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Novel surface modifications and new nanostructured titania synthesis for high-performance lithium-ion batteries and solar cells

Dongsheng Guan
Louisiana State University and Agricultural and Mechanical College, dguan4@tigers.lsu.edu

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NOVEL SURFACE MODIFICATIONS AND NEW NANOSTRUCTURED TITANIA SYNTHESIS FOR HIGH-PERFORMANCE LITHIUM-ION BATTERIES AND SOLAR CELLS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Mechanical Engineering

by

Dongsheng Guan
B.S., Harbin Institute of Technology, 2006
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To my parents and sister
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ABSTRACT

With the rapid development of electronic devices, electrical vehicles and space aerocrafts, rechargeable lithium-ion batteries (LIBs) have attract numerous interests due to high energy and power density, long lifespan and low self discharge. Spinel LiMn₂O₄ is a promising cathode material for novel LIBs thanks to high working potential, easy synthesis and low cost, but its severe capacity drop mostly due to inevitable reactions with electrolytes is a drawback. In the dissertation, ultrathin and highly-conformal Al₂O₃ coatings are grown on the surface of micro-sized and nanosized LiMn₂O₄ with atomic layer deposition. Thickness of Al₂O₃ ALD coatings can be precisely controlled by varying ALD growth cycles, notably with a growth rate of 1.5 Å per cycle on nano-LiMn₂O₄ particles. The coatings improve electrochemical performance of LiMn₂O₄ cathodes in LIB. For example, micro-LiMn₂O₄ cathode coated with 10 Al₂O₃ ALD layers shows higher discharge capacity of 53.7 mA h g⁻¹ than bare micro-LiMn₂O₄ cathode (40.2 mA h g⁻¹) over 100 cycles in half cells, and nano-LiMn₂O₄ cathode coated with 6 Al₂O₃ ALD layers delivers a capacity retention efficiency 23% higher than that of bare nano-LiMn₂O₄ cathode over 100 cycles in full cells.

One reason for popularity of nanostructured TiO₂ is its higher working potential and better safety as anode material in high-power LIBs. The effect of morphology and phase structure of anodic TiO₂ nanotube arrays on their capacity and cycleability in LIBs is investigated, as well as their thermal and electrochemical stability. The other reason is its broad use in dye-sensitized solar cells (DSSCs). One-dimensional TiO₂ nano structures have large surface area for dye loading and ordered paths for fast electron transport, good for enhanced conversion performance of TiO₂-based DSSCs. In this project, single-layer, double-layer and bamboo-type TiO₂ nanotube arrays are synthesized by anodic oxidation of Ti foils under constant- or alternating-voltage conditions. Their growth mechanisms are carefully explored to achieve morphology control, based on dominant ion diffusion-controlled mechanisms. Various bamboo-type TiO₂ nanotubes are produced by tuning the holding time of high-voltage and low-voltage steps, and denser ridges on tube walls are found to favor performance of TiO₂ nanotubes in DSSCs.
CHAPTER 1. OVERVIEW: DEVELOPMENTS OF RECHARGEABLE LITHIUM-ION BATTERIES AND DYE-SENSITIZED SOLAR CELLS

1.1 Energy Storage Techniques

1.1.1 New Power Source for Autos

The number of automobiles is drastically increased over the past two decades, since their prices are down to a level that citizens can afford. Most of these vehicles are powered by internal combustion that consumes gasoline and yields toxic waste gas and uncomfortable noises. This aggravates the pressure from exhausting fossil fuels, and also greatly worsens the environment. As a result, seeking clean, efficient and low-cost power sources for automobiles have become a worldwide topic across industrial and academic fields, in order to replace the conventional internal combustion method. One of available power sources is electricity from electric energy generation or storage devices installed in vehicles. For example, the electricity can be produced directly from vehicle-mounted solar cell or fuel cell systems. Another way is to obtain electricity from vehicle-mounted electrochemical batteries. The battery is typically a type of energy storage devices. In the present, a group of energy storage techniques, physical and chemical, have been widely developed. Figure 1.1 shows various energy storage methods, such as pumped hydro, capacitors and electrochemical batteries [1]. Among them, the electrochemical batteries are very popular due to their large specific energy capacity and portable use.

![Figure 1.1 Current energy storage techniques [1].](image)

1.1.2 Electrochemical Batteries

As the name suggests, electrochemical batteries are a kind of energy storage devices which could convert electrochemical energy into electrical energy. Martin Winter and Ralph Brodd give a rigorous definition for such battery: one or more electrically connected electrochemical cells with terminals or contacts to supply electrical energy [2]. The terminals or contacts are electrodes in cells that can be divided into anodes (negative) and cathodes (positive) by their
potential difference. The electrodes are paired where chemical energy is stored and released by redox reactions. The redox reaction describes all chemical reactions in which atoms have their oxidation state changed due to the gain and loss of electrons [3]. When a battery is at work in a closed circuit, the redox reaction occurs at the cathode and anode, and electrons are released to flow along the external circuit. The flow of electrons forms electricity that can be utilized by external loads. These characteristics distinguish the electrochemical batteries from other energy storage devices, such as fuel cells, physical and electrochemical capacitors.

Batteries have a history of more than two hundred years. It is firstly invented in 1800 by Alessandro Volta, an Italian physicist. He designed a voltaic pile that could provide a steady electrical current [4]. Since then, many types of batteries have been manufactured, and their performance has been progressively improved to meet demands from increasing household and industrial applications. In general, the electrochemical batteries are classified into two broad categories: primary battery and secondary battery. The first one is not rechargeable. That is, the primary battery can provide electricity right after assembly. When the electrode materials inside for redox reactions are exhausted, the electricity cannot be further supplied. The electrode materials cannot be re-generated by charging; otherwise it may cause fire and explosion. The primary batteries include zinc-carbon battery, zinc-chloride battery, alkaline battery, oxy nickel hydroxide battery, zinc-air battery, and silver-oxide battery [5]. In contrast, the secondary battery is rechargeable. After assembly and initial charging, they can output electrical current to external loads, and their electrode materials are continuously consumed by occurring redox reactions. This process is called “discharging”, in which chemical energy is converted into electrical energy. After the electrode materials are used up, a subsequent charging treatment can renew the material for another discharging process. In the same way, the secondary battery can be charged and discharged even for thousands of times. It includes a big group of batteries, such as nickel-cadmium (Ni-Cd) battery, Ni-Zn (nickel-zinc) battery, nickel-metal hydride battery (NiMH), lead acid (Pb-acid) battery and lithium-ion (Li-ion) battery, as shown in Figure 1.2 [6]. It can be seen that these electrochemical batteries have relatively high power density and energy density. Besides, they are portable, cheaper, in small size and with great convenience, and thus attract numerous interests. Their structures and advantages are briefly introduced as follows:

The lead-acid battery has been widely used in vehicles and aircrafts. It is low-cost and has good performance when operated at high and low temperatures. However, some drawbacks restrict its further development, such as short cycling life and low energy density. It typically contains lead oxides, porous lead metal, and dilute sulphuric acid electrolytes, and can be described as: (-) Pb | H₂SO₄ | PbO₂ (+). The voltage of a Pb-acid battery is 2.0 V.

The Ni-Cd batteries have high physical durability, large charge retention and good cycling performances, but their high production cost and severe memory effects need to be alleviated. The Ni-Cd battery contains Cd metal as negative electrode, nickel oxide hydroxide (NiOOH) as positive electrode, and KOH (or NaOH) aqueous solution as electrolyte. It can be written as: (-) Cd | KOH (or NaOH) | NiOOH (+). Their cell voltage is usually ~1.2 V.

The NiMH battery has excellent safety, and thus has been widely adopted in aero vehicles. It has large energy density and long cycling life. Its limitations are high initial cost and self discharge proportional to the pressure of hydrogen gas used. Its positive electrode is nickel oxide hydroxide (NiOOH), and negative electrode is hydrogen gas catalyzed by platinum.
The electrolyte used in NiMH is KOH or NaOH aqueous solutions. The NiMH battery can be described as: \((-\) Pt, H\(_2\) | KOH (or NaOH) | NiOOH (+)). It has a typical cell voltage of \(~1.4\) V.

The Li-ion batteries (LIBs) have many unique properties: (1) large energy capacity per mass or volume, and high power density. They contain light-weight electrode materials and have much higher output voltages (3.2–3.6 V) than other secondary batteries (1.2–2.1 V), (2) low self-discharge rates good for long-term storage, and no memory effects for fewer loss in frequent use, and (3) long life span. Hence, LIBs are broadly applied in portable electronic devices (laptops, cameras, mobile phones) and electric vehicles (bicycles, autos and planes).

![Figure 1.2 Comparisons between rechargeable electrochemical batteries [6].](image)

### 1.1.3 Structure and Working Principle of LIBs

The first commercial LIB is invented by Sony Company in 1991, a big breakthrough in battery industry. Soon after, LIBs have become a popular power source for cell phones and laptops that are spreading across the world. LIBs are also known for shape flexibility, such as coin/button cells, cylinder cells and pouch cells, invented to meet different demands. Prior to LIBs, lithium batteries are explored, such as Li-MnO\(_2\) battery, Li-SOCl\(_2\) battery and Li-SO\(_2\) battery [7]. However, lithium batteries are seldom used currently due to rapid-discharge and safety issues, except under some extremely environmental conditions. In contrast, LIBs are much safe, and similarly composed of anode, cathode, polymer separator and electrolyte. The anode and cathode materials are a series of elements or compounds that could accommodate and release Li\(^+\) ions under different potentials, as introduced in detail later. The separator is a thin polymer film used to prevent the direct contact of anode and cathode, in order to avoid short circuit inside the battery. Some special requirements for the separators are [8]:

1. Good electronic insulator, in order to eliminate electric short-circuits;
2. Minimal electrolyte (ionic) resistance, to avoid hindering migration of Li\(^+\) ions;
3. Good mechanical and dimensional stability, for easy processing;
4. Sufficient physical strength to allow easy handling;
5. Chemical resistance to degradation by electrolytes, impurities, electrode reactants and reaction products;
(6) Effective in preventing migration of particles or colloidal or soluble species between the anode and cathode
(7) Readily wetted by organic or aqueous electrolyte;
(8) Uniform in thickness and other physical properties.

The LIBs are filled with an organic electrolyte containing lithium compound salts, such as LiPF₆, LiAsF₆ and LiClO₄. The redox reactions occur at anode and cathode simultaneously. Thus, a typical LIB structure is written as: (-) C₆ | 1 mol/L LiPF₆-EC+ DEC | LiCoO₂ (+).

The working mechanism of a LIB is illustrated in Figure 1.3. In the discharging process, Li⁺ ions are extracted out of the anode material and finally inserted into the cathode material at cathode. Meanwhile, electrons move from the anode to cathode. As a result, the electrical current is generated and its direction is from the cathode to anode. In the charging process, these movements are reversed; that is, Li⁺ ions are released by the cathode and inserted into the anode material, and simultaneously the electrons are released to flow back into the anode, which forms reverse current provided by external power sources. Hence, it is understood that the number of electron or Li⁺ ions provided by cathode material and anode material for these reversible movements is very essential for the output current density, and further the specific energy and rate capability of LIBs.

In LIBs, anode materials contain graphite, silicon, germanium, metal alloys, SnO₂, TiO₂ and Li₄Ti₅O₁₂, with negative redox potential. The cathode material includes LiCoO₂, LiNiO₂, LiMn₂O₄, LiFePO₄, V₂O₅, MnO₂ and LiCo₁/₃Ni₁/₃Mn₁/₃O₂, with positive redox potential. In general, the cathode and anode materials must meet three fundamental requirements to reach the goal of high specific energy and power density for LIBs: (1) a high specific charge and charge density, i.e., a high number of available charge carriers per mass and volume unit of the material. (2) a high cell voltage, resulting from a high (cathode) and low (anode) standard redox potential of the respective electrode redox reactions, and (3) a high reversibility of electrochemical reactions at both cathodes and anodes to well maintain the specific charge for hundreds or thousands of charge-discharge cycles. Batteries made of materials with these properties could have high specific capacity, large power density (rate capability) and even excellent cycling life.

Figure 1.3 Schematic on a Li-ion battery in discharging process.
As novel electronic devices and electric vehicles are manufactured in larger scale, LIBs with higher specific capacity and power density, better safety and longer life are demanded. It gives higher-level standards for element used in LIBs, including anode and cathode materials. Many traditional or novel techniques have been employed to optimize the electrode materials for high-performance LIBs, including nano technology. For example, to downsize electrode materials into nano scale is feasible to achieve LIBs with high specific capacity and good rate capability, which is attributed to a fact that nanostructured electrode materials possess larger surface area for more Li-ion intercalation within a shorter diffusion path, allowing fast charge/discharge rate and good capacity retention especially at high current rates. Take LiMn2O4 for example. Kiani et al. firstly used sonochemical method to produce \( \gamma \)-MnO2 nanoparticles that serve as precursor for synthesis of LiMn2O4 particles in micro size (290 nm) and in nano size (35 nm), respectively [9]. The nanoparticles show a much higher discharge capacity (~145 mA h g\(^{-1}\)) than micro particles (85 mA h g\(^{-1}\)) at C/2 rate between 3.0 V and 4.5 V. In addition, a group of nanostructured anode materials have also been synthesized, such as Si nanowires, Si/carbon nanofibers, CuO nanoparticles, SnO2 nanowires, NiO nanoshfts, Co3O4 nanotubes and TiO2 nanorods. These nano structures can improve the electrochemical performance of electrode materials, but also alleviate volume change problem in Li-ion intercalation process.

1.2 New Energy Sources and Materials

1.2.1 Energy Supply Demands

Since the first industrial revolution occurred in late 18\(^{th}\) century, fossil fuels (coal, gasoline and natural gas) have been the most important energy sources for industrial manufacturing, economical growth and social progress. Figure 1.4 presents the energy consumption structure around the world from 1900s to present, as well as an assumption of consumption trend until 2050 [10]. Clearly, three conventional energy sources account for most of the percentages of energy supplies and consumption, reflecting the significance of fossil fuels on evolution of
human civilizations on earth. Unfortunately, the fossil fuels power the world for a long term, but this situation cannot continue to the future. The first reason is their inherent drawbacks. For example, their reserve on earth is limited and their production cannot be duplicated very readily, since formation of coal, crude oil and natural gas from ancient organisms (e.g. a mass of forests) passes millions of years in very special and critical conditions (e.g. high pressure and high temperatures). Each use of 42 US gallons of gasoline means a loss of one barrel of crude oil reserve on the planet, and thus the increasing number of automobiles and aerobat accelerates the exhaustion of nonrenewable crude oil. Coal and natural gas reserves also face the same problems. It is highly possible that one day all the three fossil fuels are depleted, which might cause a worldwide energy crisis.

Another concern refers to unavoidable environment pollution caused by use of fossil fuels. The combustion of coal, oil and natural gas yields millions of tons of carbon oxides (e.g. CO, CO₂), sulfides, waste water and solids every day, and brings air and water pollution, ozone holes, soil contamination and even global climate change. Hence, urgent and massive efforts are required to explore novel energy sources with exciting characteristics, such as abundance, reproducibility, cleanliness, low cost and high efficiency.

The sustainable increment in energy supply offers valuable opportunities for development of other energy resources, such as solar energy, geothermal energy, nuclear and wind energy. Figure 1.5 shows the worldwide investment on promotion of these sustainable and renewable energy resources [11]. It is seen that the wind energy, biological energy and solar energy take up eighty percents of the whole financial support, and thus their related research work draws tremendous attention across both academics and industry. However, it should be claimed that wind energy and tidal energy are restricted by locations and climate conditions, thereby with poor stability. For the artificial nuclear energy, it has ever regarded as an ultimate solution to energy crisis and space travelling, but is bothered by its safety issues. The solar energy source seems to a promising alternative or effective supplement to the fossil fuels in a broad range. The sun keeps delivering ~120,000 TW of energy to the earth, which is greatly more than the current amount of energy needs (13 TW) [12]. However, energy produced from sunlight has not become a mainstream in the current energy consumption realm, thanks to high production cost and unsatisfied conversion efficiency of energy conversion devices. Hence, it is highly demanded to modify these devices for enhanced photo-electric conversion performance.

![Figure 1.5 Global investments in sustainable energy by technology in 2006 [11].](image)
1.2.2 Development of Solar Cells

Green plants utilize solar radiation prior to man-made solar cells. Their leaves absorb solar energy and convert it into chemical or electric energy. Likewise, invented solar cells work in similar ways to provide electricity for external loads, thus considered as an energy generation or conversion device. So far, four generations of man-made solar cells have been developed based on single-element or compound materials. The first one is thin films based on silicon crystals. Silicon (Si) is a semiconductor with a bandgap of 1.12 eV, in which electrons in the valence band of Si are excited under solar irradiation, and jump to its conduction band to be free electrons eventually. The electrons with negative charge and holes with positive charge automatically move toward opposite directions to reach respective electrodes, and therefore a potential difference emerges between the two electrodes. When an external circuit connects the electrodes, electric current can be generated for usage. According to crystallinity, bulk Si used in solar cells can be generally divided into three types: amorphous Si, monocrystalline Si and polycrystalline Si. Currently reported largest efficiencies for the three Si materials are 10%, 25% and 20.4% in the labs respectively, but in practical use, Si solar cells show much lower efficiencies, such as 15% for monocrystalline Si-based solar cells and 12% for polycrystalline Si-based solar cells. Although crystalline Si solar cells are commercialized, their high production cost hinders their wide applications. For the amorphous Si solar cells, how to increase their efficiencies and long-term stability is a challenging issue.

The second one is thin films based on III-V or II-VI group compounds, such as GaAs, GaN, CdTe, GaInP and copper indium gallium selenide. These semiconductor materials exhibit far better photo-electric conversion capabilities than Si solar cells. For example, a GaAs-based triple junction metamorphic solar cell reaches an extremely high efficiency of 43.5% [13]. In addition, these materials are very applicable for thin film solar cells, since their film is thinner than Si thin films in Si solar cells usually with a thickness over 100 µm. However, problems such as expensive element sources, complex film manufacturing process and toxic attributes, restrict these compound thin film solar cells for extensive civil use.

![Figure 1.6](image_url) Schematic on structure and working mechanism of a dye-sensitized solar cell with mesoporous TiO$_2$ film as photo anode inside [15].
The third generation is dye-sensitized solar cells (DSSCs) invented by Michael Grätzel in the 1990s. One advantage of DSSCs is impressively low production cost. They are cheaper, with only 1/5~1/3 of the cost of commercial solar cells made of poly-crystalline silicon. They can even be manufactured on robust or flexible substrates in a DIY fashion. Though their best photo-electric conversion efficiency is not high (10~11% [14]), DSSCs show a very attractive price to performance ratio, which allows them to compete with electricity produced from the conventional fossil fuels.

Figure 1.6 shows the typical structure and working principle of front-side DSSCs with mesoporous TiO$_2$ film as photo anode [15]. It contains a thin dye-sensitized TiO$_2$ film on a conductive glass, and a Pt-coated conductive glass as the counter electrode. The cell is filled with a redox electrolyte. Under incident radiation, the dye absorbs the sunlight and is excited. The excited dye releases electrons that are injected into the conduction band of TiO$_2$. The electrons transfer across TiO$_2$ particles and reach the conductive glass. Through external electric circuit, these electrons finally arrive at the counter electrode. The directional flow of electrons forms usable electricity for consumption. Inside the cell, the excited dye oxidizes the redox species in the electrolyte to capture electrons and returns to its unexcited state. The oxidation process can be described by this equation:

\[
\frac{3}{2} \Gamma \rightarrow \frac{1}{2} \text{I}_3^- + e^- \tag{1.1}
\]

The \text{I}_3^- species transfer to the counter electrode and receive electrons there under the catalysis of Pt. The reduction process can be expressed by this equation:

\[
\frac{1}{2} \text{I}_3^- + e^- \rightarrow \frac{3}{2} \Gamma \tag{1.2}
\]

The renewed \text{I}^- ions move back to the anode where they react with excited dye again. In the long-term illumination, electrons are continuously generated to yield electricity. At this point, it is known that the electric circuit is completed by the electrolyte containing a redox couple (\text{I}/\text{I}_3^-), and the stability of electrolyte is critical for DSSCs’ performance. It can be liquid one made of volatile organic solvents, and thereby must be rapidly and completely sealed, but its long-term stability is still a big concern. The state-of-the-art DSSCs use solid electrolytes due to higher stability and easier processing, but slow ionic movement in solid electrolytes causes much lower efficiencies of solid-state DSSCs than that (~11% [14]) of DSSC using liquid electrolytes. Thus, ionic liquids in quasi solid state are used in DSSC to alleviate the severe problem.

The fourth one is organic or polymer solar cells. Due to advantages of low cost and easy large scale production, they draw lots of attention as well. They have a sandwiched structure similar to that of DSSCs shown in Figure 1.6; however, the biggest difference between them is the middle layer. In these organic solar cells, a layer of organic electronic material is sandwiched by two electrodes. The electronic material is a type of conductive polymers or small organic molecules and serves as sunlight absorption and charge transport medium. The newest record of organic solar cells’ efficiency is 8.3%, and there is still a big improvement anticipated in the future.

1.2.3 Current Research on DSSCs

According to the working mechanism of DSSCs shown in Figure 1.6, it can be understand
that the efficiency of DSSCs is affected by the following factors:

(1) Photo anode materials. They can be semiconductor ZnO, TiO$_2$ and oxides else. Single-crystal ZnO nanorods or nanowires with several tens of micrometer in length are easily to be synthesis, in which electrons are able to quickly transfer into the conductive glass below, with much less recombination with holes. However, the chemical bond of dye to ZnO is not as strong as that of dye with TiO$_2$, yielding a smaller electron injection efficiency. Besides, ZnO film supporter can be corroded by the dye and electrolytes, which undermines the stability of ZnO-base DSSCs. These solar cells made of other oxides (e.g. SnO$_2$, Nb$_2$O$_5$, SrTiO$_3$, Zn$_2$SnO$_4$) show relatively poorer performance than TiO$_2$-based DSSCs, due to some unique advantages in film porosity, bonding with dye, charger transport of TiO$_2$ films [16].

(2) Surface area of TiO$_2$ film supporter. The dyes are the source of electrons, but only one layer dye chemically bonds to TiO$_2$. More layers of dye coated on TiO$_2$ reduce the injection of electrons into TiO$_2$, and surprisingly yields lower efficiencies. Therefore, the amount of monolayer dye is dependent on the surface area of TiO$_2$ films. Currently, DSSCs deliver their highest efficiency of ~11%, which are based on a layer of mesoporous TiO$_2$ film with 10 µm of thickness [16]. As a result, a group of nanostructured TiO$_2$ films with larger thickness and bigger surface area are synthesized for DSSCs.

(3) Efficient utilization of supporter. The dye (e.g. Ruthenizer 535-bisTBA) is commonly a type of photovoltaic molecules in nano size, which can penetrate into and fully coat on thick mesoporous TiO$_2$ films for light harvest. Other organic dyes include N3 [17], K8 [18], K19 [19], C101 [20] and black dye [17]. However, these dyes are far expensive and even contains toxic element inside, so various new dyes in larger size are synthesized to reduce the cell cost or further improve the cell efficiency. One problem emerges that the mesoporous TiO$_2$ films are difficult for larger dyes to penetrate for complete absorption, reducing the utilization of supporter. Likewise, it makes harder for the solid-state electrolyte to infiltrate for full contact. Based on these reasons, well-order one-dimensional (1-D) nanostructured TiO$_2$ films are made for serving as photo anodes in DSSCs. Their dimensions can be tuned easily via tuning preparation conditions, in order to fit these bigger dyes and let (quasi) solid electrolytes in.

(4) Electron-hole recombination. It is seen from Figure 1.6 that the electrons jump among TiO$_2$ particles to the conductive substrate after being injected. Numerous boundaries of tiny particles greatly slow down the electron transport and increase their interfacial combination with redox species in electrolytes. In thicker mesoporous TiO$_2$ films, this recombination tends to be more intense. It significantly worsens the efficiency of DSSCs, and thus the thickness of mesoporous TiO$_2$ films usually ranges from 10−14 µm, blocking the way to improve the cell performance by making the anode films thicker. Fortunately, this problem could be solved by using ordered 1-D TiO$_2$ nanorods, nanowires and nanotubes. In these structures, electrons can quickly transfer directionally and reach conductive substrate quickly, reducing the interfacial recombination probability. Besides, the 1-D structures allow electron diffusion length as long as 100 µm, so the improvement of DSSCs’ performance achieved by increasing the thickness of sensitized 1-D TiO$_2$ nanostructured films is feasible and promising.

(5) Front-side or back-side illumination. Figure 1.6 represents a front-side DSSC, because incident light directly shines on the photo anode. In contrast, in back-side DSSCs the light
transfers through counter electrode and electrolyte to reach the anode. The reflection from the counter electrode and absorption by the electrolyte decreases the light harvest by dye at anode, and further affects the cell efficiency. Thereby, porous TiO$_2$ films are preferred to be attached on transparent conductive glass or plastics for front-side DSSCs.

(6) Other factors. The performances of DSSCs are affected by dye types, catalytic coatings on counter electrode, contact electric resistance and processing quality as well. In brief, it is a comprehensive project of improving the cell efficiency and cell stability, and decreasing the production cost. Extensive progress has been made in optimizing cell material, structures and processing technique of DSSCs. For example, morphology of TiO$_2$ films used as a supporter for dye evolves from flat thin films to porous nanoparticles films [21], and to 1-D nanostructures [22] and even 3-D nanostructures (branched TiO$_2$ nanotubes [23], forest-like TiO$_2$ films [24] and TiO$_2$ aggregates [25]). These nanostructures are designed and synthesized to either increase the surface area of photo anode, or enhance the light scattering and harvest, or reduce electron-hole recombination in DSSCS.

1.3 Motivation and Goals

This dissertation generally introduces three projects on exploring state-of-the-art materials used for cathode and anode of rechargeable LIBs, and for photo anode in DSSCs. In chapter 2 and 3, LiMn$_2$O$_4$ cathode material and its surface modification is introduced. Spinel LiMn$_2$O$_4$ is a promising cathode material for high-energy-density LIBs used in electric vehicles and hybrid electric vehicles, due to its low cost, high safety, easy production and non toxicity. However, this material shows poor stability in electrolytes due to dissolution reaction, and poor crystalline stability in overcharge and over discharge processes, especially at elevated temperatures, resulting in a huge loss of capacity during cycling. A group of surface coating techniques is employed to enhance the cycling stability of LiMn$_2$O$_4$, such as sol-gel method, melting impregnation and solid-state reaction method, but surface coatings formed by these approaches are usually not uniform and conformal, and the coating thickness is not precisely controllable. Besides, these coatings are as thick as several micrometers, inevitably causing capacity loss of LiMn$_2$O$_4$. Moreover, these coating routes are not fit for nanosized LiMn$_2$O$_4$ particles. This project adopts a cutting-edge technique to coat LiMn$_2$O$_4$; namely, atomic layer deposition. This technique enables growth of uniform, dense and conformal single-element or compound coatings with atomic thickness control on flat or porous substrate. Hence, a layer of nano-sized thin or subnanometer-thin Al$_2$O$_3$ is grown on microsized or nanosized LiMn$_2$O$_4$. Al$_2$O$_3$ is a conventional coating agent for Li-ion cell materials, and its coating on LiCoO$_2$ via ALD works very well for enchantment of the material in LIBs. At this point, improvement in electrochemical performance of LiMn$_2$O$_4$ coated with Al$_2$O$_3$ via ALD is also anticipated.

A second project on TiO$_2$ anode material for rechargeable Li-ion batteries is introduced in Chapter 4. Presently, commercial Li-ion batteries mostly contain graphite as anode, but the safety of graphite is a concern, especially when coupled with high-working-potential cathode materials. Thus, a group of new anode materials are studied, including TiO$_2$. TiO$_2$ also has higher working potential, and is a safer, low cost and chemically stable anode material with large specific capacity. TiO$_2$ nanotube arrays formed by anodic oxidation are very popular recently, thanks to their quite large surface area and excellent properties. It displays good
performance when serving as anode in LIBs. However, the effect of morphology and phase composition of anodic TiO$_2$ nanotubes on their Li-ion insertion performance remains unclear, as well as their structural stability during electrochemical cycling, which restricts the development of TiO$_2$ nanotubes for practical battery use. In this dissertation, these important factors are selected for careful examination, in order to optimize morphological features and phase structures of TiO$_2$ nanotube arrays for their better performance in LIBs.

The final project described in Chapter 5 and 6 is about synthesis of bamboo-type and multilayer TiO$_2$ nanotubes by anodization of Ti, and also about their application in DSSCs. It is demonstrated that bamboo-type nanotubes deliver enhanced conversion efficiencies when used in DSSCs, due to structural advantages. Multilayer nanotubes share some similarities in structure with the bamboo-type nanotubes, and thus their improved performance in DSSCs is expected. However, growth mechanisms of the two nano structures still remain unclear, and factors affecting their morphologies have not been fully investigated hitherto. In this project, the two types of TiO$_2$ nanotube arrays are synthesized under different anodization conditions, and the bamboo-type is then optimized for assembly in DSSCs tested. The comparison in the DSSC performance indicates the significant effect of nanotube appearance on their functions as a dye supporter and electron transport path in DSSCs.

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CHAPTER 2. NANOSIZED-THIN Al2O3 SURFACE COATINGS FOR ENHANCED ELECTROCHEMICAL PERFORMANCES OF MICRO-SIZED LiMn2O4 IN HALF BATTERY CELLS*

2.1 Introduction

Rechargeable lithium-ion batteries (LIBs) have drawn extensive attention due to their excellent properties, such as high energy density and light weight. Typical cathode materials such as LiCoO2, LiNiO2, LiMn2O4 and LiFePO4 have been widely investigated for LIBs with high energy and power density, or good cycling stability [1]. Among them, LiCoO2 has been used in commercial rechargeable LiIBs thanks to its easy production, high cell voltage (3.6 V) and specific capacity (140 mA h g⁻¹), and good cycleability. However, Co resource on earth is quite limited and causes a much high production cost of resultant LIBs. Besides, Co is a very toxic element, which may pollute nature environment if LiCoO2-based LIBs are not correctly disposed. LiNiO2 is less toxic material for LIBs, and Ni reserve on earth is much larger than LiCoO2. Its working potential is 3.6 V (vs. Li/Li⁺), with a large specific capacity of 180 mA h g⁻¹. However, LiNiO2 with precise stoichiometric ratios is much difficult to be synthesized, and its crystal structure is not much stable during Li-ion intercalation process, resulting in poor stability of LiNiO2-based LIBs. Recently, LiMn2O4 and LiFePO4 become popular cathode materials for high-energy-density LIBs used in electric vehicles. LiFePO4 is cheap, easily-synthesized and environmentally friendly, and LiFePO4-based LIBs also have excellent good long-term stability. However, its working potential (3.4 V vs. Li/Li⁺) is low, and its energy density (110 mA h g⁻¹) is too small. The biggest drawback of LiFePO4 is very poor electronic conductivity, yielding such low specific energy capacity. For LiMn2O4, it is a promising material that may be used in future commercial LIBs, due to its unique advantages. It has higher specific capacity (120 mA h g⁻¹) and output voltages (3.5–4.3 V vs. Li/Li⁺), higher safety and no memory effect [2, 3]. In addition, LiMn2O4 has abundant resource and is cheap, non-toxic, and environmentally friendly. However, a critical problem of LiMn2O4 is its poor stability with electrolyte and its capacity degradation during cycling, which limits its practical applications [4].

In general, the fast capacity fading of LiMn2O4 can be ascribed to three factors [5]: (1) dissolution of Mn²⁺ ions into solutions. Mn²⁺ ions are formed by a disproportional reaction:

\[ 2\text{Mn}^{3+} \text{(solid)} \rightarrow \text{Mn}^{4+} \text{(solid)} + \text{Mn}^{2+} \text{(solution)} \]  \hspace{2cm} (2.1)

(2) Jahn-Teller (J-T) distortion effect of Mn³⁺ ions due to the crystallographic transformation of LiₓMn2O4 (1<x<2) from cubic spinel structure to tetragonal phase that is well-known for its poor capacity retention; (3) continuous decomposition of electrolytes on the electrode partially due to formation of Mn⁴⁺ that has high oxidation ability. Thus, a variety of methods have been proposed to solve these problems. For instance, a small amount of cations, such as Al, Ga, Co, Ni, Cr and Ti, are doped into spinel LiMn2O4 in order to improve its structural stability [6-9]. Another common approach is surface modification of LiMn2O4 by coating with the oxides, metals [10], fluorides [11], phosphates [12], polymers [13], carbon [14] and

electrode materials [15, 16]. For example, oxides studied for coatings include MgO [17], Al2O3 [18], TiO2 [19], ZrO2 [20], ZnO [21], CeO2 [22], CaCO3 [23], α-MnO2 [24], SnO2 [25], SiO2 [26], Cr2O3 [27], Co3O4 [28] and Li2O•2B2O3 [29, 30]. The oxide coating on LiMn2O4 scavenges hydrogen fluoride (HF) formed from side reactions in LIBs, and thus slows down dissolution of manganese ions and degradation of electrolytes at cathode, yielding improved electrochemical performance of LiMn2O4.

Most surface modifications of lithium transition metal oxides reported in literature are carried out with wet chemical methods such as sol-gel processing or solution processing [16, 31, 32], such as soaking cathode materials into a nano-alumina sol [33]. Other methods include melting impregnation method and pulsed laser deposition [34, 35]. However, these methods are not well-controlled processes and their resultant coatings lack conformality, uniformity and completeness. One is not capable of well controlling the coating thickness and quantity using these methods, which limits the repeatability, reliability, and optimization of these processes. Moreover, wet chemistry methods require a large amount of solvent and precursor, and post-heat-treatment to obtain the desired coatings. In addition, nanostructured battery electrodes have received tremendous attention lately, owing to their high surface area and high capacities [36]. However, coatings resulted from wet processing are usually 50 – 1000 nm thick [30], which is too thick to be coated onto nanostructured electrodes. Hence, it is necessary to explore new surface coatings that are thinner and have high conformality for next-generation battery technology.

In this project, ultrathin and highly-conformal oxide coatings are deposited onto LiMn2O4 cathodes by using the atomic layer deposition (ALD) method with precise thickness control at atomic scale. This technique, originally called atomic layer epitaxy, is first reported by Suntola et al. in 1980s for growth of zinc sulfide thin films to produce electroluminescent flat panel displays [37]. ALD technique has outstanding large-area capability (large batch and easy scale-up), excellent conformality and good reproducibility, which is significantly welcomed in semiconductor manufacturing industry recently [38]. It can be applied to particles, polymers, high-aspect-ratio (up to 1:60) structures, flat substrates (e.g. Si wafers). The coating materials are in a broad range, from single elements to compounds; namely, II-VI compounds (e.g. ZnS, ZnSe, ZnTe, CdS, CdTe, MnTe, Hg1-xCdxTe, etc), III-V compounds (GaAs, AlAs, InP, GaP, AlxGa1-xAs, etc), nitrides (AlN, GaN, TiN, TaN, etc), fluorides (CaF2, SrF2 and ZnF2) and oxides (Al2O3, TiO2, In2O3, Ga2O3, YBa2Cu3O7-x, etc) [37]. ALD requires a minimal amount of precursor and can be used to deposit ultrathin and highly-conformal surface coatings [39, 40]. The basic advantage of ALD lies in the fact that the film growth is surface controlled, rather than source controlled as in many other deposition methods such as chemical vapor deposition (CVD). This is achieved by using sequential exposures, separating the (usually binary) reactions between precursor compounds into two half-reactions. During each half-reaction, only one monolayer of the reactant chemisorbs (or is chemically bound) onto the surface. Further layers which are only physisorbed are removed by an inert gas purge before the other reactant is introduced. As a result, the process proceeds step-wise in self-limiting surface reactions separated by purge steps. In some cases, the deposition process is enhanced by thermal conditions or plasma or radical conditions, in order to obtain a faster growth rate of coating materials. The films grown using ALD are typically uniform, dense, homogenous, pinhole-free and extremely
conformal to the underlying substrate. Moreover, ALD has good step coverage (~100%) and refilling ability on porous structures [41-44].

To date, there are only a few reports about surface modifications of LIB electrode material via ALD coatings and most of them focus on LiCoO₂ [45-48]. Al₂O₃ is chosen as the coating material here, because it is one of the most common coatings grown via many wet chemistry methods for LiMn₂O₄ and exhibits better effects than other oxides [30, 49, 50].

In this chapter, it is described that nanosized-thin Al₂O₃ coatings are deposited on LiMn₂O₄ (micro-sized)/carbon composite cathodes by atomic layer deposition technique. These coated cathodes are characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Electrochemical performance of bare and coated cathodes is compared to investigate the effect of thin Al₂O₃ coatings on the cycleability of LiMn₂O₄ cathodes. The results indicate that ultrathin and conformal Al₂O₃ ALD coatings reduce dissolution rate of manganese ions and thus improve cycling stability of LiMn₂O₄ cathodes at room temperature.

2.2 Experimental

Ti sheets (Alfa Aesar, 99.5%, 10×10×0.25 mm³) are degreased in ethanol and rinsed by sonicating in deionized water. A wet slurry mixture of LiMn₂O₄ powder (Alfa Aesar, 99.5%), carbon black (CB, Alfa Aesar, 99.5%), and poly(vinylidene fluoride) (PVDF, Alfa Aesar) (80:10:10 of weight ratio) is then spread on Ti sheets in a square (7×7 mm²) to produce LiMn₂O₄ composite electrodes. A two-step of heat treatment in air at 80 °C for 30 min and in vacuum at 120 °C for 9 h is conducted on the composite electrodes. The electrodes are then pressed by a MTI pressing machine with a pressure of 2 ton/cm² for 10 seconds.

Deposition of thin Al₂O₃ ALD coatings on the composite electrodes is carried out in a Savannah 100 ALD system (Cambridge NanoTech Inc., USA), as shown in Figure 2.1a. The precursors used for Al₂O₃ ALD are trimethylaluminum (TMA, SAFC Hitech) and deionized water. The coating process is shown in Figure 2.1b. The vapors of the two precursors are alternately carried by N₂ gas at a flow of 5 sccm into a sealed reaction chamber where the temperature is set at 120 °C for Al₂O₃ ALD. Self-terminating chemical reactions for Al₂O₃ film growth on the cathodes can be described as follows [45]:

\[ \text{AlOH}^* + \text{Al(CH}_3)_3 \rightarrow \text{AlO-Al(CH}_3)_2^* + \text{CH}_4 \]  

(2.2)

\[ \text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{Al-OH}^* + \text{CH}_4 \]  

(2.3)

The crystallographic structure of LiMn₂O₄ particles is determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2°/min. A scanning electron microscope (SEM, Quanta 3D FEG) is used to characterize the morphology of LiMn₂O₄ cathodes. The chemical composition of the electrodes is analyzed by an X-ray photoelectron spectroscopy (XPS, AXIS 165, Kratos Analytical Ltd.) with an AXIS 165 spectrometer from Kratos Analytical LTD by using a twin-anode Al Kα (1486.6 eV) X-ray source. The XPS spectrum is calibrated according to the binding energy of the C1s peak at 284.8 eV.

A three-electrode cell is set up in air to analyze the electrochemical properties of LiMn₂O₄ cathodes (Figure 2.1c). The electrolyte is 1 M lithium perchlorate (LiClO₄, Alfa Aesar, 99%), dissolved in anhydrous propylene carbonate. The composite electrodes are working electrode,
and a platinum mesh serves as counter electrode. A silver wire in a 0.1 mol/L AgNO₃ ethanol solution serves as the reference electrode. The galvanostatic charge-discharge measurements are carried out by using an electrochemical analyzer (Model 605C, CH Instruments, Inc) in a potential range between -0.3 V and 0.8 V (vs. Ag/Ag⁺) under a current density of 300 mA g⁻¹ (2.5 C). All the measurements are conducted at room temperature.

Figure 2.1 (a) S100 atomic layer deposition system, (b) atomic layer deposition process of Al₂O₃ on LiMn₂O₄ composite electrode, and (c) three-electrode cell bath for electrochemical measurements of LiMn₂O₄ composite electrode.

2.3 Results and Discussion

Figure 2.2 shows XRD pattern of micro-sized LiMn₂O₄ powders. All the diffraction peaks are indexed to a cubic spinel structure with a space group Fd3m (JCPDS 35-0782), where Li atoms occupy in tetragonal 8a sites, Mn atoms in 16d sites and O in 32e sites [34]. In this structure, [Mn₂]O₄ spinel framework displays a octahedral coordination of manganese ions, where Li ions can diffuse through interstitial pathways [51]. It is reported that such cubic structure gradually distorts and transforms to tetragonal phase during long-term cycling, and a rapid decrease in the Li-ion intercalation capacity of LiMn₂O₄ occurs accordingly [34].

Figure 2.3 presents SEM images of LiMn₂O₄ cathodes with and without Al₂O₃ ALD
coating, respectively. The commercial LiMn$_2$O$_4$ powders are composed of dispersed particles with a size range of 1~8 µm, which are mixed and pressed with carbon black to fabricate LiMn$_2$O$_4$ cathodes. It can be seen from Figure 2.3a that cracks appear in these micro-sized LiMn$_2$O$_4$ particles because of heavy pressing. Apart from these cracks, these particles have relatively smooth surfaces. The cracks increase the surface area of particles, and may affect the electrochemical properties of LiMn$_2$O$_4$. After the LiMn$_2$O$_4$ cathode is coated with Al$_2$O$_3$ ALD film via 20 ALD growth cycles, the coated LiMn$_2$O$_4$ particles preserve the shape and morphology of original bare particles, as clearly evidenced by SEM image in Figure 2.3b, indicating that the Al$_2$O$_3$ ALD coating is highly conformal. The growth rate of Al$_2$O$_3$ ALD film deposited on flat silicon substrates at 120 °C is about 1.0 Å per cycle; however, the growth rate of Al$_2$O$_3$ ALD coating deposited on nanoparticles is about 2.0 Å per cycle, because there is more hindrance from neighboring molecules in the absorption step on a flat substrate surface [52, 53]. Hence, thickness of Al$_2$O$_3$ ALD film grown with 20 ALD cycles here is estimated to be about 4 nm. It should be noted that the surfaces of coated particles are smoother than bare particles. During ALD growth, H$_2$O is absorbed onto the high surface

Figure 2.2 XRD pattern of micro-sized LiMn$_2$O$_4$ powders.

Figure 2.3 Top-view SEM images of (a) bare LiMn$_2$O$_4$ cathode, and (b) LiMn$_2$O$_4$ cathode coated with 20 Al$_2$O$_3$ ALD layers.
area of cathode or trapped within fine cracks on the particles, which makes it difficult to completely purge H$_2$O away from the ALD reactor. This presence of H$_2$O in the reactor or H$_2$O trapped in some fine cracks during TMA reaction would lead to a small amount of chemical vapor deposition and thus increased the growth rate, which smoothens some thin cracks [45].

To confirm deposition of Al$_2$O$_3$ coatings on the surface of LiMn$_2$O$_4$ cathodes, XPS is employed to characterize the surface elements. Therefore XPS analysis is conducted on a LiMn$_2$O$_4$ cathode coated with Al$_2$O$_3$ ALD film via 4 ALD growth cycles. The Al2p XPS spectrum is given in Figure 2.4 This figure shows Al2p peak at binding energy of 75.2 eV, which can be conformed to Al-O chemical bond of Al$_2$O$_3$ or Al(OH)$_3$ in reference to the values in NIST XPS Database [54]. XPS analysis of bare LiMn$_2$O$_4$ cathode is also carried out and the Al element is not detected. The result confirms the presence of Al$_2$O$_3$ coating on the coated cathode. For the cathodes coated with thicker Al$_2$O$_3$ ALD coatings via more ALD cycles, Al element is also observed in XPS analysis.

Figure 2.4 XPS spectrum of Al2p taken from the surface of LiMn$_2$O$_4$ cathode coated with Al$_2$O$_3$ ALD using 4 ALD cycles.

Figure 2.5 summarizes cycling performances of bare LiMn$_2$O$_4$ cathode and coated LiMn$_2$O$_3$ cathodes cycled at a current density of 300 mA g$^{-1}$ in a potential range of -0.3~0.8 V vs. Ag/Ag$.^+$ The cathodes are coated with Al$_2$O$_3$ ALD films via 10 or 20 ALD cycles. As it is discussed earlier, thicknesses of Al$_2$O$_3$ ALD coatings deposited via 10 and 20 ALD cycles are estimated to be 2 nm and 4 nm, respectively. From this figure, it can be seen that the discharge capacity of bare cathode continues to decrease from 65.7 to 40.2 mA h g$^{-1}$ over 100 cycles. According to the previous discussions, such capacity fading can be mainly attributed to dissolution of Mn$^{2+}$ ions (eqn(2.1)), J-T distortion effect of Mn$^{3+}$ ions, and decomposition of electrolyte components on the electrode. In comparison to these coated cathodes, the bare cathode delivers higher initial capacities. This result is possibly attributed to the absence of insulating Al$_2$O$_3$ coatings, and existence of cracks in LiMn$_2$O$_4$ particles that enlarges their surface area for Li-ion intercalation and deintercalation process. During discharging, a Li-ion concentration gradient is developed from the surface to the center of LiMn$_2$O$_4$ crystals, which is favorable for the formation of tetragonal Li$_2$Mn$_2$O$_4$ on the surface.
Figure 2.5 Cycling performances of (a) bare LiMn$_2$O$_4$ cathode, cathodes coated with Al$_2$O$_3$ ALD using (b) 20 ALD cycles and (c) 10 ALD cycles. These samples are cycled at a current density of 300 mA g$^{-1}$ over the voltage range of -0.3~0.8 V.

of the crystal [34]. The new phase leads to J-T distortion which induces micro strains on the surface during charging and discharging to originate new tiny cracks that accelerate the dissolution of Mn$^{2+}$ ions [34]. Consequently, the specific capacity of bare LiMn$_2$O$_4$ cathode continues to decline, along with slow electrolyte degradation.

On the other hand, Al$_2$O$_3$-coated cathodes exhibit much better capacity retention. Though thin insulating Al$_2$O$_3$ film leads to lower initial discharge capacities of coated cathodes compared to the bare sample, their capacities after long-time cycling are apparently higher than that of the bare cathode. It can be seen from Figure 2.5 that the cathode coated with Al$_2$O$_3$ ALD using 10 ALD cycles delivers an initial capacity of 43.7 mA h g$^{-1}$; however, the capacity increases and gradually becomes higher than that of the bare cathode starting from the 18th cycle, with a capacity of 53.7 mA h g$^{-1}$ at the 100th cycle. The cathode coated with Al$_2$O$_3$ ALD using 20 ALD cycles delivers an initial capacity of 24.9 mA h g$^{-1}$; its capacity also increases initially and exceeds the capacity of bare cathode starting from the 44th cycle with a capacity of 48.7 mA h g$^{-1}$ at the 100th cycle. These results demonstrate that surface modification by Al$_2$O$_3$ ALD coatings can enhance cycling performances of LiMn$_2$O$_4$ cathodes. Although the ALD coatings (< 10 nm thick) here are much thinner than the oxide coatings (50~1000 nm thick) synthesized via wet chemistry methods as reported in literature [9, 34, 35, 55]. The effect of ALD coatings is in good agreement with previous reports which showed that LiMn$_2$O$_4$ coated with oxides exhibited better cycling performance than bare LiMn$_2$O$_4$ over 100 cycles [56, 57]. Detailed work is introduced in next chapter to incorporate the ALD coated cathodes into button/coin cells with high-purity Li metal as anode and LiPF$_6$ as electrolyte, for optimizing the thickness of Al$_2$O$_3$ ALD coatings for full battery cells with best cycleability and highest capacities, and for much more fundamental surface/interface studies.

Furthermore, the effect of ALD coatings on the cycleability of LiMn$_2$O$_4$ cathodes is dependent on the thickness of ALD coatings, which can be controlled precisely by varying
ALD growth cycles. For example, LiMn$_2$O$_4$ cathode coated with Al$_2$O$_3$ ALD using 10 ALD cycles shows higher capacities and better cycleability than the cathode coated with Al$_2$O$_3$ ALD using 20 ALD cycles, due to reduced surface resistance of thinner Al$_2$O$_3$ coating. The coated cathodes using less than 10 ALD cycles or more than 20 cycles are also fabricated, which showed worse electrochemical performances than the previous two. Thus, it could be predicted that an optimal number of ALD growth cycles is between 10 and 20. If the oxide coating is too thin, it may fail to protect the cathode material over long electrochemical cycling; if the oxide coating is too thick, the capacities of the cathode material may be reduced because the oxide coating has higher electronic resistance and higher diffusion resistance for lithium ions. In addition, it is interesting to note that capacities of coated cathodes initially increase then decrease, different from capacities of bare cathode. The initial increase in capacity can be ascribed to partial dissolution of thin Al$_2$O$_3$ film into the electrolyte. Hence, Li-ion transfer between the active material and electrolyte is facilitated.

Figure 2.6 Charge-discharge curves (measured at a current density of 300 mA g$^{-1}$) and initial cyclic-voltammogram curves (measured at a scan rate of 0.1 mV s$^{-1}$) of different samples: (a-b) bare cathode and (c-d) cathode coated with 20 Al$_2$O$_3$ ALD layers.

![Figure 2.6](image_url)
To check whether there is dissolution of Al$_2$O$_3$ coating during electrochemical cycling, a coated cathode with much thinner ALD coating via 4 ALD cycles is fabricated. The coated cathode is electrochemically cycled for 100 cycles and is then examined by XPS. XPS analysis revealed that there is no Al element on the surface of this cycled sample, indicating dissolution of Al$_2$O$_3$ coating. As the initial capacities of the coated cathodes using 10 or 20 ALD growth cycles increase to a certain point and electrochemical cycling proceeds, dissolution of manganese and formation of new phases consumes LiMn$_2$O$_4$, which prevents the capacity from further increasing and the capacity starts to decrease. However, coated cathodes are better protected due to Al$_2$O$_3$ coverage, and thus deliver capacity values higher than that of bare cathode after 100 cycles.

Figure 2.6 shows the charge-discharge curves and cyclic voltammetric (CV) curves of bare cathode and coated cathode with 20 Al$_2$O$_3$ ALD layers. Apparently, the bare cathode shows capacity fading during cycling, while capacity of coated cathode initially increases then decreases. The results also confirm that thin Al$_2$O$_3$ coatings are able to enhance cycling stability of LiMn$_2$O$_4$ cathodes. However, such improvement is undermined gradually due to the loss of LiMn$_2$O$_4$, and dissolution of Al$_2$O$_3$. It can also be observed that two potential plateaus exist in the charge or discharge profiles, corresponding to a two-stage reversible intercalation and deintercalation process of Li ions. These results are in good agreement with previous reports in literature [34, 58]. Moreover, this phenomenon can be clearly seen from the first cyclic voltammetric profiles of the two cathodes. In comparison with the CV curve of bare cathode, the CV curve of coated cathode shows two less distinct oxidation current peaks at higher potential, and two less distinct reduction current peaks at lower potential, indicating occurrence of high polarization at the cathode induced by low electronic conductivity of Al$_2$O$_3$ film on the surface [3, 59].

2.4 Summary

In this chapter, it is discussed that ultra-thin and highly-conformal Al$_2$O$_3$ coatings are deposited on the surfaces of LiMn$_2$O$_4$ cathodes via ALD. The Al$_2$O$_3$ coating protects cathode material and thus alleviates the severe dissolution of manganese ions into electrolyte; the coating also reduces decomposition of electrolyte at the cathode. As a result, LiMn$_2$O$_4$ cathodes coated with Al$_2$O$_3$ ALD films show significantly enhanced cycling performances compared to the bare cathode. Moreover, cycling performances of coated cathodes can be optimized simply by turning coating thickness via varying ALD growth cycles. For example, LiMn$_2$O$_4$ cathode coated with 10 Al$_2$O$_3$ ALD layers shows much better cycling performance compared to cathode coated with 20 ALD cycles, because a thicker Al$_2$O$_3$ coating causes high polarization and increases resistance of electrode. This work can also be generalized to other electrode materials and a wide variety of surface coatings, for significant improvement of battery cycleability.

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CHAPTER 3. SUBNANOMETER-THIN Al$_2$O$_3$ SURFACE COATINGS FOR ENHANCED ELECTROCHEMICAL PERFORMANCES OF NANOSIZED LiMn$_2$O$_4$ IN FULL BATTERY CELLS*

3.1 Introduction

In Chapter 2, the concept is proved that nanosized-thin Al$_2$O$_3$ ALD coatings can be used to significantly enhance cycling stability of micro-sized LiMn$_2$O$_4$ by in air testing half batteries containing the ALD-coated cathodes. This project describes a much more comprehensive study by integrating the ALD-coated LiMn$_2$O$_4$ cathodes into full batteries (coin cells) for long electrochemical cycling, and optimizing the ALD coating thickness for maximizing the battery performance. The LiMn$_2$O$_4$ particles are in nano size here, with much larger surface area for Li-ion intercalation. Besides, the nanosized particle allows very shorter diffusion path, favorable for capacity improvement and rate capability [1, 2]. To optimize the coating, LiMn$_2$O$_4$ cathodes are assembled into coin (or button) cells. Compared to cylindrical cells and pouch cells, the coin cells have a simpler structure composed of anode cap, gasket and spring, anode material, separator, cathode material and cathode can, and its fabrication process is simplest, which thus is always used to assemble new cathode and anode materials for investigations. The coin cells produced in this work is much similar to commercial Li-ion button cells, and the result obtained is meaningful for renewing current cathode fabrication process to achieve better LiMn$_2$O$_4$-based LIBs with longer cycle life. The coins cells in this project have the following big differences from Li-ion half cells introduced in chapter 2:

1) Electrode materials and their processing procedures. The anode material is pure lithium discs fitting for coin cells, with a theoretical capacity of 3860 mA h g$^{-1}$, greatly larger than the theoretical capacity (148 mA h g$^{-1}$) of LiMn$_2$O$_4$. This big discrepancy ensures to precisely measure the specific capacity of nanosized LiMn$_2$O$_4$ without anode influence. Secondly, Li anode serves both a reference electrode and a counter electrode, minimizing errors from cell configuration, with respect to the half-cell structure shown in Figure 2.1c. Finally, the way of spreading cathode materials on Al foil is commonly used in commercial batteries in industry and simulator cells in labs, making the results more comparable to other groups’ reports.

2) Electrolyte composition. The electrolyte used is commercial for LIBs, and its chemical composition is optimized and thus errors from the electrolyte are highly reduced, such as self-degradation. One of the electrolyte compositions is LiPF$_6$, with very higher conductivity than LiClO$_4$ in the same solvents [3]. In addition, a mixture of solvents here (ethylene carbonate, dimethyl carbonate and diethyl carbonate) allows the electrolytes not only to have excellent conductivity, but also to possess good stability during battery use.

3) Assembly process. It is known that a trace of water in the LIBs is extremely harmful for cell performance, since the water can react with the salt LiPF$_6$ to generate corrosive HF. The reaction is described by this equation:

$$\text{LiPF}_6 + 4\text{H}_2\text{O} \rightarrow \text{LiF} + \text{H}_3\text{PO}_4 + 5\text{HF}$$

(3.1)

HF then reacts with active materials (LiMn$_2$O$_4$, LiCoO$_2$, etc) at cathode and causes a loss of

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Li-ion sources. It is also understood from eqn (3.1) that electrolytes degrade due to present of trace water inside. Water also involves some other side reactions in LIBs, yielding insoluble solids (Li$_2$O, Li$_2$CO$_3$, etc) precipitating at cathode that hinders Li-ion transfer, and even gases (CO$_2$, O$_2$, etc) accumulating in the cell that causes some safety issues. Therefore, the coin cell assembly in this work is conducted in high-purity Ar-gas protective environment, and all the cell part is necessarily dried or cleaned to eliminate water. Together with commercially-used separator to prevent direct contact between the anode and cathode, all the cell configuration and processing procedures aims to ensure maximum performance of cathode materials.

In this chapter, various subnanometer-thin ($\leq 1.2$ nm) Al$_2$O$_3$ coatings are deposited by ALD directly on LiMn$_2$O$_4$ (nanosized)/carbon black composite cathodes. The cathode is assembled into coin cells for electrochemical measurements. Cell performance is compared to clarify the best coating thickness for nanosized-thin LiMn$_2$O$_4$ as cathode in LIBs.

3.2 Experimental

Aluminum sheets (Alfa Aesar, 99.997%) are first cleaned by sonicating in ethanol and dried in air. A slurry is made from mixture of LiMn$_2$O$_4$ powder (MTI Corporation, 98%), carbon black (CB, Alfa Aesar, 99.5%), and poly(vinylidene fluoride) (PVDF, Alfa Aesar) in a weight ratio of 80:10:10. The slurry is then coated on the Al sheet using the blade-casting method, followed by heating in air at 80 $^\circ$C for 1 hour and in vacuum at 120 $^\circ$C for 12 hours, to produce LiMn$_2$O$_4$ composite cathodes. Afterward, the cathodes are pressed by a pressing machine (MTI Corporation) with a pressure of 10 MPa for 30 seconds, and then cut into disks with a diameter of 19 mm. Masses of LiMn$_2$O$_4$ cathodes are about 20 mg.

Depositions of Al$_2$O$_3$ ALD coatings on the LiMn$_2$O$_4$ cathodes or particles are carried out in a Savannah 100 Atomic Layer Deposition system (Cambridge NanoTech Inc., USA). The precursors used for Al$_2$O$_3$ ALD are trimethylaluminum (TMA, SAFC Hitech) and deionized water. The vapors of the two precursors are alternately carried by N$_2$ gas at a flow of 5 sccm into a reaction chamber where the temperature is set at 120 $^\circ$C for the Al$_2$O$_3$ ALD. The detailed deposition process and reactions are described in Figure 2.1c.

The crystallographic structure of as-received LiMn$_2$O$_4$ powder is determined by X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu K$_\alpha$ radiation operated at 30 kV and 15 mA with a scan rate of 2$^\circ$/min. Scanning electron microscope (SEM, Quanta 3D FEG) is used to characterize the morphology of LiMn$_2$O$_4$ powder and cathodes. The Al$_2$O$_3$ ALD coating on LiMn$_2$O$_4$ particles is observed by a high-resolution transmission electron microscope (HR-TEM, JEM-2010, JEOL LTD.). Chemical composition of cathodes is analyzed by an X-ray photoelectron spectrocope (XPS, AXIS 165, Kratos Analytical Ltd.) with an AXIS 165 spectrometer from Kratos Analytical LTD by using a twin-anode Al K$_\alpha$ (1486.6 eV) X-ray source. All the XPS spectra are calibrated according to the binding energy of the C1s peak at 284.8 eV.

Two-electrode CR2032-type coin cells (Figure 3.1b) is assembled to investigate the electrochemical behaviors of LiMn$_2$O$_4$ cathodes used as a working electrode. Lithium foils (Sigma-Aldrich, 99.9%) serves as both the counter and reference electrode. The two electrodes are separated by a porous Celgard-2320 separator composed of 20 $\mu$m thick polypropylene (PP)/polyethylene/PP trilayer film. The commercial electrolyte from MTI Corporation is composed of lithium hexafluorophosphate (LiPF$_6$, 1 mol/L) dissolved in a mixed solvent of...
ethylene carbonate, dimethyl carbonate and diethyl carbonate (1:1:1 volume ratio). All the CR2032 coin cells are assembled in an argon-filled glove box (OMNI-Lab system, Vacuum Atmosphere Co.) (Figure 3.1a). The cyclic voltammetry testing is performed on a CHI electrochemical analyzer (Model 605C, CH Instruments, Inc). The galvanostatic charge-discharge measurements are carried out using an 8-channel battery analyzer (MTI Corporation) in a potential range between 3.4 V and 4.5 V (vs. Li/Li⁺) under a specific current of 300 mA g⁻¹ (2.5 C). In summary, Al₂O₃ ALD coatings are deposited on LiMn₂O₄ particles for XRD, TEM and SEM characterizations, and deposited on LiMn₂O₄ composite cathodes for XPS surface composition analysis and electrochemical measurements.

Figure 3.1 (a) Argon-filled glove box with extremely low oxygen and moisture level (≤ 1 ppm) inside for coin cell assembly, (b) assembled CR2032-type coin cells and their initial open-circuit voltage.
3.3 Results and Discussion

Figure 3.2 presents the XRD pattern of as-received LiMn$_2$O$_4$ powder. All the diffraction peaks are indexed to a cubic spinel structure with a space group Fd-3m (JCPDS 35-0782). In this crystal, oxygen ions in 32e sites form a cubic close packed lattice, which accommodates manganese ions (Mn$^{4+}$ and Mn$^{3+}$) in octahedral 16d sites and lithium ions in tetrahedral 8a sites. The adjacent vacant octahedral 16c sites provide a three-dimensional pathway that allows lithium ions to diffuse into and out of LiMn$_2$O$_4$ crystal easily [4]. The to-and-fro motion of lithium ions induces Li-poor or Li-rich local regions on the surface of LiMn$_2$O$_4$ particles during charge/discharge, yielding the origination of Li$_x$Mn$_2$O$_4$ ($0 \leq x \leq 2$). It is reported that the non-stoichiometric spinel crystals could lead to formation of inactive tetragonal Li$_2$Mn$_2$O$_4$ (space group I4$_1$/amd), under excessive discharge below 3.0 V or high rate conditions above 3.0 V [4]. During this phase evolution, a large crystallographic (J–T) distortion (16% change in the c/a ratio and 6.5% increase in cell volume) occurs, leading to micro-strains or cracks on the surface of LiMn$_2$O$_4$, and consequent capacity loss. In addition, new phases, such as λ-MnO$_2$ and rock salt phase (Li$_2$MnO$_3$), may appear after electrochemical cycling [5]. It is noted that XRD pattern of LiMn$_2$O$_4$ particles coated with Al$_2$O$_3$ ALD films (8 Al$_2$O$_3$ ALD layers) (Figure 3.2b) shows no difference from that of bare LiMn$_2$O$_4$ particles. Eight Al$_2$O$_3$ ALD layers are deposited onto LiMn$_2$O$_4$ particles for XRD analysis, since Al$_2$O$_3$ ALD coatings deposited onto LiMn$_2$O$_4$ cathodes for electrochemical measurements do not exceed 8 ALD layers as presented in this paper later.

![Figure 3.2 XRD patterns of (a) as-received LiMn$_2$O$_4$ powder and (b) powder coated with 8 Al$_2$O$_3$ ALD layers.](image)

To investigate the Al$_2$O$_3$ ALD coating and obtain its growth rate, Figure 3.3 presents high-resolution TEM images of primary LiMn$_2$O$_4$ particles coated with relatively thin and thick Al$_2$O$_3$ ALD films using 10 or 50 ALD growth cycles (10 or 50 ALD layers). It can be seen that both the films are conformally coated on the surface of the LiMn$_2$O$_4$ particle. The average film thickness is estimated to be ~7.5 nm for 50 ALD layers, corresponding to a ALD growth rate of 1.5 Å per cycle (layer). This growth rate is higher than the rate of 1.0 Å per cycle for atomic layer deposition of Al$_2$O$_3$ on flat substrates as reported in literature [6].
In this work, the Al₂O₃ ALD film is deposited on particles and there is less hindrance from neighboring molecules in the adsorption step during the film growth on curved surface of particles. Thus the ALD growth on particles is faster than ALD growth on flat substrates, leading to higher growth rate [7]. LiMn₂O₄ primary particle coated with ultrathin Al₂O₃ film (10 Al₂O₃ ALD layers) also confirms the formation of ALD film on the surface of LiMn₂O₄, and various ultrathin ALD coatings are deposited onto LiMn₂O₄ cathodes for electrochemical measurements later on.

Figure 3.3 High-resolution TEM images of nano-sized LiMn₂O₄ primary particles coated with (a) 10 and (b) 50 Al₂O₃ ALD layers.

In order to confirm the Al₂O₃ deposition on LiMn₂O₄ cathodes, XPS analysis is used to examine the surface of bare LiMn₂O₄ cathode and cathode coated with 6 Al₂O₃ ALD layers. It should be noted that the cathode material film, with a thickness of ~30 µm, is prepared on clean and high-purity silicon wafers instead of Al disks. Figure 3.4 displays the Al2p XPS spectrum taken from the ALD coated LiMn₂O₄ cathode. In this figure, the Al2p peak at a binding energy of 74.8 eV is conformed to Al-O chemical bond of Al₂O₃, indicating the Al₂O₃ on the surface of the cathode. In contrast, Al element is not detected on bare cathode.

Figure 3.4 Al2p XPS peak taken from LiMn₂O₄ cathode coated with 6 Al₂O₃ ALD layers.
To further investigate the conformality of ALD coatings, morphological features of LiMn$_2$O$_4$ particles and ALD-coated particles are characterized by SEM. Figure 3.4a and b present SEM images of bare LiMn$_2$O$_4$ particles at low and high magnifications, respectively. It can be seen that LiMn$_2$O$_4$ consists of agglomerates (secondary particles) with a size range of 5 – 25 µm as shown in Figure 3.4a, while each agglomerate is composed of numerous primary particles with a uniform size distribution of ~220 nm as shown in Figure 3.4b. SEM is also performed on nano-sized LiMn$_2$O$_4$ particles coated with 50 Al$_2$O$_3$ ALD layers (Figure 3.4c and d) and it is observed that the shape and morphology of ALD-coated LiMn$_2$O$_4$ particles are almost identical to bare particles, suggesting that the ALD coating is highly conformal and preserve the morphology of bare particles. It should be noted that the samples shown in the HR-TEM images in Figure 3.3 are ALD-coated primary particles (nano-sized); the TEM sample is prepared via ALD coating directly on LiMn$_2$O$_4$ powder (agglomerates of primary particles) followed by vigorous sonication to well disperse these primary particles. Herein, the ALD technique demonstrates its ability to penetrate mesoporous structure and to coat ultrathin and highly-conformal coatings onto individual primary particles. As shown in Figure 3.4b, the gaps between LiMn$_2$O$_4$ primary particles are at nanometer scale, making it

Figure 3.5 SEM images of (a) bare LiMn$_2$O$_4$ agglomerates (secondary particles) shown at low magnification and (b) at high magnification, and LiMn$_2$O$_4$ agglomerates (secondary particles) coated with 50 Al$_2$O$_3$ ALD layers shown (c) at low magnification and (d) high magnification.
difficult to deposit complete and conformal coatings on primary particles via commonly-used wet chemistry method, while conformal coating on primary particles can be formed by ALD.

Figure 3.6 summarizes cycling behaviors of bare LiMn$_2$O$_4$ cathode and Al$_2$O$_3$-coated cathodes cycled at a specific current of 300 mA g$^{-1}$ in a voltage range of 3.4 – 4.5 V vs. Li/Li$^+$. The three coated cathodes are coated with 4, 6 and 8 Al$_2$O$_3$ ALD layers, corresponding to film thickness of 0.6 nm, 0.9 nm and 1.2 nm, respectively. From this figure, it can be seen that the initial discharge capacities of bare cathode and cathodes coated with 4 and 6 Al$_2$O$_3$ ALD layers are quite close, ranging from 100.6 mA h g$^{-1}$ to 105.6 mA h g$^{-1}$. However, the initial capacity of the cathode coated with 8 Al$_2$O$_3$ ALD layers is appreciably lower (~75 mA h g$^{-1}$) than bare cathode, because an insulating Al$_2$O$_3$ ALD coating with a thickness exceeding 1 nm significantly reduces the electronic conductivity of active material and results in slower charge-discharge kinetics and appreciable capacity drop [8]. It is noted that the electronic conductivity of Al$_2$O$_3$ ($< 10^{-14}$ S cm$^{-1}$) is much lower than that of spinel LiMn$_2$O$_4$ (2 × 10$^{-5}$ – 5 × 10$^{-5}$ S cm$^{-1}$) [9]. At the second electrochemical cycle, the discharge capacities of all four samples increase more or less, which is resulted from the loss of lithium ions in side reactions (e.g. electrolyte decomposition) and the formation of solid-electrolyte-interface (SEI) film in the first cycle. Afterwards, the capacity of bare cathode declines to 78.6 mA h g$^{-1}$ at the 100th electrochemical cycle. This capacity fading can be attributed to dissolution of manganese ions (Equation 1) and J–T distortion effect. Under discharging at a high current rate, a Li-ion concentration gradient is developed from the surface to the center of LiMn$_2$O$_4$ particles, which facilitates the origination of inactive Li$_2$Mn$_2$O$_4$. J–T distortion occurs simultaneously, which induces microstrains in the particles and possibly causes small cracks [10]. These cracks damage the protective SEI film and accelerate the dissolution of Mn$^{2+}$ ions. Moreover, the successive electrolyte degradation may be involved in the capacity loss of bare LiMn$_2$O$_4$ cathode as well. As shown in Figure 3.6, all the Al$_2$O$_3$-coated cathodes show enhanced cycling performances and deliver higher final capacities than bare cathode after 100 electrochemical cycles. Among them, the cathode coated with 6 Al$_2$O$_3$ ALD layers demonstrates the best cycleability and delivers the highest final capacity of 96.5 mA h g$^{-1}$ at

![Figure 3.6](image-url)  

Figure 3.6 Specific discharge capacities vs. cycle number for bare LiMn$_2$O$_4$ cathode and three cathodes coated with 4, 6, and 8 Al$_2$O$_3$ ALD layers, cycled at a current of 300 mA g$^{-1}$. 

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the 100th cycle, significantly higher than final capacity of bare cathode (78.6 mA h g⁻¹). The final capacity of the cathode coated with 6 Al₂O₃ ALD layers remains 95.1% of its initial capacity, while the final capacity of bare cathode is only 78.1% of its initial capacity. To study the change of Al₂O₃ surface coating during electrochemical cycling, XPS is used to examine the surface of the cathode coated with 6 Al₂O₃ ALD layers before and after electrochemical cycling. It is found that atomic fraction of Al [Al/(Al+Mn)] of the coated cathode before cycling is 0.69 and is 0.23 after 100 charge-discharge cycles. This result indicates that there is partial dissolution of Al₂O₃ coating during electrochemical cycling, but this dissolution is less severe than other coated-cathodes reported in literature [8].

On the other hand, the cathode coated with a thinner coating (4 Al₂O₃ ALD layers, 0.6 nm) exhibits less satisfying cycleability delivering a final capacity of 85.6 mA h g⁻¹ at the 100th cycle, because the coating is too thin to effectively protect the active material. For the cathode coated with a thicker coating (8 Al₂O₃ ALD layers, 1.2 nm), the initial capacities are significantly lower than bare cathodes, due to an overly thick insulating Al₂O₃ ALD coating as mentioned above. It can also be seen that the capacity of the cathode coated with 8 Al₂O₃ ALD layers increases gradually at the beginning and exceeds the capacity of bare cathode at the 50th cycle, then decreases slowly, reaching a final capacity of 81.5 mA h g⁻¹ at the 100th cycle. Such initial increase in capacity is likely ascribed to formation of a solid solution layer at the interface of LiMn₂O₄ and Al₂O₃ ALD coating as Al₂O₃ ALD coating is chemically bonded to LiMn₂O₄, which delivers slightly reduced charge transfer resistance during initial electrochemical cycles [11,12]. Partial dissolution of Al₂O₃ coating into the electrolyte may also occur [13], which improves the electronic conductivity of LiMn₂O₄ and thus leads to a temporary increase in the capacity.

These results prove that ALD coatings with a thickness less than 1 nm can remarkably enhance the cycleability of cathode material. In contrast, most surface coatings for lithium transition metal oxides reported in literature are as thick as 10–1000 nm [11]. These ALD-coated cathodes show comparable or even better cycling stability than those cathodes coated with much thicker coatings reported in literature, because the ALD coating is dense, robust, complete, pin-hole free, highly-conformal, long-lasting, and thus an ultrathin coating is able to effectively protect the cathode material. First, the Al₂O₃ coating scavenges HF formed by the reaction of a trace amount of H₂O and LiPF₆ in the electrolyte and thus alleviates the dissolution of manganese ions. Secondly, the Al₂O₃ ALD film can be converted to a solid electrolyte or glass state during Li-ion intercalation process [14, 15]. Liu et al. used in-situ TEM technique and observed the evolution of ultrathin amorphous Al₂O₃ surface layer (thickness 4 – 5 nm, coated on thin Al nanowires) during lithiation/delithiation cycles [16]. The Al₂O₃ layer turns into a Li-Al-O glass layer with high ionic conductivity and low electronic conductivity after intercalating lithium ions. This glass layer can prevent the direct contact between active material and electrolyte, and thus reduces the decomposition of electrolyte components [1, 14]. Also, the glass layer is mechanically robust and can serve as a mechanical constraint to prevent the lattice of electrode material from large volume change during charging/discharging processes [16, 17].

In addition, the results indicate that the protective effect of ALD coatings on the LiMn₂O₄ cathodes is dependent on the thickness of surface coatings and can be optimized by precisely controlling the thickness of ALD coatings. If an Al₂O₃ ALD coating is too thin, it cannot
protect the cathode material effectively over long electrochemical cycling, as observed for the 
LiMn$_2$O$_4$ cathode coated with 4 Al$_2$O$_3$ ALD layers. On the other hand, an overly thick Al$_2$O$_3$
ALD coating will reduce the electronic conductivity of cathode, resulting in lower capacities 
of cathode. Fortunately, ALD allows precise control of coating thickness at atomic scale and 
thus makes it ideal for accurately tuning the thickness of ALD coatings for ultimate 
optimization of Li-ion battery performances.

The cyclic voltammograms (CV) of bare cathode and cathode coated with 6 Al$_2$O$_3$ ALD 
layers are shown in Figure 3.7. Two pairs of oxidation current peaks (4.08 V and 4.20 V) and 
reduction current peaks (3.93 V and 4.06 V) for both cathodes are distinct, revealing typical 
characteristics of two-stage reversible phase transformation of the spinel LiMn$_2$O$_4$. In 
addition, the positions of the peaks for Al$_2$O$_3$-coated cathode are the same as those for bare 
cathode, which demonstrates that ultrathin Al$_2$O$_3$ ALD coating (6 ALD layers, ~0.9 nm) 
rarely undermines the electronic conductivity of LiMn$_2$O$_4$. It should be noted that the CV 
curve of a cathode coated with thick Al$_2$O$_3$ film will have appreciable peak position shift 
compared to that of bare cathode, due to the insulating nature of Al$_2$O$_3$ and reduced electronic 
conductivity of cathode. LiMn$_2$O$_4$ cathodes coated with 20 Al$_2$O$_3$ ALD layers are fabricated, 
and it is found that the coating caused high polarization evidenced by peak shifting in its CV 
plot [13]. Similar phenomenon is also observed in Se-Hee Lee group’s work [8].

Figure 3.8 illustrates the charge-discharge plots of bare cathode and cathode coated with 6 
Al$_2$O$_3$ ALD layers. Apparently, both cathodes show two voltage plateaus in charge and 
discharge profiles, which are compatible with the two oxidation and reduction peaks in their 
C-V plots above. These voltage plateaus correspond to a two-stage reversible intercalation/
decintercalation process of lithium ions in LiMn$_2$O$_4$. The coated cathode delivers much higher 
discharge capacity and capacity retention after 100 cycles than the bare one. Besides, it is 
found that the oxidation plateau of the bare cathode moves up distinctly and its reduction 
plateau moves down over 100 electrochemical cycles, while the coated cathode almost shows 
no shifting in its oxidation and reduction plateaus over 100 cycles, indicating that the 
ultrathin Al$_2$O$_3$ ALD coating greatly improves the structural stability of LiMn$_2$O$_4$ during the 
electrochemical cycling.

Figure 3.7 Cyclic-voltammetric curves of (a) bare LiMn$_2$O$_4$ cathode and (b) cathode coated 
with 6 Al$_2$O$_3$ ALD layers, cycled between 3.3 V and 4.6 V vs. Li/Li$^+$. 

Figure 3.8 Charge-discharge plots of (a) bare LiMn$_2$O$_4$ cathode and (b) cathode coated 
with 6 Al$_2$O$_3$ ALD layers, showing two voltage plateaus in charge and discharge profiles.
Figure 3.8 Galvanostatic discharge-charge curves of (a) bare LiMn$_2$O$_4$ cathode and (b) cathode coated with 6 Al$_2$O$_3$ ALD layers, cycled at a specific current of 300 mA g$^{-1}$ between 3.4 V and 4.5 V vs. Li/Li$^+$. 

3.4 Summary

In this chapter, subnanometer-thin and highly-conformal Al$_2$O$_3$ coatings are deposited on LiMn$_2$O$_4$ composite cathodes by using the atomic layer deposition method, for enhanced electrochemical performances of cathode materials. Thickness of Al$_2$O$_3$ ALD coatings can be tuned and precisely controlled by varying ALD growth cycles, with a growth rate of 1.5 Å per cycle in this study. All the ALD-coated cathodes demonstrate enhanced cycleability compared to bare cathodes. Among cathodes coated with ALD films of different thicknesses, LiMn$_2$O$_4$ cathode coated with 6 Al$_2$O$_3$ ALD layers (0.9 nm thick) shows the best cycling performance, demonstrating that it is facile to accurately tuning thickness of ALD coatings and thus optimize the electrochemical performances of ALD-coated cathodes simply via varying ALD growth cycles. The Al$_2$O$_3$ ALD coating alleviates dissolution of manganese ions into electrolyte by scavenging HF, and retards the electrolyte decomposition by isolating...
LiMn$_2$O$_4$ from the electrolyte. As a result, ALD-coated cathodes show significantly enhanced cycling performances compared to bare cathode. And lastly, the methods presented in this study can be generalized to other cathode materials and other coatings as long as the coatings can be fabricated via ALD.

### 3.5 References


CHAPTER 4. SYNTHESIS OF ANODIC TiO₂ NANOTUBE ARRAYS FOR APPLICATIONS AS ANODE MATERIALS IN RECHARGEABLE Li-ION CELLS*

4.1. Introduction

In the above two chapters, cathode materials (e.g. LiMn₂O₄) for rechargeable lithium-ion batteries (LIBs) and their surface modification ways are introduced. The cathode is a positive electrode with respect to the anode in a LIB. In order to achieve high-performance LIBs, the anode material also need meet some basic requirements described Chapter 1, such as high specific capacity and power density, properly high working potential and excellent electrochemical cycleability. After the invention of graphite as an anode material for commercial LIBs in 1991, a group of novel anode materials have been developed for LIBs with enhanced cell performance. Presently, nanotechnology involves in the synthesis of electrode materials, and thereby more and more nanostructured anode materials have been produced to achieve better-performance LIBs. The anode materials are generally classified into four categories:

(1) Carbon materials. Graphite is the most commonly used anode material in current commercially available LIBs. It is cheap, easy synthesized and processed, which a theoretical capacity of 372 mA h g⁻¹. However, the graphite has some limitations which hinder the development of new LIBs with higher operation voltages and larger power density. For example, lithium dendrites may appear in graphite-based LIBs and induce short-circuit or an explosion if exposed to air, because the potential for Li-ion intercalation into graphite is close to that of the Li/Li⁺ redox couple [1].

(2) Single metal or semiconductor. Silicon has extremely high theoretical capacity (4200 mA h g⁻¹), low cost and abundant source. However, a 400% volume variation of bulk Si electrodes during insertion/extraction processes collapses the structure of the electrode and cause huge capacity loss. Hence, various nano-sized silicon structures have been synthesized. For example, silicon nanowires (NWs) grown by Cui et al. directly on the metallic current collector substrate is integrated into the anode of a LIB, with much less volume change during charge-discharge process [2]. Tin (Sn) has a voltage of 0.3 V and Li/Sn alloy has a high specific capacity of 990 mA h g⁻¹, but drastic volume variation (> 300%) greatly limits their practical applications. Germanium (Ge) is a promising material for anode as well, thanks to its Li-ion transfer coefficient that is 400 times larger than that of silicon at room temperature.

(3) Metal (oxide)-carbon composites. Si-C composites deliver larger capacity than bare carbonaceous material (i.e. graphite), and better cycling performance than bare silicon electrodes. The reason is that the carbon material enhances the electronic conductivity of the anode, but also alleviates the drastic volume change of silicon. Si-C composites with a silicon/graphite/CNTs structure is prepared by a ball milling technique [3]. In the same way, the Sn-C composites deliver large charge-discharge capacity and excellent cycling performance when used as anode material in a LIB.

(4) Metal oxides and transitional-metal oxides. SnO₂ almost has twice capacity (781 mA h
than graphite as anode materials, but its volume changes drastically during cycling. One solution is to downsize SnO$_2$ into nano scale, and these nanosized SnO$_2$ is able to maintain considerable its charge-discharge capacities after long-term cycling. A second solution is to synthesize SnO$_2$-C composites or carbon-coated SnO$_2$. Cupric oxides (CuO) deliver good capacity retention capability. CuO materials have various morphologies for use as anode in Li-ion battery, such as nano cubes, nano spheres, nano rods and nano particles. Nickel oxides (NiO) are also used as an anode material in LIBs. It has various structures, such as nano walls, nano shafts and nano particles. Among these nano structures, NiO nano walls exhibit the best electrochemical performance with a capacity of ~680 mA h g$^{-1}$. Co$_3$O$_4$ has a theoretical Li-ion insertion/extraction capacity two times higher than that of graphite. Nanosized Co$_3$O$_4$ particles are prepared via a combination of chemical decomposition and a spray conversion process, which show a good reversible discharge capacity of 360 mA h g$^{-1}$ [4].

Semi-conducting TiO$_2$ is a kind of transitional-metal oxides that can be used in LIBs. It is a promising alternative to the graphite due to its high operation voltage or working potential (~1.75 V vs. Li/Li$^+$ redox couple), high safety and low self-discharge and excellent capacity retention during cycling. For instance, the high operation voltage of TiO$_2$ makes it possible to combine with novel cathode materials (LiCoPO$_4$ and LiCo$_{0.5}$Mn$_{1.5}$O$_4$) to achieve LIBs with high output voltages (5 V). In addition, the high chemical stability, low cost and non-toxicity of TiO$_2$ are also favorable for its broad applications in LIBs.

The electrochemical performance of TiO$_2$ mainly depends on its morphology, structure and phase composition. It is reported that various polymorphs of TiO$_2$ display Li-ion insertion/deinsertion properties. For example, Reddy et al. discovered that a maximum of 0.95 Li/TiO$_2$ (molar ratio) can be inserted into brookite TiO$_2$ nanocrystallites with a size of 10 nm and 0.23 Li/TiO$_2$ into brookite nanocrystallites with a size of 33 nm [5]. Noailles et al. discovered that hollandite-type TiO$_2$ shows relatively low Li-ion intercalation capacity [6]. On the other hand, nanostructured B-phase TiO$_2$ shows a large capacity with a theoretical value of 335 mA h g$^{-1}$ and excellent cycleability when used as anode material for LIBs [7, 8]. Additionally, anatase and rutile TiO$_2$ are potential anode materials for rechargeable Li-ion batteries as well.

The reaction for Li-ion insertion/deinsertion into anode TiO$_2$ can be written as [9]:

$$\text{TiO}_2 + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{TiO}_2$$  \hspace{1cm} (4.1)

Figure 4.1 Li-ion insertion and deinsertion processes on crystal structure of anatase TiO$_2$. 

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Both anatase phase and rutile phase have tetragonal structures, which are described by the space group I41/amd and P42/mnm, respectively. In such a structure, a Ti ion is surrounded by a distorted oxygen octahedron, and numerous vacant octahedral and tetrahedral sites exist between these octahedrons. Li ions can be accommodated in these vacant sites. It should also be noted that Li-ion insertion can lead to a phase transition from a Li-poor (tetragonal) phase to a Li-rich (orthorhombic, cubic spinel, cubic rocksalt, etc.) phase [10, 11].

Despite fast Li-ion transfer inside, TiO\(_2\) is limited by its low electronic conductivity (~10\(^{-12}\) S/cm) that leads to poor cycling stability. One solution is to combine TiO\(_2\) with carbonaceous materials. The TiO\(_2\)-carbon composite works as anode in LIBs and demonstrates enhanced kinetics of Li-ion insertion/extraction processes and increased electronic transfer coefficient. Fu et al. synthesized TiO\(_2\)-C core-shell composites and found that the carbon shells encase TiO\(_2\) cores and prevent agglomeration of TiO\(_2\) nanoparticles [12]. A hydrothermal method followed by heat treatment [13] has been used to produce a composite of TiO\(_2\) nanotubes and carbon materials in which nanosized carbon particles are dispersed in TiO\(_2\) matrix. This composite is a porous, with large specific surface area. The dispersed nanosized carbon helps to reduce the bulk resistance, SEI resistance and charge transfer resistance at the anode, and thus is able to maintain a high discharge capacity of ~138 mA h g\(^{-1}\) over 70 cycles.

Besides modification with carbon materials, various 1-D nanostructures are also beneficial to enhancement of cell performance of TiO\(_2\), because this structure allows faster Li-ion and electronic transfer inside. For example, since amorphous TiO\(_2\) delivers a high Li-ion diffusion coefficient [14], nanostructured amorphous TiO\(_2\) with large surface area has been fabricated, such as nanorods and nanotubes. These nanostructures not only provide large surface area for Li-ion insertion/deinsertion process, but also facilitate Li-ion and electron transport to greatly improve the cell performance. At the same time, much less volume change occurs (< 3%) in nanostructured TiO\(_2\) during electrochemical cycling, favorable for the stability of TiO\(_2\)-based LIBs. It is also confirmed that randomly-dispersed amorphous TiO\(_2\) nanotubes prepared via a hydrothermal method have been reported to deliver a discharge capacity of 168 mA h g\(^{-1}\) [15], while well-aligned TiO\(_2\) nanotubes exhibit a higher capacity than these disordered nanotubes. As a result, order 1-D nanostructures of TiO\(_2\), such as nanotubes, nanowires and nanorods are preferred for its battery applications.

There are many methods to fabricate 1-D TiO\(_2\) tubular structure. The anodic oxidation of Ti metal, a simpler and cheaper technique than common template-based approaches, is often adopted to produce self-ordered TiO\(_2\) nanotube arrays [16]. The metallic Ti beneath the TiO\(_2\) nanotube arrays directly functions as a current collector. More importantly, the growth of anodic TiO\(_2\) nanotube arrays is controllable: their morphology can be optimized by tuning preparation conditions, such as voltages (DC [17] or AC [18]), electrolyte composition and anodization time. For instance, different electrolyte compositions lead to three generations of anodic TiO\(_2\) nanotube arrays. The first-generation nanotubes only have a length up to 500 nm, due to the high rate of chemical dissolution of TiO\(_2\) in acid HF-based aqueous electrolytes where they are formed [16, 19, 20]. Schmuki et al. found that a reasonable pH gradient within the growing nanotube is very important to the formation of long anodic TiO\(_2\) nanotubes [21], and thus neutral fluoride-based aqueous solutions are utilized to grow TiO\(_2\) nanotubes with a length up to 6.4 \(\mu\)m [20, 22]. Afterwards, anhydrous glycerol is employed as a solvent in the electrolyte, yielding smooth TiO\(_2\) nanotubes of 7 \(\mu\)m long [23]. Herein,
more and more high-aspect-ratio TiO$_2$ tubes are produced with fluoride-containing organic electrolytes [24-26]. The most common one is ethylene glycol solutions with a small amount of NH$_4$F and H$_2$O [27-30], in which the formed TiO$_2$ nanotubes can be as long as 500 μm, and with good surface morphology [31].

According to the field-assisted dissolution model [32], anodic TiO$_2$ nanotube arrays result from competition between electrochemical etching process and chemical dissolution process on Ti. The two processes refer to three simultaneously occurring chemical reactions [33]: (1) field-assisted oxidation of Ti: Water molecules decompose near the metal and produce O$^{2-}$ ions and H$^+$ ions; the O$^{2-}$ ions then travel through an electrolyte-oxide interface to oxidize Ti. (2) field-assisted dissolution of titanium oxides: In the electric field, the Ti-O bond undergoes polarization and is weakened, promoting dissolution of the oxides. (3) chemical dissolution of titanium oxides: Herein, Ti$^{4+}$ ions cations become soluble hexafluorotitanium complexes [TiF$_6$]$^{2-}$ that go into the electrolyte, while free O$^{2-}$ anions transfer to the oxide-metal interface and react with Ti. In general, growth of anodic TiO$_2$ nanotube arrays is divided into three stages: (1) formation of an initial compact layer. Once a proper voltage is applied initially, water is decomposed fast at anode and Ti is oxidized fast to generate a compact oxide film (Figure 4.2a). (2) pit and pore formation. Some electrolyte species, especially F$^-$ ions, aggregate in regions with high surface energy (e.g. micro cracks) and selectively dissolve oxides there to start origination of tiny pits and pores in the compact film (Figure 4.2b and c). Afterwards, the pores develop towards metal substrate. Since formed oxide layer hinders O$^{2-}$ ion transfer, and thereby some metallic part between the pores survives (Figure 4.2d). Electric charges aggregate in the arising metallic portions to generate stronger local electric field, and further cause non-uniform surface energy distribution of the oxide layer. (3) cavity and tube formation. Again, the electrolyte species aggregate in regions with high surface energy and dissolve oxides faster to start origination of cavities between the pores, and turn the porous film into a tubular structure (Figure 4.2e and f). The tubes continue to grow in depth. When the etching rate of Ti equals the dissolution rate of tube tops, the tube length is unchanged.

![Figure 4.2 Growth process of anodic TiO$_2$ nanotube arrays: (a) formation of initial compact oxide layer, (b) pit formation inside, (c) pore formation inside, (d) pore development, (e) inter-pore cavity formation, (d) tube formation with inter-tube cavities.](image-url)
Based on the growth model above, ways are easily found to extend the tube length, such as increasing anodic voltages to enhance oxidation rate, decreasing water content in electrolytes to reduce dissolution rate, or prolong anodic time to allow sufficient growth of TiO$_2$ tube. For example, Ti substrate is secondly oxidized in ethylene glycol electrolytes with 0.3 wt% NH$_4$F and 5.0 vol% H$_2$O for 40 min and 50 min, which yields ordered TiO$_2$ nanotube arrays with a thickness of 5.35 µm and 8.07 µm, respectively (Figure 4.3). Clearly, these nanotubes have an open entrance, which shows an average outer diameter of ~140 nm.

![Image](a.png) ![Image](b.png) ![Image](c.png) ![Image](d.png)

Figure 4.3 Top and cross-sectional SEM images of amorphous TiO$_2$ nanotubes formed at 60 V in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O for (a-b) 40 min and (c-d) 50 min at room temperature.

Anodic TiO$_2$ nanotube arrays have drawn much scientific endeavor when they act as anode material in LIBs. Wang et al. has set up a LIB by incorporating TiO$_2$ nanotube arrays as the anode and ordered porous carbon as the cathode, which delivers an energy density of 25 Wh kg$^{-1}$ and a power density of 3000 W kg$^{-1}$ at a current-draining time of 30 s, twice higher than previous hybrid electrochemical cells [34]. Fang et al. found that the capacity of amorphous TiO$_2$ nanotube arrays is higher than that of anatase TiO$_2$ nanotubes arrays with identical morphological features, due to the faster Li-diffusion in amorphous TiO$_2$ [14]. Ortiz et al. also compared the capacities of 0.92-µm long amorphous and anatase TiO$_2$ nanotubes grown
on Ti foils, and found that at a rate of 5 μA cm⁻² the former deliver a capacity of 77 μA h cm⁻² in the first reversible discharge, while the latter show a capacity of 68 μA h cm⁻² [35]. Interestingly, 0.6 μm-long amorphous TiO₂ nanotubes formed on Ti-coated Si chips exhibit larger capacities of 89 μA h cm⁻² in the first discharge and 56 μA h cm⁻² over 50 cycles, suggesting that such electrode is compatible with IC technology and is a promising candidate for the fabrication of on-chip 2D micro-batteries [36]. Besides the phase composition, the morphology is a second factor affecting Li-ion intercalation properties of the material. Wei et al. produced amorphous TiO₂ nanotubes arrays with different pore size and wall thickness using voltages of 20~80 V, and thought such morphological differences as a critical reason for the discharge capacities of these nanotubes increasing with their anodic voltages [37]. Moreover, the influence of chemical composition on the Li-ion insertion performance of TiO₂ nanotube arrays is also an important issue. For example, the charge-transfer conductivity of anatase TiO₂ nanotube arrays can be enhanced by Ag coatings and an increase in the capacity of material occurs accordingly [38]. In the same sense, 1.1 μm-thick TiO₂ nanotube arrays annealed at 400 °C in CO gas have a larger initial discharge capacity (223 mA h g⁻¹) than those annealed in N₂ gas (163 mA h g⁻¹) at a current density of 320 mA g⁻¹ [39, 40].

As discussed above, a variety of routes has been proposed to improve the electrochemical performance of anodic TiO₂ nanotube arrays. However, few detailed research work has been reported hitherto on the relationship between tube length and energy storage of the material, though the tube length is a well-known factor that determines the specific surface area of TiO₂ nanotubes where the Li-ion insertion/deinsertion reactions occur. In addition, anatase TiO₂ nanotubes have some advantages over amorphous nanotubes, such as higher mechanical strength [41] and higher resistance to erosion of fluoride species, and thus the improvement in their capacity is also worth scientific effort. This chapter presents a study on synthesis and electrochemical characterization of TiO₂ nanotube arrays with various dimensions and phase compositions. The lengths and diameters of these nanotubes can be tuned by tailoring several preparation conditions. Heat treatment at elevated temperatures converts the amorphous TiO₂ nanotubes into nanotubes of pure anatase phase and nanotubes of mixed phases containing anatase and rutile crystallites. TiO₂ nanotube arrays show high thermal structural stability and there is no morphological change after the nanotube arrays are annealed at high temperatures. However, TiO₂ nanotubes of different phases show distinct electrochemical behaviors, and amorphous TiO₂ nanotubes deliver the highest discharge capacity and the best cycleability.

4.2 Experimental

The Ti foils (99.5 wt%) (10×10×0.25 mm³) in this study are purchased from Alfa Aesar. Prior to any electrochemical treatment, Ti foils are first chemically etched by immersing into a mixture of HF and HCl acid. The mixture ratio of HF: HCl: H₂O is 1:4:5 in volume. The foils are then degreased in acetone and rinsed by sonicating in deionized water. A two-electrode cell with a Pt mesh (23×14 mm²) as the counter electrode is assembled for electrochemical anodization (Figure 4.4a). Electrolytes are anhydrous ethylene glycol (EG) with 0.3 wt% NH₄F and 2~10 vol% H₂O. All the solutions are prepared from reagent grade chemicals and deionized water. During the anodizing process, a potential ramp from 0 V to 30 V or 60 V with a sweep rate of 1 V s⁻¹ is firstly conducted, and then the end voltage is maintained for 1~10 h. The voltage is supplied by a DC power supply with digital display
(Model 1623A, PK Precision). All the experiments are carried out at room temperature.

After completing the anodization, the samples are immediately rinsed in deionized water and dried in air. TiO₂ nanotube arrays are formed on both front side and back side of Ti foils. Subsequent heat treatments at 110 °C for 1 h, 480 °C for 3 h and 580 °C for 3 h are conducted on these nanotubes in air with heating and cooling rates of 4°C/min. A FEI Quanta 3D FEG scanning electron microscope (SEM) and a Hitachi S-3600N scanning electron microscope are used to characterize the morphology of TiO₂ nanotubes. The crystallographic structure of TiO₂ nanotube arrays is determined by an X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2°/min.

The electrochemical performance of TiO₂ nanotube arrays is investigated by experiments carried out in anhydrous propylene carbonate electrolytes containing 1 M LiClO₄. The TiO₂ nanotubes on the backside of Ti foils are scraped off prior to electrochemical measurements. A three-electrode electrochemical cell is constructed for chrono-potentiometric and cyclic voltammetric measurements (Figure 4.4b). The cell is consisting of TiO₂ nanotubes on the Ti foil as working electrode, Pt mesh as the counter electrode, and Ag wire inserted into AgNO₃ (0.1 M) alcohol electrolyte as the reference electrode. All the measurements are conducted using an electrochemical analyzer (Model 605C, CH Instruments. Inc.) at room temperature.

Figure 4.4 Illustration schematics showing experimental set-ups for (a) anodic oxidation of Ti, and (b) electrochemical measurements of TiO₂ nanotube arrays as anode material.

4.3 Results and Discussion

As we mentioned above, the morphologies of anodic TiO₂ nanotube arrays highly depend on preparation conditions, such as voltage, electrolyte composition and anodization time [42]. Figure 4.5 presents the SEM images of as-prepared TiO₂ nanotubes formed in EG electrolytes.
Figure 4.5 Top and cross-sectional SEM images of amorphous TiO$_2$ nanotubes formed at 30 V in EG electrolytes containing 0.3 wt% NH$_4$F and 10 vol% H$_2$O for (a-b) 1 h, (c-d) 4 h, (e-f) 10 h, and (g-h) at 60 V in EG electrolyte with 0.3 wt% NH$_4$F and 2 vol% H$_2$O for 3 h.
containing NH₄F and H₂O at voltages of 30 V and 60 V. These nanotubes are well-aligned with open ends on the top; they are perpendicular to the Ti substrate, with a high aspect ratio up to 158. The shape of the nanotubes resembles bamboos, with ridges on the surface. TiO₂ nanotubes formed by anodizing Ti in EG electrolyte with 10 % H₂O at 30 V for 1 h have an outer diameter of ~106 nm, a wall thickness of ~15 nm and a tube length of ~1.9 μm (Figure 4.5a and b). As the anodization time extends to 4 h, the outer diameter of formed nanotubes is ~125 nm; the wall thickness is ~15 nm; and the tube length is ~3 μm (Figure 4.5c and d). Anodization of Ti in the same electrolyte at 30 V for 10 h yields nanotubes with an outer diameter of 125 nm, a wall thickness of 15 nm and a tube length of 4.7 μm (Figure 4.5e-f). TiO₂ nanotubes with an outer diameter of ~158 nm and a length of ~25 μm can be obtained (Fig. 4.5g-h) at 60 V in the EG electrolyte with 2 vol% H₂O. Besides, it is found that identical TiO₂ nanotube arrays are grown on the front side and back side of the bare metal substrate. The nanotube arrays on the backside are removed before electrochemical testing. It is obvious that longer anodization time and higher voltages lead to longer nanotubes.

Figure 4.6 shows the XRD patterns of Ti substrate, TiO₂ nanotubes anodized at 30 V in EG electrolytes containing 0.3 wt% NH₄F and 10 vol% H₂O, and anodic TiO₂ nanotubes annealed at 110 °C for 1 h, 480 °C for 3 h and 580 °C for 3 h in air. The XRD patterns of Ti substrate and as-prepared nanotubes only have Ti diffraction peaks, such as the typical peak (101) at 2θ = 40.0°, which indicates that the as-prepared nanotubes are amorphous. This is in agreement with previous reports [43, 44]. TiO₂ nanotubes annealed at 110 °C for 1 h are also amorphous, as evidenced by their XRD pattern where anatase peaks or rutile peaks cannot be found. However, the heat treatment at higher temperatures can convert the amorphous nanotubes into crystalline ones. Metastable anatase crystallites are found to emerge at 480 °C, which is evidenced by its typical diffraction peaks (101) at 2θ = 25.2° and (200) at 2θ = 47.9°. The diffraction peaks of Ti substrate are also found in the XRD pattern of TiO₂ nanotube arrays annealed at 480 °C. Due to heat treatment at 580 °C, stable rutile phase appears in TiO₂.
nanotube arrays, which is shown by its representative diffraction peak (110) at 2θ = 27.5° in the XRD pattern of annealed TiO2 nanotube arrays. The anatase phase is also found in TiO2 nanotube arrays annealed at 580 °C. The intensity of anatase (101) peak is much higher than that of rutile (110) peak, suggesting that only a small portion of anatase crystallites transform to rutile phase at 580 °C resulting in TiO2 nanotube arrays of mixed phases.

Figure 4.7 shows the galvanostatic discharge/charge curves at a current density of 400 μA cm⁻² and cyclic voltammetric curves cycled between -0.6 V and -2.3 V for the three different TiO2 nanotube arrays with a tube length of 3 μm. The nanotubes on the back side of Ti foils after anodization are removed for these tests. The absence of voltage plateaus in the curves for amorphous TiO2 nanotubes (Figure 4.7a and b) is attributed to the considerable disordered structures and defects contained in them. The disordered structures and defects provide many sites for Li-ion insertion at relatively higher potential during discharging, and thus expand the potential range for Li-ion insertion reaction [14]. The shape of curves for crystalline TiO2 nanotubes (Figure 4.7c-f) is in accordance with those reported earlier for anatase TiO2 [35] and rutile TiO2 electrodes [45]. Voltage plateaus can be observed in the curves for crystalline TiO2 nanotubes, which correspond to Li-ion insertion into or deinsertion from the crystal matrix of anatase or rutile TiO2. In addition, the first discharge capacity of amorphous nanotubes (0.0912 mAh cm⁻²) is apparently higher than that of anatase nanotubes (0.0538 mAh cm⁻²) and nanotubes of mixed phases (0.0631 mAh cm⁻²) at the same current density of 400 μA cm⁻², thanks to the higher Li-ion diffusion coefficient in amorphous TiO2. The disordered structures and defects in amorphous TiO2 not only create large spatial channels for Li-ion diffusion, but also function as scattering sites for electron transport resulting in low electronic conductivity [14]. However, for the nanotubes which are not very long, the Li-ion diffusion coefficient plays a more important role in the cell capacity than the electronic conductivity of the material. Moreover, the Li-ion diffusion coefficient in rutile TiO2 is found to be larger than that in anatase by 4–5 orders of magnitude at room temperature [46], which may explain why TiO2 nanotubes of mixed phases has higher capacity than that of anatase nanotubes. In other words, the rutile crystallites in anatase nanotubes facilitate the Li-ion transportation in TiO2. It can be understood that the Li-ion insertion reaction occurs at the electrolyte-oxide interface on the anode. Large surface area is beneficial for TiO2 nanotube arrays to work as a medium that accommodates Li ions, because there are more sites for the Li-ion insertion/deinsertion reaction. Table 4-1 summarizes the electrochemical performance of different amorphous TiO2 nanotubes with various tube lengths at a current density of 400 μA cm⁻². Clearly, for the nanotubes on the single side (front side) of Ti foils, the first discharge capacity of nanotubes increases by 11.6 times as the tube length extends from 1.9 μm to 25 μm to create more reaction sites per electrode area. TiO2 nanotube arrays on double sides of the Ti foil yield more reaction sites resulting in a higher discharge capacity (0.158 mAh h cm⁻²). It has been reported that the amorphous TiO2 compact layer delivers a capacity of 0.009 mAh cm⁻² at a current density of 5 μA cm⁻² [35]. The amorphous TiO2 nanotubes with a length of 1.9 μm exhibit a capacity of 0.046 mAh cm⁻² at a current density of 400 μA cm⁻², as shown in Table 4-1. Hence, the nanotube array shows a capacity five times higher than that of TiO2 compact layer even when the nanotube array is cycled at a current density 80 times higher than that for the compact layer. These results also indicate that the surface area of TiO2 nanotube arrays does have significant influence on their areal capacity. Since the
length of the nanotubes can reach up to hundreds of micrometers, their discharge capacity may be further improved drastically. The charge process (Li-ion deinsertion) charged to -0.6 V for these TiO$_2$ nanotubes delivers charge capacities in a range from 0.042 mA h cm$^{-2}$ to

![Figure 4.7](image)

Figure 4.7 Galvanostatic discharge/charge curves at a rate of 400 $\mu$A cm$^2$ and cyclic voltammetric curves cycled between -0.6 V and -2.3 V for the three different TiO$_2$ nanotube arrays: (a-b) amorphous TiO$_2$ nanotubes, (c-d) anatase TiO$_2$ nanotubes, and (e-f) TiO$_2$ nanotubes of mixed phases.
The first discharge/charge areal capacities and coulombic efficiencies at a current density of 400 μA cm$^{-2}$ for different amorphous TiO$_2$ nanotube arrays annealed at 110 °C.

<table>
<thead>
<tr>
<th>TiO$_2$ nanotubes on the surface of Ti foils</th>
<th>Tube length (μm)</th>
<th>1$^{st}$ discharge capacity (mAh cm$^{-2}$)</th>
<th>1$^{st}$ charge capacity (mAh cm$^{-2}$)</th>
<th>Coulombic efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-side</td>
<td>1.9</td>
<td>0.046</td>
<td>0.042</td>
<td>92</td>
</tr>
<tr>
<td>Single-side</td>
<td>3.0</td>
<td>0.091</td>
<td>0.079</td>
<td>87</td>
</tr>
<tr>
<td>Single-side</td>
<td>4.7</td>
<td>0.115</td>
<td>0.104</td>
<td>91</td>
</tr>
<tr>
<td>Single-side</td>
<td>25</td>
<td>0.533</td>
<td>0.467</td>
<td>88</td>
</tr>
<tr>
<td>Double-side</td>
<td>3.0</td>
<td>0.158</td>
<td>0.135</td>
<td>85</td>
</tr>
</tbody>
</table>

0.468 mA h cm$^{-2}$, indicating the influence of the lengths of TiO$_2$ nanotubes on their charge capacities. Moreover, these amorphous nanotubes all exhibit good coulombic efficiency (ratio of charge to discharge capacity) up to 92%, which is beneficial to their cycling performance. Figure 4.8 shows the cycling performance of amorphous and crystalline TiO$_2$ nanotube arrays at a current density of 400 μA cm$^{-2}$ for 50 cycles. The nanotubes on the back side of Ti foils are removed for these tests. The results clearly confirm that the specific capacity of amorphous nanotubes is much higher than that of crystalline nanotubes, which suggests that many more Li ions are inserted into amorphous TiO$_2$ than into crystalline TiO$_2$. The capacity retention efficiencies measured for amorphous nanotubes, anatase nanotubes and nanotubes of mixed phases are 77%, 67%, and 72%, respectively. The capacity retention efficiency of the amorphous TiO$_2$ nanotubes is compatible with previous ones obtained at a much lower current density [35]. The poorer cycling performance of anatase TiO$_2$ nanotube array is possibly attributed to the smaller quantity of structural defects in the crystal that favor Li-ion insertion and deinsertion.

Figure 4.8 Specific discharge capacity vs. cycle number for the amorphous TiO$_2$ nanotube arrays (solid squares), anatase TiO$_2$ nanotube arrays (circles), and TiO$_2$ nanotubes of mixed phases (solid triangles), cycled at a current density of 400 μA cm$^{-2}$.
Figure 4.9 SEM images of (a) amorphous TiO$_2$ nanotubes before cycling, (b) amorphous TiO$_2$ nanotubes after cycling, (c) anatase TiO$_2$ nanotubes before cycling, (d) anatase TiO$_2$ nanotubes after cycling, (e) TiO$_2$ nanotubes of mixed phases before cycling, and (f) TiO$_2$ nanotubes of mixed phases after cycling. The nanotubes are cycled at 400 $\mu$A cm$^{-2}$ for 50 times. The inset images are the cross-sectional view of these TiO$_2$ nanotubes.

The structural stability of TiO$_2$ nanotube arrays during cycling is also explored. Figures 4.9a, c, and e present SEM images of various TiO$_2$ nanotube arrays (amorphous, anatase and mixed phases) before electrochemical cycling. These nanotubes are synthesized at 30 V in the
EG electrolytes containing 0.3 wt% NH₄F and 10 vol% H₂O, and subsequently annealed at 110 °C for 1 h, 480 °C for 3 h or 580 °C for 3 h in air. It can be clearly seen that the tubular structure is well-reserved after the annealing process. Amorphous and crystalline TiO₂ nanotubes stand separately and are well-aligned, with an average outer diameter of ~119 nm and a length of ~3 μm. A small amount of floccules appear on the surface, possibly due to the shrinkage of tube walls at the top ends of the nanotubes during heat treatment. Overall, the morphology of TiO₂ nanotube arrays almost remains unchanged after annealing, showing a high structural stability at elevated temperatures. Figures 4.9b, d and f show the SEM images of these nanotube arrays (amorphous, anatase, mixed phases) after electrochemical cycling at a current density of 400 μA cm⁻² for 50 cycles. It can be seen that both amorphous and crystalline tubular structure are well preserved after cycling, and no discernable damage is found on the walls of these nanotubes. Such high structural stability of TiO₂ nanotube arrays will lead to good capacity retention efficiency as shown in Figure 4.8.

4.4 Summary

In this project, high-aspect-ratio TiO₂ nanotube arrays are successfully synthesized by anodizing Ti foils in EG electrolytes containing NH₄F and H₂O. The dimensions of these nanotubes are controllable by tuning synthesis conditions, such as applied voltage, electrolyte composition and anodization time. The as-prepared TiO₂ nanotubes are amorphous, and heat treatment can convert them into crystalline nanotubes with identical morphologies. During the annealing process, the TiO₂ nanotube arrays show high thermal structure stability. The amorphous nanotubes, anatase nanotubes, and nanotubes of mixed phases (anatase and rutile) exhibit excellent electrochemical properties. Among the three, the amorphous TiO₂ nanotubes deliver the largest Li-ion intercalation capacity because the Li-ion diffusion coefficient is higher in amorphous TiO₂ than that in crystalline TiO₂. The TiO₂ nanotubes of mixed phases have higher capacity than pure anatase nanotubes, because the formation of rutile phase in anatase nanotubes facilitates the Li-ion transportation. The amorphous TiO₂ nanotube array shows good cycling performance, with a capacity retention efficiency of 77% after 50 cycles. The anatase nanotube array shows less good capacity retention, possibly due to fewer structural defects present in Li-ion diffusion in anatase TiO₂. However, all amorphous and crystalline nanotubes show excellent structural stability during cycling tests. These results further confirm that anodic TiO₂ nanotube arrays could be a potential alternative material for the anode of high-performance Li-ion batteries.

4.5 References


CHAPTER 5. SYNTHESIS AND GROWTH MECHANISM OF DOUBLE LAYER TiO₂ NANOTUBE ARRAYS BY ANODIC OXIDATION*

5.1 Introduction

As introduced in Chapter 1, one of broad applications for TiO₂ is dye-sensitized solar cell, a type of photo-to-electric conversion device or electric generation device. Well-ordered TiO₂ nanostructures (nanorods, nanowires or nanotubes) have drawn immense attention due to their much less excited charger recombination within much longer lengths, and pretty more accommodation for new efficient dyes in big size. Anodic TiO₂ nanotube array is an excellent nature support for the dye in DSSCs. As discussed in Chapter 4, an advantage of TiO₂ nanotubes is easy controllable fabrication via anodic oxidation. The length, diameter and wall features of TiO₂ nanotubes can be adjusted by tuning preparation conditions, such as applied voltages (constant [1] or alternating [2, 3]), electrolyte composition and anodic oxidation duration. The controllability in synthesis allows quite easy optimization of tube morphologies for targeted properties and performance. To date, three generations of anodic TiO₂ nanotube arrays have been synthesized and studied: The first-generation nanotubes only have a length up to 500 nm, due to a high dissolution rate of TiO₂ in acid HF-based aqueous electrolytes [2, 4]. The second-generation nanotubes are fabricated in neutral fluoride-based aqueous solutions where the fast oxide dissolution is alleviated, and thus their length extends to 6.4 μm [15, 5]. Afterwards, water in the electrolytes is found to play a significant role in the TiO₂ dissolution, and organic liquids start to replace water as the main solvent in electrolyte, yielding smooth or bamboo-type (with ridges on outer tube walls) TiO₂ nanotubes with a length up to 500 μm (Figure 5.1a) [6-9]. These nanotubes formed in organic electrolytes are denoted as the third-generation TiO₂ nanotube arrays that have much more flexibility in tube length.

Numerous efforts have been made to further increase the surface area of anodic TiO₂ nanotubes, which is favorable for surface reactions and related applications. For example, Chen et al. [10] and Butail et al. [11] synthesized hierarchically branched TiO₂ nanotubes with tailored diameters and branch numbers by adjusting anodization voltages. To improve the surface area of long TiO₂ nanotubes grown in water-poor organic electrolytes that have smooth outer and inner walls, some groups coat anodic TiO₂ nanotubes with nano-sized TiO₂ particles, and such hierarchical nanostructure delivers higher power conversion efficiencies than uncoated nanotubes when used in DSSCs (Figure 5.1a and b) [12]. In addition, Schmuki et al. fabricated bamboo-type TiO₂ nanotubes with regular ridges on outer tube walls by anodizing titanium sheets under alternating voltages (Figure 5.1c) [13]; the bamboo structure delivers more dye loading per unit volume when used in dye-sensitized solar cells (DSSCs), and yields a photo conversion efficiency which is 55% higher than that of smooth-walled tubes with identical film thickness [13]. Xie et al. synthesized various bamboo-type TiO₂ nanotubes via alternating-current anodization, and also found that their photo conversion efficiency is up to 49% higher than smooth nanotubes with the same length, when assembled in DSSCs [14]. These improvements are either due to increased surface area for more dye.

http://pubs.rsc.org/en/Content/ArticleLanding/2012/NR/C2NR30315A
loadings or due to enhanced light scattering for more light harvest inside the photo anode. Likewise, multilayer TiO$_2$ nanotube arrays will also have higher surface area due to extra layers or interfaces present between two neighboring nanotube layers, while retaining the vertically ordered structure of the one-dimensional nanostructures. In addition, multilayer nanotubes provide more light scattering when used in DSSCs and offer more flexibility for dimension tuning and morphology engineering [13, 15]. Yasuda et al. have prepared the layers of zirconium titanate nanotubes by using a multi-step anodization process of Ti-Zr alloys [16]. Li et al. and Wang et al. both fabricated multilayer TiO$_2$ nanotube arrays by applying high and low voltages alternately for anodization steps [17, 18]. Macak et al. and Yang et al. obtained multilayer TiO$_2$ nanotubes via anodizing titanium sheets in different electrolytes alternately [19, 20]. To date, there are only a few short papers about synthesis of multilayer nanotubes arrays as summarized above; there are no fundamental explorations of growth mechanism underlying these synthesis and no clear understanding of factors that control the formation of different nanostructures.

In this chapter, it is introduced that ethylene glycol-based electrolyte containing a small amount of NH$_4$F and H$_2$O is employed to synthesize various TiO$_2$ nanotube structures such as single-layer nanotubes, bamboo-type nanotubes and multilayer nanotubes; this electrolyte is different from those used in previous reports [27, 28] and offers more flexibility for tuning voltage/time and water content to explore growth mechanisms of various TiO$_2$ nanotube structures. Double-layer nanotubes with closed-bottom tubes in the upper layer are first described and bamboo-type nanotubes with concave waists are synthesized for the first time by adjusting high and low voltages in the alternating anodization sequence. It is found that the growth process of different TiO$_2$ nanotube array structures is ion-diffusion controlled.

![Figure 5.1 Illustration on various TiO$_2$ nanotube structures as anode in dye-sensitized solar cells: (a) smooth nanotubes, (b) TiO$_2$ nanotubes coated with TiO$_2$ or ZnO nanoparticles, and (c) TiO$_2$ nanotubes with rough walls (bamboo ridges).]
Fundamental understanding of growth characteristics of double-layer TiO₂ nanotubes offers much more flexibility in engineering morphology, tuning dimensions and phase compositions of multilayer TiO₂ nanotubes, and double-layer TiO₂ nanotube arrays with two phases in different layers is achieved.

5.2 Experimental

Ti foils (99.5 wt%) (10×10×0.25 mm³) in this study are purchased from Alfa Aesar. Prior to any electrochemical treatment, Ti foils are degreased and rinsed by sonicating in ethanol and deionized water. A two-electrode cell with a Pt mesh as the counter electrode is assembled for electrochemical anodization. Electrolytes are anhydrous ethylene glycol (EG) with 0.3 wt% NH₄F and 0~20 vol% H₂O. Water content is varied from 0 to 20 vol% for the synthesis of different TiO₂ nanostructure and understanding growth mechanism. All the solutions are prepared from reagent grade chemicals and deionized water. The voltage is supplied by a DC power supply with digital display (Model 1623A, PK Precision). To prepare multilayer TiO₂ nanotubes, the anodization process consists of three sequences as shown in Figure 5.2. The voltage is first increased from zero to V_high with a ramp rate of 1 V s⁻¹ and remains for t₁ time, then drops to V_low and is kept at V_low for t₂ time, followed by increasing to V_high with a rate of 1 V s⁻¹ and being kept at V_high for t₃ time. For comparison purpose, single-layer TiO₂ nanotubes are prepared by anodizing Ti sheets at 60 V for 1 h and 2 h, respectively. Except that one sample is annealed at 300 °C for 1 h between the first and second anodization steps, all the experiments are carried out at room temperature.

After anodization is completed, the samples are immediately rinsed in deionized water and dried in air. A FEI Quanta 3D FEG scanning electron microscope (SEM) is employed to characterize the morphology of TiO₂ nanotube arrays. The crystallographic structure of TiO₂ nanotube arrays is determined by an X-ray diffraction (XRD) using a Rigaku MiniFlex diffractometer with Cu Kα radiation operated at 30 kV and 15 mA with a scan rate of 2°/min. Transmission electron microscopy (TEM, JEM-2010, JEOL LTD.) coupled with EDAX is used to characterize the morphology and composition of a single TiO₂ nanotube. Chemical composition of the nanotubes is also analyzed by an X-ray photoelectron spectroscope (XPS, AXIS 165, Kratos Analytical Ltd.) with an AXIS 165 spectrometer from Kratos Analytical LTD by using a twin-anode Al Kα (1486.6 eV) X-ray source. All the XPS spectra are calibrated according to the binding energy of C1s peak at 284.8 eV.

5.3. Results and Discussion

5.3.1 Effect of Anodization Time Ratio

To synthesize multilayer TiO₂ nanotube arrays, we use a multi-step anodization process by applying high and low voltages alternately as shown in Figure 5.2. The ratio of high-voltage anodization time (t₁, t₃) to low-voltage anodization time (t₂) affects the structural features of TiO₂ nanotube arrays. To simplify the investigation, t₁ is set equal to t₃ and thus the ratio of t₂ to t₁ is under the consideration. Figure 5.3a shows SEM images of double-layer TiO₂ nanotube arrays formed by an anodization sequence with 60 V for 2 min followed by 10 V for 2 min and 60 V for 2 min, as illustrated in Figure 5.3b. The two nanotube layers have the same thickness of 500 nm, and there is a rough porous barrier layer in between. The upper-layer nanotubes have an outer diameter of 80 nm and nanotubes underneath have a
Figure 5.2 Anodization sequence for formation of multilayer TiO$_2$ nanotube arrays.

larger outer diameter of 120 nm. Nanotubes in both layers are well-organized and cylindrical with spherical bottoms as a characteristic of closed ends of anodic TiO$_2$ nanotubes. As we increase the anodization time to 10 min but keep $t_2/t_1$ ratio (=1:1) unchanged as shown in Figure 5.3d, double-layer TiO$_2$ nanotubes are yielded with longer tube length; total thickness of upper layer and lower layer reaching $\sim$3.5 µm; and nanotubes in both layers have a larger outer diameter of $\sim$140 nm (Figure 5.3c). Figure 5.4a presents the top-view SEM image of these double-layer nanotubes, showing the upper layer with open entrances.

Length of TiO$_2$ nanotubes can be further increased by using even longer anodization time. To study the growth mechanism of multilayer TiO$_2$ nanotubes, we use long anodization time which allows for varying $t_2/t_1$ ratio, and prepare single-layer TiO$_2$ nanotubes for comparison purpose. When a constant voltage (60 V for 2 h) is applied, the absence of low-voltage anodization ($t_2 = 0$) leads to formation of single-layer TiO$_2$ nanotube arrays (Figure 5.5a and b). The formed tubular structure is composed of hollow nanotubes that are well-aligned with an open entrance (Figure 5.4b) and a closed bottom. The tubes have smooth inner walls and outer walls, with an outer diameter of 170 nm and a length of $\sim$13 µm. When low-voltage anodization is added for a short time ($t_2 = 10$ min, $t_2/t_1 = 1:6$), bamboo-type TiO$_2$ nanotube arrays are yielded with ridges (or bamboo rings) in the middle of outer tube walls and a total tube length of 9.5 µm (Figure 5.5c and d). The ridges form a connecting layer to bind tubes above and underneath; the ridges also divide a whole tube into two sections. The upper section is formed during $t_1$ period and the lower section during $t_3$ period. The outer diameter of nanotubes in the upper section (170 nm) is smaller than that in the lower section (200 nm), though the inner tube walls of two sections are both smooth and vertical to the substrate. Open entrances are also found in the upper-section TiO$_2$ nanotubes, as shown in its top-view SEM image (Figure 5.4c). Gaps among nanotubes are much wider in the upper section, indicating that dissolution of oxides in the inter-tube cavities becomes much more difficult due to the block of the ridge-layer and thus there is less dissolution of oxides when growing nanotubes in lower section during anodization in $t_3$ period.

When $t_2$ is increased to 60 min with $t_1$ and $t_3$ kept at 60 min ($t_2/t_1 = 1:1$), a double-layer structure composed of smooth TiO$_2$ nanotubes in each layer emerges, with a total thickness of two layers at 9.0 µm (Figure 5.5e-h). In each layer, all nanotubes have open entrance (Figure 5.4d) and a closed bottom. The outer diameter of upper-layer nanotubes is about 170 nm, while the more closely-packed lower-layer nanotubes have a slightly larger outer tube
diameter. This difference in nanotube diameters is ascribed to different current densities between the first and second high-voltage anodization steps. The higher the current density is, the larger the tube diameter is [21-23]. These two layers of nanotubes are connected by a thin porous barrier layer in between, which is considered to be the origination of lower-layer nanotubes [26]. Based on these results, it could be concluded that layer structure of TiO$_2$ nanotube arrays is largely affected by duration of anodization voltages. Constant-voltage anodization in organic electrolyte usually gives single-layer smooth-walled tubes. When a low-voltage anodization step is added, ridges will be formed on the outer tube walls initially, leading to formation of bamboo-type TiO$_2$ nanotubes. If the low-voltage anodization step proceeds for sufficiently long time (e.g., $t_2/t_1$ ratio increased from 1:6 to 1:1), the previous single layer turns to be two distinct layers of smooth nanotubes with closed bottoms, which are connected by a thin porous layer in between.

Figure 5.3 Cross-sectional SEM images and corresponding anodization sequences of TiO$_2$ nanotube arrays synthesized in EG electrolyte with 0.3 wt% NH$_4$F and 5 vol% H$_2$O: (a-b) 60 V for 2 min followed by 10 V for 2 min and 60 V for 2 min; (c-d) 60 V for 10 min followed by 10 V for 10 min and 10 V for 10 min. $t_2/t_1 = 1:1$ for both samples.

Evolution of layered structure with anodization time ratio can be confirmed in other cases where $t_1$ ($t_3 = t_1$) and $t_2$ are changed but using the same $t_2/t_1$ ratios as above. For example,
anodization of titanium at 60 V for 60 min leads to formation of single-layer smooth TiO$_2$ nanotubes (Figure 5.6a-b), while an anodization sequence composed of 60 V for 30 min followed by 10 V for 5 min ($t_2/t_1 = 1:6$) and 60 V for 30 min results in bamboo-type nanotubes with ridges in the middle (Figure 5.6c-d). When the anodization time at 10 V is increased to 30 min ($t_2/t_1 = 1:1$), two layers of smooth nanotubes with closed bottoms are formed (Figure 5.6e-f). Hence, it can be concluded that $t_2/t_1$ ratio equal to 1:1 is a critical electrochemical parameter for initiation of double-layer TiO$_2$ nanotubes in EG electrolytes with an addition of 0.3 wt% NH$_4$F and 5 vol% H$_2$O at room temperature. It should be noted here that tube length in each layer is dependent on corresponding anodization time [16], and thus thickness of double-layer TiO$_2$ tubes can be adjusted by tuning the anodization time.

Figure 5.4 SEM images showing top-view of various TiO$_2$ nanotube arrays formed in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O via different anodization sequences: (a) 60 V for 10 min, followed by 10 V for 10 min ($t_2/t_1 = 1:1$) and 60 V for 10 min (short double-layer nanotubes); (b) 60 V for 2 h (single-layer nanotubes), (c) 60 V for 60 min, followed by 10 V for 10 min ($t_2/t_1 = 1:6$) and 60 V for 60 min (bamboo-type nanotubes); (d) 60 V for 60 min followed by 10 V for 60 min ($t_2/t_1 = 1:1$) and 60 V for 60 min (double-layer nanotubes).
Figure 5.5 Cross-sectional SEM images and corresponding anodization sequences of TiO$_2$ nanotube arrays formed in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O: (a-b) 60 V for 2 h; (c-d) 60 V for 60 min followed by 10 V for 10 min ($t_2/t_1 = 1:6$) and 60 V for 60 min; (e-f) 60 V for 60 min followed by 10 V for 60 min ($t_2/t_1 = 1:1$) and 60 V for 60 min; (g-h) same sample in e, but is bent to show the closed bottoms of nanotubes.
Figure 5.6 Cross-sectional SEM images and corresponding anodization sequences of TiO$_2$ nanotube arrays formed in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O: (a-b) 60 V for 60 min; (c-d) 60 V for 30 min followed by 10 V for 5 min ($t_2/t_1 = 1:6$) and 60 V for 30 min; (e-f) 60 V for 30 min followed by 10 V for 30 min ($t_2/t_1 = 1:1$) and 60 V for 30 min.

TEM and EDAX are used to analyze the morphological feature and chemical composition of anodic TiO$_2$ nanotubes. Figure 5.7 shows the TEM image of a single TiO$_2$ nanotube and EDAX signals are captured from three different spots of this nanotube. All the EDAX spectra from the three spots are similar (inset of Figure 5.7), revealing the presence of Ti and
O from the nanotube in addition to Cu and C from the TEM sample membrane consisting of copper grid and carbon film. To further examine the composition of nanotubes, the Ti2p and O1s XPS spectra of as-synthesized single-layer TiO$_2$ nanotube arrays and double-layer nanotube arrays are given in Figure 5.8. These tubular oxide films are scratched off the metal substrate, and then put on conductive adhesive copper tapes upward for elemental analysis on top surface or downward for analysis on nanotube base. Two characteristic peaks of Ti 2p1/2 at 464.3 eV and Ti 2p3/2 at 458.5 eV ($\Delta E = 5.8$ eV) are clearly seen in XPS spectra of both surface and base of single-layer nanotubes, which correspond to Ti$^{4+}$ (Figure 5.8a) [24, 25]. O1s peaks taken from the top and base of nanotubes have the same binding energy of 530.1 eV, corresponding to Ti-O bond of TiO$_2$ [34]. Similarly, the Ti2p and O1s XPS spectra taken from the surface of upper-layer nanotubes and the base of lower-layer nanotubes in the double-layer nanotubes also reveal the formation of fully oxidized Ti and resultant Ti$^{4+}$ oxides (Figure 5.8b). Hence, it can be concluded that titanium is fully oxidized during growth of either single-layer or double-layer structure with anodic oxidation of Ti, yielding ordered arrays of true TiO$_2$ nanotubes on the substrate at anode.

5.3.2 Barrier Layer in Multilayer TiO$_2$ Nanotube Arrays

In order to investigate the growth process of lower-layer nanotubes (the second layer), the upper layer nanotubes are removed by bending the sample and the upper layer is delaminated and peeled off. The double-layer nanotubes are made by an anodization sequence composed of 60 V for 10 min followed by 10 V for 10 min ($t_2/t_1 = 1:1$) and 60 V for 10 min. After the upper-layer nanotubes are removed, a porous barrier layer is revealed to cover the lower-

Figure 5.7 TEM image and EDS spectra (inset) of a nanotube in single-layer TiO$_2$ nanotube arrays formed at 60 V for 2 h in EG electrolyte containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O (Note: EDS analysis is performed at spots 1, 2 and 3, respectively).
Figure 5.8 Ti2p XPS peaks and O1s XPS peaks (insets) taken from the top and the bottom of (a) single-layer TiO2 nanotubes synthesized at 60 V for 2 h, and (b) double-layer TiO2 nanotube arrays synthesized at 60 V for 60 min followed by 10 V for 60 min \((t_2/t_1 = 1:1)\) and 60 V for 60 min, in EG electrolytes containing 0.3 wt% NH4F and 5 vol% H2O.

layer TiO2 nanotube arrays, as shown in Figure 5.9a. The barrier layer is formed during the low-voltage anodization stage. It can be seen that the barrier layer has a very rough surface, full of regular concave regions. These concave regions correspond to the semi-spherical bottoms of upper-layer nanotubes. Besides, numerous fine pores or pits exist in the barrier layer, which function as channels for ion diffusion into or out of the lower layer. The pores or pits may also act as originations of new layer of nanotubes below. This is confirmed by a tubular barrier layer in the double-layer structure formed via a longer anodization sequence (60 V for 30 min, then 10 V for 30 min \((t_2/t_1 = 1:1)\) and 60 V for 30 min), as shown in Figure 5.9b (upper-layer nanotubes are removed). This barrier layer has a thickness of about 150 nm and is composed of a large amount of directional small nanotubes. The small tubes cover the entrance of the large tubes below, and some of them even become part of walls of large tubes. Similarly, such tubular barrier layer also exists in the double-layer structure formed via an even longer anodization sequence (60 V for 60 min, then 10 V for 60 min \((t_2/t_1 = 1:1)\) and 60 V for 60 min), as shown in Figure 5.9c (upper-layer nanotubes are removed). These results indicate that a thin layer of small nanotubes is formed at low voltage (10 V) for a certain period, leading to a sandwiched structure. To confirm this, an anodization sequence containing a very long low-voltage anodization time (even longer than high-voltage anodization time) (60 V for 10 min, then 10 V for 60 min \((t_2/t_1 = 6:1)\) and 60 V for 10 min) is carried out on titanium. The layer of small nanotubes formed at 10 V is clearly seen between diameter of small nanotubes is 37 nm, much smaller than that of upper-layer nanotubes (~111 nm) and lower-layers (~170 nm) tubes grown at high voltage. The much smaller diameter of nanotubes grown during the low voltage anodization is due to the smaller current density when the low voltage is applied [32, 33]. The formation of TiO2 nanotubes at low-voltage step (10 V) is accordance with tube growth directly on the surface of Ti sheet at the same voltage. Figure 5.10a shows two-step anodization of Ti substrate and resultant TiO2 nanotube at 10 V after 30 min. The removed former nanotubes (grown at 60 V) leave concave hexagonal areas on substrate where much smaller pores or tubes are originated
Figure 5.9 SEM images of double-layer TiO₂ nanotube arrays with the upper layer removed. All samples are synthesized in EG electrolyte containing 0.3 wt% NH₄F and 5 vol% H₂O using different anodization sequences: (a) 60 V for 10 min followed by 10 V for 10 min and 60 V for 10 min; (b) 60 V for 30 min followed by 10 V for 30 min and 60 V for 30 min; (c) 60 V for 60 min followed by 10 V for 60 min and 60 V for 60 min; (d) 60 V for 10 min followed by 10 V for 60 min (t₂/t₁ = 6:1) and 60 V for 10 min, with t₂ much longer than t₁.

Figure 5.10 Top-view SEM images of TiO₂ nanotube arrays synthesized in EG electrolyte containing 0.3 wt% NH₄F and 5 vol% H₂O at 10 V for (a) 30 min, and (b) 60 min.
at 10 V, suggesting probability of tube formation at the low-voltage anodization step. Figure 5.10b presents TiO$_2$ nanotubes grown at 10 V for 60 min on a fresh Ti substrate, indicating tube development with time.

### 5.3.3 Growth Mechanism of Multilayer TiO$_2$ Nanotube Arrays

It is well-known that the growth of anodic TiO$_2$ nanotube arrays is divided into three stages. Initially, a compact oxide layer is formed once voltage is applied; later, pits and pores emerge in the compact layer and turn this layer into a porous film; finally, the pores are separated by inter-pore cavities, eventually resulting in an ordered tubular layer [26]. In fact, this morphological evolution of anodic TiO$_2$ film is a result of the competition between electro-chemical etching process and chemical dissolution process on Ti [27]. The two processes involve three simultaneously occurring chemical reactions as follows [28]:

1. **Field-assisted oxidation of Ti**: water molecules decompose near the metal and produce O$^{2-}$ ions and H$^+$ ions [29]; the O$^{2-}$ ions then travel through an electrolyte-oxide interface to oxidize Ti. The reactions are described as:

   \[
   \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{O}^{2-} \quad (5.1) \\
   \text{Ti} + 2\text{O}^{2-} \rightarrow \text{TiO}_2 + 4\text{e} \quad (5.2)
   \]

2. **Field-assisted dissolution of titanium oxides**: due to electric field, the Ti-O bond undergoes polarization and is weakened, promoting dissolution of the oxides.

   \[
   \text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \quad (5.3)
   \]

3. **Chemical dissolution of titanium oxides**: herein, Ti$^{4+}$ cations become soluble hexafluorotitanium complexes [TiF$_6$]$^{2-}$ that go into the electrolyte, while the free O$^{2-}$ anions transfer to the oxide-metal interface and react with Ti. The reaction is described as:

   Under the applied electrical field, three chemical reactions occur simultaneously at the anode. Figure 5.11a presents the ion profiles inside a tube or an inter-tube cavity present in an oxide film on Ti substrate [30]. In the neutral electrolyte, H$^+$ ions mostly come from water decomposition at the tube bottom (eqn (5.1)), which partly diffuse towards bulk electrolyte and establish a pH profile. After the anodization starts, ion diffusion gradients are gradually established in the first two stages that finally allow stable growth of TiO$_2$ nanotubes under a high voltage [23]. The shaded area in Figure 5.11b represents stable pH gradient decreasing from the tube bottom to tube entrance. Under constant-voltage anodization (60 V), Ti is continuously oxidized (eqn (5.2)) and the oxide/metal interface moves towards the substrate, while tube-bottom oxides are dissolved (eqn (5.3)) and the electrolyte/oxide interface moves towards the substrate as well. This system results in formation of single-layer TiO$_2$ nanotubes with controllable length and an oxide barrier layer (thinner than tube walls) below these nanotubes.

   Once this system is altered to a lower voltage (10 V), fewer H$^+$ ions are yielded and the pH profile is changed to less steep gradient (Figure 5.11c). It would slow down or even cease dissolution of oxides at the tube bottom, yielding a thicker compact barrier layer there. After a certain period of time, origination of small pits and pores in the barrier layer occurs under the low voltage, just like the first stage of tube formation introduced above. In this situation, a subsequent step back to the high voltage (60 V) would restart the growth of previous tubes.
Figure 5.11 Schematic showing growth of single-layer, bamboo-type and double-layer TiO$_2$ nanotube arrays via anodic oxidation: (a) ion diffusion profiles inside nanotubes, (b) pH gradient profile in nanotubes during their steady growth stage at a high voltage, (c) less steep pH gradient and pit or pore formation after the voltage is altered to a low value, (d) formation of bamboo-type nanotubes, (e) further less steep pH gradient and tube formation when the low voltage is kept for a longer period, (f) formation of double-layer TiO$_2$ nanotubes.

and cavities toward the substrate, and the formed pits and pores in the barrier layer are eaten or consumed by them. However, part of the thick barrier layer between two neighboring nanotubes survives and residues on the tube walls to form ridges as shown above, yielding bamboo-type tubes (Figure 5.11d). If the low-voltage anodization is kept for longer time (e.g. $t_2/t_1$ ratio $\geq 1$), the barrier layer becomes thinner and the pits and pores grow to become small tubes (Figure 5.11e). Now the H$^+$ ions become much fewer due to outward diffusion and participation in the oxide dissolution, and the pH gradient is much less steep. At a critical point, this system is able to induce a second formation and growth of bigger TiO$_2$ nanotubes at subsequent high-voltage (60 V), as shown in Fig. 5.11f, yielding double-layer nanotubes.
arrays. The existing small nanotubes cover the newly-formed lower layer, and some of them are even integrated into the walls of bigger nanotubes in the lower layer.

This model can be used to explain the effect of anodization time ratio $t_2/t_1$ on the morphology of anodic TiO$_2$ nanotubes. The key to formation of double-layer nanotubes is an adequate change of the ion concentration inside the tubes. As the anodization voltage is reduced, the yield of H$^+$ ions and diffusion rate of ions are decreased accordingly, and the ion concentration profiles in nanotubes tends to be similar to that in the bulk electrolyte, which brings more probability for forming new nanotubes during the second high-voltage anodic oxidation ($t_3$). If $t_1$ is longer, nanotubes in the upper layer (first layer) are longer; thus it takes ions outside more time to diffuse through these longer nanotubes to reach the bottom of tubes, and more time for ions inside nanotubes to move out the tubes, hence, the ion concentration profiles need longer time to change to the critical point for initiation of subsequent nanotube formation. In addition, the tube length is linear to the anodization time, and the diffusion time for ions that travel through the tubes is proportional to the tube length, so the variation of ion concentration profiles in tubes during $t_2$ period is related to previous anodic time ($t_1$). Therefore, it can be seen that the low-voltage anodization time $t_2$ needs to be extended until the $t_2/t_1$ ratio reaches a critical value (e.g. 1:1) to grow double-layer nanotube arrays, if the first high-voltage anodization proceeds for longer time.

5.3.4 Effect of Water Content in Organic Electrolytes

The variation of ion concentration profiles inside TiO$_2$ nanotubes largely depends on the ion diffusion through the tube, and more exactly on the diffusion coefficients of ions in the electrolyte. The diffusion coefficients are further influenced by the viscosity of electrolytes used [17]. Figure 5.12a shows TiO$_2$ nanotubes grown via an anodization sequence composed of 60 V for 60 min followed by 10 V for 60 min ($t_2/t_1 = 1:1$) and 60 V for 60 min in anhydrous EG electrolyte containing 0.3 wt% NH$_4$F. The resulted structure is single-layer smooth nanotubes, rather than bamboo-type nanotubes or double-layer nanotubes formed using the same anodization sequence in electrolyte containing 5 vol% water shown earlier. This is attributed to few variations occur in the ion concentration profiles inside the tubes. In such anhydrous electrolyte, traces of water decompose at tube bottom to support oxidation of metal and dissolution of oxides. Diffusion of various ions, including H$^+$ ions, is quite slow in the tubes. Even though the duration of low-voltage anodization is as long as that of high-voltage anodization, the ion concentration profiles almost remain unchanged. As a result, formation of bamboo-type or double-layer nanotubes is suppressed. Once the high voltage is applied again, traces of water are decomposed merely to continue the nanotube growth.

In contrast, more water in electrolyte allows faster ion diffusion and concentration change in nanotubes when switching voltages. Figure 5.12b shows SEM images of bamboo-type TiO$_2$ nanotubes via an anodization sequence composed of 60 V for 60 min followed by 10 V for 10 min ($t_2/t_1 = 1:6$) and 60 V for 60 min in EG electrolyte with 0.3 wt% NH$_4$F and 10 vol% H$_2$O. The resulted nanotubes become shorter due to faster dissolution of oxide on tube walls by water. When water content in electrolyte is increased into 15 vol%, the double-layer TiO$_2$ nanotube array emerges, rather than bamboo-type TiO$_2$ nanotube arrays (Figure 5.12c). It is due to the accelerated ion diffusion in less viscous electrolyte, and efficient ion diffusion and ion concentration variation inside nanotubes to induce origination of new layer of TiO$_2$
nanotubes during \( t_3 \) period. The upper layer is composed of well-ordered nanotubes with closed bottoms, but the nanotubes in the lower layer have ordered bottoms but disordered tops, indicating certain instability occurs during growth of the lower layer. This instability becomes more distinct when water content in electrolyte is increased into 20 vol\%, resulting in a very disordered spongy structure under which some small and short nanotube rudiments appear randomly (Figure 5.12d).

Figure 5.12 SEM images of TiO\(_2\) nanotube arrays synthesized (a) at 60 V for 60 min, 10 V for 60 min \((t_3/t_1 = 1:1)\) and 60 V for 60 min in anhydrous EG electrolyte containing 0.3 wt\% NH\(_4\)F; and at 60 V for 60 min, 10 V for 10 min \((t_1/t_2 = 6:1)\) and 60 V for 60 min in EG electrolyte with 0.3 wt\% NH\(_4\)F and (b) 10 vol\% H\(_2\)O, (c) 15 vol\% H\(_2\)O, (d) 20 vol\% H\(_2\)O.

### 5.3.5 Effect of Voltage Gaps

The model discussed in section 5.3.3 can also explain the effect of voltage gap on the layer structure of anodic TiO\(_2\) nanotube arrays. Figure 5.13a shows cross-section SEM images of TiO\(_2\) nanotubes grown via an anodization sequence composed of 60 V for 60 min followed by 40 V for 60 min \((t_2/t_1 = 1:1)\) and 60 V for 60 min (Figure 5.13b). This process with increased low voltage (40 V instead of 10 V) yields bamboo-type TiO\(_2\) nanotubes with outer ridges that connect all nanotubes, while the same anodization time for a voltage pair of 60 V and 10 V results in double-layer TiO\(_2\) nanotube arrays as shown in Figure 5.6e earlier. The
reason for the difference is that the gap or difference between high voltage and low voltage is too small in the case of 60 V and 40 V to cause drastic change of the ion concentration profiles in nanotubes for the electrolyte used. In other words, when voltage becomes 40 V, the production of H⁺ ions and ion diffusion inside nanotubes is still fast in the electric field [39] and the pH gradient and ion concentration profiles do not change much [40]. As a result, the barrier layer becomes a little thicker for the formation of ridges on outer walls, but the subsequent tube growth during $t_3$ period maintains the initial tubular structure. Moreover, it is worthy to note that a concave waist appears under the ridge of each nanotube, because the tube diameter is smaller due to smaller current density when a voltage of 40 V is applied.

Figure 5.13 (a) Cross-sectional SEM images of bamboo-type TiO₂ nanotubes synthesized in EG electrolyte containing 0.3 wt% NH₄F and 5 vol% H₂O via (b) an anodization sequence composed of 60 V for 60 min followed by 40 V for 60 min ($t_2/t_1 = 1:1$) and 60 V for 60 min.

5.3.6 Phase Control of Multilayer TiO₂ Nanotube Arrays

Controllable synthesis of multilayer TiO₂ nanotubes via anodic oxidation allows us to optimize morphology and phase structure of the material. Figure 5.14a shows XRD patterns of two types of double-layer TiO₂ nanotube arrays. Both are produced via an anodization sequence composed of 60 V for 60 min followed by 10 V for 60 min ($t_2/t_1 = 1:1$) and 60 V for 60 min in EG electrolyte containing 0.3 wt% NH₄F and 5 vol% H₂O. However, one sample is annealed in air at 300 °C for 1 h prior to the low-voltage anodization at 10 V. The XRD pattern of unheated sample only shows diffraction peaks from Ti substrate, indicating that both the upper-layer and low-layer TiO₂ tubes are amorphous [11, 31]. On the other hand, the annealed sample shows crystalline structure of anatase TiO₂. In its XRD pattern, typical peaks (101) and (200) of metastable anatase are found to be at $2\theta = 25.2^\circ$ and at $2\theta = 47.9^\circ$ respectively [32, 33]. Since the lower-layer tubes are as-prepared one, the anatase crystallites exist in the heated upper-layer nanotubes, and thus multilayer TiO₂ nanotubes composed of anatase upper layer and amorphous lower layer is obtained (Figure 5.14b).
Figure 5.14 (a) XRD diffraction patterns of double-layer TiO$_2$ nanotubes synthesized via an anodization sequence composed of 60 V for 60 min followed by 10 V for 60 min ($t_2/t_1 = 1:1$) and 60 V for 60 min in EG electrolyte containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O: blue pattern: double-layer nanotubes without heat treatment, red pattern: double-layer nanotubes with heating treatment at 300 °C for 1 h prior to the low voltage anodization at 10 V and growth of the lower layer; (b) cross-sectional SEM images of double-layer TiO$_2$ nanotube arrays with anatase phase in the upper layer and amorphous phase in the lower layer.

5.4 Summary

In summary, three types of TiO$_2$ layer structures are successfully synthesized: single-layer smooth TiO$_2$ nanotubes, bamboo-type TiO$_2$ nanotubes, and double-layer TiO$_2$ nanotubes. Growth mechanisms of the three are introduced and compared based on variation efficiency of pH and ion concentration profiles inside tubes and pores. A sufficient ion concentration change is the key to the formation of bamboo-type and double-layer TiO$_2$ nanotube nanotubes. The ratio of low-voltage anodization time to high-voltage anodization time ($t_2/t_1$) affects morphology of TiO$_2$ nanotubes. The higher the time ratio is, the easier the formation of double-layer TiO$_2$ nanotubes. Likewise, for a proper electrolyte, a bigger gap between the high voltage and the low voltage is favorable for the formation of double-layer nanotubes. Appropriate water content in electrolytes is also beneficial for the formation of double-layer nanotubes, but too much water renders the tubular structure unstable and even converts the ordered tube arrays to disordered spongeous structure. Based on the controbility of synthesis of double-layer TiO$_2$ nanotube arrays, phase composition of each layer can be manipulated through heating and multilayer nanotubes with different phases in different layers can be achieved. Additionally, the work can be generalized to grow multilayer TiO$_2$ nanotube arrays consisting of more layers (e.g., three or more layers), by tuning voltages, anodization time ratio, and electrolyte composition.

Double-layer TiO$_2$ nanotubes with closed bottoms have higher surface area due to extra layers or interfaces present between two neighboring nanotube layers and offer more flexibility for morphology engineering and dimension tuning, while retaining the vertically ordered structure of one-dimensional nanostructure. Furthermore, double-layer nanotube arrays provide more light scattering when used in DSSCs. Therefore, double-layer TiO$_2$
nanotube arrays find wide applications as anodes in lithium-ion batteries and photo-anodes in dye-sensitized solar cells. In particular, for the double-layer TiO$_2$ nanotube arrays with different phases (anatase phase in the upper layer and amorphous phase in the lower layer), the anatase upper layer has higher mechanical strength and stronger corrosion resistance, which may facilitate growth of ultra-long nanotubes in the lower layer. In addition, the amorphous lower layer is more vulnerable to some chemical solvents (e.g. H$_2$O$_2$) and thus its dissolution readily yields free-standing anatase TiO$_2$ nanotube arrays that can be transferred to conductive glass or plastic substrates for DSSC assembly.

5.5 References


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CHAPTER 6. GROWTH MECHANISM AND MORPHOLOGY CONTROL OF DOUBLE-LAYER AND BAMBOO-TYPE TiO₂ NANOTUBE ARRAYS FOR HIGH-EFFICIENCY DYE-SENSITIZED SOLAR CELLS

6.1 Introduction

As described in Chapter 5, there have been extensive research efforts to further increase the surface area of anodic TiO₂ nanotubes recently, such as fabrication of multilayer TiO₂ nanotube arrays with extra porous interlayers [1, 2], or bamboo-type TiO₂ nanotubes with ridges on outer tube walls by anodizing Ti under alternating-voltage (AV) conditions [3, 4]. These new TiO₂ nanostructures provide larger surface area due to extra interfaces or rough walls, while retaining the vertically ordered one-dimensional nanostructure. In addition, they enable more light scattering when used in DSSCs, and provide more flexibility for dimension tuning and morphology engineering. For example, double-layer and sandwich-structured smooth-walled TiO₂ nanotube arrays are synthesized via modified AV anodic conditions and their growth mechanism is explored [5]. Double-layer smooth-walled TiO₂ nanotube arrays can also be prepared using stepping-voltage anodization [6], or by anodizing Ti in alternating aqueous and organic electrolytes [7, 8]. Regarding bamboo-type TiO₂ nanotube arrays, Zhang et al. achieved ordered bamboo-type TiO₂ nanotubes in electrolytes with different viscosity and water content [9]. Li et al. employed AV anodization to synthesize ordered TiO₂ nanotubes with bamboo-shaped upper section and smooth-walled lower section [10, 11]. Schmuki et al. integrated bamboo-type TiO₂ nanotube arrays into DSSCs; the new DSSCs yielded photo conversion efficiency 55% higher than DSSCs based on smooth-walled nanotubes with identical film thickness of 8 µm, due to larger surface area of bamboo-type nanotubes for more dye loading and enhanced light scattering for more photon absorption [12]. In addition, Xie et al. synthesized bamboo-type TiO₂ nanotubes with various ridge densities on tube walls, which found applications in DSSCs for up to 49% photo conversion efficiencies than smooth-walled nanotubes [13]. Consequently, much attention is focused on the bamboo-type TiO₂ nanotube due to its unique advantages and potential applications in photo catalysts, LIBs and DSSCs [14].

To date, there are only a few papers about bamboo-type TiO₂ nanotubes arrays as summarized above, which rather focus on synthesis and device applications. Though formation process of bamboo-type TiO₂ nanotubes is briefly outlined [3], there is no report about fundamental explorations of growth mechanism underlying the synthesis and no clear understanding of factors that control morphological features such as ridge spacing on bamboo-type nanotubes. Ridge spacing provides a simple way for measuring the actual growth rate of anodic TiO₂ nanotubes. It should be noted that the actual growth rate of TiO₂ nanotubes cannot be calculated directly from the final tube length divided by total anodic time, since the length of nanotubes is decided by both the growth process of their roots towards substrate and the dissolution process of their tops into electrolyte. However, ridge spacing on bamboo-type TiO₂ nanotubes is the intact outcome from the actual tube growth within a given time period, and thus it can be used to calculate the actual growth rate of TiO₂ nanotubes. The relationship between the ridge spacing and actual growth rate is profound for
fundamentally understanding the adjustment of growth rate or tube length by various approaches, such as voltage, electrolyte composition, anodic time, temperature and substrate structures. For example, it is known that ultralong TiO₂ nanotubes (~×10² µm) can be grown in ethylene glycol (EG) electrolytes containing a limited amount of water (≤ 2 wt%) [15], and rapid growth of TiO₂ nanotubes can be achieved by adding excess fluorides [16] or H₂O₂ [17], or even using chlorides as solute for anodization. Since the theoretical tube length can be calculated by multiplying the rate with total anodic time, the dissolution rate of TiO₂ tube tops may be estimated with the difference between measured tube length and theoretical length divided by the total time. Given that the influence of a preparation parameter on actual growth rate and dissolution rate of TiO₂ nanotubes is clear, it makes it viable to design anodic procedures to achieve long nanotubes efficiently by balancing the two rates.

In this chapter, double-layer TiO₂ nanostructures composed of smooth-walled nanotubes in the upper layer and bamboo-type nanotubes in the lower layer are synthesized from EG-based electrolytes containing a small amount of NH₄F and H₂O by applying multiple high/low voltage steps, and their growth mechanisms are carefully explored. For comparison purposes, single-layer smooth-walled TiO₂ nanotubes and double-layer smooth-walled TiO₂ nanotubes are fabricated as well. Real-time current measurements are used to study the growth process and morphological evolution of these anodic TiO₂ nanostructures. Formation mechanism of double-layer TiO₂ nanotubes with or without a bamboo-type layer is proposed based on ion diffusion-controlled process inside tubes and inter-tube cavities. Fundamental factors that affect the morphology of the bamboo-type TiO₂ nanotubes are studied with both experimental approaches and theoretical calculation and by manipulating water content in electrolyte and adjusting high or low voltage anodization time. To the best of the knowledge, so far there is no report about the effect of water content and low-voltage anodization duration on ridge formation and ridge spacing. This work is also the first effort to calculate and measure the actual growth rate of anodic TiO₂ nanotubes.

In addition, the thermal stability of double-layer and bamboo-type TiO₂ nanotubes is studied, in order to ensure their structural stability during annealing or crystallization process. Since the controllable growth of anodic TiO₂ nanotube arrays is achieved, a couple of bamboo-type nanotubes are produced with different ridge densities. These nanotubes are then assembled into DSSCs to evaluate the photo-electric conversion ability of solar cells.

6.2 Experimental

Ti foils (99.5 wt%) (10 ×10 × 0.25 mm³) in this study are purchased from Alfa Aesar. Prior to any electrochemical treatment, Ti foils are degreased and rinsed by sonicating in ethanol and deionized water. A two-electrode cell with a Pt mesh as the counter electrode is assembled for electrochemical anodization. Electrolytes are anhydrous ethylene glycol (EG) with 0.3 wt% NH₄F and 2–15 vol% H₂O. All the solutions are prepared from reagent grade chemicals and deionized water. The voltage is supplied by a DC power supply with digital display (Model 1623A, PK Precision). A Data Acquisition/Data Logger Switch Unit (Aglient 34970A) is employed to record real-time anodic current. To prepare multilayer TiO₂ nanotubes, the anodization process consists of several alternating high and low-voltage anodic oxidation steps, as shown in Figure 1. The voltage is first increased from zero to V_{high} with a ramp rate of 1 V s⁻¹ and remains for a time t₁, then drops to V_{low} and is kept at V_{low} for a time
$t_2$, followed by increasing to $V_{\text{high}}$ with a rate of 1 V s$^{-1}$ and being kept at $V_{\text{high}}$ for a time $t_3$. Such voltage alteration is repeated for different TiO$_2$ nanotube structures. For comparison purpose, single-layer TiO$_2$ nanotubes are prepared by anodizing Ti sheets at 60 V for 20 min. All the experiments are carried out at room temperature. After anodization is completed, the samples are immediately rinsed in deionized water and dried in air. A FEI Quanta 3D FEG scanning electron microscope (SEM) is used to characterize the morphology of TiO$_2$ nanotube arrays formed on the front side of Ti foils.

![Figure 6.1 Anodization sequence for the formation of multilayer TiO$_2$ nanotube arrays.](image)

Figure 6.1 Anodization sequence for the formation of multilayer TiO$_2$ nanotube arrays.

Figure 6.2a shows the fabrication process of dye-sensitized TiO$_2$ nanotube arrays as photo anode in DSSCS. At the beginning, a layer of well-ordered nanotubes are produced by anodic oxidation of Ti under specific conditions. The film is then converted into photo active anatase phase with heat treatment at 450 °C in air for 2 h. Later, the oxide film is scratched into an area of 5×5 mm$^2$ in the center. 0.2 M TiCl$_4$ aqueous solution is prepared at freezing point and partial hydrolysis of TiCl$_4$ in water yields TiOCl$_2$ and HCl and a 2 M TiOCl$_2$ solution, which is described by the following equation:

$$\text{TiCl}_4 + \text{H}_2\text{O} \rightarrow \text{TiOCl}_2 \text{ (solution)} + 2\text{H}^+ \text{ (solution)} + 2\text{Cl}^- \text{ (solution)} \quad (6.1)$$

The TiCl$_4$ treatment is conducted by soaking crystalline TiO$_2$ nanotubes in 20 ml of the TiCl$_4$ solution in a 70 °C water bath for 30 min, and further hydrolysis of TiOCl$_2$ (solution) yields fine TiO$_2$ particles (~1 nm) covering TiO$_2$ porous film, which is able to effectively reduce the recombination of electrons injected to the conduction energy band of anatase TiO$_2$ film with the electrolyte species. A subsequent heat treatment in air at 450 °C for 30 min is performed to bond the particles and substrate film. After they are rinsed and dried, the film is immersed into Ruthenizer 535-bisTBA dye (N719, cis-diisothiocyanato-bis(2,20-bipyridyl-4, 40-dicarboxylato) ruthenium(II) bis(tetrabutylammonium), Solaronix Co.) ethanol solution (0.2 mM) and kept in it in darkness for 24 h. For fabrication of counter electrode, a drop of H$_2$PtCl$_6$ (chloroplatinic acid hexahydrate, Sigma-Aldrich) isopropanol (Alfa Aesar) solution (0.5 mM) falls on FTO glass and spreads uniformly, followed by heating at 400 °C in air for 20 min. In the cell fabrication process (Figure 6.2b), the TiO$_2$ samples are taken out of dye solution and rinsed with ethanol and dried softly. A piece of hot seal film (100 µm thick, Solaronix Co.) with a centric square hole is put on the sample, which is then covered by Pt-coated FTO glass with its conductive side facing inside, in order to form a sandwiched
structure. By proper hot press, the seal film is softened to bond the anode and cathode together without electric short-circuits. Since the TiO$_2$ film is trapped into the spacing of the assembly, the redox electrolyte, an ionic liquid containing 0.60 M BMIM-I, 0.03 M I$_2$, 0.5 M TBP, and 0.10 M GTC in a mixture of acetonitrile and valeronitrile (v:v = 85:15) (ES-0004, io.li.tec, Germany), is then injected into the spacing via one hole of FTO glass. Make sure that no air bubble exist in the spacing, especially between TiO$_2$ film and counter electrode. The holes in FTO glass are then sealed with Scotch tape or hot seal film plus two pieces of transparent glass. Finally, a dye-sensitized solar cell based on TiO$_2$ nanotube arrays is made for cell measurements.

![Fabrication of anodic TiO$_2$ nanotube arrays](a) Heat treatment, TiCl$_4$ modification and dye sensitization, and (b) assembly of dye-sensitized TiO$_2$ film with hot seal film and Pt-coated FTO glass to obtain a solar cell subsequently filled with organic electrolyte.

The working performance of the DSSC is tested by recording the current–voltage (I–V) curves with a Keithley 2400 source meter (Oriel) under illumination of simulated AM 1.5G solar light (100 mW cm$^{-2}$) coming from a 150 W Xenon arc lamp (Oriel-6256 equipped with an AM 1.5G filter) controlled by a solar light simulator (Oriel-67005). The light intensity is calibrated using a calibrated standard Si solar cell at 100 mW cm$^{-2}$ (Newport 91150) fitted with a KG-5 filter (Schott). The current density can be obtained by four times of current read from the I-V curves. Hence, short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$) and
maximum output power density \( P_{\text{max}} \) are read or calculated. Another important parameter is the Fill Factor (FF), which is described by this equation:

\[
\text{FF} = P_{\text{max}} \times (V_{\text{oc}} \times J_{\text{sc}})^{-1}
\]

(6.2)

The most important parameter of a solar cell is the photo-light conversion efficiency \( \eta \), and can be obtained from this equation:

\[
\eta = V_{\text{oc}} \times J_{\text{sc}} \times \text{FF} \times \text{incident light energy}^{-1} \times 100\%
\]

(6.3)

where the incident light energy is 100 mW cm\(^{-2}\).

### 6.3 Results and Discussion

#### 6.3.1 Morphology Evolution of TiO\(_2\) Nanotube Arrays

Figure 6.3 show SEM images of TiO\(_2\) nanotube arrays synthesized by constant-voltage or alternating-voltage conditions in EG electrolytes containing 0.3 wt\% NH\(_4\)F and 5 vol\% H\(_2\)O at room temperature. The direct anodization at 60 V leads to formation of single-layer TiO\(_2\) nanotube arrays perpendicular to the Ti substrate (Figure 6.3a-b). The tubular structure is composed of well-aligned hollow nanotubes with an open entrance (Figure 6.3c) and a semi-hemispherical closed bottom. These tubes have smooth walls, with an average length of \( \sim 3.10 \mu m \). Their outer diameter is slightly increased from the top (120 nm) to bottom (152 nm), and the gaps among them tend to be narrower at the bottom, due to dissolution of formed tube walls by electrolyte. The wall dissolution makes the tube with V-like hollow structure [18]. These gaps serve as ion diffusion channels for development of inter-tube cavities toward the Ti substrate and thus narrowing gaps is not favorable for ions outside to diffuse and reach the bottom.

The previous results demonstrate that the 1:1 ratio of high-voltage anodization time \( t_1 \) to low-voltage anodization time \( t_2 \) is a critical parameter for synthesis of double-layer TiO\(_2\) nanotube arrays by using three high/low-voltage anodization steps in EG electrolytes containing 0.3 wt\% NH\(_4\)F and 5 vol\% H\(_2\)O at room temperature [5]. This in-situ preparation of double-layer TiO\(_2\) nanotubes is much more convenient than reported two-step anodization method using alternating electrolytes with different compositions [7, 8]. Figure 6.3e shows double-layer TiO\(_2\) nanotubes synthesized by an anodization sequence with 60 V for 10 min followed by 10 V for 10 min \((t_1/t_2 = 1:1)\) and 60 V for 10 min (Figure 6.3c), with the total high-voltage anodization time (20 min) the same as that for growing single-layer nanotubes in Figure 6.3a. Both nanotubes in the upper layer and lower layer are smooth-walled and highly ordered. The upper layer reaches a thickness of \( \sim 1.6 \mu m \) where the nanotubes have an outer diameter of \( \sim 152 \) nm, and the lower layer is 1.7 \( \mu m \) thick and the outer tube diameter becomes a little larger (\( \sim 172 \) nm). Figure 6.3f presents the top-view SEM image of these hollow double-layer nanotubes, showing the upper-layer tubes with round open entrances. In addition, it is worth noted that that titanium element is fully oxidized during formation of either single-layer or double-layer structure by anodization, yielding true TiO\(_2\) nanotubes [5]. Likewise, as reduce the anodization time to 4 min but keep time ratio of high-voltage and low-voltage anodization \((t_1/t_2 = 1:1)\) unchanged, shorter double-layer TiO\(_2\) nanotubes are yielded (Figure 6.4a-b).
Figure 6.3 Cross-sectional SEM images and anodization sequence of TiO$_2$ nanotubes formed in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O under different conditions: (a-c) 60 V for 20 min (inset: whole nanotube array), (d-f) 60 V for 10 min, followed by 10 V for 10 min and 60 V for 10 min (inset: whole double-layer nanotube arrays).

The high/low-voltage anodization steps are then performed for more times to explore morphological evolution of TiO$_2$ nanotubes. Anodic oxidation of Ti with three anodization steps at 60 V for 20/3 min separated by two steps at 10 V for 20/3 min (Figure 6.4c) does not produce TiO$_2$ nanotubes of more layers such as 3 layers, but yields a new type of double-layer nanotube arrays that consists of closed-bottom smooth-walled nanotubes in the upper
layer and bamboo-type nanotubes (one ridge on each tube) in the lower layer (Figure 6.4d). In this process, the total high-voltage anodization time is 20 min and resultant double-layer structure is ~3.0 µm, and the spacing between the bamboo ridge and tube base is about 1050 nm. Furthermore, another anodization with four steps at 60 V for 5 min separated by three steps at 10 V for 5 min (Figure 6.4e) does not yield nanotubes of more layers such as 4 layers either, but produces similar double-layer nanotube arrays with smooth-walled nanotubes in the upper layer and bamboo-type nanotubes (two ridges on each tube) in the lower layer (Figure 6.4f). The total high-voltage anodization time remains as 20 min, the same as that for growing nanotubes in Figure 6.3a, d and Figure 6.4 d. This double-layer structure has a total thickness of ~2.9 µm, and the spacing between the two ridges on the lower-layer nanotubes is ~800 nm (Figure 6.4f). It is noted that the total thicknesses of the four different nanotube arrays in Figure 6.3a, d and Figure 6.4 d, f are quite close (2.9 – 3.3 µm), since the total high-anodization voltage time for growing these nanotubes is the same (20 min).

It is observed that more high-voltage anodization steps does not produces TiO$_2$ nanotubes of more layers but induces more ridges on the bamboo-type tubes in the lower layer while the whole TiO$_2$ structure remains as double-layer. For example, an anodization sequence of five steps at 60 V for 4 min separated by four steps at 10 V for 4 min (Figure 6.5a) results in one layer of smooth-walled nanotubes above and the other layer of bamboo-type nanotubes with three ridges on each below (Figure 6.5b). In this structure, the top layer is composed of small closed-bottom nanotubes with a length of ~0.5 µm and an outer diameter of ~94 nm, which covers a layer of bamboo-type nanotubes that are larger (~160 nm in outer diameter) and much longer (~2.6 µm). The spacing between two neighboring ridges (or the length of tube sections) is estimated to be ~645 nm, a little longer than the length of top-layer nanotubes, since the top layer suffers from dissolution by electrolyte during the anodization process. Open entrances can be also observed in top-layer TiO$_2$ nanotubes, as shown in its top-view SEM image (Figure 6.5c). The evolution of smooth nanotubes into bamboo-type nanotubes in the lower layer in a double-layer structure indicates some spontaneous changes in the local electrochemical conditions for growth of TiO$_2$ nanotubes under prolonged anodization sequences.

Furthermore, if we increase both high-voltage and low-voltage anodization time while keeping $t_1/t_2$ as 1 in the multiple-step anodization sequence, double-layer TiO$_2$ nanotube arrays are still resulted. For instance, an anodization sequence of five steps at 60 V for 10 min separated by four steps at 10 V for 10 min (Figure 6.5d) yields a double-layer TiO$_2$ structure composed of smooth nanotubes on the top and bamboo-type nanotubes at the bottom (Figure 6.5e). In this structure, the upper-layer nanotubes are smooth and closed-bottom with a length of ~1.3 µm and the lower-layer bamboo-type nanotubes is ~5.7 µm long. Open entrances are also observed in the top-view SEM image of upper-layer nanotubes (Figure 6.5f). Some lower-layer nanotubes only have one bamboo ridge on their outer walls, different from those bamboo-type nanotubes with three ridges produced using the same number of voltage pairs but shorter high-voltage and low-voltage anodization time (4 min). The spacing from this single ridge to tube top (or the length of 1st section) is ~1.6 µm, almost one fourth of the total length of bamboo-type nanotubes, and thus it is assumed that two ridges disappear on these tubes during subsequent alteration of high/low-voltage
Figure 6.4 Cross-sectional SEM images and anodization sequences of TiO₂ nanotube arrays synthesized in EG electrolytes containing 0.3 wt% NH₄F and 5 vol% H₂O under different conditions: (a-b) 60 V for 4 min, followed by 10 V for 4 min (t₁/t₂ = 1:1) and 60 V for 4 min (inset: whole double-layer nanotube arrays), (c-d) three anodization steps at 60 V for 20/3 min separated by two steps at 10 V for 20/3 min (inset: whole double-layer nanotube arrays), (e-f) four anodization steps at 60 V for 5 min separated by three steps at 10 V for 5 min (inset: whole double-layer nanotube arrays).
Figure 6.5 Anodization sequences and cross-sectional SEM images of TiO$_2$ nanotubes formed in EG electrolytes containing 0.3 wt\% NH$_4$F and 5 vol\% H$_2$O under different conditions: (a-c) five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min (inset: whole double-layer structure), (d-f) five anodization steps at 60 V for 10 min separated by four steps at 10 V for 10 min (inset: whole double-layer structure).

Anodization conditions for tube growth beneath a thicker upper layer and a longer tube section. It is ensured that the closely-packed long tubes hinder inward diffusion of ionic species (e.g. F$^-$ ions and H$_2$O) from reaching tube bases, which creates a different electrolyte
environment there, with respect to anodization shown in Figure 6.5a which produces shorter upper-tubes and tube sections.

6.3.2 Anodic Current versus Time Transients

It is well known that current-time transients during anodic oxidation of Ti under constant-voltage or alternating-voltage conditions reveal details about different stages of the film growth process and corresponding morphologies [19-22]. Figure 6.6a and b show typical current-time transients for anodizing Ti at a constant voltage of 60 V for 20 min in agitated electrolyte. When the applied voltage goes up to 60 V at the beginning, the initial anodic current is increased as well and reaches to its maximum. In this process, water is decomposed fast at anode and Ti is oxidized quickly to form a compact oxide film. The related reactions are as follows:

\[ \text{H}_2\text{O} \rightarrow 2\text{H}^+ + \text{O}^{2-} \quad (6.4) \]
\[ \text{Ti} + 2\text{O}^{2-} \rightarrow \text{TiO}_2 + 4\text{e} \quad (6.5) \]

The resultant compact oxide film hinders Ti4+ ion transport into the electrolyte and thus stops the current from increasing. The oxide film is then further thickened, yielding an abrupt current drop. According to the high field-assisted ionic transport mechanism [23], the relationship between anodic current and the potential difference across the oxide film can be expressed by the following equation:

\[ j = A \exp(BU/d) \quad (6.6) \]

where \( j \) is the ionic current, \( A \) and \( B \) are electrolytic constants, \( U \) is the applied voltage and \( d \) refers to the oxide film thickness. Hence, a thicker compact oxide film (larger \( d \)) leads to a weaker electric field across the film (\( U/d \)), and a smaller ionic current (\( j \)). The formation of an initial compact film is commonly regarded as the stage I of TiO2 nanotube growth, as noted in the current plot in Figure 4b. Later, some species, especially F- ions, aggregate in regions with high surface energy (e.g. micro cracks) and selectively dissolve oxides there to start origination of tiny pits and pores in the compact film [24]. The dissolution reaction is described as:

\[ \text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow \text{TiF}_6^{2-} + 2\text{H}_2\text{O} \quad (6.7) \]

The development of pits and pores converts the film into a porous structure and attenuates the film thickness (reduced \( d \) in eqn(3)), which facilitates ion transport through this film to slow down the current drop (or usually to increase the anodic current slightly during anodization of Ti in static electrolytes) [21, 22]. Formation of the porous film is the growth stage II of TiO2 nanotube arrays. As the pores grow deeper, the inter-pore sites become high-surface-energy regions attracting F- ions for faster dissolution of oxides there [24, 25]. As a result, cavities emerge between the pores, and turn the porous film into a tubular structure. An array of parallel nanotubes appears with a thin compact barrier layer underneath, and their primary development in depth continues to attenuate the oxide film and retard the current drop, but later their steady-state growth yields relatively stable current as shown in Figure 4b. Formation of the tubular film is the growth stage III of anodic TiO2 nanotubes. Hence, it can be concluded that the current transient measurement provides
insight for exploring the morphological evolution of anodic oxide film grown on Ti substrate under constant voltage steps.

Figure 6.6d displays the current-time plots recorded during the anodization of Ti under a sequence of 60 V for 10 min, followed by 10 V for 10 min and 60 V for 10 min (Figure 6.5d). Similarly, a current peak appears after the initial voltage ramp to 60 V, due to the formation of a compact oxide film (stage I), and then the current drops at a reducing rate due to the origination of pores or tubes in the oxide film (stage II and III). Within the tube growth, the voltage is quickly altered to 10 V at ~660 s, yielding an instant current drop by ~5.8 times. However, the current quickly recovers a little and then drops (Inset of Figure 6.6d), suggesting that the oxide film becomes a little thinner first and then thicker. The temporarily thinning oxide film is due to weaker oxidation of Ti and slower movement of barrier layer at 10 V, while H⁺ and F⁻ ion profiles achieved at 60 V continue to dissolve oxides of barrier layer at a fast speed. After a short while, these species are mostly consumed and their profiles are finally adjusted according to anodization conditions at 10 V. The barrier layer grows to be thicker, yielding a small current drop, but the subsequent pit or pore formation in this layer yields an increased current. If the anodization step at 10 V is performed for a sufficient time (e.g. ≥ 30 min), small tubes can be formed under the barrier layer, but the holding time of 10 min here only allows origination of tiny pores, as described in the earlier work [5]. When the voltage is tuned to be 60 V again, the current increase/decrease/increase sequence vividly indicates the three growth stages of a new layer of nanotubes under the first one [19, 20]. Surprisingly, this current variation sequence represents typical current-time behaviors of anodizing Ti in static hydrous electrolytes [20, 22], indicating that ion diffusion process dominates the mass transfer inside the nanotube layer, rather than the convection process in stirred bulk electrolyte [5]. The final current plateau tells a steady growth state of the new-layer nanotubes at 60 V, and its height is lower than the small current peak before it.

Figure 6.6f presents the current-time plots recorded during anodic oxidation of Ti with five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min (Figure 6.6e). The first two high-voltage anodization steps produce similar current changes as in Figure 4d, suggesting formation of double-layer TiO₂ nanotube arrays. However, the subsequent three anodization steps at 60 V yield different current-time transients featured by their current plateaus higher than the peak before it. For example, the current starts to rise at ~1108s and reach a peak, as the voltage goes back to 60 V, but later drops a little due to thickened barrier layer under the lower-layer nanotubes. Then the pit or pore origination attenuates the barrier layer, which could only cause the current to increase until reaching a plateau the same as the previous one. However, the current keeps increasing to form a plateau higher than the peak right before it. It is assumed that growth of bigger pores in the barrier layer involves after the voltage returns to 60 V, and further attenuates the barrier layer. In the presence of formed tube section above, these tubes and inter-tube cavities are most likely to be the bigger pores, which are much larger than nascent pits originated at 60 V. Besides, identical current-time plots appear in the final two high-voltage steps as well, suggesting that the same morphological features for the tubes emerge in the three anodization steps. At this point, it is understood that there is a competitive relation between growth of former tube sections and nascent pits along the vertical direction to the Ti substrate. Since ion diffusion to the bottom is slowed down by the closely arrayed nanotube
Figure 6.6 Anodization sequences and current-time curves for growth of TiO$_2$ nanotube arrays in stirred EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O under different conditions: (a-b) 60 V for 20 min, (c-d) 60 V for 10 min, followed by 10 V for 10 min ($t_1/t_2 = 1:1$) and 60 V for 10 min, (e-f) five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min, (g-h) five anodization steps at 60 V for 10 min separated by four steps at 10 V for 10 min.
layer and a compact thin barri er layer above, pit development is difficult inside the base bar rrier layer, which is incomparable to the re-started growth of formed tubes and cavities. Therefore, the newly-born pits are consumed or eaten, which greatly reduces the probability of developing a new nanotube layer from these pits. Moreover, the temporarily thickened barrier layer leaves some debris on tube walls to generate ridges, yielding bamboo-type tubes [5], as shown in Figure 6.5b and e.

Figure 6.6h exhibits current-time transient recorded during anodization of Ti via five anodization steps at 60 V for 10 min separated by four steps at 10 V for 10 min (Figure 6.6g) to obtain longer nanotubes on each layer. It can be seen that this current time plot is much like that shown in Figure 6.6f, suggesting some similarities in the growth of double-layer TiO$_2$ nanotubes during multi-voltage alterations. However, one distinct difference between the two plots is the current changes in the final two voltage switches from 10 V to 60 V. The current increases after the voltage is back to 60 V, then drops slightly, and soon after rises to a current plateau higher than the current peak right before it. The reduced current drop indicates that the barrier layer changes very little in thickness at the voltage switch, thanks to much fewer ions reaching the base barrier layer through further thicker tube layer and tube sections above. Consequently, pit formation tends to be slowed down or even suppressed in barrier layer, which is easier to be replaced by re-started growth of former tubes and inter-tube cavities, yielding smooth tube sections shown in Figure 6.5e.

6.3.3 Growth Mechanism of Multilayer TiO$_2$ Nanotubes

The previous findings reveal that the evolution from single-layer TiO$_2$ nanotubes to double-layer nanotubes is attributed to efficient variations of ion concentration profiles inside tubes and inter-tube cavities on the switch of high and low anodic voltages. Based on the analysis on real-time current transients and post morphological observations, growth mechanism of double-layer TiO$_2$ nanotubes is proposed here. To simplify the model, we only take H$^+$ ion concentration (or pH) gradient profile inside TiO$_2$ nanotubes for example to explain their formation process. In neutral electrolytes, H$^+$ ions are mostly generated from water decomposition at the tube bottom (eqn(6.4)), which partly diffuse towards bulk electrolyte and establish a pH profile decreasing from the tube bottom to tube entrance (shaded area in Figure 6.7a). After the anodization starts, H$^+$ gradient profile is gradually established in the first two stages (I and II) that finally allows stable growth of TiO$_2$ nano tubes under high voltage [3]. During constant-voltage anodization (60 V), Ti is continuously oxidized (eqn (6.5)) and the oxide/metal interface moves towards the substrate, while the oxides at the tube bottom are dissolved (eqn (6.7)) and the electrolyte/oxide interface moves towards the substrate as well. This system would yield single-layer TiO$_2$ nanotube arrays with controllable lengths, with a compact oxide barrier layer (thinner than tube walls) below. These nanotubes grow in a steady state, and the corresponding anodic current-time plot is smooth but drops at a slow rate.

Once this system is altered to a lower voltage (10 V), fewer H$^+$ ions are yielded and the pH profile is changed to less steep gradient (Figure 6.7b). It would slow down dissolution of oxides at the tube bottom, yielding a thicker compact barrier layer there. After a certain period, tiny pits and pores emerge in the barrier layer and grow when the low-voltage anodization proceeds. Now H$^+$ ions become much fewer due to outward diffusion and
Figure 6.7 Schematic showing growth of double-layer structure containing smooth TiO$_2$ nanotubes or bamboo-type TiO$_2$ nanotubes via anodic oxidation: (a) pH gradient profile in nanotubes during their steady growth at a high voltage, (b) much less steep pH gradient and tube formation when a low voltage is kept for a sufficiently long period ($t_2/t_1 \geq 1$), (c) formation of double-layer smooth TiO$_2$ nanotubes, (d) pH gradient profile in double-layer nanotubes during their steady growth at a high voltage, (e) less steep pH gradient in the lower-layer nanotubes and pit or pore formation in the barrier layer after the voltage is altered to a low value, (f) formation of double-layer structure with long bamboo-type nanotubes in the lower layer.
participation in the oxide dissolution, and the pH gradient is much less steep. At a critical point, this system is able to induce a second formation of a new layer of nanotube arrays below the upper layer, under a subsequent high voltage (60 V), based on the existing bigger pits and pores, yielding a double-layer structure (Figure 6.7c).

In the second high-voltage anodization process, a steady pH gradient profile is established to allow the steady growth of lower-layer nanotubes (Figure 6.7d). If the voltage is switched to a lower value (10 V) again, fewer H⁺ ions are produced and the pH gradient profile in lower-layer nanotubes becomes less steep (Figure 6.7e). After a short while, tiny pits and pores are originated in the barrier layer under the low voltage (Figure 6.7e), but their growth is relatively slow since the closed-bottom upper-layer tubes with a barrier layer below hinders ions outside (e.g. F⁻ ions) from diffusion to the bottom of lower-layer tubes, and ions inside (e.g. H⁺ ions) from diffusion to the entrance of upper-layer tubes. Hence, within the holding time of low voltage that is equal to time of previous high voltage step, the pH gradient profile in the lower layer fails to have sufficient variation for initiation of a third tube formation at the subsequent high-voltage step. A subsequent step back to a high voltage (60 V) would thicken the barrier layer near the substrate, which then is attenuated by growth of existing pits and pores. However, the restarted growth of former tubes and inter-tube cavities is faster than them, and thus they are consumed. This helps to attenuate the barrier layer and facilitate ion transport through it, and further increase the anodic current as shown in current-time plots in Figure 6.6. In particular, the concave cavity deepens relatively fast towards the convex triangular pillar of metal among three neighboring tube bases, leaving some residues of thickened barrier layer on walls of two neighboring tubes to form ridges, yielding bamboo-type features (Figure 6.7f). Thereby, the first tube section of bamboo-type nanotubes is generated in the lower layer. More ridges are formed in the same way during the following high/low-voltage anodization steps, since the formed upper-layer tubes and ridge layers retard ion diffusion through the whole tubular layer. Hence, the anodic current transients for the final three voltage switches from 10 V to 60 V are the same, as shown in Figure 6.6f.

So far it has been known that ion diffusion inside nanotubes and cavities is very significant not only for initiation of new nanotube layer below, but also for formation of bamboo ridges on the lower-layer tubes. In some cases, high-voltage anodization proceeds for a long period, resulting in long upper-layer tubes and long tube sections with large spacing between ridges shown in Figure 6.5e. These nanotubes are closely packed, and their gaps become narrow when near to the bottom, which makes ion diffusion much more difficult. As the voltage is altered back to a high value, thickness of the barrier layer changes very little in which tiny pits possibly emerge later. However, these pits grow so slowly that the re-grown tubes and cavities consume them immediately. As a result, formation of other bamboo ridges after the first one is suppressed, yielding long smooth tube walls with fewer ridges. At this point, it is assumed that the smooth tube section is easier to be produced in organic solvent-based electrolytes with higher viscosity (e.g. reduced water content) and slower ion diffusion.

### 6.3.4 Role of Low-Voltage Anodization

According to the growth model above, ion diffusion at low-voltage anodization plays an
important role in the formation of a new tube layer or a ridge layer. A sufficiently long low-voltage anodization step is critical for growth of double-layer nanotubes, and even for origination of an extra layer of small nanotubes between the upper layer and lower layer [5]. Since ion diffusion length relies on the time given, herein we vary the duration of low-voltage anodization to study its influences on the growth of lower-layer bamboo-type nanotubes. Figure 6.8b show SEM image of double-layer nanotubes formed by four anodic oxidation steps at 60 V for 4 min separated by three steps at 10 V for 4 min, 10 min and 20 min, respectively (Figure 6.8a). The resulted structure is also composed of short closed-bottom nanotubes in the upper layer and bamboo-type nanotubes with two ridges on each in the lower-layer. The spacing between bamboo ridges is ~640 nm, which is close to the ridge spacing formed by five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min shown in Figure 6.5b, indicating that different low-voltage anodization time has no effect on the ridge spacing. Moreover, it is noted earlier that the total thicknesses of four different TiO$_2$ nanotube arrays in Figure 6.3b, 6.3e, 6.4d, 6.4f and 6.5b are quite close (2.9–3.3 µm) due to the same total time (20 min) of high-voltage anodization steps, though their total low-voltage anodization time ranges from 0 min to 16 min. These results indicate that the ridge spacing and nanotube length are dependent on high-voltage anodization time, rather than low-voltage anodization. This can also be understood from the current-time plots in Figure 6.6f and h showing much smaller anodic current at low-voltage steps than at high-voltage steps. Theoretically, within the same time period, much larger quantity of electric charge is transferred at a high-voltage step than at a low-voltage step, and Ti is mostly oxidized (eqn(6.5)) to form oxides during high-voltage anodization to achieve nanotube growth, according to Faraday’s law [26].

On the other hand, a proper low-voltage anodization step is indispensable for ridge formation on the lower-layer bamboo-type nanotubes. To find out the minimum low-voltage anodization time required for the formation of new nanotube layer or ridge layer, we apply an anodization sequence consisting of different low-voltage steps with decreasing time. Figure 6.8d shows SEM image of double-layer TiO$_2$ nanotubes formed by four anodization steps at 60 V for 4 min separated by three steps at 10 V for 4 min, 2 min and 1 min, respectively (Figure 6.8c). The first low-voltage anodization step (10 V for 4 min) helps initiation of a new tubular layer under short upper-layer nanotubes. The second low-voltage step (2 min) facilitates formation of a ridge on each nanotube in the lower layer. However, no more ridges are observed in the SEM image in Figure 6d, indicating that the third low-voltage step (1 min) is too short to induce the ridge formation due to low-voltage anodization step for 1 min is added. This can be explained by the ion-diffusion-controlled in-situ growth mode of double-layer and bamboo-type TiO$_2$ nanotubes above. Inside the lower-layer bamboo-type tubes, ion diffusion is so slow that the ion concentration profile established at previous high-voltage anodization (60 V for 4 min) can change little within too short time (1 min), and thus pit formation cannot be induced here. Once the high voltage is applied again, only growth of tubes and inter-cavities is re-started, yielding smooth tube sections. Hence, it is known that a proper ratio of high/low-voltage anodization time is critical for wall features of lower-layer nanotubes in double-layer structures. In summary, low-voltage anodization time needs to be long enough to induce ridges on bamboo-type nanotubes, but overly long low-voltage anodization time has no effect on the ridge spacing.
6.3.5 Self-Assembly Capability of TiO₂ Nanotubes

In addition to the time ratio of high-voltage and low-voltage anodization steps, electrolyte composition also affects formation and morphology of double-layer TiO₂ nanotube arrays. It is found in the earlier work that formation of bamboo-type or double-layer TiO₂ nanotubes does not occur either in anhydrous EG electrolytes due to too slow ion diffusion, or in EG electrolytes with more than 20 vol% H₂O due to induced growth instability by too fast ion diffusion [5]. There is an inherent relation between electrolyte viscosity and ion diffusion coefficients (D), which can be expressed by Stokes-Einstein equation [27]:

\[
D = \frac{k_B T}{6 \pi \eta r}
\]  

(6.8)

Where \(k_B\) is Boltzmann's constant, \(T\) is temperature, \(\eta\) is viscosity of the electrolyte, \(r\) is the radius of ion species. As a result, for the same ion species, a reduced viscosity gives higher diffusion coefficients and results in faster ion diffusion, which could definitely influence the morphological features of double-layer TiO₂ nanotubes according to the growth model.
discussed above. Figure 6.9a presents an SEM image of double-layer TiO$_2$ nanotubes formed in EG electrolyte with 0.3 wt% NH$_4$F and 10 vol% H$_2$O via an anodization sequence shown in Figure 6.5a. Due to the increased water content and thus enhanced dissolution of oxides by water, the length of upper-layer nanotubes is reduced to be $\sim$250 nm, almost half of upper-layer tubes formed in EG electrolytes containing less water (5 vol%) via identical anodization steps (Figure 6.5a). Below the upper-layer nanotubes are a thin porous film and a layer of bamboo-type nanotubes with only one ridge. The ridge spacing is $\sim$460 nm. The ridge is supposed to be generated in the final voltage switch from 10 V to 60 V, and the disordered porous film emerges under the upper layer during other voltage alterations. Hence, we continue to increase the water content to 15 vol% for anodization via the same sequence shown in Figure 6.5a. Disordered porous layers are formed below a tube layer (Figure 6.9b).

Figure 6.9 Cross-sectional SEM images of TiO$_2$ nanotube arrays grown by five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min (shown in Figure 6.5a) in EG electrolytes containing 0.3 wt% NH$_4$F and (a) 10 vol% H$_2$O, (b) 15 vol% H$_2$O.

Figure 6.10 Cross-sectional SEM images of double-layer TiO$_2$ nanotubes synthesized in EG electrolytes with 0.3 wt% NH$_4$F and 15 vol% H$_2$O by an anodization sequence of 60 V for 60 min, followed by 10 V for 10 min and 60 V for 60 min: (a) double-layer nanotubes shown at low magnification, (b) lower-layer nanotubes shown at higher magnification.
Sometimes, such disordered structure can be overcome by self-assembly ability of porous anodic TiO$_2$ films, and thus an ordered tubular structure appears again, as shown in the SEM images of double-layer TiO$_2$ nanotubes obtained via a sequence composed of 60 V for 60 min, 10 V for 10 min and 60 V for 60 min in EG electrolyte containing 0.3 wt% NH$_4$F and 15 vol% H$_2$O (Figure 6.10). In these SEM images, tubular structure appears under disordered structure in the lower layer of TiO$_2$ nanostructure. Therefore, we come to a conclusion that faster F$^-$ ion transport and H$^+$ ion yield may accelerate the oxide dissolution and render tube growth instable because the viscosity of EG electrolyte is reduced by increasing water content to facilitate the ion diffusion. If beyond self-assembly ability of anodic TiO$_2$ films under specific conditions, the instability leads to formation of disordered or even spongeous oxide films. On the other hand, some cylindrical tube embryos and corresponding concave regions below are observed inside the porous layers in Figure 6.9b, suggesting probability of achieving multiple layers of closed-bottom nanotubes by anodizing other valve metals (e.g. Zr, Ti-Zr, Ti-Nb alloys) [28-30], since their resultant oxide nanotubes have higher structural robustness and flexibility in hydrous electrolytes.

6.3.6 Effects of Time and Water Content on Ridge Spacing

It has been reported in literature that bamboo-type TiO$_2$ nanotubes with dense ridges have larger surface area and thus show enhanced DSSC efficiency as photo-anodes compared to smooth-walled TiO$_2$ nanotubes [12, 13]. The study above has demonstrated that the ridge spacing is dependent on high-voltage anodization steps. Therefore, we can manipulate and optimize morphological features of bamboo-type TiO$_2$ nanotubes for device applications. Figure 6.11b shows SEM image of double-layer TiO$_2$ nanotubes formed by five anodization steps at 60 V for 2 min separated by four steps at 10 V for 2 min (Figure 6.11a). This structure contains one layer of short closed-bottom nanotubes (~182 nm long) covering a layer of longer bamboo-type nanotubes with three ridges on each. The ridge spacing is about ~330 nm, much shorter than that of nanotubes grown by similar anodization sequence but with double time for each step shown in Figure 6.5a. When the anodization time is further reduced to 1 min (Figure 6.11c), the ridges become much denser with a spacing of ~165 nm (Figure 6.11d), while the total thickness of the nanotube array in Figure 6.11b (1.43 µm) remains similar to that in Figure 6.11d (1.48 µm) are quite close due to the same total time of high-voltage anodization steps (10 min). These results suggest that the ridge spacing or density can be modified by varying duration of high-voltage anodization steps. As more high/low-voltage anodization steps are applied, dissolution of upper-layer nanotubes is more severe, yielding a layer of directional nanowires on the top of bamboo-type nanotubes as shown in Figure 6.11d.

Additionally, water content also affects ridge spacing in bamboo-type nanotubes of lower layer. For example, the ridge spacing is 165 nm for double-layer nanotubes grown in EG electrolyte with 5 vol% H$_2$O, and 270 nm for those formed in EG electrolyte with 2 vol% H$_2$O (Figure 6.12a), by using the same anodization sequence shown in Figure 6.11c. When an anodization sequence of five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min is performed in the two electrolytes, the ridge spacing is increased from 645 nm to 1100 nm (Figure 6.12b). The discrepancy could be explained by this fact: less water in electrolytes allows for thinner barrier layers at the substrate because the donation of
oxygen becomes difficult (eqn(6.4) and (6.5)) and results in a reduced tendency to form oxide [31, 32]. Ionic transport across the barrier layer is enhanced, and thus accelerates the motion of this layer toward substrate, yielding faster growth of nanotubes. This explanation is evidenced by the current-time plot recorded during anodization of Ti in EG electrolyte containing 0.3 wt% NH₄F and 3.3 vol% H₂O, via a sequence composed of five steps at 60 V for 10 min separated by four steps at 10 V for 10 min (Figure 6.13a). Current plateaus for high-voltage anodization steps corresponds a current of ~10 mA, which is larger than those (~ 6.4 mA) recorded during anodization in EG containing more water (5 vol%) via the same anodization sequence, indicating faster oxidation of Ti in the electrolyte with less water. A double-layer nanotube structure is formed, and some lower-layer tubes only have one ridge on their outer walls. The ridge spacing is ~2550 nm (Figure 6.13b), much larger than that (~1600 nm) on tubes synthesized in EG containing more water (5 vol%) via the same anodization sequence. The upper layer is consisting of agglomerated long nanotubes with closed bottoms (Figure 6.13c), and the other wall section below the ridge of lower-layer nanotubes is smooth (Figure 6.13d). In contrast, a thicker barrier layer is formed to hinder

Figure 6.11 Cross-sectional SEM images and anodization sequences of double-layer TiO₂ nanotube arrays formed in EG electrolytes with 0.3 wt% NH₄F and 5 vol% H₂O in different conditions: (a-c) five anodization steps at 60 V for 2 min separated by four steps at 10 V for 2 min (inset: the whole double-layer nanotube array), (e-f) ten anodization steps at 60 V for 1 min separated by nine steps at 10 V for 1 min (inset: the whole nanotube array).
Figure 6.12 Cross-section SEM images of lower-layer bamboo-type TiO$_2$ nanotubes in the double-layer structure synthesized in EG electrolytes containing 0.3 wt% NH$_4$F and 2 vol% H$_2$O with different anodization sequences: (a) ten anodization steps at 60 V for 1 min separated by nine steps at 10 V for 1 min as shown in Figure 6.8d, (b) five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min as shown in Figure 6.5a.

Figure 6.13 Cross-sectional SEM images of lower-layer bamboo-type TiO$_2$ nanotubes in a double-layer structure synthesized in EG electrolytes containing 0.3 wt% NH$_4$F and 3.3 vol% H$_2$O by using an anodization sequence of five anodization steps at 60 V for 10 min separated by four steps at 10 V for 10 min as shown in Figure 6.6g.
ionic transport and reduce the growth rate of tubes when the water content is increased. As a result, the ridge spacing is shorter, as evidenced by 645 nm to 460 nm for bamboo-type tubes formed by the same anodization sequences in EG electrolytes with increasing water content from 5 to 10 vol%.

Figure 6.14 summarizes the correlation between ridge spacing observed in various SEM images presented earlier and high-voltage anodization time and water content. It can be clearly seen that the ridge spacing increases linearly from 165 nm to 1600 nm, with the high-voltage anodization time from 1 min to 10 min. Such correlation and the theoretical ridge spacing can be derived from growth length (L) of nanotubes estimated by using eqn (1) and (2) and Faraday’s law below:

$$L = \frac{QM}{(Fn\delta)} \tag{6.9}$$

where Q is the circulated charge (C cm$^{-2}$), M is molecule weight of TiO$_2$ (79.9 g mol$^{-1}$), F is the Faraday constant (96500 C equiv$^{-1}$), n is the number of electrons involved in the reaction and $\delta$ is density of TiO$_2$ (3.8~4.1 g cm$^{-3}$) [33]. The circulated charge is calculated by integrating the corresponding current-time plot. Therefore, the theoretical ridge spacing can be calculated using eqn(6.9). For example, the current-time plot corresponding to the fourth high-voltage anodization (1650 s to 1950 s in Figure 6.6e) gives a total circulated charge of 2.160 C cm$^{-2}$, and leads to a theoretical oxide growth length of ~1120 nm. However, the oxide film appears on both the front side and back side of Ti substrate, and simultaneous growth of nanotubes at the two sides is lopsided: tube length is longer at the front side than at the back side [34]. For anodization in EG electrolyte with 0.3 wt% NH$_4$F and 2 vol% H$_2$O at 60 V, the tube length is ~29% bigger at the front side than at the back side [34] and thus we estimate the theoretical ridge spacing of the sample to be ~650 nm, very close to the actual spacing of 645 nm between ridges on nanotubes formed by four min-long high-voltage anodization step. Correspondingly, the theoretical (or actual) grow rate of these nanotubes is ~162 nm per minute. If the back side is covered so that anodization only occurs on the front side of Ti substrate, more precise theoretical spacing can be calculated from

![Figure 6.14 Relationship between ridge spacing and time for high-voltage anodization steps used for synthesis of double-layer structures with lower-layer bamboo-type TiO$_2$ nanotubes in EG electrolytes containing 0.3 wt% NH$_4$F and 2~10 vol% H$_2$O.](image-url)
current-time plots. Furthermore, it is seen from Figure 6.6e and g that the partial circulated charge mostly depends on width of current plateaus of high-voltage anodization steps. Since the plateaus are parallel to the time axis, the linear relationship between ridge spacing and high-voltage anodization time can be anticipated.

6.3.7 Thermal Stability of Multilayer TiO$_2$ Nanotube Arrays

As we mentioned in chapter 4, the as-formed TiO$_2$ nanotubes by anodic oxidation of Ti are amorphous, which are demanded to be transformed to anatase phase for use in dye-sensitized solar cells. Anatase TiO$_2$ film is a crystalline semiconductor solid with inherent band energy structure matched with energy levels of dyes used in DSSCs. Therefore, the thermal stability of single- and double-layer TiO$_2$ nanotubes is investigated here. Figure 6.15a and b show the single-layer nanotubes after heat treatment at 450 °C for 2 h. Clearly, these smooth tubes are well-preserved after annealing, but it is found from the top-view SEM image that their tube walls become a little thick due to the crystallization process at elevated temperature.

![Figure 6.15 Cross-sectional and top-view (insets) SEM images of TiO$_2$ nanotube arrays synthesized in EG electrolytes containing 0.3 wt% NH$_4$F and 5 vol% H$_2$O under different conditions and annealed at 450 °C in air for 2 h: (a) 60 V for 20 min, (b) five anodization steps at 60 V for 4 min separated by four steps at 10 V for 4 min.](image-url)
Likewise, the double-layer tubular structure also survives after annealing (Figure 6.15c), as well as the ridges in lower-layer bamboo-type nanotubes. The upper layer is delaminated and peeled off when the sample is bent for SEM observation. In addition, the tube walls become thick, as seen from the tube entrance (Figure 6.15d). Based on previous studies in Chapter 4 and 5, it is believed that the annealed TiO₂ nanotubes are in anatase phase. These results indicate that the ordered structure of single-layer and bamboo-type and even double-layer nanotubes remains stable upon the heat treatment at 450 °C in air, which is favorable for their DSSC applications.

6.3.8 DSSCs Based on Bamboo-Type TiO₂ Nanotubes

One of conventional applications of TiO₂ nanotubes is to serve as photo anode in dye-sensitized solar cells. Anatase TiO₂ is a photo active material, which can absorb incident blue and ultra-violet light energy to generate free electrons. However, the short-wavelength light only takes a small portion of solar radiation, yielding too low photo conversion efficiencies of pure TiO₂ film. Therefore, photo active organic dyes are synthesized to coat on TiO₂ film and absorb more energy from solar light. The quantity of dye loading on TiO₂ plays a great role in the generation of free electrons. Since only a single layer of dye can chemisorbs on the surface of TiO₂ substrate, the surface area is an affecting factor of DSSC performance. Hence, thick porous TiO₂ films are preferred to improve the dye loading. However, the thickness of mesoporous TiO₂ films for DSSCs cannot exceed 10 µm, because electron-hole recombination becomes more severe and reduces the cell efficiency. Besides, a group of new low-cost and non-toxic dyes with much larger size has been synthesized for economic DSSCs recently, and their penetration into thick mesoporous TiO₂ films for absorption is an issue. Moreover, (quasi-) solid-state DSSCs using solid polymer electrolytes have attracted lots of interest, thanks to their greatly higher long-term stability than DSSCs using liquid electrolytes, but the penetration of higher-viscosity polymer electrolyte into mesoporous TiO₂ film tends to be difficult. According to these problems, ordered one-dimensional TiO₂ or ZnO structures seem to be very promising as the substrate of dye loading for DSSCs. Crystalline ZnO absorbs solar light in a broader wavelength than crystalline TiO₂, and one-dimensional single-crystal ZnO structures are easier to be synthesized than single-crystal TiO₂ structures. However, the chemical bond of dyes onto ZnO substrate is weaker than that between dye and TiO₂ substrate and ZnO films are unavoidably corroded by common dyes and electrolytes, so a ZnO-based DSSC usually has smaller energy conversion efficiencies and poorer stability than a TiO₂-based DSSC.

Anodic TiO₂ nanotube arrays have very higher surface area for dye loading than flat thin films, since usually a single layer of dyes chemisorbs on a TiO₂ substrate. More layers of dye increase the recombination of electrons and holes and reduce injection efficiency of electrons into conduction band of crystal TiO₂ structure. Besides, the order tubular structure facilitates electron transfer into FTO glass below and further decreases electron-hole recombination. It is found that mean free path of electrons in single-crystal TiO₂ nanorods and nanotubes is ~100 µm long, which validates the work on enhancing DSSC performance by prolonging the length of TiO₂ nanotubes. The penetration of dyes in larger size or solid polymer electrolytes into the one-dimensional structure is out of question, for their morphologies can be tuned.
Figure 6.16 Cross-sectional SEM images of TiO$_2$ nanotube arrays synthesized in EG electrolytes with 0.3 wt% NH$_4$F and 5 vol% H$_2$O under different conditions: (a-b) smooth TiO$_2$ grown at 60 V for 60 min, (c-d) bamboo-type nanotubes (NTs, 1 min), grown under AV conditions, with a periodical sequence at 60 V for 1 min and at 40 V for 1 min for 80 cycles; (e-f) bamboo-type nanotubes (NTs, 2 min), grown under AV conditions, with a periodical sequence at 60 V for 2 min and at 40 V for 2 min for 40 cycles.

Figure 6.16 exhibits smooth-walled TiO$_2$ nanotubes and various bamboo-type nanotubes at the same length of 8 µm. The smooth nanotube is produced by anodizing Ti at a constant-
voltage of 60 V in EG electrolyte with 0.3 wt% NH₄F and 5 vol% H₂O (Figure 6.16a and b). The bamboo-type nanotubes are formed under alternating-voltage conditions. A periodical anodization sequence composed of 60 V for 1 min and 10 V for 1 min results in bamboo-type tubes with ridge spacing of 100 nm (Figure 6.16c and d). It should be noted that the ridge spacing here is shorter than that (165 nm) in bamboo-type nanotubes shown in Figure 6.11d, because in this sequence the low voltage of 10 V drastically goes up to 60 V during each voltage switch, without a voltage ramp of 1 V s⁻¹. At this point, it can be seen that the voltage ramp step affects the growth rate of TiO₂ tubes. Similarly, a periodical anodization sequence composed of 60 V for 2 min and 10 V for 2 min results in bamboo-type tubes with ridge spacing of 200 nm (Figure 6.16e and f). The linear increase of ridge spacing with the holding time is in agreement with former analysis in section 6.3.6.

The smooth and bamboo-type TiO₂ nanotubes are then assembled into DSSCs for electrical measurements. Figure 6.17 presents the current-voltage (I-V) plots of these DSSCs under AM 1.5 simulated solar radiation. It could be seen that bamboo-type nanotubes with ridge spacing of ~100 nm gives the largest short-circuit current (Jsc) of 11.60 mA cm⁻², while smooth tubes shows the lowest Jsc of 6.96 mA cm⁻². Table 6.1 lists detailed photovoltaic parameters of the solar cells. Their open-circuit voltages are close due to same materials and processing process used. However, the short-circuit current and cell efficiency are increased with ridge density. The more ridges per unit length of tubes, the higher cell efficiency is. The enhanced performance of DSSCs based on TiO₂ nanotubes at the same thickness is attributed

Table 6.1 Photovoltaic parameters of the solar cells under the simulated sunlight irradiation (AM 1.5, 100 mW cm⁻²).

<table>
<thead>
<tr>
<th></th>
<th>Jsc (mA cm⁻²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
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<tr>
<td>Smooth</td>
<td>6.96</td>
<td>0.85</td>
<td>0.66</td>
<td>3.90</td>
</tr>
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<td>Bamboo NTs-1</td>
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<td>0.81</td>
<td>0.60</td>
<td>5.64</td>
</tr>
<tr>
<td>Bamboo NTs-2</td>
<td>9.44</td>
<td>0.78</td>
<td>0.60</td>
<td>4.42</td>
</tr>
</tbody>
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to extra surface area from multiple ridge layers from more dye loading, but also to the improved light harvest from more light scattering between the ridge layers

6.4 Summary

The double-layer smooth-walled TiO$_2$ nanotubes and double-layer TiO$_2$ nanotubes with bamboo-type nanotubes in the lower layer are synthesized via alternating-voltage anodic oxidation of Ti in NH$_4$F-containing ethylene glycol electrolytes. Anodic current is recorded during growth of various TiO$_2$ nanotube arrays, in order to evaluate their morphological evolutions at different stages. With the voltages applied, the increase/decrease/increase sequences of current represent formations of oxide barrier layer, pores and nano tubes, respectively. A plateau of current appears upon stable growth of TiO$_2$ nanotubes. Based on these findings, growth mechanisms of double-layer structures containing smooth-walled or bamboo-type nanotubes are proposed and ion diffusion in nanotubes is considered to be a dominant factor. A sufficient variation of ion concentration profiles in upper-layer nanotubes during high/lower-voltage alteration can induce formation of a new tube layer underneath. The morphology of lower-layer nanotubes can be tuned by repeating the high-voltage and low-voltage anodization steps, and thus bamboo-type nanotubes are obtained. Sufficient time of low-voltage anodization step is required for formation of ridges, but the spacing between neighboring ridges relies on the time of high-voltage anodization step. In particular, the ridge spacing is found to be increased linearly from 164 nm to 1600 nm, with the time of high-voltage anodization step from 1 min to 10 min, for lower-layer bamboo-type nanotubes formed in EG electrolytes with 0.3 wt% NH$_4$F and 5 vol% H$_2$O. In addition, the effect of water content in electrolyte on double-layer TiO$_2$ nanotube arrays is also investigated due to the relation between viscosity and ion diffusion coefficients. More water in EG electrolytes causes instability for growth of double-layer nanotubes. If the instability cannot be overcome by self-assembly nature of anodic TiO$_2$ film, a disordered porous oxide layer is formed on Ti finally. On the other hand, decreasing water content in electrolyte results in larger ridge spacing on lower-layer bamboo-type nanotubes, owning to origination of a thin barrier layer.

Smooth and bamboo-type TiO$_2$ nanotubes in anatase phase could be used in dye-sensitized solar cells (DSSCs). All the DSSCs consisting of bamboo-type nanotubes show better energy conversion capability than those made of smooth nanotubes. In particular, the photo-electric conversion efficiency can be improved by increasing the ridge density and length of anodic TiO$_2$ nanotubes.

6.5 References


CHAPTER 7. CONCLUSIONS

In general, this dissertation introduces three projects about exploring novel micro-sized or nanosized materials and structures for energy applications. The first is to use a cutting-edge technique (atomic layer deposition) to modify cathode materials for high-performance Li-ion batteries (LIBs). The second project is to synthesize nanostructured anode material for high-performance LIBs, and the final project is to synthesize and optimize nanostructures to achieve better solar cells. Conclusions from these projects are described as follows:

Nanosized-thin and highly-conformal Al₂O₃ coatings are directly deposited on the surfaces of micro-sized and nanosized LiMn₂O₄ by atomic layer deposition (ALD). The Al₂O₃ ALD coating has a growth rate of ~1.5 Å per cycle on LiMn₂O₄ nanoparticles. The Al₂O₃ coating scavenges HF species, protects cathode material and thus alleviates the severe dissolution of manganese into electrolyte; the coating also reduces decomposition of electrolytes at cathode. Therefore, micro-LiMn₂O₄ cathodes with Al₂O₃ ALD coatings show significantly enhanced cycling performances compared to the bare cathode. Moreover, the cycling performance of coated cathodes could be optimized by turning coating thickness via changing ALD growth cycles. For example, micro-LiMn₂O₄ cathode coated with 10 Al₂O₃ ALD layers delivers much better cycleability than cathode coated with 20 Al₂O₃ ALD cycles, and nano-LiMn₂O₄ cathode coated with 6 Al₂O₃ ALD layers presents the best cycling performance among cathodes coated with ALD coatings of different thicknesses and bare nano-LiMn₂O₄ cathode.

In addition to the cathode material, TiO₂ as anode material for LIBs is also been explored. Single-layer ordered TiO₂ nanotube arrays are synthesized by anodic oxidation of Ti foils in EG electrolytes with NH₄F and H₂O. The dimensions of these nanotubes are controllable by voltages, electrolyte composition and anodization time. The as-prepared TiO₂ nanotubes are amorphous and become crystalline by proper heat treatment, with structures well preserved. The amorphous and anatase nanotubes and nanotubes of mixed phases show excellent electrochemical properties. Among them, the amorphous ones deliver the largest Li-ion charge/discharge capacity. Those of mixed phases have larger capacities than pure anatase nano tubes, because rutile crystallites in anatase nanotubes facilitate the Li-ion transport. The amorphous tubes also show the best cycleability and the anatase nanotubes show less good capacity retention. However, all amorphous and crystalline tubes show excellent structural stability during electrochemical cycling.

Moreover, anodic TiO₂ nanotubes arrays can also serve as photo anode in DSSCs. Single-layer, bamboo-type and double-layer TiO₂ nanotubes are fabricated by using constant- or alternating-voltage anodization conditions. Growth mechanisms of the three are described. Sufficient ion concentration variations inside tubes and cavities at the voltage switch is the key to growth of bamboo-type and double-layer nanotubes. The ratio of low-voltage holding time to high-voltage holding time \((t_2/t_1)\) affects morphology the tubular layer structure. A bigger gap between the high voltage and low voltage is favorable for the formation of double-layer nanotubes. Proper water content in electrolytes favors the growth of double-layer tubes, but too much water renders the tubular structure unstable and even converts the ordered tube arrays to disordered spongeous structures.

The growth mechanism of double-layer structures containing smooth or bamboo-type TiO₂ nanotubes is further developed on the basis of their formation under multiple voltage
switch conditions. A sufficient variation of ion concentration in the upper-layer nanotubes during high/low-voltage alteration can induce formation of a new tube layer underneath. The morphology of lower-layer nanotubes can be tuned with more high-voltage and low-voltage anodization steps, and thus bamboo-type tubes are obtained. The formation of ridges requires enough time for low-voltage anodization steps, but their spacing relies on time of high-voltage anodization steps. In particular, the ridge spacing is found to be increased linearly with the high-voltage anodization time in ten minutes. More water in EG electrolytes causes instability for growth of double-layer nanotubes and even leads to a disordered porous oxide layer on Ti anode.

In the end, various bamboo-type nanotubes with different ridge spacing or ridge densities have been synthesized by varying the step anodization period, for assembly into back-side DSSCs. It is observed that bamboo-type TiO$_2$ nanotubes show much better performance as photo anode in DSSC than smooth-walled TiO$_2$ nanotubes with the same thickness, due to larger surface area for more dye loading and ridge layers for more efficient light harvest. The light conversion can be improved by using bamboo-type nanotubes with denser ridges.
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VITA

Dongsheng Guan was born in Changning, Hunan, China in 1982. He earned his bachelor’s and master’s degrees in Materials Physics & Chemistry from Harbin Institute of Technology, Harbin, China, in 2006 and 2008, respectively. He joined in the doctoral program in the Department of Mechanical Engineering at Louisiana State University in fall semester, 2009.

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