Electrochemical Nanowire Devices for Energy Storage

Liqiang Mai, Qiulong Wei, Xiaocong Tian, Yunlong Zhao, and Qinyou An

Abstract—**Green energy has been increasingly demanded with the rapid development of economy and population. The electrochemical performance of energy storage devices could be improved by using nanomaterials, but their fast capacity fading is still one of the key limitations. The intrinsic reasons of capacity fading need to be further understood. Here, we review some single nanowire electrode devices designed as a unique platform for *in situ* probing the direct relationship between electrical transport, structure, and other properties of the single nanowire electrode before and after cycling. It is found that the conductivity decrease of the nanowire electrode and the structural change during electrochemical reaction limited devices' lifespan. Some strategies, such as prelithiation, conductive coating and structural construction, are designed and used to restrain the conductivity decrease and structural disorder/destruction, which improve the lifespan and rate capability of energy storage devices. Further, the stand-alone rechargeable nanobatteries built up by nanowires are able to meet the needs of energy storage in self-powered nanosystems.**

Index Terms—**Energy storage, nanodevices, nanoelectronics, nanowire, one-dimensional nanomaterials.**

I. INTRODUCTION

THE demand for green energy has significantly increased with the rapid development of economy and population [1]–[3]. Most of fossil fuels are nonrenewable energy resources and produce large amount of greenhouse gases, leading to the global warming. Thus, there is a strong need to develop renewable energy such as solar energy, hydroenergy, and wind energy, as well as safe and economic energy storage systems [4]–[6]. Rechargeable lithium batteries and supercapacitors have been widely used for consumer electronics and are desirable for applications in efficient large-scale electrical energy storage, hybrid electric vehicles, and electric vehicles, due to their high energy density and good environment compatibility [7]–[11]. Remarkably, as the highest energy density among the chemical batteries, Li-air batteries have captured worldwide attention and been regarded as next-generation energy storage devices.

The continuous development of energy storage devices is requiring higher capacity, longer operating cycles and shorter charge/discharge time. The key of achieving high-rate capability is known to solve kinetic problems involving slow ion diffusion and electron transport in the electrode materials. Based on the $t \approx L^2 / D$ [2] (where t is the diffusion time of lithium ion, L is the diffusion length, and D is the diffusion coefficient), the most effective method to improve the rate capability is reducing the characteristic dimensions of the electrochemical active materials. In this regard, numerous nanoscale materials have widely been synthesized and demonstrated to improve electrochemical performance [3], [11]–[16].

One-dimensional nanostructural materials, especially nanowires whose widths are at nanoscale but length can be up to hundred micrometer or even to centimeter, have attracted intense interest in recent years, which leads to the development of structures with rationally controlled geometry, composition, and electronic properties [1], [17]–[20]. The rational controls during synthesis processes have enabled nanowires to act as powerful building blocks for the bottom-up assembly of functional devices with application in photonics [1], energy storage [8], [9], energy conversion [19], nanoelectronics [21], and biosciences [22]. The nanowires can offer large electrolyte-electrode contact area, short Li-ion diffusion distance, effective electronic transport pathway, and facile strain relaxation during cycling, which are able to improve both capacity and rate performance of energy storage devices. Although the electrochemical properties can be improved, the fast capacity fading is still one of the key limitations and the intrinsic reasons need be further understood.

To find out the reasons of fast capacity fading, it was usually studied *ex situ* after disassembling the devices. Recently, *in situ* probing has been increasingly employed in the nanotechnology, such as *in situ* XRD [23], NMR [24], or TEM [25]–[27], which could provide some hint on material's structural changes during the electrochemical test, without being disturbed by other components. In this review, we introduce some single nanowire electrode devices designed as unique platforms for *in situ* probing the direct relationship between electrical transport, structure, and electrochemical properties of the single nanowire electrode before and after cycling [28]. Then, the intrinsic reason for electrode capacity fading in Li-ion-based energy storage devices is concluded, which may push the fundamental limits of the nanowire materials for energy storage applications. Based on

Fig. 1. Schematic of assembling a single nanowire electrode device.

Fig. 2. (a) Schematic diagram of a single nanowire electrode device design. (b) Optical images of a typical nanowire electrochemical device. (c–g) Single vanadium oxide nanowire transport properties at different charge/discharge states: (c) initial state, (d) after shallow discharge at 100 pA for 200 s, (e) after shallow charge at −100 pA for 200 s, (f) after deep discharge with 100 pA for 400 s, and (g) after deep charge with −100 pA for 400 s. Adapted from [28] (American Chemical Society, copyright 2009).

these results, the conductivity decrease of the nanowire electrode and the structural change during the electrochemical reaction limit the lifespan of the devices. In order to overcome these limitations, some strategies are designed and used to restrain the conductivity decrease and structural disorder/destruction, which largely improve the cycle life and rate capability of energy storage devices.

II. SINGLE NANOWIRE ELECTROCHEMICAL DEVICES

A traditional electrochemical cell consists of two electrodes (anode and cathode) separated by the electrolyte. Some recent reports focused on the single nanowire electrochemical behavior of Li ion or electron transport in the nanowire and aimed to study the relationship between electrode material composition, structure, transport properties, charge/discharge status, and electrochemical performance, revealing the intrinsic reason for fast capacity fading at nanoscale.

To assemble the single nanowire electrochemical devices [28], two different working electrodes, vanadium oxide nanowire, and silicon nanowire, were taken as examples. The PEO-LiClO$_4$-PC-EC polymer was used as the electrolyte. Binders or conductive carbon additives were not introduced into the systems. So the insights of intrinsic reason for electrode capacity fading can be studied without any additional effect, which the traditional battery test can not offer. The detailed steps of assembling the single vanadium oxide nanowire electrochemical devices are schematically shown in Fig. 1. First, highly ordered pyrolytic graphite (HOPG) flakes were dry transferred onto a marked substrate. Second, vanadium oxide nanowires were deposited onto the region close to the HOPG flake. Third, current collector patterning was written by E-beam lithography, then
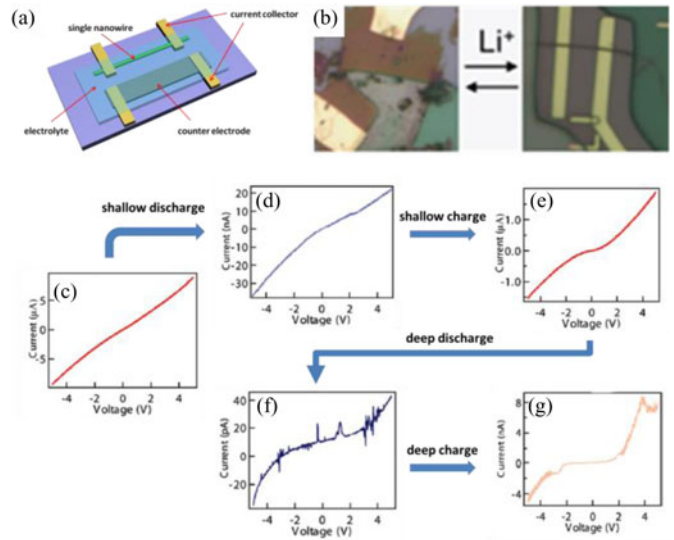
Cr/Au (10/100 nm) and Si$_3$N$_4$ layer (300 nm) were deposited by thermal evaporation and plasma-enhanced chemical vapor deposition, respectively. At last, the polymer electrolyte was drop cast onto the marked region. Compared to single vanadium oxide nanowire, the HOPG flake has much larger surface area, on which the influence is little during the electrochemical test.

The optical image of a typical nanowire electrochemical device is shown in Fig. 2(b). The transport properties of the vanadium oxide nanowire at different charge/discharge status were characterized immediately after the electrochemical performance test [see Fig. 2(c)–(g)]. During charge or discharge, Li ions moved out of or into the cathode materials, along with oxidizing or reducing reaction. Initially, the vanadium oxide nanowire was highly conductive [see Fig. 2(c)], agreeing with its original intact crystal structures. After discharge (Li-ion insertion) at 100 pA for 200 s, the nanowire conductance decreased over two orders [see Fig. 2(d)]. And, the conductance was restored to previous scale when charged (Li-ion deinsertion) at –100 pA for another 200 s [see Fig. 2(e)]. However, when deeply discharged at 100 pA for 400 s, the nanowire conductance dropped over five orders [see Fig. 2(f)]. The change was permanent and could not be recovered even after deep charging at –100 pA for 400 s [see Fig. 2(g)]. The aforementioned results indicated that structure change became permanent with too many Li ions inserting into the vanadium oxide layered structures.

Meanwhile, single silicon nanowire device was assembled with a Si/a-Si core/shell nanowire (as anode) and LiCoO$_2$ thin film (as counter cathode) [see Fig. 3]. As shown in Fig. 3(c), the silicon nanowire expanded after Li-ion insertion and became Li$_x$Si alloy, along with a layer of SEI forming at the surface of the silicon nanowire [10]. After Li-ion deinsertion, the
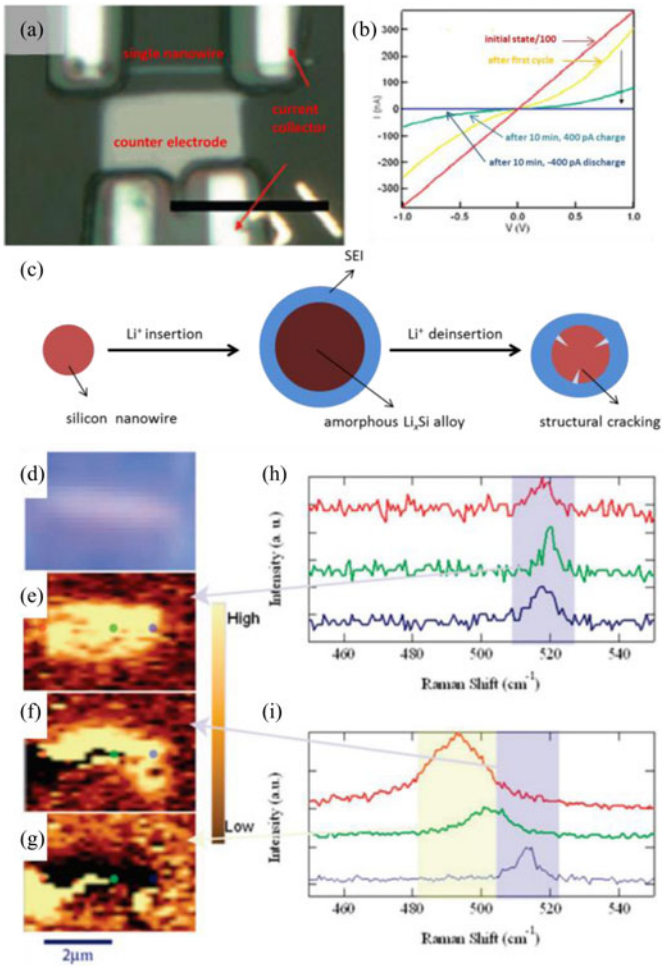
Fig. 3. (a) Optical images of a typical Si/a–Si nanowire/LiCoO$_2$ electrode device. (b) Transport property evolution of Si/a–Si nanowire along with an electrochemical test: red, initial state/100; yellow, after first cycle; green, after 400 pA charge 10 min; blue, after −400 pA discharge 10 min. (c) Schematic of silicon naonwire changes during charge and discharge. (d) Optical image of Si/a–Si nanowire. Raman mapping (e) before and (f) and (g) after electrochemical cycling. The Raman spectra of the three spots denoted in (e–g) are displayed in (h) and (i). The shaded area is the region employed for respective Raman mapping. Adapted from [28] (American Chemical Society, copyright 2009).

silicon structures shrank leading to structural cracking and deterioration [29]. Instead of reversible conductive change in vanadium oxide [see Fig. 2(c)–(g)], the conductance of the silicon nanowire monotonously decreased along with charge/discharge process [see Fig. 3(b)], which was accorded with the previous *ex situ* electrode conductive test [10]. Raman spectra were measured to reveal the structure change at the single nanowire level [see Fig. 3(d)–(i)]. It showed clear red shifts and broadening because crystalline silicon lost its order and a metastable amorphous Li$_x$Si alloy forms, along with the nanowire conductance degradation and the capacity fading. Notably, the single nanowire electrochemical device was also a stand-alone rechargeable nanobattery, which could meet the needs of micro-/nanodevices to build self-powered nanosystems.

Recently, *in situ* transmission electron microscope (TEM) has been largely developed, which enabled direct real-time visualization of electrochemical reaction, inducing structural changes, phase evolution, fracture behavior and atomic-level variations during lithiation/delithiation. Huang *et al*. constructed a nanoscale electrochemical device inside a TEM and *in situ* observed the Li-ion insertion and diffusion in SnO$_2$ nanowire during electrochemical charge [25]. It was clearly observed that a reaction front propagated progressively along the nanowire, causing the nanowire to swell, elongate, and spiral upon charging. The dislocations were continuously nucleated in the crystal regions, and then, moved away from the highly stressed region. After charge, the initially straight SnO$_2$ nanowire became highly distorted, with a total elongation of 90% and a total volume expansion of 250%. Further, the surface crack formation in ZnO nanowire was clearly observed during the electrochemical cycles [26]. Recently, Cui and his coworkers [30] used *in situ* TEM to observe the lithiation/ delithiation of amorphous Si nanospheres and revealed that the first lithiation occurred via a two-phase mechanism.

III. NANOWIRE ELECTROCHEMICAL DEVICES WITH ENHANCED PERFORMANCE

Based on the *in situ* measurements, the nanowire electrode conductivity decrease and the structural disorder/destruction caused by phase transformation and volume change during the electrochemical reaction limit the cycle lifetime of the devices. The key of improving the electrochemical performance is to concurrently optimize electrical and ionic conductivity, and maximize the active material utilization, as well as minimizing the strain induced damage.

A. Prelithiation

From the inherent characteristic of materials, Mai *et al.* used prelithiation to restrain the conductivity decrease and improve the cycling performance of electrochemical devices [31]. The conductivity of the lithiated MoO$_3$ nanowire was evidently increased and exhibited enhanced cycling capability [see Fig. 4]. Moreover, ultralong LiV$_3$O$_8$ nanowires were synthesized by topotactic Li intercalation in H$_2$V$_3$O$_8$ nanowires [32]. The LiV$_3$O$_8$ nanowires cathode displayed decreased charge transfer resistance and excellent high-rate performance. Also, the lithiated silicon [33] and graphene [34] anode were investigated with remarkably improved the electrochemical performance. The prelithiated technology opens up new avenues of pairing Li-free electrodes for the next-generation high-energy lithium ion batteries [31]–[34].

B. Coating Technology

The conductive coating technique is another effective way to increase the electronic conductivity, such as coating carbon, conductive polymers, metal, or metal oxides. Coating other material on the backbone nanowires is the most facile and common way to synthesize coaxial nanowires [14]. Coaxial MoO$_3$/PTh [35], MnO$_2$/CNT [36], and Polymer/Si [37] nanowires have exhibited superior advantages in terms of electrical conductivity, mechanical stability, and electrochemical performance. Moreover,
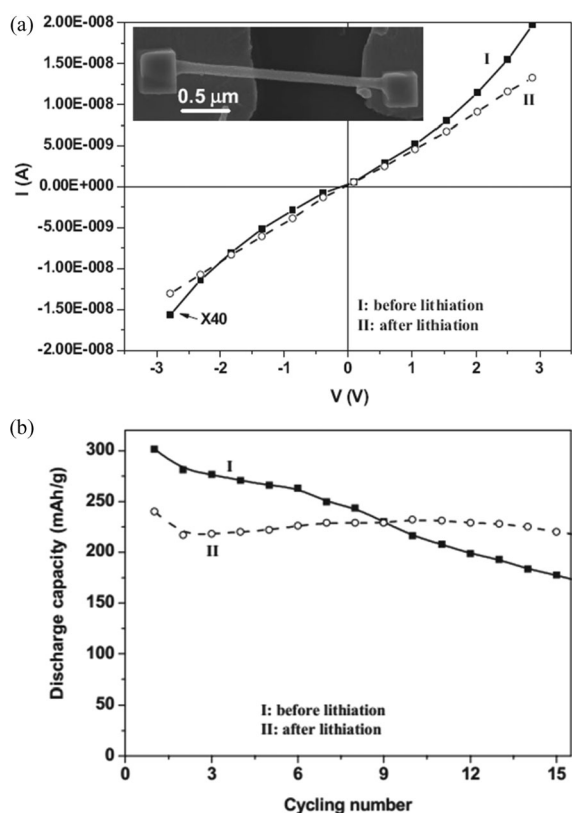
Fig. 4. (a) *I–V* transport measurements of single nanobelt fabricated devices using the samples before and after lithiation. (b) Cycle performance for the MoO_3 nanobelts cathode before and after lithiation. Adapted from [31] (Wiley-VCH, copyright 2007).
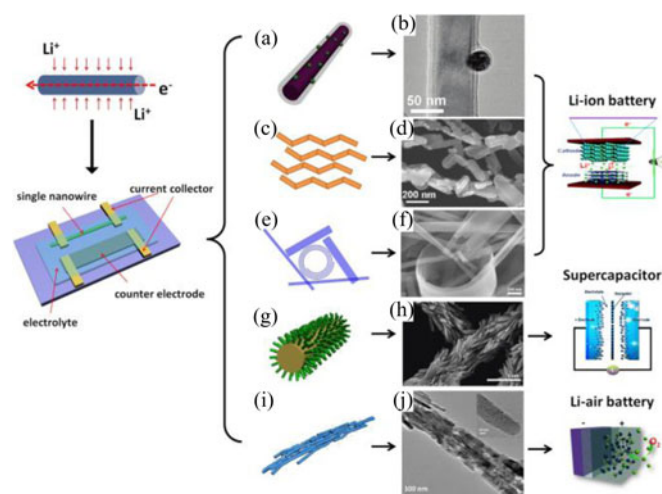

Fig. 5. Nanowire electrochemical devices with enhanced performance. (a) and (b) Silver vanadium oxides/polyaniline triaxial nanowires from [39]. (c) and (d) Utralong herarchical vanadium oxide nanowires from [40]. (e) and (f) Nanoscroll buffered hybrid nanostructure vanadium dioxide from [41]. (g) and (h) Hierarchical $MnMoO_4$/$CoMoO_4$ heterostructured nanowires from [42]. (i) and (j) Hierarchical mesoporous perovskite $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanowires from [45].

triaxial nanowires with conductive coating and increased active sites may further improve the cycling and rate performance [38]. Silver vanadium oxides/polyaniline triaxial nanowires [see Fig. 5(a) and (b)] [39] were synthesized by combining *in situ* chemical oxidative polymerization and interfacial redox reaction, demonstrated as an effective and facile technique for improving the electrochemical performance and stability of nanowire electrodes.

C. Structural Construction

The enhanced electrochemical performance of electrodes depends on not only the material intrinsic characteristics, but also the designed morphologies. Owing to the high surface energy, nanomaterials are often self-aggregated, which reduces the effective contact areas of active materials. Ultralong hierarchical vanadium oxide nanowires constructed from attached short vanadium oxide nanorods with length up to several millimeters were synthesized by electrospinning [40]. The self-aggregation in the unique "nanorod-in-nanowire" structures [see Fig. 5(c) and (d)] could be reduced because of the attachment of nanorods in the ultralong nanowires, which kept the effective contact areas of active materials and fully realized the advantage of nanomaterial-based cathodes. The ultralong hierarchical vanadium oxide nanowire cathode exhibited an initial capacity of 390 mAh g^{-1}.

The volume changes during cycles lead to the structural damage. Nanostructure with some buffered section in the interior

of structure could promptly accommodate the volume changes during rapid ion insertion/deinsertion, which may enhance the structure stability. Nanoscroll buffered hybrid nanostructural vanadium dioxides composed of nanobelts and nanowires were synthesized through hydrothermal-driven splitting and self-rolled method [see Fig. 5(e) and (f)] [41]. The hybrid nanostructure with buffered section was able to offer facile strain relaxation and shorten the lithium ion diffusion distances. Excellent cycle life with capacity retention over 82% after 1000 cycles at ∼9 C was achieved.

Heterogeneous materials with the synergistic contribution from different active materials have the advantages of further improving the electrochemical performance. Hierarchical $MnMoO_4$/$CoMoO_4$ heterostructures were successfully prepared on the backbone material $MnMoO_4$ by a simple refluxing method under mild conditions [see Fig. 5(g) and (h)] [42]. The asymmetric supercapacitors based on the hierarchical heterostructured nanowires showed a high specific capacitance and good reversibility with a cycling efficiency of 98% after 1000 cycles. Similarly, heterogeneous Co_3O_4 nanowire at MnO_2 ultrathin nanosheet core/shell arrays [43] and Graphene/MnO_2 nanostructured textiles [44] exhibited excellent electrochemical performance, much better than the individual parts. Further, the design of some desirable interfaces was able to build multifunctional nanostructures, which would be promising for a large spectrum of device applications.

Li-air battery theoretically offers very high specific energy because oxygen (the cathode active material) is not stored in the battery, but can be accessed from the environment. To enhance the performance, one method for enhancing the mobility of oxygen ions is to provide disorder-free channels of oxygen vacancies. To provide continuous oxygen channels, hierarchical mesoporous perovskite $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanowires were

synthesized by a facile multistep microemulsion followed slow annealing [see Fig. 5(i) and (j)] [45]. Li–air batteries fabricated by using hierarchical mesoporous nanowires exhibited an ultra-high capacity of more than 11000 mAh g^{-1}.

IV. CONCLUSION AND PROSPECTS

In situ methods have been developed for understanding the mechanisms governing battery performance and the properties change of electrode during Li-ion insertion/deinsertion. Single nanowire electrode devices are designed as unique platforms for *in situ* probing the direct relationship between electrical transport, structure, and electrochemical properties of the electrode before and after cycles. Based on the research, the key of improving the electrochemical performance is to concurrently optimize electrical and ionic conductivity, and maximize the active material utilization, as well as minimize the strain-induced damage.

The design and synthesis of structurally stable materials with high electron and ion conductivity have the potential to impact both small- and large-scale applications. Further, the concept of a stand-alone rechargeable nanobattery using individual nanowires as electrodes is quite appealing, while the self-power nanosystem or nanorobot needs an extreme miniaturization of power supply [4]. The ultimate advantages of the nanoscale in rechargeable energy storage devices are the formation of nanoarchitectured cells, in which electrons and ions can transport rapidly and effectively. Nanoarchitectures will be important research features in the future years, which may lead to energy storage devices with high energy density and power density.

ACKNOWLEDGMENT

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