclability.	
S/CNT composite	In situ TEM	The huge volume expansion without any fractures. The direct transformation of S into Li_2S without any formation of polysulfide	[211]
	In situ Raman	The characteristic Raman peak of long S chains disappeared after discharge below 1.45 V corresponding to the breaking of ordered S chains.	[212]

Notes: (SIBs: [158] [160] [162] [213] [166] [170] [214] [172]; Supercapacitors: [184] [185] [187] [188] [189] [190] [191] [192] [196]; Li-air and Li–S batteries: [201] [207] [208] [211] [212]).



Fig. 13. (a) Schematic diagram of a single NW electrode device design. (b) Optical image of a typical c-Si/a-Si coaxial NW electrode device. (c) Schematic diagram of a single H₂V₃O₈ NW device with multicontacts. (d) SEM image of the device with only one end of the NW exposed in the electrolyte. (a and b) Reprinted with permission from Ref. [217]. Copyright 2010 American Chemical Society. (c and d) Reprinted with permission from Ref. [222]. Copyright 2012 American Chemical Society.

- a) Some important characterization methods (e. g., neutron diffraction and atomic force microscopy) are absent. Many necessary characterization methods which have been used in the bulk materials showed great potential in observing the electrochemical phenomena of high-performance 1D nanomaterials. New electrochemical mechanisms are expected to be addressed with the help of more advanced characterization instruments.
- b) Compared with the 1D anode nanomaterials, the development of 1D cathode nanomaterials which was also important for constructing high-performance full batteries is insufficient. More new-type 1D cathode nanomaterials should be given more attention.
- c) There is a big gap between the nanobatteries and the real batteries. For example, the geometry that the electrode is inserted into the electrolyte in TEM is a good choice to some extent only when the reduced spatial resolution can be averted. In addition, necessary but complex modification for characterization instruments increases the test cost and the wide applications of *in situ* characterization. A general design of *in situ* cell which can be used in similar instruments (e. g., TEM and SEM, XRD and XAS, etc.) should be developed.
- d) Due to the inherent limitation of individual test instrument, the simultaneous detection of all changes of the electrode materials (e. g., composition variation, structural transformation, the change of electric transport properties) during the electrochemical processes is still a challenge. A new nanodevice integrated with *in situ* technology, such as building a micro-nano battery may give a chance to gain better understanding of the electrochemical processes. As a low-cost tool, nanodevice which can be constructed to reveal the intrinsic reason at single NW level for capacity fading will be a new and unique platform for studying and solving the key problems of LIBs, SIBs, supercapacitors, Li–S and Li–air batteries. This nanodevice can be expected to serve as a guide in constructing

high energy and power density, long circle life and safe electrochemical storage device.

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