Nanostructured vanadium-based cathodes for rechargeable lithium ion batteries

Rui, Xianhong

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**NANOSTRUCTURED VANADIUM-BASED
CATHODES FOR RECHARGEABLE LITHIUM
ION BATTERIES**

RUI XIANHONG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Rechargeable lithium ion batteries (LIBs) with high specific volumetric and gravimetric energy densities are seen to be the most promising electrochemical energy storage systems for wide applications in portable electronic devices, electric vehicles (EVs), and hybrid electric vehicles (HEVs). However, with increasing demands in electronic industry, it is highly desirable to design LIBs capable of higher energy storage, faster lithium charge/discharge, and lighter weight. Cathode materials, which are the limiting factor in improving the capacities of LIBs, are strongly in need of further research study. The host materials with a layered or open structure are favorable for fast and reversible lithium intercalation/deintercalation. Amongst them, vanadium-based compounds (*e.g.*, VO₂(B), V₂O₅, Li₃V₂(PO₄)₃) with oxidation states ranging from V⁵⁺ to V³⁺ have attracted much attention recently. Unfortunately, their electronic and ionic conductivities are quite low, limiting the power capabilities of LIBs. The charge transfer kinetics can be largely improved in nanoscale electrodes, which offer a range of unique advantages over their bulk counterparts including shorter lithium ion transport distance, larger contact area between the electrode and electrolyte, and facile strain relaxation upon repeated lithium uptake and removal.

Firstly, uniform carbon-coated VO₂(B) nanobelts are synthesized by a simple hydrothermal reduction method using sucrose as both the reducing agent and carbon source. The one-dimensional nanobelt growth is attributed to the anisotropic structure of VO₂(B) with fast growth along the [010] direction. On the other hand, the thickness of carbon shell can be tuned from 3.0 to 6.9 nm by changing the amount of sucrose in the reaction. Although carbon can enhance the electrical conductivity of the VO₂(B)

nanobelts, too much carbon would block Li^+ diffusion. The electrochemical tests indicate that the $\text{VO}_2(\text{B})$ nanobelts with a carbon content of 6.6 wt% (carbon thickness: 4.3 nm) exhibit highest capacities, and best rate capabilities (*e.g.*, 100 mAhg^{-1} at 12.4 C).

To further improve the reversible specific capacity and working potential, V_2O_5 active materials are extensively investigated. Hydrated V_2O_5 ($\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O}$) nanobelts are initially prepared by a facile hydrothermal method with the assistance of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). These nanobelts are highly flexible with lengths of up to several hundred micrometers. Binder-free bulky paper electrodes are then fabricated by oven drying of these flexible nanobelts. The flexible hydrated V_2O_5 cathodes deliver high reversible capacities (*e.g.*, 163 mAhg^{-1} at 6.8 C). Afterwards, ultrathin V_2O_5 nanosheets and reduced graphene oxide supported porous V_2O_5 spheres consisting of nanoparticles ($\text{V}_2\text{O}_5/\text{rGO}$) are synthesized to further improve the charge transfer kinetics of V_2O_5 . Ultrathin V_2O_5 nanosheets with thicknesses of 2.1-3.8 nm are prepared by a liquid-phase exfoliation method. The thickness of the V_2O_5 nanosheets allow fast Li^+ diffusion and electron transportation, resulting in remarkable power and energy densities (*e.g.*, 117 mAhg^{-1} at 50 C). $\text{V}_2\text{O}_5/\text{rGO}$ (rGO content: 46 wt%) hybrids, prepared by a facile solvothermal approach followed by heat treatment exhibit a reversible capacity of 128 mAhg^{-1} at 13 C.

Furthermore, high-voltage $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes are also investigated. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nanocrystals (5-8 nm) embedded in a nanoporous carbon matrix attached onto rGO sheets were fabricated by a sol-gel process followed by heat treatment. Such unique nanostructure allows fast Li^+ and electron transfer, allowing the electrode to display a capacity of 109 mAhg^{-1} at a high rate of 30 C when cycled between 3.0 and 4.8 V.

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Chapter 1: Introduction

1.1 Background

Rechargeable lithium-ion batteries (LIBs) with high energy densities and long cycling life are currently considered to be the most promising energy storage devices in mobile electronics, such as iPads, iPhones, notebook PCs, and camcorders, as well as in electric vehicles (EVs) and hybrid electric vehicles (HEVs). The worldwide market demand for LIBs is expected to be more than 10 billion dollars per annum and is still growing. With current economic development, there is an ever-growing need for LIBs with various specifications, such as lighter-weight, lower-cost, thinner, smaller, more powerful, and even flexible and rollable, promoting extensive investigations on LIBs including its cathodes, anodes, electrolytes, binders, and separators.¹⁻³

The first lithium-ion battery commercialized by Sony Corp. in 1991 employed graphite as the anode and LiCoO_2 as the cathode. Nonetheless, this battery offered energy densities of only 200 WhL^{-1} and 80 Whkg^{-1} . Since then, great achievements have been made in terms of battery design, reduction of inactive materials, and optimization of the utilized active materials, and the energy densities were more than doubled. The recent market growth results in a further increase of research activities towards lithium ion batteries. Accordingly, many new electrode materials are investigated for their capability to reversibly store more lithium even in a fast charge/discharge manner in order to meet the demands of future large-scale applications such as EVs, HEVs, as well as stationary energy storage systems.

Compared to the theoretical capacities of anodes (e.g., graphite: 372 mAhg^{-1} , metal oxides: $500\text{-}1000 \text{ mAhg}^{-1}$), the capacities of cathodes (e.g., LiCoO_2 : $\sim 140 \text{ mAhg}^{-1}$) are

rather low. Besides, the high cost and toxicity of Co have encouraged materials researchers to investigate on alternative candidates.

1.2 Motivations

Among the many candidate cathode materials that could potentially replace commercial LiCoO_2 , vanadium-based cathode materials such as $\text{VO}_2(\text{B})$, V_2O_5 , and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ have received considerable attention as they offer advantages of high capacities and energy densities due to the multiple vanadium valence variation ranging from +2 to +5, low cost, facile sample preparation, and high safety.⁴⁻⁷ For example, layered V_2O_5 is a typical intercalation compound for reversible lithium uptake and removal, which has a theoretical capacity of as high as 294 mAhg^{-1} between 2.0 and 4.0 V vs. Li/Li^+ . This capacity is significantly higher than not only LiCoO_2 , but also other commonly used cathodes such as LiMn_2O_4 (148 mAhg^{-1}) and LiFePO_4 (170 mAhg^{-1}). However, the vanadium-based cathodes have its own drawbacks such as low electrical conductivity and sluggish lithium ion diffusion, which limit their practical large-scale applications.

Nanostructures are highly favourable for developing high-performance vanadium-based cathodes. They have many unique advantages over their traditional bulk counterparts including shorter distances for lithium ion and electron transport, higher electrode/electrolyte contact area which results in a high Li^+ flux across the interfaces of active materials, better accommodation of the strain upon lithium (de)intercalation, more facile electrochemical reactions. Therefore, it is interesting to fabricate nanostructured

vanadium-based electroactive materials through novel synthetic routes to achieve high lithium storage capacities and superior rate capabilities for high-performance LIBs.

1.3 Objectives of Research

The aim of this PhD research is to develop unique nanostructured vanadium-based cathode materials for high-performance LIBs. Specifically, the objective of this thesis mainly includes the following five categories:

(1) One-pot Synthesis of Carbon Coated $\text{VO}_2(\text{B})$ Nanobelts for High-Rate Lithium Storage

- To synthesize carbon-coated one-dimensional $\text{VO}_2(\text{B})$ ($\text{VO}_2(\text{B})@\text{C}$) nanobelts via a hydrothermal process
- To characterize the as-synthesized $\text{VO}_2(\text{B})@\text{C}$ nanobelts
- To evaluate the lithium storage properties of the as-synthesized $\text{VO}_2(\text{B})@\text{C}$ nanobelts
- To study the effect of amorphous carbon coating thicknesses on the lithium storage properties of the as-synthesized $\text{VO}_2(\text{B})@\text{C}$ nanobelts

(2) Facile Preparation of Hydrated Vanadium Pentoxide Nanobelts Based Bulky Paper as Flexible Binder-free Cathodes for High-performance Lithium Ion Batteries

- To synthesize single-crystalline hydrated vanadium pentoxide (HVO) nanobelts via a hydrothermal process
- To characterize the as-synthesized HVO nanobelts

- To fabricate flexible bulky papers using the as-synthesized HVO nanobelts for application as binder-free electrode for lithium ion battery application
- To evaluate the lithium storage properties of the as-fabricated HVO bulky-paper electrodes

(3) Ultrathin V_2O_5 Nanosheet Cathodes: Realizing Ultrafast Reversible Lithium Storage

- To synthesize two-dimensional ultrathin V_2O_5 nanosheets via a facile liquid-phase exfoliation method
- To characterize the as-synthesized V_2O_5 nanosheets
- To evaluate the lithium storage properties of the as-synthesized V_2O_5 nanosheets as cathode materials for high-power lithium ion batteries

(4) Reduced Graphene Oxide Supported Highly Porous V_2O_5 Spheres as a High-Power Cathode Material for Lithium Ion Batteries

- To synthesize reduced graphene oxide (rGO) supported porous polycrystalline V_2O_5 spheres (V_2O_5 /rGO) via a facile solvothermal approach followed by thermal treatment
- To characterize the as-synthesized reduced graphene oxide (rGO) supported porous polycrystalline V_2O_5 spheres
- To evaluate the lithium storage properties of the as-synthesized reduced graphene oxide (rGO) supported porous polycrystalline V_2O_5 spheres as cathode materials for lithium ion batteries

(5) $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Nanocrystals Embedded in a Nanoporous Carbon Matrix Supported on Reduced Graphene Oxide Sheets: Binder-Free and High-Rate Cathode Material for Lithium-Ion Batteries

- To synthesize $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nanocrystals embedded in a nanoporous carbon matrix attached onto rGO sheets (LVP-NC@NPCM@rGO) via a facile sol-gel process followed by thermal treatment
- To characterize the as-synthesized LVP-NC@NPCM@rGO
- To evaluate the lithium storage properties of the as-synthesized LVP-NC@NPCM@rGO as high-power cathode materials for lithium ion batteries

1.4 Organization

Chapter 1 gives a brief background of this PhD study, an overview of the motivation, and the objectives of this thesis. In Chapter 2, literature review on the basic mechanism of lithium ion batteries, commonly used cathode materials, anodes materials, electrolytes, some vanadium-based cathodes, nanostructured electrode materials, and the synthesis of vanadium-based nanomaterials is carried out. Chapter 3 summarizes the common material characterizations and electrochemical measurements. In Chapter 4, a simple one-pot hydrothermal approach is presented to synthesize the $\text{VO}_2(\text{B})@\text{C}$ nanobelts, and their lithium storage properties are investigated. Chapter 5 describes the synthesis of single-crystalline $\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O}$ nanobelts by a simple hydrothermal reaction and subsequent fabrication of binder-free bulky paper on the basis of intertwining of these nanobelts, and their electrochemical performances are examined. In Chapter 6, a facile liquid-phase exfoliation method is proposed to produce ultrathin V_2O_5

nanosheets (thickness: 2.1-3.8 nm), and their lithium storage properties are investigated. Chapter 7 presents a facile solvothermal approach combined with the subsequent thermal treatment to prepare rGO supported porous V_2O_5 spheres, and their Li-ion battery properties are evaluated. In Chapter 8, a facile sol-gel process followed by heat treatment is employed to prepare $Li_3V_2(PO_4)_3$ nanocrystals (5-8 nm) embedded in a nanoporous carbon matrix attached onto rGO sheets, and their Li-ion battery properties are evaluated. Conclusions and some recommendations for future research are then presented in Chapter 9.

Chapter 2: Literature Review

2.1 Lithium Ion Rechargeable Batteries

Human civilization and its progress are very closely related to the use of energy. Currently, most of the energy in used in the world today comes from the burning of fossil fuels. However, high oil costs and environmental issues have encouraged human to move from the use of fossil fuels to other greener energy sources such as solar, wind, and hydroelectric power. Since these green energies are intermittent in nature, energy storage remains a major challenge in order to promote their widespread usage. Batteries are such devices that can store chemical energy and, when needed, directly convert this stored energy into electrical energy for powering a variety of applications.

The history of battery development can be dated all the way back to 1800 when Italian physicist Alessandro Volta immersed a zinc plate and a silver plate in brine and discovered that current flows in the external wire connecting these two pieces of metal. Following, he invented the very first battery known as the “Volta’s pile” or “voltaic pile”. This battery is formed by connecting a number of cells in series where each cell consists of a pair of zinc and silver discs separated by a saltwater-wetted cloth where the saltwater functions as the electrolyte. The invention of the “Volta’s pile” provided a new concept for energy conversion and storage and, at the same time, it also serves as a prelude to chemical power sources. Since then, many different types of chemical power sources started to be developed gradually. In 1859, French physicist Gaston Planté invented the first lead-acid battery. After using this battery for a period of time and after its voltage decreased, the lead-acid battery can be electrically charged to increase its voltage. This implies that the lead-acid battery can not only convert its stored chemical energy to

electrical energy, it can also convert electrical energy back into chemical energy and store it. As this type of battery can be charged and discharged repeatedly, the lead-acid battery is also known as a “rechargeable battery”. In fact, lead-acid battery is the oldest type of rechargeable battery. Following, numerous advancements have been made to the field of energy storage. Some notable developments include the invention of MnO_2 -Zn primary battery with NH_4Cl as the electrolyte by Frenchman Leclanché in 1868; the discovery of $\text{Ni}(\text{OH})_2$ -Cd battery by Swedish inventor Waldemar Jungner in 1899 and the invention of iron-nickel battery by Edison in 1900. With the improvement in technology, higher requirements are imposed on the properties and design of batteries, constantly pushing it towards smaller size, lighter weight, and higher capacity, longer cycling life and greener chemistry.

In the past few decades, sales of two types of rechargeable batteries start to emerge in the commercial market. One of these two types of batteries is the nickel-metal hydride battery which enters the market in 1989. This battery has a volumetric energy density that is twice that of a lead-acid battery and became the best choice of power source for portable electronics in the 1990s. The nickel-metal hydride battery successfully replaced its nickel-cadmium counterpart in many different fields of applications. It is also chosen over other batteries to be used in the hybrid electric car, Toyota Prius launched by Toyota in 1997. The other popular battery choice in the market would be the lithium ion battery. The lithium ion battery is a secondary battery that originated and evolved from lithium battery. As lithium metal has the lowest electrode potential (-3.04V) and atomic mass (6.94 g mol^{-1}) amongst all the elemental metals, hence employing lithium metal as the anode material can allow us to achieve a higher battery output voltage and gravimetric

energy density. Besides, lithium has a very small atomic radius of 0.78 Å, enabling it to be easily inserted and extracted from the crystal structures of metal oxides. Although lithium primary battery is already an established commercial product in the 1970s, lithium secondary battery did not manage to gain widespread industrial applications. This is mainly due to the safety issues related to repeated cycling of a lithium battery. After charging and discharging a lithium battery several times, lithium dendrites could form at the lithium anode. These lithium dendrites could poke through the separator between the electrodes to reach the cathode, resulting in internal short-circuiting of the battery, greatly reducing its cyclability and poses serious safety issues.

Research on lithium ion batteries (LIBs) started around late 1980s and, in 1991, Japan's Sony Corporation commercialized the first lithium secondary battery. They used petroleum coke as the anode material and LiCoO_2 as the cathode material, greatly lowering the lithium ion deintercalation potential at the anode and increasing the operating voltage of the battery. This is a very important milestone in the history of battery development. Following, Dahn et al. reported on lithium ion battery with a $\text{Li}_y\text{C}_6|\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{EC}+\text{DME}|\text{Li}_{1-y}\text{NiO}_2$ structure, while Tarascon and Guyomard reported one with a $\text{Li}_y\text{C}_6|\text{LiClO}_4/\text{EC}+\text{DME}|\text{Li}_{1-y}\text{Mn}_2\text{O}_4$ structure. Since then, lithium ion batteries have gain attention from researchers worldwide, promoting the rapid development in commercialization of LIBs. In recent years, LIBs have moved from applications in small items such as mobile phones and notebook computer to powering items in other fields such as power tools, hybrid vehicles, satellites and aerospace applications.

Figure 2.1 Schematic illustration of the working principle of a lithium ion battery.⁸

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Like other electrochemical power sources, LIBs mainly consists of electrodes which lithium ions can intercalate and de-intercalate into, electrolyte which can conduct lithium ions and a separator that prevents direct contact between the anode and the cathode. A schematic diagram of a LIB is shown in Figure 2.1. When the LIB is in its discharged state, lithium ions are “stored” in the cathode. During charging, the lithium ions in the cathode are extracted and transported through the electrolyte and separator to the anode, where the lithium ions gained one electrons, get reduced back to elemental lithium and are inserted into the crystal structure of the negative electrode (Figure 2.1). At this time, the cathode is at a higher potential, lithium-poor state, while the anode is at a lower

potential, lithium-rich state. During discharging, the lithium in the anode will lose an electron to become Li^+ and these lithium ions will move through the electrolyte and separator and get “stored” in the cathode, changing the cathode to a lithium-rich state. As the energy conversion process in a LIB occurs via the transportation of lithium ions between the two electrodes, such a cell is also referred to as a rocking-chair battery.

If the anode material in the battery is graphite and the cathode material is layered-structured LiCoO_2 , then the chemical reactions at the electrodes during charging and discharging of the battery will be as shown below.

Commercialized lithium ion battery, like the prismatic LIB cell shown above, usually include cathode, anode, electrolyte, separator, anode lead, cathode lead, insulator, safety vent, PTC (Positive Temperature Control) and battery casing (Figure 2.2). The material choice for the positive electrode are usually lithiated metal oxides that have an electrode potential greater than 3 V with respect to Li and is air stable such as LiCoO_2 , LiNiO_2 and LiMn_2O_4 . On the other hand, the anode choices are usually materials that can store lithium ions and have an electrode potential that is close to that of Li such as graphite, synthetic carbon, carbon fibers and metal oxides. Most of the commercialized LIB uses

LiPF_6 dissolved in either ethylene carbonate (EC) or propylene carbonate (PC) or diethylene carbonate which is less viscous or a mixture of any of these three solvents as the electrolyte. Microporous membrane made of polyethylene or polypropylene or their co-polymer is generally used as separator in commercialized LIB, while its casing is mainly made using steel or aluminum.

Figure 2.2 Structure of a lithium ion battery.⁹ *Reprinted with permission from ref. 9. Copyright 2001, John Wiley & Sons, Inc. and The Japan Chemical Journal Forum.*

Lithium ion batteries have gained wide spread attention and rapid development in the past few decades mainly because of its various advantages compared to other secondary batteries like Ni/Cd battery, Ni/MH battery and lead acid batteries. Lithium ion batteries have the following advantages:

- (1) High operating voltage. Single lithium ion battery cell typically have an operating voltage of about 3.6 V and, sometimes, it can reach as high as more than 4 V. This high operating voltage is almost 3 times that of nickel-cadmium and nickel-metal hydride battery and twice that of lead-acid battery. In fact, this is the most outstanding advantage of LIB.
- (2) High specific energy and great potential for further development. The gravimetric energy density of LIB is usually twice that of nickel-metal hydride battery and four times that of lead-acid battery; the volumetric energy density of LIB can reach as high as 270 Wh L^{-1} , allowing the LIB to be half the size of a nickel-cadmium battery if both batteries were to have the same capacity. Thus, compared to other secondary batteries, LIB of the same capacity can be made lighter and smaller (Figure 2.3). This is very significant especially for applications in portable electronics where size and weight are of great importance.
- (3) Long cycling life. After 1200 charge-discharge cycles, LIB can still maintain at least 60% of its rated capacity. This capacity retention is much higher than other types of rechargeable batteries, making LIB a more economical battery power choice.
- (4) Low self-discharge rate. The self-discharge rate of LIB is typically around 10%, which is obviously lower than Ni/Cd and Ni/MH batteries.
- (5) No memory effect. LIB can undergo charging and discharging any time. In case of emergency, it can display its excellent performance.
- (6) Good safety. The electrochemical reaction in a LIB will not result in the formation of lithium dendrites, greatly improving its safety aspect.

- (7) Environmentally-friendly. LIB is a fully-sealed system and does not contain toxic substances like cadmium, lead and mercury. Hence, it can be considered as a clean and green power source.

Figure 2.3 Comparison of different battery technology performance in a Ragone plot.¹⁰

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Lithium ion batteries have gained a lot of attention as an energy storage system because of the above stated advantages, allowing it to constantly achieve better performance. Currently, work on LIB has been aimed at improving its performance, widening its variety, lowering its cost and improving its safety aspect so that it can be used in a vast range of applications.

2.2 Cathode Materials

The key requirements and criteria for a material to be successfully applied as a cathode (positive electrode) in a lithium rechargeable battery are as follows:¹¹

- (1) The material contains a redox ion (e.g., a transition metal).
- (2) The material can react with lithium reversibly. This indicates an intercalation-type reaction, in which the host structure is retained as lithium is inserted/extracted.
- (3) A high free energy of electrochemical lithium reaction is required (i.e., high storage capacity, high working voltage, and high energy density).
- (4) Rapidly lithium insertion and extraction are desired (i.e., high power density).
- (5) It is better that the material has a good electronic conductor. This means that the electrons can be easily added or removed during the electrochemical reaction.
- (6) The material must be stable to overdischarge and overcharge.
- (7) The raw materials are cheap.
- (8) The material is environmentally benign.

Figure 2.4 shows voltage versus capacity of several cathode materials. Almost all of the cathode materials have focused on two categories of materials.¹²⁻¹⁴ The first contains layered lithium transition metal oxides, comprising compounds with formula of $\text{Li}_x\text{M}_y\text{O}_z$ (where M = Mn, Co, and Ni). The second group has more open structures, e.g., vanadium oxides, manganese dioxide, and most recently the transition-metal phosphates such as the olivine LiFePO_4 .

Figure 2.4 Voltage versus capacity of several cathode materials.¹² Reprinted with permission from ref. 12. Copyright 2010, American Chemical Society.

Figure 2.5 Crystal structure of HT-LiCoO₂.¹⁵ (a) Lithium ions horizontally between CoO₂ octahedra. (b) Projection along the [110] zone axis displaying lithium, cobalt and oxygen atoms in columns. Reprinted with permission from ref. 15. Copyright 2003, Rights Managed by Nature Publishing Group.

2.2.1 Layered Lithium Cobalt Oxide, LiCoO_2

Since the first report by Goodenough et al.¹⁶ in 1980, LiCoO_2 has received tremendous attention owing to the convenience and simplicity of preparation, good thermal stability, high capacity, high output-voltage and long cycle life. LiCoO_2 has two crystal structures, i.e., the hexagonal and cubic structures.¹⁷ High temperature lithium cobalt oxide (HT- LiCoO_2) exhibits a hexagonal $\alpha\text{-NaFeO}_2$ layered structure (Figure 2.5), while the low temperature lithium cobalt oxide (LT- LiCoO_2) has a cubic spinel-related structure. Unlike LT- LiCoO_2 , HT- LiCoO_2 shows superior electrochemical stability upon repeated lithium insertion and removal.¹⁷

Figure 2.6 First galvanostatic charge-discharge cycle of a $\text{Li}/\text{HT-Li}_x\text{CoO}_2$ cell.¹⁸

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The first galvanostatic charge-discharge curve of $\text{Li}/\text{HT-LiCoO}_2$ cell is presented in Figure 2.6. The electrochemical mechanism of Li extraction on HT- Li_xCoO_2 can be summarized as below: firstly, an expansion of the interlayer c axis due to the electrostatic

repulsion of the oxygen layers $x \leq 0.5$;¹⁹ afterwards, a hexagonal-monoclinic transition (i.e., an order-disorder transition) occurred at $x \approx 0.5$; finally, a phase transition of O3 LiCoO_2 (oxygen close-packed with an ABCABC stacking sequence) into O1 Li_xCoO_2 (ABAB stacking sequence) at $x \approx 0.05$. Although almost all of lithium can be extracted to yield a theoretical capacity of 274 mAh g^{-1} , only around half of lithium can be reversibly cycled ($\leq 4.2 \text{ V vs Li/Li}^+$). There is a serious capacity fading upon extraction of > 0.5 lithium. When the lithium is extracted from Li_xCoO_2 , Co^{3+} is oxidized to unstable Co^{4+} . High concentration of Co^{4+} will damage the crystallinity of the electrode, and the phase transition could reduce the c -axis dimension, which results in the mechanical failure of LiCoO_2 active materials.²⁰ Besides the poor stability of phases at low lithium contents, it has been evidenced by Tarascon et al.²¹ that the capacity degradation is also associated with the dissolution of Co^{3+} in the electrolyte solution.

Doped $\text{LiM}_x\text{Co}_{1-x}\text{O}_2$ ($\text{M} = \text{Al, Cr, et al.}$)²²⁻²⁵ have been proved to be an effective way to improve the electrochemical performance. For example, Needham et al.²⁵ prepared layered intercalation compounds $\text{LiM}_{0.02}\text{Co}_{0.98}\text{O}_2$ ($\text{M} = \text{Mo}^{6+}, \text{V}^{5+}, \text{Zr}^{4+}$). The electrochemical tests showed that the first cycle irreversible capacity loss was in an order of $\text{Zr} (15 \text{ mAhg}^{-1}) < \text{Mo} (22 \text{ mAhg}^{-1}) < \text{V} (45 \text{ mAhg}^{-1})$, and with prolonging cycles, the Mo-doped electrode displayed the best performance of all dopants with a stable reversible capacity of 120 mAhg^{-1} during the 30th cycle. Another strategy was coating insertion metal oxides (e.g., SnO_2 , MgO , and Al_2O_3)²⁶⁻²⁹ and phosphates³⁰ on the LiCoO_2 surface. Among them, Al_2O_3 -coated LiCoO_2 illustrated the most excellent cycling performance. It was suggested that a solid solution of $\text{LiCo}_{1-y}\text{Al}_y\text{O}_2$ was formed to enhance the structural stability of LiCoO_2 during the repeated lithium insertion and removal. Huang et al.²⁹

developed a facile co-precipitation approach to coat Al_2O_3 or MgO on commercial LiCoO_2 or nano- LiCoO_2 . As seen from Figure 2.7a, an amorphous Al_2O_3 layer with a thickness of 4 nm was uniformly coated on nano- LiCoO_2 surface. Figure 2.7b exhibits the effect of an Al_2O_3 coating layer on improving the capacity retention of nano- LiCoO_2 . Although LiCoO_2 dominates the lithium ion battery market, alternatives to LiCoO_2 are highly desired due to its toxicity, high cost, and poor safety, which is not suitable for large-scale energy-storage applications.

Figure 2.7 (a) TEM image of Al_2O_3 -coated nano- LiCoO_2 sintered at 300 °C for 2 h. (b) Cycling performance of A) bare commercial LiCoO_2 , B) Al_2O_3 -coated nano- LiCoO_2 sintered at 300 °C for 2 h, and C) Al_2O_3 -coated nano- LiCoO_2 sintered at 600 °C for 2 h.²⁹

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2.2.2 Spinel LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

Recently, spinel LiMn_2O_4 and its derivatives have become promising cathode materials for transportation and large-scale Li-ion batteries because of its abundance, low cost, environmental friendliness, easy preparation, good structural stability, and enhanced

safety compared with currently used LiCoO_2 cathode.³¹⁻³³ As shown in Figure 2.8a, LiMn_2O_4 has a face-centered spinel structure (space group $Fd3m$), in which Li, Mn, and O

Figure 2.8 (a) The crystal structure of spinel LiMn_2O_4 .³⁴ Reprinted with permission from ref. 34. Copyright 2012, Elsevier. (b) The initial discharge curves of LiMn_2O_4 spinels annealed at different temperatures.³⁵ Reprinted with permission from ref. 35. Copyright 2004, The Electrochemical Society.

Table 2.1 Reasons for the capacity fading of LiMn_2O_4 .³⁴ *Reprinted with permission from ref. 34. Copyright 2012, Elsevier.*

Detrimental effect	Mechanism of the detrimental effect	General solution	Limitation of current solution	Prospect on how to improve
Jahn-Teller distortion	Severe volume change	Nonstoichiometric spinel, metal ion doping	Low capacity	Reduce particle size
Dissolution of Mn	Disproportionation reaction	Surface modification	Low capacity	Reduce coating materials
Formation of two cubic phases	Structure instability	Nonstoichiometric spinel	Low capacity	Reduce particle size
Loss of crystallinity	Structure degradation	Nonstoichiometric spinel	Low capacity	Reduce particle size
Development of micro-strain	Volume change	Metal ion doping	Low capacity	Reduce particle size

ions occupy the 8a tetrahedral, 16d octahedral, and 32e sites, respectively. The structure is based on the three-dimensional edge-shared octahedral Mn_2O_4 , which is highly stable and possesses a large number of vacancies formed by the face-sharing of 8a tetrahedral lithium sites and empty 16c octahedral sites. These vacancies allow the three-dimensional Lithium diffusion. The Li^+ intercalation/deintercalation into/from the tetrahedral (8a) sites occurs at around 4 V (vs. Li/Li^+) with keeping of cubic spinel symmetry. A maximum of one lithium can be intercalated into the spinel LiMn_2O_4 to form $\text{Li}_2\text{Mn}_2\text{O}_4$ occurred at around 3 V with a phase transition of cubic to tetragonal structure (Figure 2.8b). Such phase transformation often known as Jahn-Teller distortion, is accompanied by a volume increase (6.5%), which could damage the electrode structure and result in a rapid capacity fading.³⁶ To avoid the Jahn-Teller distortion, LiMn_2O_4 was normally used at around 4 V with a limited theoretical capacity of 148 mAh g^{-1} (the theoretical capacity of $\text{Li}_2\text{Mn}_2\text{O}_4$ is 296 mAh g^{-1}). However, the capacity of LiMn_2O_4 still tended to decrease even within the 4 V region during the cycling process, especially at an elevated temperature (e.g., 55°C). Several reasons have been considered for the capacity fading:³⁴

- (1) Jahn-Teller distortion occurred at the surface of active materials under non-equilibrium cycling;
- (2) dissolution of Mn^{2+} into the electrolyte through the

disproportional reaction $2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$; (3) formation of two cubic phases on the 4 V region; (4) loss of crystallinity; and (5) formation of micro-strain during lithium insertion/extraction. These main reasons are summarized in Table 2.1.

Doping with low valence cations (e.g., Al, Mg, Co, and Ni)³⁷⁻³⁹ has been widely explored to enhance the cycling stability of LiMn_2O_4 , which not only can reduce the amounts of Mn^{3+} to alleviate the Jahn-Teller distortion and, but also can stabilize the cubic spinel structure. However, monovalent Li seems to be the best doping agents since

Figure 2.9 Scanning electron micrographs of (a) bare and (b) ZnO-coated LiMn_2O_4 . Specific discharge capacity of (c) bare and (b) ZnO-coated LiMn_2O_4 at 30 °C.⁴⁰ Reprinted with permission from ref. 40. Copyright 2003, The Electrochemical Society.

Li can provide a larger valence difference to Mn than other high valence cations. On the other hand, the structure of lithium-rich $\text{Li}_x\text{Mn}_2\text{O}_4$ was found to be more stable and own better cycleability.⁴¹ For example, lithium-rich spinels $\text{Li}[\text{Li}_x\text{Mn}_{2-x}]\text{O}_{4-\delta}$, where $0 < x < 0.33$ and $\delta < 0.2$ exhibited good rechargeability at ~ 0.3 C with a capacity retention of around 95% during 50 cycles.⁴² Surface modifications such as coating ZnO, MgO, Al_2O_3 , CuO and CeO_2 on LiMn_2O_4 surface have been considered another effective approach to improve the cycleability of LiMn_2O_4 .⁴³⁻⁴⁶ For instance, Sun et al.⁴⁰ have investigated the improvement of ZnO coating on cycling performance of LiMn_2O_4 . ZnO nanoparticles were uniformly coated on LiMn_2O_4 surface as indicated by scanning electron microscopy (Figure 2.9a and b). As shown in Figure 2.9c and d, both bare LiMn_2O_4 and ZnO-coated LiMn_2O_4 delivered the nearly same discharge capacity (120 mAh g^{-1}). However, the ZnO-coated LiMn_2O_4 exhibited almost no capacity loss during 50 cycles, which was remarkably better than the bare LiMn_2O_4 , suffering a 10% capacity loss during 50 cycles. The enhanced cycling performance was mainly attributed to significantly reduced HF content in the electrolyte solution, which results in the decrease of Mn^{2+} dissolution.

Another widely studied spinel cathode is $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because of its good cycling behavior, relatively high capacity and high voltage plateau at around 4.7 V. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is different from pure spinels since the redox activity happens on Ni and the Mn is still remained in 4+ state. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel possess two different crystal structures: non-stoichiometric disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ with the space group of $Fd3m$ and stoichiometric ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with the space group of $P4_332$.^{31, 47} The non-stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ possess face-centered cubic spinel structure, in which the Li, Mn, Ni and O ions occupy the 8a tetrahedral, 16d octahedral, 16d octahedral and 32e

Figure 2.10 Lithium diffusion path in the disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$.⁴⁸ Reprinted with permission from ref. 48. Copyright 2007, The Electrochemical Society.

sites, respectively. In this structure, Mn and Ni ions are randomly distributed in the 16d sites. While in the stoichiometric ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (possessing primitive simple cubic structure), the Li, Mn, and Ni ions occupy the 4c, 12d and 4a sites, respectively, and the O ions occupy the 8c and 24e sites. In this structure, Mn and Ni ions are ordered regularly. It was found that the disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ had better electrochemical properties than ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.⁴⁷ In disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$, Li moves from 8a site to the neighboring empty octahedral 16c site, and then to the next 8a site. The three-dimensional lithium 8a-16c-8a diffusion paths are illustrated in Figure 2.10. All Li ions extraction can give a theoretical capacity of 147 mAh g^{-1} for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Unfortunately, the cycling performance of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, especially at high rates, is not satisfactory. One reason is that the redox couple ($\text{Ni}^{3+}/\text{Ni}^{4+}$) occurs at the

potential of electrolyte decomposition (e.g., ~4.6 V for 1.0 M LiPF₆ in ethylene carbonate and diethyl carbonate). Additionally, spinel LiNi_{0.5}Mn_{1.5}O₄ can lose oxygen and formation of Li_xNi_{1-x}O or NiO when it was heated above 650 °C. Thus, it is difficult to synthesize the pure spinel LiNi_{0.5}Mn_{1.5}O₄, and it also shows a degradation of electrochemical performances because of the Mn³⁺ ions.

Cations or anions doping have been proposed as an effective way to improve the high voltage electrochemical properties of LiNi_{0.5}Mn_{1.5}O₄ spinel. Titanium (Ti) doped LiNi_{0.5}Mn_{1.5}O₄ can improve the disordering of the transition metals, and hence lower the symmetry from simple cubic structure (*P4₃32*) to face-centered spinel (*Fd3m*). It is reported by Sun et al.⁴⁹ that Ti doped LiNi_{0.5}Mn_{1.5-x}Ti_xO₄ showed higher working voltages, faster Li⁺ diffusion, and better rate performance than undoped LiNi_{0.5}Mn_{1.5}O₄. *Ex-situ* XRD analysis of delithiated LiNi_{0.5}Mn_{1.5-x}Ti_xO₄ (*x* = 0, 0.3 and 0.5) indicated that with increasing Ti content, the phase transition was suppressed. However, large amount of Ti substitution could lower discharge capacity, which was possibly because of the blocking of electron migration pathways in octahedral sites. Ruthenium (Ru) could also be added as a dopant to the LiNi_{0.5}Mn_{1.5}O₄ spinel. The rate performance and cycling stability of the LiNi_{0.5}Mn_{1.5}O₄ were significantly improved by Ru doping.⁵⁰ Specifically, the as-synthesized Li_{1.1}Ni_{0.35}Ru_{0.05}Mn_{1.5}O₄ and LiNi_{0.4}Ru_{0.05}Mn_{1.5}O₄ exhibited discharge capacities of 108 and 117 mAh g⁻¹ at a 10 C rate in the voltage range of 3.0-5.0 V, respectively. Furthermore, as shown in Figure 2.11a, Li_{1.1}Ni_{0.35}Ru_{0.05}Mn_{1.5}O₄ and LiNi_{0.4}Ru_{0.05}Mn_{1.5}O₄ could retain 91% and 84% of their initial capacities during the 500th cycle under a fast 10 C charge/discharge rate, respectively, suggesting that Ru-doping

could be an effective way to improve the electrochemical properties of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

Fluorine (F) could be another common anion dopant in lithium-ion batteries. It has been found that the reversible capacities of 5 V- $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel could be improved by F-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.975}\text{F}_{0.05}$,⁵¹ which is mainly due to suppression of the formation of NiO impurity during the sample preparation. As proposed by Yang et al.,⁵² the lattice parameters and bonding energies could be changed by the fluorine doping in the oxygen sites. SEM images (Figure 2.11b) showed that, with increasing the amount of F substitution, the particle size became larger and the size distribution was more uniform. Although the discharge capacity decreased with increasing the F amount, which may be due to the strong Li-F bond hindering the Li^+ transportation, the cyclic stability was significantly improved for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{3.9}\text{F}_{0.1}$ (Figure 2.11b).

Figure 2.11 (a) Capacity retention of Ru-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinels.⁵⁰ Reprinted with permission from ref. 50. Copyright 2009, Elsevier. (b) SEM images and cycling stability of F-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-x}\text{F}_x$ ($0.05 \leq x \leq 0.2$) at 0.2 C rate.⁵² Reprinted with permission from ref. 52. Copyright 2008, Elsevier.

It is worth mention that lithium transition metal oxides suffer safety issues due to the reaction with electrolyte. Significant researches have been made to improve the stability of lithium transition metal oxide electrodes. Surface modifications by coating $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ with various metal oxides (e.g., ZnO^{53}), phosphates (e.g., AlPO_4^{54}), and metals (e.g., Ag^{55}) have been verified as effective approaches to enhance the stabilities of electrodes, and thus improve the capacity retentions during cycling. In the case of ZnO-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$,⁵³ the electrode exhibited superior electrochemical properties and structural stabilities. The as-synthesized bare and ZnO-coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes demonstrated capacity retentions of 27% and 99% during the 50th cycle at 55 °C, respectively. It was found that the ZnO coating layer could significantly reduce the HF content in the electrolyte solution. In a similar manner, AlPO_4 protecting layer⁵⁴ could effectively suppress the formation of undesirable solid electrolyte interface layer, and partially absorb the stress resulted from the volume change during the repeated lithium uptake and removal.

2.2.3 Olivine LiFePO_4

LiFePO_4 has been widely considered as the most attractive cathode for the next-generation Li-ion batteries for large-scale applications such as hybrid electric vehicles (HEVs) and electric vehicles (EVs), due to advantages of low cost, environmentally benign Fe and PO_4 , long cycle life and high safety.⁵⁶ The olivine LiFePO_4 (Figure 2.12a) possess of a polyoxyanionic framework of edge-shared LiO_6 octahedra and corner-shared FeO_6 octahedra paralleling to the *b*-axis, linking together by the PO_4 tetrahedra. Upon complete lithium extraction, FePO_4 still retains the olivine framework. The oxygen atoms

Figure 2.12 (a) The crystal structure of olivine LiFePO_4 .¹ Reprinted with permission from ref. 1. Copyright 2001, Rights Managed by Nature Publishing Group. (b) Curved Li^+ transport trajectory along the $[010]$ channel in olivine LiFePO_4 , shown with red arrows.¹⁴ Reprinted with permission from ref. 14. Copyright 2010, American Chemical Society.

in LiFePO_4 structure is highly stable even at high states of charge due to the strong P-O bonds in $(\text{PO}_4)^{3-}$ polyanionic clusters, which makes LiFePO_4 more stable and safety than the lithium transition metal oxide cathodes such as LiCoO_2 . The high structure stability leads to excellent capacity retention during cycling. Unfortunately, the strong covalent oxygen bonds also result in poor electronic conductivity ($\sim 10^{-9} \text{ cm s}^{-1}$).⁵⁷

It has been shown by the atomistic modeling and first-principle calculations that the lowest energy for lithium movement is the pathway along the [010] projection, with a curved, nonlinear trajectory between adjacent lithium sites (Figure 2.12b).¹⁴ Although the calculated Li^+ ionic diffusion coefficient of LiFePO_4 can reach as high as $10^{-8} \text{ cm}^2 \text{ s}^{-1}$, the one-dimensional *b*-axis transport pathways are easily blocked by impurities and defects. Thus, the practical Li^+ diffusion coefficients are lower than the theoretical one. For example, it has been reported by Takeda et al.⁵⁸ that the Li^+ diffusion coefficients in LiFePO_4 were measured to be 10^{-14} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ by the potentiostatic intermittent titration technique (GITT), 10^{-15} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ by the electrochemical impedance spectroscopy (EIS), and $10^{-14} \text{ cm}^2 \text{ s}^{-1}$ by the cyclic voltammetry (CV), respectively. Therefore, in order to achieve high-power density and high-energy density, it is necessary to improve both electronic conductivity and lithium ion diffusion.

Since the discovery of LiFePO_4 in 1997, many efforts have been devoted to improve the electrochemical properties of this material through various routes, which are summarized in Table 2.2. Carbon coating is the most common way to improve the electronic conductivity by introduction of carbonaceous organic compounds in the sample preparation and annealing in a reducing atmosphere. The pioneering research was realized by Armand et al.⁵⁹ The theoretical capacity could be almost achieved by coating

a carbon layer on LiFePO_4 surface. Afterwards, numerous work associated with carbon-coated LiFePO_4 (LiFePO_4/C) have been widely reported regarding to the sample synthesis and the electrochemical behavior analysis. Until now, a large number of carbonaceous organic molecules, such as glucose,⁶⁰ sucrose,⁶¹ oxalate,⁶² citrate,⁶³ and polymers,⁶⁴ have been used as carbon sources for LiFePO_4 . For example, as reported by Bewlay et al.,⁶⁵ the electronic conductivity of LiFePO_4 had a seven-order-of-magnitude increase by adding sucrose to coat carbon on its surface. It has been found that the carbon effect on the electrochemical properties of LiFePO_4 was strongly depended on the carbon content, the morphology, the degree of graphitization, and the carbon distribution on LiFePO_4 surface.⁶⁶ The graphitization degree of carbon is mainly influenced by the used carbon sources and the calcination temperatures, which has an important effect on the conductivity and rate capability of LiFePO_4 . Li^+ diffusion through the sp^2 carbon is much easier than the sp^3 carbon. Thus, LiFePO_4 coated with more graphitic carbon has higher conductivities and displays better electrochemical properties.

Carbon can not only improve the electronic conductivity of LiFePO_4 , but also act as a nucleating agent to reduce the particle size of LiFePO_4 . On the other hand, carbon acts as a reductant to prevent the formation of ferric impurities. Recently, Mauger et al.⁶⁷ reported that the surface properties of LiFePO_4 nanoparticles (30-40 nm) could be changed by the carbon coating. Before carbon coating, the particles were well-crystallized in bulk and no impurities, but were surrounded by a disordered surface layer ($\sim 8 \text{ \AA}$ thick), in which the iron ions were in the Fe^{3+} low-spin ($S = 1/2$) configuration, whereas the carbon coating could reduce the disorder at the surface and the Fe^{3+} ions were switched to the high-spin ($S = 5/2$) configuration. However, excess carbon may

Table 2.2 Various approaches to improve electrochemical performances of LiFePO_4 .⁶⁸*Reprinted with permission from ref. 68. Copyright 2011, Royal Society of Chemistry.*

Methods	Catalogue	Advantages	Disadvantages
Size reduction	Micro (10 μm)	High tap density	Low rate performance
	Sub-micro (0.5–1.0 μm)	Medium tap density	Medium performance
	Sub-micro (0.5 μm)	Medium tap density	Medium performance
	Nano-size (100–200 nm)	High rate performance	Low tap density
	Nano-size (20 nm)	High rate performance	Low tap density
Conductive surface coating	Metal (Cu/Ag)	High conductivity	High cost non-uniform
	Polymer (PPy/PANI) ^a	High conductivity	Poor mechanical properties
	Carbon	High conductivity	No improving intrinsic conductivity
Lattice engineering	Supervalent cation doping	—	No convincing evidences
	Anion doping	—	Possible structure change
Surface engineering	Ion-conducting polyphosphate	—	Mechanism debates
	Metal oxide coating	Improving cycle performance	High cost, non-uniform

^a PPy: polypyrrole, PANI: polyaniline.

Figure 2.13 Preparation process of core-shell structured LiFePO_4/C nanoparticles including an *in-situ* polymerization reaction and two typical restriction processes.⁶⁹ Reprinted with permission from ref. 69. Copyright 2008, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

generate by-products (e.g., Fe_2P).⁷⁰ Moreover, too much carbon will significantly lower the tap density of LiFePO_4 . It is thus very necessary to optimize the carbon content. Generally, the optimal amount of carbon in LiFePO_4/C is $< 5 \text{ wt\%}$.

Much effort has also been carried out on controlling the morphology and distribution of carbon on LiFePO_4 surfaces. A complete, homogeneous, thin coating carbon is highly desired, which ensures that the electrons can transport from all directions to LiFePO_4 and the lithium ions can fluently pass through the carbon layer without large polarization. Zhou et al.⁶⁹ developed an in-situ polymerization restriction method to synthesize core-

shell structured LiFePO_4/C nanoparticles, in which the LiFePO_4 was completely coated with carbon (Figure 2.13). Such core-shell structured LiFePO_4/C showed a discharge capacity of 168 mAh g^{-1} at a rate of about 0.6 C. After 1100 cycles, the discharge capacity could retain about 95% of the initial one, suggesting an excellent cycling stability. Moreover, the electrode still delivered a capacity of 90 mAh g^{-1} even at a high rate of 60 C, indicating a high-power performance. Drummond et al.⁷¹ prepared several porous LiFePO_4/C composites with featured pores ranging from 10 to 100 nm on the basis of a solution-based templating technique. The LiFePO_4/C electrode with the largest pores (around 100 nm diameters) had the largest discharge capacities with values of 160 mAh g^{-1} at 0.1 C and 115 mAh g^{-1} at 5 C. As demonstrated above, the great improvement on the rate performances of the LiFePO_4/C composites is not only attributed to the proper carbon content, but also related to the architecture of the coated carbon.

2.3 Anode Materials

2.3.1 Carbonaceous Anodes

In terms of energy density, metallic lithium is the most attractive anode material for rechargeable Li-ion batteries. However, it has proved risky in Li-ion batteries due to the lithium dendrites, which may cause an internal short circuit and result in a serious safety problem. Carbonaceous materials are promising alternatives and dominate current commercial Li-ion battery market due to their low cost, high availability, favorable stability, and outstanding electrochemical properties. Carbonaceous materials for reversible lithium intercalation/deintercalation can be divided into two types: graphitic and non-graphitic (disordered) carbons. Graphitic carbons have a crystallographic layered

Figure 2.14 Structures of hexagonal graphite (a) and non-graphitic carbon (b).⁷²

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Figure 2.15 Structure of LiC₆. (a) AA stacking order and (b) perpendicular view.⁷²

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structure with a perfect stacking order of AB (hexagonal graphite, Figure 2.14a). Non-graphitic carbons consist of hexagonal arranged carbon atoms in a planar, but without far-

reaching crystal order along the *c*-direction. These carbons normally have amorphous areas embedding and crosslinking with some graphitic ones (Figure 2.14b).

For highly crystalline graphitic carbons, a maximum lithium content of one Li per six carbon atoms can be achieved ($x \leq 1$ in Li_xC_6). During lithium intercalation, the stacking order of the carbon layers (i.e., graphene layers) changes into AA, meaning that two neighboring graphene layers directly face each other (Figure 2.15a). In fully lithiated graphite, lithium ions occupy the direct neighboring gaps between the carbon layers by forming a $\text{Li-C}_6\text{-Li-C}_6$ chain along the *c*-axis. The interplanar distance is increased from 3.35 Å at $x = 0$ to 3.70 Å at $x = 1$. In LiC_6 , the lithium is arranged in such a way associated with a hexagonal carbon ring within a plane to avoid the occupation of nearest neighbor sites (Figure 2.15b).

Lithium intercalation into graphite undergoes the staging mechanism. The staging phenomenon is a thermodynamic result related to: 1) the energy required to overcome the van der Waals interactions to expand the graphene layer gap, and 2) the repulsive interactions between lithium species. Such phenomenon was clearly demonstrated by the voltage profiles for lithium intercalation/deintercalation into graphite (Figure 2.16a). The voltage plateaus suggested two-phase regions (coexistence of two phases). The stages of intercalation have also been confirmed by X-ray diffraction and Raman spectroscopy.⁷² Theoretically, lithium intercalation into graphite is fully reversible, giving a capacity of 372 mAh g⁻¹. However, it is obvious from Figure 2.16a that the first charge capacity exceeds the theoretical value of 372 mAh g⁻¹. The excess capacity is generally because of the formation of solid electrolyte interphase (SEI) film and corrosion-like reactions of Li_xC_6 .

Figure 2.16 The initial charge-discharge curves of (a) graphite,⁷³ (Reprinted with permission from ref. 73. Copyright 2009, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) and (b) “high specific charge” carbon (poly(*p*-phenylene), calcined at 700 °C).⁷² Reprinted with permission from ref. 72. Copyright 1998, WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.

In terms of the capability of lithium storage, non-graphitic carbons can be classified as:

- 1) “low specific charge” carbons such as cokes and carbon blacks, which typically have maximum x values of ~ 0.5 to ~ 0.8 in Li_xC_6 , and
- 2) “high specific charge” carbons, which can store more lithium than graphite (i.e., $x > 1$ in Li_xC_6).

Recently, many studies have been carried out to develop of “high specific charge” carbons. As shown in Figure 2.16b, non-graphitizing (hard) carbons calcined at 700 °C exhibit very high specific capacity, and display a voltage hysteresis: lithium insertion close to 0 V whereas lithium removal at much high potential. The hysteresis is related to the hydrogen in the carbon. Several models were proposed to explain the high specific capacities (Figure 2.17). As revealed by

Figure 2.17 Some proposed lithium storage mechanisms for “high specific charge” carbons. (a) Lithium storage in the form of Li_2 covalent molecules.⁷⁴ Reprinted with permission from ref. 74. Copyright 1994, American Association for the Advancement of Science. (b) Cavity mechanism.⁷⁵ Reprinted with permission from ref. 75. Copyright 1995, The Electrochemical Society. (c) Lithium storage on the carbon particle edges and surfaces.⁷⁶ Reprinted with permission from ref. 76. Copyright 1995, Elsevier. (d) Lithium adsorption on the two sides of the individual graphene sheet.⁷⁷ Reprinted with permission from ref. 77. Copyright 1996, Elsevier.

the nuclear magnetic resonance spectrum, Sato et al.⁷⁴ indicated that lithium occupied the nearest neighbor sites (i.e., the existence of Li_2 covalent molecules) in carbons (Figure

2.17a). Another model is that nanoscopic cavities are also capable of storing lithium species (Figure 2.17b).⁷⁵ Additionally, considerable amount of lithium species can be stored on the carbon particle edges and surfaces (Figure 2.17c).⁷⁶ Dahn et al.⁷⁷ suggested that the disordered carbons contained large amount of single-layer graphene sheets and the lithium species could be adsorbed on both sides of the sheets (Figure 2.17d).

2.3.2 Transition Metal Oxides

Transition metal oxides M_xO_y ($M = \text{Fe, Co, Ni, Mn, Cu, etc.}$) have been extensively studied as promising anode materials for lithium rechargeable batteries due to their diverse chemical and physical properties and capability of incorporating more than one Li per transition metal species, giving much higher electrochemical capacities (ranging from 500 to 1000 mAh g^{-1}) than graphite anodes. The electrochemical lithiation mechanism of M_xO_y electrodes is different from the Li-intercalation reaction mechanism. These M_xO_y oxides are reduced to a metallic state, accompanying the formation of Li oxide (Li_2O) during the first lithiation process through a conversion reaction: $M_xO_y + 2y\text{Li}^+ + 2ye^- \leftrightarrow y\text{Li}_2\text{O} + xM$. This reaction can be reversibly oxidized to its initial state after delithiation. Although these oxides can deliver high reversible charge/discharge capacities and high energy densities, they often exhibit much low initial Coulombic efficiency, large voltage hysteresis, formation of unstable SEI film, large volume variation upon the electrochemical cycling and poor cycling stability.⁷⁸ Consequently, efficient approaches such as synthesis of nanosized oxides, nanostructured porous oxides or oxide/carbon nanocomposites to solve these problems.

Iron oxides (e.g., hematite Fe_2O_3 and magnetite Fe_3O_4), are highly attractive for conversion reaction-based anodes owing to their non-toxicity and low cost. Fe_2O_3 can be reversibly electrochemically reacted with lithium in a wide voltage range of 1.5–4.0 V vs. Li/Li^+ . When discharging the potential to 0.005 V, a total 8.5 moles of lithium can be inserted, which gives a theoretical capacity of 1007 mAh g^{-1} by reduction of Fe^{3+} to Fe^0 . Tarascon et al.⁷⁹ indicated that the particle size had a significant effect on the lithium reactivity to Fe_2O_3 . At the initial stage of lithiation, nanosized Fe_2O_3 (20 nm) could be inserted with one Li per formula unit ($\text{Li}_{1.0}\text{Fe}_2\text{O}_3$) before the structural transformation of hexagonal to cubic stacking, whereas the large particles ($\sim 0.5 \mu\text{m}$) reacted with a very small amount of lithium ($x < 0.1$ in $\text{Li}_x\text{Fe}_2\text{O}_3$). However, capacity fading still occurred during the long-term cycling. Zhang et al.⁸⁰ reported the synthesis of macroporous fiberlike Fe_2O_3 by calcination of the as-prepared cellulose fibers involving Fe_2O_3 nanoparticles. The fiberlike Fe_2O_3 showed a very high discharge capacity of 2750 mAh g^{-1} during the first cycle and retained a capacity of 732 mAh g^{-1} during the 50th cycle. The extremely high initial discharge capacity was probably because of the large surface area of Fe_2O_3 and remained carbon remained after heat treatment.

Cobalt oxides Co_3O_4 and CoO with theoretical capacities of 890 and 715 mAh g^{-1} , respectively, have also been widely investigated as anode materials for rechargeable lithium batteries. Until now, a large number of nanostructured Co_3O_4 materials have been fabricated for Li-ion battery applications, such as Co_3O_4 nanorods,⁸¹ Co_3O_4 nanowire arrays,⁸² needle-like Co_3O_4 nanotubes,⁸³ Co_3O_4 nanosheets,⁸⁴ and mesoporous Co_3O_4 .⁸⁵ For example, Wu et al.⁸² reported the large-area growth of self-supported Co_3O_4 nanowire arrays on various foils via a template-free method. As shown in Figure 2.18a-b,

Figure 2.18 SEM images of Co₃O₄ nanowire arrays grown on Ti foil viewed from (a) the top and (b) when tilted by 40°. (c) Cycling performance of Co₃O₄ nanowire arrays, unsupported Co₃O₄ nanowires, and commercial Co₃O₄ powders at a rate of 1 C. (d) Rate capability of Co₃O₄ nanowire arrays at rates of 20 and 50 C.⁸² Reprinted with permission from ref. 82. Copyright 2008, American Chemical Society.

Co₃O₄ nanowires with the length of 15 mm and the diameter of 500 nm grew vertically from the substrate. These nanowire arrays demonstrated excellent electrochemical properties as compared to unsupported Co₃O₄ nanowires and commercial Co₃O₄ powders. Co₃O₄ nanowire array electrodes exhibited high discharge and charge capacities of around 1124 and 859 mAh g⁻¹, respectively, during the first cycle at a rate of 1 C. The discharge capacity of nanowire arrays could maintain at about 700 mAh g⁻¹ during the

20th cycle (Figure 2.18c). In contrast, under the same testing conditions, unsupported Co₃O₄ nanowires gave a moderate discharge capacity of 350 mAh g⁻¹ during the 20th cycle, and the commercial powders only showed a significantly low discharge capacity of 80 mAh g⁻¹ during the 20th cycle (Figure 2.18c). Furthermore, the self-supported Co₃O₄ nanowire arrays also exhibited a superior high-C-rate capability (Figure 2.18d). This array electrode could still relieve a capacity of 450 mAh g⁻¹ at rate of 20 C, and 240 mAh g⁻¹ at 50 C during the 20th cycle. The large capacities and excellent high-rate capability of Co₃O₄ nanowire arrays was believed to result from their unique hierarchical architecture.

Manganese oxides (e.g., MnO, Mn₃O₄, and Mn₂O₃) are also attractive for Li-ion battery anodes. Their theoretical capacities are around 700-1000 mAh g⁻¹. However, the manganese oxides have poor electrical conductivity and suffer from large volume change during reported lithium uptake and removal. A promising approach to solve these problems is fabrication of nanostructured manganese oxides, such as nanocrystalline MnO thin film,⁸⁶ porous MnO/C nanotubes,⁸⁷ MnO nanoflakes,⁸⁸ and Mn₃O₄/graphene hybrids.⁸⁹ The electrochemical performance of Mn₃O₄ materials can also be improved by substitution of Mn by Zn or Co.⁹⁰ Recently, porous manganese oxide/carbon composite prepared by electrospinning of PAN/Mn(CH₃COO)₂ precursor combined with a heat treatment step, showed promising lithium storage performance.⁹¹ Porous MnO_x/carbon nanofibers can avoid large local volume change, and the porous carbon matrix can act as a structural buffer due to its strong mechanical strength, preventing aggregation and disintegration of MnO_x. As a result, this composite showed high reversible capacities, stable capacity retention, and high rate capability. A reversible capacity of 600 mAh g⁻¹ was obtained during the 50th cycle (current density: 50 mA g⁻¹), which was 76% of the

initial discharge capacity. Moreover, the porous MnO_x /carbon nanofibers could be charged/discharge at higher current densities.

Copper oxides (e.g., Cu_2O and CuO) are well-known p-type semiconductors and can also be served as anode materials for rechargeable lithium batteries. Similar to manganese oxides, bare CuO and Cu_2O electrodes also have large volume change during cycling. Thus, various nanostructured copper oxides and nanocomposites were fabricated to reduce the volume expansion and enhance the cycling stability. Tarascon et al.⁹² revealed that the lithiation of CuO involved the formation of a solid solution of $\text{Cu(II)}_{1-x}\text{Cu(I)}_x\text{O}_{1-x/2}$ ($0 \leq x \leq 0.4$), a phase transformation into Cu_2O , and then formation of Cu nanograins embedded into a Li_2O matrix. However, subsequent re-oxidization of metallic Cu was only back to Cu_2O instead of CuO . Wu et al.⁹³ showed the fabrication of hierarchical CuO spheres with radiating nanoplates, which delivered the initial discharge and charge capacities of 800 and 250 mAh g^{-1} , respectively. The charge capacity value suggested that the reduced metallic Cu was just re-oxidized to Cu_2O .

2.3.3 Lithium Alloys

A large number of semi-metallic and metallic elements in groups IV and V, such as Si , Sn , Ge , Sb , Al , Au , In , Ga , and Zn , can electrochemically alloy with a large quantity of lithium at a low potential.⁷⁸ Representatively, Si , Ge , and Sn can alloy with Li up to 4.4 per metals ($\text{Li}_{4.4}\text{M}$), yielding theoretical capacities of as high as 4200, 1600, and 990 mAh g^{-1} , respectively. The main challenge for using of these alloy anodes is their dramatic volume expansion and contraction during Li alloying/dealloying processes. For example, a volume expansion of 400% was happened for the formation of $\text{Li}_{4.4}\text{Si}$ alloy.

The large volume expansion leads to severe crumbling and cracking of the electrode materials and then loss of electrical contact between active materials and the current collector, resulting in large irreversible capacity and rapid capacity decline. For silicon anode, another difficulty is its poor electronic conductivity, which hinders fast lithium transportation.

Several strategies have been proposed to overcome these hurdles. One is preparation of unique nanostructures. The resultant unique nanostructures can accommodate the large strain during cycling, and reduce the distance of electronic and ionic transport.⁹⁴ Another strategy is formation of hybrid nanocomposites by introduction of a second component, such as coating metal nanoparticles with carbon or dispersion of metal nanoparticles in a carbon matrix. In this strategy, the coating carbon/carbon matrix can act as a structure buffer to alleviate the volume expansion and enhance the electric conductivity of the electrode materials. The third strategy is to introduce an electrochemically active or inactive phase M to form a new alloy. The second phase M can absorb the dramatic volume expansion and contraction during cycling, and also improve the electronic conductivity of the electrode.

On the basis of the above mentioned three approaches, Si nanowires,⁹⁵ Si nanotubes,⁹⁶ nest-like Si nanospheres,⁹⁷ Si/carbon nanocomposites,⁹⁸ Si/graphene hybrids,⁹⁹ and Si-metal alloys,¹⁰⁰ etc., have been synthesized to enhance the structural stability of Si-based electrodes during the cycling and result in stable cycling performance. For example, Cui et al.⁹⁵ reported the direct vapor-liquid-solid growth of Si nanowires onto the stainless steel current collector, which showed significantly enhanced electrochemical properties as compared to large particle and thick film electrodes (Figure 2.19). As schematically

Figure 2.19 (a and b) Schematic illustration of the morphological changes for Si film, particle, and nanowire array electrodes during cycling. (c) The voltage profiles of Si nanowire arrays tested at different current densities. (d) Capacity vs. cycle number for Si nanowire arrays at a rate of C/20. (e and f) SEM image of Si nanowire arrays before (e) and after (f) lithiation.⁹⁵ Reprinted with permission from ref. 95. Copyright 2007, Rights Managed by Nature Publishing Group.

shown in Figure 2.19a-b, there is sufficient space between adjacent nanowires for Si nanowire array to buffer the volume expansion during alloying and de-alloying processes. Moreover, each Si NW is electrically connected to the current collector, which makes sure the efficient charge transport. These features made Si nanowire array electrodes to achieve the discharge capacity close to the theoretical value, and obtain a charge capacity close to 75% of discharge one, which were little fading during 10 cycles (Figure 2.19c-d). The morphology change of Si nanowires before and after electrochemical reactions was also investigated (Figure 2.19e-f). Pristine Si nanowires were smooth sidewalls and had a diameter of around 90 nm (Figure 2.19e). After electrochemical lithiation, the Si nanowires had roughly textured sidewalls, and the diameter increased to about 140 nm (Figure 2.19d). Although the volume was largely increased, the nanowire morphology was still remained and did not pulverize into smaller particles.

Sn and Ge are also promising alloy anode materials for rechargeable lithium batteries. For example, Maier et al.¹⁰¹ reported a composite of Ge/carbon nanospheres (Ge nanoparticles embedded in carbon matrix) using the solid-state pyrolysis of tetraallylgermane. As shown in Figure 2.20a-b, the average diameter of Ge/carbon nanospheres was around 60 nm. This composite showed a highly stable and reversible discharge capacity of around 900 mAh g⁻¹ during the 50th cycle at a current density of 150 mA g⁻¹ (Figure 2.20c). As seen from Figure 2.20d, as the current density increased to 300, 600, and 900 mA g⁻¹, the reversible capacities of about 774, 650, and 613 mAh g⁻¹ were still obtained, respectively, indicating a superior rate capability. The good lithium storage properties of the Ge/carbon nanosphere electrode were attributed to its unique nanostructure. The nanosized Ge grains reduced the Li transfer distance, and the carbons

kept a well electrical connection with the current collector and prevent the agglomeration of Ge nanograins.

Figure 2.20 (a and b) SEM images of Ge/carbon nanospheres. (c) Galvanostatic charge/discharge curves of Ge/carbon nanospheres at a current density of 150 mA g⁻¹. (d) Rate capability of Ge/carbon nanospheres.¹⁰¹ Reprinted with permission from ref. 101. Copyright 2008, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

2.4 Electrolytes

In addition to the cathodes and anodes, the electrolyte, referring to a solution containing of the salts and solvents, is considered to be the third key component of a Li-

ion battery. The requirements for a successful electrolyte in Li-ion batteries are as follows:^{12, 102}

- (1) The electrode/electrolyte interface should be stable during cycling even for the electrode materials with a large volume change.
- (2) Li-ion conductivity (σ_{Li}) $> 10^{-4} \text{ S cm}^{-1}$ at the battery operation temperature.
- (3) Electronic conductivity (σ_{e}) $< 10^{-10} \text{ S cm}^{-1}$.
- (4) Transference number ($\sigma_{\text{Li}}/\sigma_{\text{total}}$) ≈ 1 , where σ_{total} is the conductivity including other ions, σ_{Li} and σ_{e} in the electrolyte.
- (5) The electrolyte must be chemically stable at room temperature.
- (6) Chemical stability to the electrode materials, including quick formation of a passivating solid/electrolyte-interface layer.
- (7) Safety such as nonflammable and nonexplosive if short-circuited.
- (8) Low cost and low toxicity.

Generally, the electrolyte is fabricated for special battery application. Table 2.3 exhibits several different electrolyte materials that have been applied for Li-ion batteries.

One is organic liquid electrolyte. Carbonates are common organic liquids, which are good solvents for a lot of Li salts. Their oxidation potential is around 4.7 V, and the reduction potential is near 1.0 V.¹⁰³ On the other hand, the viscosity of carbonates is relatively low, suggesting low activation energy for Li^+ transfer. Carbonates or carbonate blends commonly consist of one or more of the following: ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), propylene carbonate (PC) or ethylmethyl carbonate (EMC). For carbon anodes, ethylene carbonate (EC) can provide a passivating SEI layer on the surface of carbons, which protects the further electrolyte

Table 2.3 Nonaqueous electrolytes for lithium rechargeable batteries.¹² *Reprinted with permission from ref. 12. Copyright 2010, American Chemical Society.*

Electrolytes	Example of classical electrolytes	Ionic conductivity ($\times 10^{-3}$ s/cm) at room temp	Electrochemical window (V) vs Li^+/Li^0		Remark
			Reduction	Oxidation	
Liquid organic	1M LiPF_6 in EC:DEC (1:1)	7	1.3	4.5	Flammable
	1M LiPF_6 in EC:DMC (1:1)	10	1.3	> 5.0	
Ionic liquids	1M LiTFSI in EMI-TFSI	2.0	1.0	5.3	Non-flammable
	1M LiBF_4 in EMI- BF_4	8.0	0.9	5.3	
Polymer	LiTFSI -P(EO/MEEGE)	0.1	< 0.0	4.7	Flammable
	LiClO_4 -PEO ₈ + 10 wt % TiO_2	0.02	< 0.0	5.0	
Inorganic solid	$\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$ ($x = 0.75$)	2.2	< 0.0	> 5.0	Non-flammable
	$0.05\text{Li}_4\text{SiO}_4 + 0.57\text{Li}_2\text{S} + 0.38\text{SiSi}_2$	1.0	< 0.0	> 8.0	
Inorganic liquid	$\text{LiAlCl}_4 + \text{SO}_2$	70	-	4.4	Non-flammable
Liquid organic + Polymer	$0.04\text{LiPF}_6 + 0.2\text{EC} + 0.62\text{DMC} + 0.14\text{PAN}$	4.2	-	4.4	Flammable
	$\text{LiClO}_4 + \text{EC} + \text{PC} + \text{PVdF}$	3.0	-	5.0	
Ionic liquid + Polymer	1M $\text{LiTFSI} + \text{P}_{13}\text{TFSI} + \text{PVdF-HFP}$	0.18	< 0.0	5.8	Less flammable
Ionic liquid + Polymer + Liquid organic	56 wt % LiTFSI - $\text{Py}_{24}\text{TFSI} + 30$ wt % $\text{PVdF-HFP} + 14$ wt % EC/PC	0.81	1.5	4.2	Less flammable
Polymer + Inorganic solid	2 vol % LiClO_4 -TEC-19 + 98 vol% 95 (0.6 $\text{Li}_2\text{S} + 0.4\text{Li}_2\text{S}$) + 5 Li_4SiO_4	0.03	< 0.0	> 4.5	Non-flammable

decomposition after SEI formation. However, carbonates are highly flammable (flash points: < 30 °C). In addition, the LiPF_6 salt can autocatalytic decompose into LiF and PF_5 . The PF_5 can easily irreversible react with water ($\text{PF}_5 + \text{H}_2\text{O} \rightarrow \text{PF}_3\text{O} + 2\text{HF}$) and, with carbonates at above 60 °C. These reactions result in the capacity fading of batteries and lead to safety hazards.

Recently, room-temperature ionic liquids (RTILs) have been also attracted significantly interesting for Li-ion battery electrolytes due to their advantages of non-flammability, low vapor pressure, good thermal stability, high oxidation potential (~ 5.3 V vs Li^+/Li), high boiling points, low toxicity, and high Li-salt solubility.¹² Unfortunately, RTILs have a low Li-ion conductivity due to their high viscosity. Imidazolium-based RTILs would be considered as more suitable electrolytes for Li-ion batteries owing to

their lower viscosity. But their stability is relatively poor at potentials below 1.1 V. Thus, additives such as EC or VC are needed to stabilize the SEI film on carbon anodes.

Solid polymer electrolytes can not only keep contact over an electrode/electrolyte interface, but also act as the separators of batteries. One of common solid polymer electrolytes is polyethylene oxides (PEOs) containing a lithium salt such as LiPF_6 or LiAsF_6 , which have advantages of nontoxic, low-cost, and good chemical stability. Unfortunately, its Li^+ conductivity is relatively low ($\sigma_{\text{Li}} < 10^{-5} \text{ S cm}^{-1}$) at room temperature, which can not apply for high-power battery system. An approach to enhance the σ_{Li} and Li^+ transference number is introduction of oxide particles (e.g., Al_2O_3 , SiO_2 , TiO_2 , or ZrO_2) to create a more amorphous polymer matrix.¹⁰⁴ Additionally, inorganic solid electrolytes with a Li-ion conductivity $> 10^{-4} \text{ S cm}^{-1}$ have also been extensively used for rechargeable lithium batteries due to their wide electrochemical windows.¹⁰⁵

2.5 Promising Vanadium-Based Cathodes for Li-Ion Batteries

2.5.1 Metastable Vanadium Dioxide, $\text{VO}_2(\text{B})$

As a metal oxide, vanadium dioxide (VO_2) with excellent physical and chemical properties has various functional applications. VO_2 has four different polymorphic structures: the most stable rutile structure of $\text{VO}_2(\text{R})$, slightly distorted rutile structure of monoclinic $\text{VO}_2(\text{R})$, tetragonal structure of $\text{VO}_2(\text{A})$, and the metastable monoclinic structure of $\text{VO}_2(\text{B})$. Among them, the metastable $\text{VO}_2(\text{B})$ received a lot of attention for Li-ion battery applications due to its layered structure, consisting of bilayers of edge sharing VO_6 octahedra (Figure 2.21). In this structure, the layers are simply linked by bridging oxygen atoms, which are suitable for the intercalation/deintercalation of guest

Figure 2.21 Crystal structure of $\text{VO}_2(\text{B})$ viewed down b -axis.¹⁰⁶ Reprinted with permission from ref. 106. Copyright 2008, Elsevier.

ions. Manthiram et al.¹⁰⁷ showed that $\text{VO}_2(\text{B})$ structure delivered an initial capacity of above 300 mAh g^{-1} between 3.5 and 1.0 V, which is equivalent to one Li per V. Tarascon et al.¹⁰⁸ exhibited the preparation of nanotextured $\text{VO}_2(\text{B})$ from the heat treatment of vanadium oxide aerogels in vacuum. Increasing the annealing temperature from 280 to 400°C , the surface areas of samples decreased from 185 to $122 \text{ m}^2 \text{ g}^{-1}$. Particle sizes were estimated to be 6 to 20-25 nm from the X-ray diffraction pattern by the Scherrer equation. The sample sintered at 280°C with the smallest particle size showed a specific capacity in excess of 500 mAh g^{-1} between 4 and 1.5 V, but it faded rapidly during cycling, which was ascribed to the dissolution of vanadium at low voltages. Stable performance at 175 mAh g^{-1} could be observed when the cell was cycled between 4 and 2.4 V.

Figure 2.22 (a, b) SEM images of VO₂(B) hollow spheres calcined at 700 °C in Ar/H₂. (c) Its initial charge/discharge voltage profile and cycling stability (inset) at 50 mA g⁻¹.⁵ Reprinted with permission from ref. 5. Copyright 2009, Royal Society of Chemistry.

Nanomaterials with unique physical and chemical properties are highly popular for Li-ion battery applications. Compared with the bulk materials, nanosized vanadium dioxides can improve the electrochemical properties. Many efforts have been devoted to preparation of nanostructured VO₂(B), including nanowires, nanoribbons, nanorods, and nanotubes.¹⁰⁹ The charge capacities were largely improved by nanostructured VO₂(B). Unfortunately, nanostructured VO₂(B) suffered from poor cycling stability, which

hinders its large-scale practical applications. Recently, Zhou et al.⁵ reported the preparation of three-dimensional (3D) superstructures of nanothorn $\text{VO}_2(\text{B})$ hollow microspheres (Figure 2.22a-b). Such unique 3D superstructure can effectively prevent the aggregation of the electrode materials, which results in the enhanced cycling performance (inset in Figure 1.22c). The $\text{VO}_2(\text{B})$ electrode showed superior capacity stability with almost no capacity fading during the 20 cycles. Moreover, the hollow core and porous shell can provide more active sites for lithium adsorption/desorption, giving large charge/discharge specific capacities (Figure 2.22c).

2.5.2 Vanadium Pentoxide, V_2O_5

Vanadium pentoxides (V_2O_5) have been intensely investigated for several decades owing to its special structural characteristics. Crystalline V_2O_5 belongs to orthorhombic structure (space group: $Pmmn$, $a = 11.512 \text{ \AA}$, $b = 3.564 \text{ \AA}$, $c = 4.368 \text{ \AA}$).¹¹⁰ As shown in Figure 2.23a, crystalline V_2O_5 exhibits a layered structure. Each layer consists of distorted VO_5 square pyramids linked by sharing of edges and corners. These VO_5 square pyramids arrange in a manner of up-up-down-down. The weak interactions (i.e., van der Waals force) between the adjacent layers give the possibility of intercalation of guest ions (e.g., lithium ions).

The electrochemical lithium insertion/extraction into crystalline V_2O_5 is shown in Figure 2.23b. Initial lithium intercalation formed α phase of $\text{Li}_x\text{V}_2\text{O}_5$ at $x < 0.01$ and ϵ phase of $\text{Li}_x\text{V}_2\text{O}_5$ at $0.35 < x < 0.7$ was formed by small amount of lithium intercalation with retaining V_2O_5 structure. At $x = 1.0$, δ -phase LiV_2O_5 was formed by gliding of one ($x > 1.0$) resulted in an irreversible transition into γ -phase due to crystal reconstruction.

Figure 2.23 (a) Crystal structure of orthorhombic V_2O_5 along c -axis.¹¹¹ Reprinted with permission from ref. 111. Copyright 2010, Royal Society of Chemistry. (b) Lithium insertion/extraction behavior into crystalline V_2O_5 at various current densities.¹¹² Reprinted with permission from ref. 112. Copyright 2009, Royal Society of Chemistry.

The γ -phase $\text{Li}_x\text{V}_2\text{O}_5$ could be reversibly cycled in the range of $0 \leq x \leq 2.0$, which gives a theoretical capacity of around 300 mAh g^{-1} . The third lithium intercalation occurring below $1.9 \text{ V vs Li}^+/\text{Li}$ led to an irreversible phase transformation from γ -phase to rock-

salt type ω -phase. On the other hand, hydrated vanadium pentoxide ($V_2O_5 \cdot H_2O$) has also been extensively investigated for Li-ion batteries. The crystallization of $V_2O_5 \cdot H_2O$ is relatively low as compared to the V_2O_5 . For Li-ion battery application, $V_2O_5 \cdot H_2O$ has characteristics of large area providing more active sites, low density, low volume expansion, and high Li^+ diffusion coefficient. However, the practical application of V_2O_5 and $V_2O_5 \cdot H_2O$ limits by their cycling stability. It is because of vanadium dissolution and sluggish kinetic in the state of deep discharge.

The vanadium oxide nanomaterials are highly favorites for the improvement of lithium storage properties due to the reduced lithium transfer distance and buffer the strain during cycling. For example, Martin et al.¹¹³ reported the template synthesis of polycrystalline V_2O_5 nanorod arrays (Figure 2.24a). The nanorod array electrode obtained a high capacity of 145 mAh g^{-1} under 1 C at room temperature between 4.0 and 2.8 V, and still cycled even at low temperatures of -20°C with a capacity of 78 mAh g^{-1} at a rate of 0.2 C. Such superior electrochemical properties, especially for the low-temperature performances, were ascribed to its unique array structure, which offered high contact area between the electrode and electrolyte and largely shortened the lithium diffusion length. To further improve the lithium intercalation/deintercalation processes in V_2O_5 , Cao et al.¹¹⁴ developed a template-based electrodeposition method to synthesize single-crystal V_2O_5 nanorod arrays (Figure 2.24b). [010]-orientated single-crystalline V_2O_5 nanorods with lengths of around $10 \mu\text{m}$ and diameters of 100-200 nm were successfully fabricated. Such nanorod array electrode showed higher lithium storage capacities, e.g., about 5 times higher than those of sol-gel-derived film. Afterwards, Cao et al.¹¹⁵ further prepared amorphous V_2O_5 nanotube arrays using similar template-based electrodeposition method.

Figure 2.24 (a) SEM image of polycrystalline V_2O_5 nanorod (diameter = 70 nm) arrays produced from a current-collector surface.¹¹³ Reprinted with permission from ref. 113. Copyright 2005, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (b) SEM image of single-crystal V_2O_5 grown from the template-based electrodeposition.¹¹⁴ Reprinted with permission from ref. 114. Copyright 2004, American Chemical Society.

Figure 2.25 SEM images of the $\text{V}_2\text{O}_5 \cdot 0.9\text{H}_2\text{O}$ nanobelts (a) and $\text{V}_2\text{O}_5 \cdot 0.6\text{H}_2\text{O}$ nanorolls (b).¹¹⁶ Reprinted with permission from ref. 116. Copyright 2006, IOP Publishing.

Figure 2.26 SEM (a) and TEM (b) images of V_2O_5 hollow microspheres.¹¹⁷ Reprinted with permission from ref. 117. Copyright 2005, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Electrochemical investigation indicated that this amorphous V_2O_5 nanotube array electrode obtained an initial capacity of as high as 300 mAh g^{-1} , which was around twice that of V_2O_5 film fabricated by electrochemical approach.

Furthermore, one-dimension (1D) hydrated vanadium pentoxide $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ was also extensively investigated. For example, Xie et al.¹¹⁶ developed a facile hydrothermal route to synthesize ultra-long $\text{V}_2\text{O}_5 \cdot 0.9\text{H}_2\text{O}$ nanobelts and $\text{V}_2\text{O}_5 \cdot 0.6\text{H}_2\text{O}$ nanorolls (Figure 2.25). The electrochemical analysis showed that the $\text{V}_2\text{O}_5 \cdot 0.6\text{H}_2\text{O}$ nanorolls exhibited an initial discharge capacity of $253.6 \text{ mA h g}^{-1}$ at a current density of 0.6 mA cm^{-2} , which was a little higher than that of $\text{V}_2\text{O}_5 \cdot 0.9\text{H}_2\text{O}$ nanobelts (223.9 mAh g^{-1}).

In addition to the 1D vanadium (V) oxide nanomaterials, 3D superstructures are also attractive. Wan et al.¹¹⁷ developed a mediated polyol process to synthesize hollow microspherical superstructures self-assembled by V_2O_5 nanorods (Figure 2.26). This superstructure electrode exhibited a discharge capacity of as high as 286.4 mAh g^{-1} with a

Coulombic efficiency of up to 97% between 2.0 and 4.0 V. On the basis of above investigations, nanoarchitected V_2O_5 is a very promising cathode material for rechargeable lithium batteries.

2.5.3 Lithium Vanadium Phosphate, $Li_3V_2(PO_4)_3$

Lithium transition metal phosphates are recently attracted much interest as promising cathode materials for lithium rechargeable batteries due to their relatively high energy densities and good thermal stabilities as compared to unstable lithium transition metal oxides such as $LiCoO_2$, and $LiNiO_2$. Furthermore, these lithium transition metal phosphate materials show high redox potentials. Among phosphate-based cathodes, monoclinic lithium vanadium phosphate $Li_3V_2(PO_4)_3$ have been attracted more attention owing to its rapid ionic mobility, high theoretical capacity (197 mAh g^{-1}) and high working voltage (3.6-4.1 V).

$Li_3V_2(PO_4)_3$ crystallizes has two structures: the rhombohedral (NASICON) phase and monoclinic phase. Monoclinic structure is thermodynamically more stable, which is suitable for lithium intercalation and deintercalation. The monoclinic $Li_3V_2(PO_4)_3$ is isotypic with the α - $Li_3Fe_2(PO_4)_3$ (space group: $P2_1/n$). The 3D framework of monoclinic $Li_3V_2(PO_4)_3$ is shown in Figure 2.27, consisting of PO_4 tetrahedra, and VO_6 octahedra linked through oxygen atoms, and corner-shared Li polyhedral. This framework has relatively large interconnected interstitial space, giving an opportunity of fast lithium ion transportation. Two lithium can be reversibly extracted from the monoclinic $Li_3V_2(PO_4)_3$ with a theoretical capacity of 132 mAh g^{-1} on the basis of the redox couple of V^{3+}/V^{4+} in the voltage range of 3.0-4.3 V. Increasing the cut-off voltage to 4.8 V, the third lithium

Figure 2.27 Crystal structure of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

can also be reversibly extracted by formation a mixed state of $\text{V}^{4+}/\text{V}^{5+}$, giving a theoretical capacity of 197 mAh g^{-1} , which is the highest value for the phosphate-based cathodes. Unfortunately, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ suffers from a problem of poor electronic conductivity, which limits its large-scale industrial Li-ion battery applications.

Various strategies has been proposed to improve the electronic conductivity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. Coating a thin carbon layer on the $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ surfaces is a common method.¹¹⁹⁻¹²¹ The in-situ carbon coating was achieved by adding an organic molecular

(e.g., sucrose, glucose, and citric acid) in the starting materials and heat treated in an inert atmosphere. During the heat process, the organic molecular was decomposed into electronically amorphous conductive carbon. For example, Chen et al.¹²² investigated the effect of different carbon sources (citric acid, glucose, PVDF and starch) on the electrochemical properties of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ under the same solid state reaction conditions. With the same molar ratio of C to V in the starting materials, the residual carbon contents were different for different carbon sources. Based on thermogravimetric analysis, the carbon content in the $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ was 1.33%, 13.27%, 12.68% and 10.46% for citric acid, glucose, PVDF and starch derived samples, respectively. As shown in Figure 2.28, the rate capability investigation revealed that the PVDF sample had the best

Figure 2.28 The rate capabilities of $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ samples prepared by different carbon sources in the voltage range of 3.0-4.8 V.¹²² Reprinted with permission from ref. 122.

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Figure 2.29 Cycling stabilities of $\text{Li}_3\text{Fe}_x\text{V}_{2-x}(\text{PO}_4)_3$ at 0.2 C. (a) $x = 0.00$, (b) $x = 0.01$, (c) $x = 0.02$, (d) $x = 0.04$ and (e) $x = 0.06$.¹²³ Reprinted with permission from ref. 123. Copyright 2006, Elsevier.

capacity retention with increasing the discharge current densities. It is because that the carbon layer was relatively uniform on surface of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ for PVDF sample.

Another approach is cation doping such as Fe^{3+} , Al^{3+} , Ti^{4+} , Zr^{4+} , and Co^{2+} .¹²³⁻¹²⁵ For example, Zhou et al.¹²³ studied the effect of Fe-doping on the lithium (de)intercalation properties in $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The Fe-doping content in $\text{Li}_3\text{Fe}_x\text{V}_{2-x}(\text{PO}_4)_3$ ($x = 0.02-0.04$) was optimized. As shown in Figure 2.29, the cycling stabilities were significantly improved by Fe-doping, and the $\text{Li}_3\text{Fe}_{0.02}\text{V}_{1.98}(\text{PO}_4)_3$ sample exhibited the best capacity retention with an initial discharge capacity of 177 mAh g^{-1} and a capacity of 126 mAh g^{-1} during the 80th cycle. The enhanced lithium storage properties are believed to result from the

incorporation of Fe^{3+} , which could increase the structural stability, and electronic conductivity of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

2.6 Nanostructured Electrode Materials

Nanomaterials, differing from the bulk materials, play an important role in recent advanced nanotechnologies. For electrochemical lithium storage applications, nanostructured materials have several advantages:¹²⁶⁻¹²⁸

- (1) Shorter distances for lithium ion and electron transport. According to the time constant (t) equation for lithium diffusion: $t = L^2/D$ (L : diffusion length, D : diffusion constant), the t for lithium insertion/removal squarely decreases as by replacing micro-sized materials with nano-dimensional electrodes.
- (2) Higher electrode/electrolyte contact area, resulting in a high Li^+ flux across the interfaces of active materials.
- (3) Better accommodation of the strain upon the lithium (de)intercalation, leading to the improvement of the cycling stability.
- (4) Facile electrochemical reactions, which may not be occurred for micro-sized materials.
- (5) Possible modification of the chemical potentials of lithium ions and electrons.

With these advantages, various nanostructured materials ranging from 0D nanoparticles to 3D complex heterogeneous nanoframworks, were developed for Li-ion battery applications, which is summarized in Figure 2.30.

Figure 2.30 Various nanostructured materials for rechargeable lithium batteries.⁸

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One of the recent achievements in nanoelectrodes is tin nanoparticles encapsulated into hollow carbon spheres (TNHCs).¹²⁹ As shown in Figure 2.31a, the hollow carbon spheres have a uniform size of around 500 nm, and thickness of ~20 nm. Sn nanoparticles with sizes of 5-10 nm encapsulate into hollow carbon spheres. Such special TNHCs delivered high specific capacities of above 800 mAh g⁻¹ during the initial 10 cycles, and retained more than 550 mAh g⁻¹ during the 100th cycle, indicating a good cycling performance for alloy anodes with a large volume expansion during lithium insertion/removal. Such superior electrochemical behavior is believed to result from the largely empty space in the hollow carbon spheres, which could accommodate the expanded lithiation products of

Figure 2.31 (a) TEM image of TNHCs. (b) Charge/discharge scheme of TNHCs.¹²⁹

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Figure 2.32 (a and b) Schematic illustration of synthesis (a) and facile lithium storage (b) of SnO_2/GNS . (c) SEM and (d) TEM images of SnO_2/GNS .¹³⁰

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$\text{Li}_{4.4}\text{Sn}$ nanoparticles (Figure 2.31b). Furthermore, the carbon sphere is conductive which could keep a good electrical conductivity through the whole electrode.

Recently, two-dimensional (2-D) nanomaterials have received much interest for energy storage and conversion applications. Honma et al.¹³⁰ fabricated rutile SnO_2 nanoparticles on graphene nanosheets (GNS). As shown in Figure 2.32a, the preparation was carried out by the reassembling of well-dispersed reduced graphene nanosheets with existence of SnO_2 nanoparticles. The molar ratio of SnO_2 to GNS was controlled to 1.5. According to the SEM and TEM observation (Figure 2.32c-d), SnO_2 nanoparticles with an average particle size of about 5 nm were homogeneously attached on the GNS. The SnO_2/GNS composite delivered a high initial reversible capacity of 810 mAh g^{-1} . As compared to the bare SnO_2 nanoparticle, the capacity retention of SnO_2/GNS was also significantly improved with a capacity of 570 mAh g^{-1} during 30th cycle. The enhanced electrochemical property of SnO_2/GNS is mainly because that the SnO_2 nanoparticles surrounded by the GNS can largely suppress the volume expansion during cycling.

2.7 Synthesis of Vanadium-Based Cathode Nanomaterials

The battery performances of nanostructured vanadium-based electrode materials are largely dependent on their morphologies, sizes, and phases, and thus several methods have been developed to synthesize the targeted vanadium-based nanomaterials.

2.7.1 Hydrothermal Method

Hydrothermal synthesis has been studied over many decades, especially in recent 10 years, for the synthesis of various nanostructured materials with special morphologies

Figure 2.33 Photograph of stainless steel autoclaves with different volumes.¹³¹ Reprinted with permission from ref. 131. Copyright 2013, Royal Society of Chemistry.

Figure 2.34 (a) SEM and (b, c) TEM images of VO₂(B) nanobelts. Inset in (c): SAED pattern of an individual nanobelt.¹³² Reprinted with permission from ref. 132. Copyright 2004, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

and sizes. The hydrothermal reaction adopts water as the reaction solvent, which is then put in a Teflon-lined steel vessel (Figure 2.33), and finally heated to a targeted

temperature. The advantages of hydrothermal synthesis mainly include the formation of high purity and high crystalline phases, and facile control of the solution reaction by changing the reaction parameters such as reagent ratios, surfactants, temperatures, and reaction times.

Figure 2.34 shows the single-crystal monoclinic vanadium dioxide $\text{VO}_2(\text{B})$ nanobelts prepared by a direct hydrothermal reaction of ammonium metavanadate and formic acid at 180 °C for 48 h.¹³² $\text{VO}_2(\text{B})$ nanobelts have the lengths of up to several micrometers, widths of 50-100 nm, and thicknesses of 10-20 nm. The selected area electron diffraction (SAED) pattern in the inset of Figure 2.34c indicates that the $\text{VO}_2(\text{B})$ nanobelt grew along the [010] direction.

2.7.2 Solvothermal Method

Solvothermal synthesis also involves high pressure and high temperature (normally 100-200 °C) occurred in an organic solution. Different organic solvents have different properties (e.g., polarity, viscosity, solubility, and transport behavior) in the liquid synthesis, which will result in the products with different morphologies, sizes and phases.

Corr et al. reported the synthesis of $\text{VO}_2(\text{B})$ nanorods by the solvothermal treatment of vanadium(V) oxide in formaldehyde or isopropanol solution at 180 °C for 48 h. As seen from Figure 2.35a-b, $\text{VO}_2(\text{B})$ nanorods prepared in the formaldehyde solution have an average length up to about 1 μm , thickness of 22 nm, and width of 100 nm. $\text{VO}_2(\text{B})$ nanorods with lower aspect-ratio (length over the width) were prepared in the presence of isopropanol (Figure 2.35c-d). The nanorod length is typical around 650 nm. The thickness and width are similar to those of formaldehyde-derived sample.

Figure 2.35 (a) SEM and (b) TEM images of formaldehyde-formed $\text{VO}_2(\text{B})$ nanorods. (c) SEM and (d) TEM images of isopropanol-formed $\text{VO}_2(\text{B})$ nanorods.¹³³ Reprinted with permission from ref. 133. Copyright 2009, Royal Society of Chemistry.

One of recent example is yolk-shell V_2O_5 microspheres prepared in the assistant of a facile template-free solvothermal reaction of vanadium (IV) acetylacetonate in *N,N*-dimethylformamide solution at 220 °C for 24 h combined with a calcinations process in air.¹³⁴ As seen from Figure 2.36, the as-prepared yolk-shell V_2O_5 microspheres have diameters ranging from 1.5 to 2 μm. The shell thickness of microsphere is around 100-200 nm as revealed by the broken yolk-shell microspheres (Figure 2.36d).

Figure 2.36 (a-d) SEM and (e-f) TEM images of yolk-shell V_2O_5 microspheres.¹³⁴

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2.7.3 Sol-Gel Reaction

The development of the sol-gel method can be traced back to 1846 when the SiO_2 gel was prepared by hydrolyzing of $\text{Si}(\text{OEt})_4$. The sol-gel process mainly includes steps of: precursor $\rightarrow$ hydrolysis $\rightarrow$ reactive monomer $\rightarrow$ condensation $\rightarrow$ sol gelation $\rightarrow$ gel $\rightarrow$ further treatment.¹³⁵ On the basis of this sol-gel procedure, various nanostructured materials were fabricated by changing different solvents, organic/inorganic ligands, precursors, as well as further treatment.

In the case of V_2O_5 , different sol-gel routs and precursors could result in different morphology products, leading to different lithium storage properties. For example, Musić et al.¹³⁶ prepared nano-fibrillar V_2O_5 by the sol-gel reaction of vanadium (V)-triisopropoxide oxide in the presence of isopropanol. The detailed synthetic procedure is

Figure 2.37 (a) Sol-gel procedure for synthesis of fibrillar V_2O_5 . (b) Its TEM image without heat treatment.¹³⁶ Reprinted with permission from ref. 136. Copyright 2003, Elsevier.

showed in Figure 2.37a. The sol-gel product displayed fine fibrillar morphology as revealed by the TEM observation in Figure 2.37b.

Another sol-gel example for synthesis of vanadium based nanomaterials is nanocrystalline $Li_3V_2(PO_4)_3$ /carbon composite.¹³⁷ $V_2O_5 \cdot nH_2O$ hydro-gel was firstly synthesized by vigorously stirring of a H_2O_2 aqueous solution containing dissolved V_2O_5 for 3 days. Afterwards, the as-obtained $V_2O_5 \cdot nH_2O$ hydro-gel was mixed with stoichiometric $NH_4H_2PO_4$, Li_2CO_3 , and 100 wt.% excess carbon, and then calcined at 850 °C for 24 h. In the SEM image (Figure 2.38a), the final product was fine particles with a good uniformity. TEM image (Figure 2.38b) indicates that the particle size is ~90 nm.

Figure 2.38 (a) SEM and (b) TEM images of nanocrystalline $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{carbon}$ composite.¹³⁷ Reprinted with permission from ref. 137. Copyright 2006, Elsevier.

2.7.4 Other Methods

Figure 2.39 SEM images of porous V_2O_5 thin film prepared at 260 °C with different deposition time. (a) 4 h, (b) 6 h, (c) 8 h, and (d) 12 h.¹³⁸ Reprinted with permission from ref. 138. Copyright 2011, Royal Society of Chemistry.

Besides these common three methods, there are also many other routes to prepared nanostructured vanadium-based materials, such as template method,¹³⁹ precipitation process,¹⁴⁰ electrospinning,¹⁴¹ sonochemical route,¹⁴² pulsed-laser-deposition,¹⁴³ chemical vapor deposition,¹⁴⁴ electrostatic spray deposition,¹³⁸ and so on.

One of examples is 3D porous V_2O_5 thin film fabricated by electrostatic spray deposition as reported by Chen et al.¹³⁸ Ammonium metavanadate dissolved in a mixed solution of 1,2-propylene glycol, ethanol and water was served as the precursor solution for electrostatic spray deposition. The morphology could be well controlled by changing of precursor solvents, deposition temperatures and time. It was found that the highly porous V_2O_5 thin film could be obtained at a deposition temperature of 260 °C and time of 4-6 h (Figure 2.39).

Chapter 3: Experimental Section

3.1 Material Characterizations

X-ray powder diffraction (XRD) patterns were recorded on a Bruker AXS D8 advance X-ray diffractometer using Cu K α radiation. The morphology of samples was investigated by using a field-emission scanning electron microscopy (FESEM) system (JEOL, Model JSM-7600F), and the nanostructure was characterized by using a transmission electron microscopy (TEM) system (JEOL, Model JEM-2010) operating at 200 kV. Thermogravimetry analysis was carried out from room temperature to the targeted temperature at a heating rate of 10 K min⁻¹ in air using TGA Model Q500. Raman spectra were obtained by WITec CRM200 confocal Raman microscopy system at a laser wavelength of 488 nm and a spot size of 0.5 mm. X-ray photoelectron spectroscopy (XPS) measurement was performed on VG Escalab 250 spectrometer using Al K α 1846.6 eV anode.

3.2 Electrochemical Measurements

The coin-type cells were assembled in an argon-filled glove-box, where both moisture and oxygen levels were less than 1 ppm. The cathodes were fabricated by mixing the as-prepared active materials, carbon black and poly(vinylidene fluoride) (PVDF) at a weight ratio of 70:20:10 for VO₂(B) and V₂O₅, and 80:10:10 for Li₃V₂(PO₄)₃ in N-methylpyrrolidone (NMP) solvent. The resulting mixture was then pasted onto the aluminum foil and punched into small disks ($\varnothing$ =14 mm). The mass loading was around 1.0-2.0 mg. Lithium foils were used as anodes and the electrolyte solution was made of

1M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). The cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage range of 4.0-2.0 V for $\text{VO}_2(\text{B})$ and V_2O_5 , and 3.0-4.3 and 3.0-4.8 V for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. The electrochemical impedance spectra (frequency range: 0.001~10⁵ Hz) were performed with an electrochemical workstation (CHI 660C). Cyclic voltammetry were performed with a Solartron analytical equipment (model 1470E) at different scan rates.

Chapter 4: One-pot Synthesis of Carbon Coated VO₂(B) Nanobelts for High-Rate Lithium Storage†

4.1 Introduction

Vanadium oxides with multiple valence states from +2 in VO to +5 in V₂O₅ have been extensively studied as well-known transition-metal oxides for the potential applications in catalysis,¹⁴⁵ sensors,¹⁴⁶ optical switching devices¹⁴⁷ and high energy density lithium ion batteries (LIBs).¹⁴⁸⁻¹⁵⁰ For LIBs application, vanadium oxides (*e.g.* V₂O₅, V₆O₁₃ and VO₂(B) *etc.*) offer the advantages of high capacity, simple synthesis procedure, low cost and being abundant with respect to the commercial cathode LiCoO₂.^{148,151-153} Among them, VO₂(B) is found to show a better cycling stability than V₂O₅. For example, VO₂(B) nanofibers aerogels prepared through a sol-gel method exhibited a capacity retention of ~80% between 4.0 and 1.5 V at C/8 after 20 cycles, while V₂O₅ nanorods obtained by annealing the VO₂(B) aerogels under air only attained a capacity retention of ~55% under the same testing condition.¹⁴⁸ This is mainly due to the higher structural stability of VO₂(B), which arises from the increased edge sharing and the consequent resistance to lattice shearing during cycling.¹⁵⁴

To develop high-performance VO₂(B) based cathode, especially at high current densities, one-dimensional (1D) nanowires or nanobelts are the most favourable as they can offer a range of unique advantages over their traditional counterparts including large

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interfacial contact area between the electrode and electrolyte, short Li⁺ transport distance, efficient 1D electron transport pathways and facile strain relaxation upon electrochemical cycling.^{155,95} For example, an electrode platform⁹⁵ was developed to enable silicon nanowires growing directly onto the current collector to accommodate the large volume change and to avoid capacity fading. Similar enhanced Li storage properties could also be obtained in 1D VO₂(B) nanofibers,¹⁴⁸ nanorods,¹⁵⁶ nanowires,¹⁰⁶ and nanobelts.¹⁵⁷ Although the VO₂(B) nanostructures were reported to show improved cyclability at relatively low current densities (*e.g.* capacity retention: 75% during the first 100 cycles at 1 C)¹⁵⁷, their rate capabilities are still not satisfying. For example, VO₂(B) nanobelts/multiwall carbon nanotube composite¹⁵⁷ exhibited capacity retentions of 77% (0.3 C), 65% (1 C), 49% (3 C) and 39% (5 C), respectively, on the basis of the 2nd discharge capacity (327 mAh g⁻¹) at 0.1 C. Such performance is significantly lower than other reported high-performance cathodes such as flower-shaped LiFePO₄/C/polypyrrole microspheres,¹⁵⁸ with capacity retentions of 92% (2 C), 81% (5 C) and 63% (10 C), respectively, based on the 2nd discharge capacity of 136 mAh g⁻¹ at 0.5 C. Hence, further performance improvement on VO₂(B) based cathode electrodes is highly desired.

Coating active materials with a conductive and elastic carbon layer is a simple and effective strategy to improve the rate capability and cycling stability of electrodes, where the carbon coating can effectively (1) enhance the kinetics of charge transfer, (2) buffer the strain caused by structural or volume changes and (3) prevent the aggregation of active materials during cycling.^{69, 119, 159} In this regard, cathodes with superior performance for LIBs have been successfully developed by coating a thin carbon layer onto the surface of LiCoO₂,¹⁶⁰ LiMn₂O₄,¹⁶¹ LiFePO₄^{69,159} and Li₃V₂(PO₄)₃.^{119,162} However,

thick carbon coating layer would hinder the Li⁺ diffusion.^{162,163} Therefore, the thickness of the carbon layer needs to be adjusted to achieve optimized Li storage performance.

Herein, we report a facile one-pot hydrothermal approach to synthesize uniform carbon-coated VO₂(B) (denoted as VO₂(B)@C) nanobelts. The thickness of carbon coating layer is controlled by changing the concentration of the precursors, which can affect the Li storage performance of the VO₂(B)@C samples. The VO₂(B)@C samples with different thicknesses of the carbon layer show high specific capacities and stable cyclability at a current density of 100 mA g⁻¹ (0.6 C). It is found that a thick carbon layer may decrease the apparent diffusion coefficient of lithium ions although it can increase the electrical conductivity and buffer the structural strain during the lithiation process. The VO₂(B)@C cathode with a carbon content of 6.6 wt% (*e.g.* the thickness of carbon shell is ~4.3 nm) shows an optimized Li ion storage performance at high current densities, achieving a highly reversible discharge capacity of 100 mAh g⁻¹ at a current density of 2000 mA g⁻¹ (12.4 C).

4.2 Material Preparation

In a typical procedure, 50 mg V₂O₅ (Alfa Aesar) and 10 mg sucrose (C₁₂H₂₂O₁₁, Sigma-Aldrich) were put in 40 mL distilled water under ultrasonication to give a yellow suspension. Successively, the suspension was transferred to a 50 mL autoclave and kept in an oven at 180 °C for 24 h. After cooling to room temperature, a black product was collected and washed with distilled water and ethanol solution several times, and then dried in a vacuum oven at 70 °C for 12 h. During the hydrothermal process, sucrose serves as a carbon precursor for the carbon shell as well as a reductant to reduce V₂O₅ to

VO₂(B), since the sucrose possesses the same hydroxyl group as the alcohol.¹⁶⁴ To obtain thicker carbon coating layer, the quantity of sucrose was sequentially increased to 20, 30 and 40 mg.

4.3 Results and Discussion

The crystal structure of the as-prepared samples obtained at different weight ratio of V₂O₅ to sucrose (herein known as I_{V₂O₅:sucrose}) in the hydrothermal process was examined by X-ray diffraction (XRD). Figure 4.1 reveals that all the reflection peaks of the four samples can be indexed to the monoclinic VO₂(B) phase (space group: C2/m, JCPDS 31-1438). No detectable crystalline carbon peak can be observed. It has been reported that the carbon derived from the sucrose (or glucose) under hydrothermal condition is amorphous.¹⁶⁵ The nature of the carbon coating of the VO₂(B) products was studied using Raman spectroscopy (Figure 4.2a). Two characteristic bands of carbonaceous materials were detected at 1370 cm⁻¹ (D-band) and at 1600 cm⁻¹ (G-band), which agree well with those of amorphous carbon.^{158,166} The carbon structure was further analyzed by X-ray photoelectron spectroscopy (XPS) C 1s spectrum (Figure 4.2b). The spectrum was fitted with two components, centered at 284.5 and 285.7 eV, which correspond to sp² and sp³ bonded carbon, respectively. The ratio of sp² to sp³ was then determined to be as high as ~2.5, which is comparable to that of amorphous carbon thin films prepared by magnetron sputtering and cathodic arc deposition,¹⁶⁷ implying a relatively high electronic conductivity.

To determine the carbon content in the VO₂(B)@C composites, thermogravimetric analysis (TGA) was carried out in air (Figure 4.3). The weight loss of 1.7% below 100 °C

Figure 4.1 XRD patterns of the as-prepared samples obtained at different $I_{V_2O_5:sucrose}$ in the hydrothermal process. (a) $I_{V_2O_5:sucrose} = 5.00$, (b) $I_{V_2O_5:sucrose} = 2.50$, (c) $I_{V_2O_5:sucrose} = 1.67$ and (d) $I_{V_2O_5:sucrose} = 1.25$.¹⁶⁸ Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.

Figure 4.2 (a) Raman spectra of the as-prepared samples obtained at different $I_{V_2O_5:sucrose}$ in the hydrothermal process. (i) $I = 5.00$, (ii) $I = 2.50$, (iii) $I = 1.67$ and (iv) $I = 1.25$. (b) XPS C 1s region for the sample prepared at $I = 1.25$.¹⁶⁸ Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.

Figure 4.3 TGA curves of VO₂(B)@C composites prepared at different $I_{V_2O_5:sucrose}$ values, (a) = 5.00, (b) = 2.50, (c) = 1.67 and (d) = 1.25.¹⁶⁸ Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.

is attributed to the evaporation of free water and physically adsorbed water. The weight changes in the temperature range of 100–450 °C is ascribed to the burning-out of amorphous carbon (weight loss) and oxidization of VO₂ to V₂O₅ (weight gain). Based on the total weight changes, the carbon contents are estimated to be 4.2 wt%, 6.6 wt%, 8.4 wt% and 9.6 wt% for VO₂(B)@C composites prepared with $I_{V_2O_5:sucrose}$ = 5.00–1.25, respectively. Thus, these four samples are named as VO₂(B)@C(4.2 wt%), VO₂(B)@C(6.6 wt%), VO₂(B)@C(8.4 wt%) and VO₂(B)@C(9.6 wt%).

The field emission scanning electron microscopy (FESEM) images shows that the sample prepared with $I_{V_2O_5:sucrose}$ = 5.00 is nanobelts (Figure 4.4a–c) of 1–2 μm in length and 120–160 nm in width with a thickness of ~25 nm. Decreasing the $I_{V_2O_5:sucrose}$ values during the hydrothermal process from 5.00 to 2.50 and 1.67 does not lead to obvious change in the nanobelt shape except for the slight decrease in the length (Figure 4.4d–i).

Further decreasing $I_{\text{VO}_2\text{B}:\text{sucrose}}$ value to 1.25 results in significant decrease in the length of the sample to 200~500 nm, making the sample nanosheets like (Figure 4.4j-l). This is mainly attributed to the binding of the sucrose molecules onto the surface of VO₂(B) nanocrystals and hence confines their growth under high sucrose concentration. Thus, the sucrose acts not only as the carbon sources but also as the effective surfactants similar to the synthesis of other reported nanocrystals.^{169,170} Here, the formation of the VO₂(B)@C nanobelts is mainly ascribed to the anisotropic bonding of its layered

Figure 4.4 FESEM images of VO₂(B)@C nanobelts. (a-c) VO₂(B)@C(4.2 wt%), (d-f) VO₂(B)@C(6.6 wt%), (g-i) VO₂(B)@C(8.4 wt%) and (j-l) VO₂(B)@C(9.6 wt%). Representative high-magnification FESEM images of (b, e, h and k) and (c, f, i and l) are the magnified view of VO₂(B)@C nanobelts to show the width and thickness of the nanobelts, respectively.¹⁶⁸ Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.

Figure 4.5 Representative HRTEM images of VO₂(B)@C nanobelts. (a) VO₂(B)@C(4.2 wt%), (b) VO₂(B)@C(6.6 wt%), (c) VO₂(B)@C(8.4 wt%) and (d) VO₂(B)@C(9.6 wt%). The inset in Figure 4.5d is the FFT pattern of Figure 4.5d.¹⁶⁸ *Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.*

structure, resulting in the faster growth along the [010] direction and the slower growth along [001] direction.¹³² Meanwhile, the 1D soft templates formed by the stacking of the sucrose molecules may also contribute to the growth of 1D VO₂(B) nanocrystals.¹⁷⁰

The nanostructure of VO₂(B)@C nanobelts was further examined by using the high resolution transmission electron microscopy (HRTEM). Figure 4.5 reveals that VO₂(B) nanocrystals are coated with a layer of amorphous carbon, which forms the VO₂(B)@carbon core-shell structure. Here, the carbon shell forms through the carbonization of the sucrose under the hydrothermal condition. The thickness of the

carbon shell can be simply tuned by changing the values of $I_{V2O5:sucrose}$ during the hydrothermal process. The thickness of the carbon layer increases from ~3.0 to ~6.9 nm when $I_{V2O5:sucrose}$ is decreased from 5.00 to 1.25 (Figure 4.5). The lattice fringes observed from the HRTEM images indicate the single crystalline nature of the VO₂(B) nanobelts. The observed interplanar spacing of 0.34 nm in the HRTEM images of these four samples agrees well with the d value of the (110) plane of the monoclinic VO₂(B) (JCPDS 31-1438). The inset in Figure 4.5d is the indexed fast Fourier transform (FFT) pattern of Figure 4.5d.

To study the Li-ion storage properties of VO₂(B)@C nanobelts, a series of electrochemical measurements were carried out based on the half cell configuration. Figure 4.6a shows the initial galvanostatic discharge (Li⁺ insertion) and charge (Li⁺ extraction) voltage profiles of the VO₂(B)@C electrodes at a current density of 100 mA g⁻¹ (0.6 C) between 4.0 and 2.0 V vs Li⁺/Li. A typically long plateau at around 2.5 V is clearly observed in the discharge curves, which corresponds to a phase transition of crystalline VO₂(B) to Li_{0.5}VO₂(B) and the corresponding electrochemical reaction is written as:¹⁷¹

Half lithium insertion into VO₂ yields a theoretical capacity of 161 mAh g⁻¹. This reaction is highly reversible as indicated by the long plateau at ~2.6 V in the subsequent charge process. As shown in Figure 4.6a, the VO₂(B)@C(4.2 wt%), VO₂(B)@C(6.6 wt%), VO₂(B)@C(8.4 wt%) and VO₂(B)@C(9.6 wt%) electrodes depict initial discharge capacities of 160, 161, 159 and 158 mAh g⁻¹ with the subsequent charge capacities of 160, 161, 159 and 158 mAh g⁻¹, respectively, indicating no irreversible capacity loss (e.g.

the coulombic efficiency is ~100%). During the 50th cycle, the discharge capacities are 125, 128, 120 and 116 mAh g⁻¹ for VO₂(B)@C(4.2 wt%), VO₂(B)@C(6.6 wt%), VO₂(B)@C(8.4 wt%) and VO₂(B)@C(9.6 wt%) electrodes (Figure 4.6b), which are 78%,

Figure 4.6 Cathode performance of VO₂(B)@C nanobelts in the voltage range of 4.0-2.0 V. (a) Initial galvanostatic charge-discharge voltage profiles at a current density of 100 mA g⁻¹. (b) Cycling performance at a current density of 100 mA g⁻¹. (c) Discharge capacities of VO₂(B)@C electrodes at various current densities of 200 to 2000 mA g⁻¹. (d) Electrochemical impedance spectra of VO₂(B)@C electrodes measured at the 4th fully discharged state. The high-middle frequency semicircle represents the charge-transfer process and a straight sloping line at low frequencies corresponds to Li⁺ diffusion in VO₂(B)@C electrodes known as Warburg impedance.¹⁶⁸ Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.

80%, 76% and 73% of the initial capacity, respectively. Although initial capacities are relatively lower as compared to flexible free-standing VO₂(B) nanobelt films (218.7 mAh g⁻¹ at current density of 10 mA g⁻¹ in the voltage range of 4.0-1.5 V),¹⁷² these cycling performances are much better than that electrode (53% of capacity retention at 50 mA g⁻¹ during the first 50 cycles) as well as other reported VO₂(B) and V₂O₅ cathodes, *e.g.*, 50% of capacity retention for VO₂(B) nanorods between 3.44 and 1.5 V at 0.1 C during the 17 cycles,¹⁷³ 68% of capacity retention for VO₂(B) nanowires at 50 mA g⁻¹ (0.3 C) between 3.2 and 2.0 V during the first 50 cycles¹⁰⁶ and 61% of capacity retention for V₂O₅ submicron spheres at 0.125 C between 3.8 and 1.8 V during the first 35 cycles.¹⁷⁴

Good rate capability is one of the keys in developing high power/fast charging lithium ion batteries. The cycling responses of the VO₂(B)@C electrodes at different C rates are evaluated and is shown in Figure 4.6c. Among the four types of cathodes, the VO₂(B)@C(6.6 wt%) electrode shows the best rate capability, delivering discharge capacities of 157, 155, 146 and 136 mAh g⁻¹ during the 2nd cycle at current densities of 200 (1.2 C), 500 (3.1 C), 800 (5.0 C) and 1000 mA g⁻¹ (6.2 C), respectively. Even at a very high current density of 2000 mA g⁻¹ (12.4 C), the VO₂(B)@C(6.6 wt%) electrode can still achieve a high specific capacity of 100 mAh g⁻¹ during the 2nd cycle. The retention of the rate capacity is calculated to be 99% (3.1 C), 93% (5.0 C), 87% (6.2 C) and 64% (12.4 C) on the basis of the capacity value of 157 mAh g⁻¹ at 1.2 C. The other three electrodes exhibit relatively low specific capacities, especially at high C rates, *e.g.* showing discharge capacities of 90, 69 and 41 mAh g⁻¹ at 12.4 C for VO₂(B)@C(4.2 wt%), VO₂(B)@C(8.4 wt%) and VO₂(B)@C(9.6 wt%), respectively. The difference of the rate capabilities of these four cathodes is verified by the electrochemical impedance

spectra (Figure 4.6d). The VO₂(B)@C(6.6 wt%) cathode shows the smallest radius of semi-circle in the Nyquist plots as compared to the other three, indicating the smallest charge-transfer resistance and the correspondence fastest kinetics of the Faradic reaction.

Figure 4.7 CV plots of VO₂(B)@C electrodes with different scan rates of 0.1, 0.2, 0.3 and 0.5 mV s⁻¹ during the 3rd cycle. (a) VO₂(B)@C(4.2 wt%), (b) VO₂(B)@C(6.6 wt%), (c) VO₂(B)@C(8.4 wt%) and (d) VO₂(B)@C(9.6 wt%).¹⁶⁸ Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.

It is interesting to find out that the VO₂(B)@C(6.6 wt%) electrode shows the best rate capabilities among these four samples. Generally, a high carbon content should improve the electrical conductivity of the VO₂(B)@C composites. However, a thick layer of

carbon coating may also block the lithium ions diffusion.^{162,163} To verify this, cyclic voltammetry (CV) was used to estimate the apparent diffusion coefficient of lithium ions (D_{Li^+}) in VO₂(B)@C nanobelt cathodes. Figure 4.7 shows the CV plots of VO₂(B)@C nanobelts with different scan rates: 0.1, 0.2 0.3 and 0.5 mVs⁻¹. A pair of redox peaks is clearly seen in the CV curves, corresponding to the phase transition between VO₂ and Li_{0.5}VO₂ as indicated in Equation (4.1), which is consistent with the potential plateaus observed in the charge-discharge curves (Figure 4.6a). As shown in Figure 4.8, it is found that the current of oxidation peaks (i_p) has a linear relationship with the square root of scan rate ($v^{1/2}$), which is a typical case of the equilibrium behaviour of an intercalation type electrode.¹⁷⁵ If the charge transfer at the interface is fast enough and the limiting step of the Li transfer is the lithium diffusion in the electrode, the relationship of the peak current and the CV sweep rate is given as:

$$i_p = (2.65 \times 10^5) n^{3/2} S D_{\text{Li}^+}^{1/2} C_{\text{Li}^+} v^{1/2} \quad (4.2)$$

where i_p is the peak current (A), n is the charge-transfer number, S is the contact area between electrode and electrolyte (here the geometric area of electrode, 1.54 cm², is used for simplicity), v is the potential scan rate (V s⁻¹), and C_{Li^+} is the concentration of lithium ions in the cathode (mol cm⁻³), which is calculated as:

$$C_{\text{Li}^+} = m/(N_A/V) \quad (3)$$

here, $m = 0.5$ is the lithium number in the unit cell of Li_{0.5}VO₂, N_A is Avogadro's constant (6.02×10^{23}), and V is the volume of unit cell of VO₂ ignoring slight volume changing during the lithium insertion and extraction processes. In addition, owing to comparable capacities (161-156 mAh g⁻¹) for four cathodes during the 3rd cycle (Figure 4.6b), it is reasonable to assume that the concentrations of Li⁺ within these cathodes are the same.

Figure 4.8 The relationship of the oxidation peak current (i_p) and the square root of scan rate ($v^{1/2}$).¹⁶⁸ Reprinted with permission from ref. 168. Copyright 2011, Royal Society of Chemistry.

Thus, based on the slopes in Figure 4.8, the D_{Li^+} is calculated to be 8.6×10^{-10} , 4.7×10^{-10} , 3.6×10^{-10} and $2.6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for VO₂(B)@C(4.2 wt%), VO₂(B)@C(6.6 wt%), VO₂(B)@C(8.4 wt%) and VO₂(B)@C(9.6 wt%) cathodes, respectively. With increasing of carbon content, the value of D_{Li^+} decreases slightly, which results from the following two aspects: (1) it is more difficult for lithium ions to transport through thicker carbon coating layer; (2) thicker carbon layer hinders the electrolyte penetration into electrode and thus reduces the interfacial contact area for Li⁺ insertion/extraction. Thus, in order to achieve high electrical conductivity, buffering of the structural strain and high value of

D_{Li^+} , a thickness of ~4.3 nm for the carbon layer is ideal to achieve high Li storage properties, especially at high current densities, for the VO₂(B)@C cathodes.

4.4 Conclusions

We have developed a facile one-pot hydrothermal approach to synthesize uniform carbon-coated VO₂(B) nanobelts. The thickness of carbon coating layer is tunable from 3.0 to 6.9 nm by changing the ratio of the precursors. The electrochemical test shows that the VO₂(B)@C is promising as a high-power cathode material for LIBs. For example, the VO₂(B)@C electrode with a 4.3-nm carbon layer (*e.g.* carbon content: 6.6 wt%) depicts high specific capacities, good cycling stabilities and excellent rate capabilities (*e.g.* 100 mAh g⁻¹ at 12.4 C).

Chapter 5: Facile Preparation of Hydrated Vanadium Pentoxide Nanobelts Based Bulky Paper as Flexible Binder-free Cathodes for High-performance Lithium Ion Batteries†

5.1 Introduction

Nowadays, there are rapid growing demands for portable electronic devices with various specifications, e.g. low-cost, paper-thin, lightweight, flexible and even rollable. Therefore the development of power sources, such as rechargeable Li-ion batteries, is desired to further improve their power and energy density, operational safety, cycling stability and even flexibility (working well even under the twisting condition). For traditional Li-ion battery electrodes, polymer binders or adhesives are added to improve the binding of active materials to substrates, which, however, also causes an undesirable decrease in the film electrical conductivity. Binder-free electrodes also open up a possibility for high temperature applications in excess of 200 °C, at which most conventional binders are not stable.¹⁷⁶ Currently, binder-free and bulky-paper-formed flexible electrodes were prepared by using carbon based materials, including carbon nanotubes (CNTs)¹⁷⁷ and graphene nanosheets.¹⁷⁸ However, their applications are limited to Li-ion battery anodes. In addition, there are concerns that the cost of CNTs is high and the preparation of graphene sheets is tedious. Hence there is a need to search for other flexible active materials with good electrochemical performance and low-cost especially

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for cathode applications.

Vanadium pentoxide (V_2O_5) has been extensively studied as a well-known cathode material for Li-ion batteries owing to its essential advantages of low cost, easy synthesis process, high safety, high specific capacity and energy density.¹⁷⁹⁻¹⁸¹ It is a typical intercalation compound with a layered crystal structure, which can act as a good host for the reversible insertion and extraction of Li^+ and can attain a large theoretical capacity of 294 mAh g^{-1} in the voltage range of 4.0-2.0 V vs Li/Li^+ . This value is rather higher than those of commonly used cathode materials, e.g., LiCoO_2 (140 mAh g^{-1}), LiMn_2O_4 (148 mAh g^{-1}) and LiFePO_4 (170 mAh g^{-1}). Moreover, converting V_2O_5 to hydrated vanadium pentoxide ($\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$) can lead to higher Li-ion storage capacities¹⁸²⁻¹⁸⁴ due to its unique crystal structure, which consists of a double layer of V_2O_5 stacked along the *c*-axis of a monoclinic unit cell with water molecules intercalated between the layers.¹⁸⁵ These water molecules expand the distance between the layers, and hence increase the Li-ion-intercalation capacities. For example, a specific energy of over 700 Wh Kg^{-1} has been achieved for Li-ion batteries with a $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ xerogel positive electrode.¹⁸²

The cathode application of V_2O_5 is limited by its low diffusion coefficient of Li^+ ($\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$)¹⁸⁶ and moderate electrical conductivities (10^{-2} to $10^{-3} \text{ S cm}^{-1}$).¹⁸⁷ Many studies have been conducted to improve its lithium diffusion and electrical conductivity by modifying the crystal structure towards a more open framework¹⁸⁸ and by adding conductive coatings.¹⁸¹ In particular, nanostructured materials are considered as a promising approach to solve these problems by decreasing the polarization and shortening diffusion paths of Li ions.^{181,189} Among the nanostructured materials, one-dimensional (1D) nanowires or nanobelts are the most favorable to construct high-

performance Li-ion batteries as they can offer a range of unique advantages over their traditional counterparts including large specific surface area, short Li^+ transport distance, efficient 1D electron transport pathways and facile strain relaxation upon electrochemical cycling.¹⁹⁰⁻¹⁹² For example, an electrode platform was developed⁹⁵ that silicon nanowires grew directly on the current collector to accommodate the large volume change and to avoid capacity fading. Numerous authors have reported the synthesis of V_2O_5 nanowires/nanobelts by using vapor transport,¹⁹³ electrospinning,¹⁹⁰ electrodeposition¹⁹⁴ and hydrothermal approach.¹¹⁶ Some of these methods, however, may only be suitable for small scale sample preparation,^{190, 193, 194} while others may require long synthesis time of about 4-7 days,^{195, 196} and insulating surface capping such as soft template poly (ethylene oxide).¹⁹⁶ For cathode performance evaluation, it was reported¹⁹⁵ that V_2O_5 nanowires delivered an initial discharge capacity of 351 mAh g^{-1} in the enlarged voltage range of 4.0-1.5 V (corresponding to three Li^+ insertion/extraction) at the current density of 50 mA g^{-1} , which degraded rapidly to 175 mAh g^{-1} after 20 cycles with a capacity retention of 49.9%. Further improvement is desired. On the other hand, fabrication of flexible cathodes using these nanowires/nanobelts has not been demonstrated. Developing binder-free flexible cathodes based on the V_2O_5 1D nanostructure has thus great potential as it can build up flexible Li ion battery with possibly higher operation temperature ranges and improved Li storage performance. Besides, it also offers the opportunity to explore an energy-saving, low-cost and simple fabrication route to enable large scale production of V_2O_5 nanostructures for practical applications.

Herein, a simple high-yield (close to 100%) hydrothermal approach was developed to prepare single-crystalline hydrated vanadium pentoxide ($\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O}$) nanobelts

having the length up to several hundred micrometers and the diameter of only ~20 nm. These $\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O}$ (hereafter abbreviated as HVO) nanobelts were further used to prepare bulky papers without addition of any binders, which were mechanically strong upon bending. The HVO bulky paper was formed by the intertwining HVO nanobelts, which created hierarchical porous channels and facilitated the strain relaxation during the charge and discharge processes. The electrochemical tests revealed that the flexible HVO cathode could deliver high reversible specific capacities, especially at high C rates such as capacity of 163 mAh g^{-1} at 2000 mA g^{-1} (6.8 C).

5.2 Material Preparation

In a typical synthesis, 1 mM V_2O_5 powder (Alfa Aesar) and 30 mL H_2O were mixed under vigorous magnetic stirring at room temperature, and then 5 mL of 31% H_2O_2 was added and kept continuously stirred for about 20 min to give a yellow solution. Then, 1.5 mM ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, Sigma-Aldrich) was dissolved in above solution. The resulting solution was transferred to a 50 mL autoclave and kept in an oven at 180°C for 48 h. The product was washed and separated by centrifugation-redispersion cycles with distilled water and ethanol and then dried at 70°C to give a yield of ~99% (i.e. ~180 mg).

To fabricate bulky paper, half of the product (90 mg) was redispersed in 40 mL ethanol solution under vigorous magnetic stirring for about 8 h. The solution was then poured into a petri dish ($100 \times 20 \text{ mm}$) with a weighing paper at the bottom and dried in an oven at 70°C under normal pressure. After the evaporation of ethanol, a flexible yellow HVO bulky paper was easily obtained by peeling it off from the weighing paper.

5.3 Results and Discussion

The phase purity and crystal structure of the product obtained in the presence of 1.5 mM $\text{NH}_4\text{H}_2\text{PO}_4$ was examined by X-ray diffraction (XRD). Figure 5.1a reveals that reflection peaks are indexed to the monoclinic $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ (JCPDS 07-0332), which is similar to the previous report.¹¹⁶ To determine the content of coordinated water in the sample, thermogravimetric analysis (TGA) was carried out in air (Figure 5.1b). The weight loss of 4.3% below 200 °C is attributed to the release of free water and physically adsorbed water, and the 4.0% weight loss in the temperature range of 200-400 °C is ascribed to the loss of coordinated water in the sample. Thus, the molar ratio of the coordinated water to V_2O_5 is determined to be ~0.44. To further confirm the oxidation state of vanadium, the X-ray photoelectron spectroscopy (XPS) analysis was also carried out on the as-prepared sample (Figure 5.1b). The V 2p_{3/2} band at 517.7 eV and the O 1s band at 530.6 eV correspond to the V(5+)-O stretch, which agrees well with the previous report.¹⁹⁷

The field emission scanning electron microscopy (FESEM) images shows that the as-prepared sample is 1D nanostructures (Figure 5.2a-b) with the length of 100-400 μm. The transmission electron microscopy (TEM) image (Figure 5.2c) reveals that the as-prepared HVO is nanobelt structure with width in the range of 20-600 nm. As some of the HVO can be rolled up to provide the side view of the nanobelts (Figure 5.2d), the thickness of the nanobelts is estimated to be around 10 nm. Here, it is noted that the width of HVO nanobelts determined through TEM is much smaller than that observed in the FESEM, due to the fact that FESEM images mainly show bundles of HVO nanobelts. The high resolution (HR) TEM image (Figure 5.2e) and the selected area electron diffraction

Figure 5.1 (a) The XRD pattern of the sample obtained in the presence of 1.5 mM $\text{NH}_4\text{H}_2\text{PO}_4$. (b) Weight loss curve with respect to temperature ($^{\circ}\text{C}$) for the as-prepared sample. (c) The corresponding XPS spectra for the O 1s and V 2p bands. (d) A relationship of yields of dried products to different ADP concentrations (I_{ADP}), ignoring the weight loss during the water and ethanol washing processes.¹⁹⁸ Reprinted with permission from ref. 198. Copyright 2011, Royal Society of Chemistry.

(SAED) pattern (inset of Figure 5.2e) indicated that these nanobelts are single crystalline. The HRTEM observation also indicates that the long axis of the nanobelts is oriented along [010] direction with the observed interfringe spacing of 0.67 nm and this corresponds well to the (200) planes of monoclinic HVO (JCPDS 07-0332). It is noted

Figure 5.2 (a) Low- and (b) high-magnification FESEM images of HVO nanobelts. (c) TEM image of nanobelts. The inset in (c) is magnified view to show the width of the nanobelts. (d) Side view of a rolled up nanobelt giving a thickness of ~ 10 nm. (e) HRTEM image of an individual nanobelt with its corresponding SAED pattern (inset). (f) Optical image of a free-standing HVO bulky paper based on the intertwining network of above HVO nanobelts without addition of any binders.¹⁹⁸ *Reprinted with permission from ref. 198. Copyright 2011, Royal Society of Chemistry.*

that the (200) lattice spacing of HVO is larger than that of crystalline V_2O_5 (e.g. 0.58 nm),¹⁹⁹ which may facilitate lithium intercalation.

The growth of 1D HVO nanobelts is attributed to the anisotropic bonding of its layered structure resulting in selected growth. The [010] or b -axis is the fastest growth direction and [001] is the slowest due to the weak c -axis bonding. Moreover, in our

Figure 5.3 FESEM images of products synthesized by hydrothermal reactions at 180 °C for 48 h with different ADP concentrations. (a) 0.0 mM, (b) 0.5 mM, (c) 1.0 mM and (d) 2.0 mM.¹⁹⁸ Reprinted with permission from ref. 198. Copyright 2011, Royal Society of Chemistry.

reaction system, the presence of $\text{NH}_4\text{H}_2\text{PO}_4$ (hereafter abbreviated as ADP) during the synthesis is noted to affect the yield of HVO products (Figure 5.1d) and the sample morphology (Figure 5.3). Here, the yield of the products is determined by the weight percentage of dried products to the V_2O_5 reactant. It is found that the product yield is only ~0.2% without ADP during the synthesis. The yield of products increases to ~78.6% and ~99.0% when ADP is added at concentration (I_{ADP}) of 0.5 and 1.5 mM, respectively.

Figure 5.4 (a) Digital photograph of a free-standing HVO bulky paper with 25 wt% acid-treated MWCNTs as conductive additives to improve cathode's electrical conductivity. (b) FESEM image of acid-treated MWCNTs, revealing a network of entangled CNTs with diameters of around 20-30 nm and lengths up to the micrometer scale. Low- (c) and high-resolution (d) FESEM images of above bulky paper, indicating a uniform mixture of the MWCNTs and HVO nanobelts.¹⁹⁸ *Reprinted with permission from ref. 198. Copyright 2011, Royal Society of Chemistry.*

Further increase in ADP concentration does not show significant change. FESEM images of the HVO nanobelts prepared under different I_{ADP} values reveal that increasing I_{ADP}

from 0 to 1.5 mM does not show obvious changes in morphology and nanostructure (Figure 5.3a-c), however nanorods are observed when I_{ADP} is increased to 2.0 mM (Figure 5.3d) with shorter length, e.g. 10-50 μm , and larger width, e.g. 50-100 nm.

The HVOs products are further used to fabricate the bulky paper as per described in the experimental section. The bulky papers prepared from the long nanobelts synthesized with appropriate amount of ADP (0.5~1.5 mM) are robust upon bending and a representative one is shown in Figure 5.2f, while the bulky paper prepared with HVO nanorods is fragile and easily broken upon bending, which is probably due to that the shorter nanorods can not form intertwining networks. For Li ion battery cathode applications, HVO nanobelts were chose as the electrode materials and were further mixed with 25 wt% acid-treated multi-walled carbon nanotubes (MWCNTs) to make flexible battery electrodes (Figure 5.4a), to make it mechanically stronger than the acetylene black. The FESEM images (Figure 5.4c-d) indicate uniform mixture of the MWCNTs and HVO nanobelts in the bulky paper electrodes. The thickness of the bulky-paper cathodes was controlled around $\sim 50\ \mu\text{m}$.

To study the Li-ion storage properties of binder-free bulky paper cathodes made from HVO nanobelts, a series of electrochemical measurements were carried out based on the half cell configuration. Figure 5.5a depicts representative cyclic voltammograms (CVs) of the HVO electrodes for the first three cycles at a scan rate of $0.2\ \text{mV s}^{-1}$ in the voltage range of 4.0 to 2.0 V. The CVs exhibited two pairs of reduction and oxidation peaks associated with the phase transitions of HVO during Li^+ intercalation and deintercalation processes. The two reduction peaks located at ~ 2.84 and ~ 2.47 V, respectively, are attributed to the reduction of V^{5+} to V^{4+} through the reaction of $\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O} + x\text{Li}^+ +$

Figure 5.5 Cathode performance of binder-free bulky paper made from HVO nanobelts in the voltage range of 4.0-2.0 V. (a) CV curves of the first three cycles at a scan rate of 0.2 mV s⁻¹. (b) Galvanostatic charge-discharge voltage profiles at a current density of 50 mA g⁻¹. (c) A comparison of charge/discharge capacities of binder-free bulky paper electrode and PVDF-added HVO electrode at various current densities of 100 to 2000 mA g⁻¹. Here, the PVDF was not counted into the active material weight. Inset in (c): cycling performance of binder-free HVO bulky paper electrode at a high current density of 2000 mA g⁻¹. (d) Electrochemical impedance spectra of above two electrodes measured at the 4th fully discharged state. The high-middle frequency semicircle represents the charge-transfer process and a straight slopping line at low frequencies corresponds to Li⁺ diffusion in HVO electrode known as Warburg impedance.¹⁹⁸

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$x\text{e}^- \rightarrow \text{Li}_x\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O}$, where x is around 2. The reverse reactions are then indicated by the two corresponding oxidation peaks at around 2.70 and 2.94 V. The symmetrical feature of the CV curves suggests a good reversibility of the cycling processes. Figure 5.5b exhibits galvanostatic charge-discharge voltage profiles of the HVO nanobelts electrode between 2.0 and 4.0 V at a current density of 50 mA g^{-1} (0.17 C). The obscure potential plateaus observed in the charge-discharge curves are consistent with redox peaks in the CV curves. In addition, the symmetrical characteristic of potential plateaus in the charge and discharge profiles suggests the highly reversible phase transition processes. The insertion process gives an initial discharge capacity of 297 mAh g^{-1} and a subsequent charge capacity of 297 mAh g^{-1} with no irreversible capacity loss. Although slightly decreased, the reversible discharge capacity still can reach 231 mAh g^{-1} during the 20th cycle with Coulombic efficiency consistently being maintained at ~100%. This cycling performance is better than those previously reported for V_2O_5 ^{174,200} and $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ ¹¹⁶ cathodes.

The cycling responses of the HVO bulky-paper electrode at different C rates were evaluated and shown in Figure 5.5c. The electrode shows a high discharge capacity of 283 mAh g^{-1} during the 2nd cycle at a current density of 100 mA g^{-1} (0.34 C) and subsequently reduces to 241, 212, 194 and 183 mAh g^{-1} at current densities of 200 (0.68 C), 500 (1.7 C), 800 (2.7 C) and 1000 mA g^{-1} (3.4 C), respectively. Even at a high current density of 2000 mA g^{-1} (6.8 C), the HVO binder-free bulky-paper electrode can still deliver a high capacity of 163 mAh g^{-1} during the 2nd cycle. For comparative studies, another HVO electrode was prepared by conventional tap-casting process with 17 wt% polyvinylidene fluoride (PVDF). It is found that the HVO nanobelts cathode with PVDF

binder exhibits an inferior performance (Figure 5.5c), giving discharge capacities of 271, 219, 193, 178, 168 and 143 mAh g⁻¹ during the 2nd cycle at current densities of 200 (0.68 C), 500 (1.7 C), 800 (2.7 C), 1000 (3.4 C) and 2000 mA g⁻¹ (6.8 C), respectively. The inferior Li storage properties of PVDF-added HVO cathodes is mainly attributed to their low electrical conductivity as verified by the electrochemical impedance spectra (Figure 5.5d). The PVDF-added HVO cathodes shows a larger radius of semi-circle in the Nyquist plots compare to that of the binder-free HVO electrodes and thus indicates higher charge-transfer resistance. As compared to V₂O₅ based electrodes prepared by other reported processes^{174,201-203}, the above demonstrated Li storage performance of HVO bulk paper electrode is outstanding. There are reports on achieving high discharge capacities for nanostructured V₂O₅ electrodes²⁰²⁻²⁰⁴. For example, nano-sized V₂O₅²⁰² showed a 2nd-cycle discharge capacity of 148 mAh g⁻¹ at a current density of 2352 mA g⁻¹; V₂O₅ nanobelt arrays grew on a Ti substrate²⁰³ depicted a 2nd-cycle discharge capacity of 192 mAh g⁻¹ at 1000 mA g⁻¹; V₂O₅/carbon tube-in-tube (CTIT) nanocomposites²⁰⁴ delivered a 2nd-cycle discharge capacity of 200 mAh g⁻¹ at 2352 mA g⁻¹. However, it is worth to point out that the higher performances reported by others are achieved in thin film V₂O₅ electrodes (2.5-3 μm thickness²⁰³) while this paper reports on thick films of ~50 μm. For evaluation of the effective energy density of the full battery cell, the average weight of current collectors and other inactive components will be added in. Thin film electrodes then will result in low effective energy densities. Moreover, our HVO bulky-paper electrode exhibits an excellent cyclability at a high current density of 2000 mA g⁻¹ (6.8 C) as shown in the inset of Figure 3c, delivering a discharge capacity of 118 mAh g⁻¹ during the 300th cycle. Such high-C-rate performance is better than other well-reported

cathodes, e.g. spinel LiMn_2O_4 nanorods²⁰⁵ showed a capacity of 85 mAh g^{-1} during the 100th cycle at 1 C rate and flowerlike LiFePO_4/C microspheres¹⁵⁸ delivered a stable capacity of 85 mAh g^{-1} during the 400th cycle at 5C rate. The superior performance of HVO flexible electrodes is believed to result from the following aspects: (1) the 10-nm thick HVO nanobelts with large specific surface area provide efficient electron transport pathways and short diffusion distances for Li^+ intercalation/deintercalation; (2) the binder-free preparation process of the electrodes increases their electrical conductivity; (3) the hierarchical porous channels in the intertwining network of HVO nanobelts relax the mechanical strain generated upon the charge-discharge cycling.

5.4 Conclusions

We have developed a simple hydrothermal approach to prepare HVO nanobelts with high production yield up to ~99%. Flexible bulky-paper cathodes without addition of any binder are prepared using these HVO nanobelts. These flexible electrodes show high reversible Li storage capacities, good high C-rate performance with ~100 % coulombic efficiency. These promising properties of binder-free flexible electrodes can be an important step for development of rollable rechargeable battery with desired energy storage performance.

Chapter 6: Ultrathin V₂O₅ Nanosheet Cathodes: Realizing Ultrafast Reversible Lithium Storage †

6.1 Introduction

Two-dimensional (2D) nanosheets, especially those with a thickness of < 5 nm and lateral dimension of submicron to micrometers, can be considered as a new class of inorganic macromolecules with exotic electronic properties and high specific surface areas that are important for sensing,²⁰⁶ catalysis,²⁰⁷ and energy storage applications.²⁰⁸⁻²¹² In particular, 2D nanosheets are ideal structures for fast lithium storage, which provide stability, high active surface area and shortened diffusion path for lithium ions.²¹⁰ Graphene is the most well-known 2D nanosheets while transition metal oxides, such as V₂O₅, also play important roles as electrode materials for lithium ion batteries (LIBs).^{4, 213-214} Owing to its high theoretical gravimetric capacity of 294 mAh g⁻¹ with 2 Li insertion/extraction per unit formula, which is more than twice the currently commercialized LiCoO₂ (~140 mAh g⁻¹), V₂O₅ is regarded as one of the most promising candidates as cathode materials.^{138, 215} However, the preparation of V₂O₅ nanosheets has not been well-reported due to the lack of a simple method to produce mono- or few-layer structures in large quantities.

Orthorhombic V₂O₅ consists of distorted VO₆ octahedral building blocks linked together to form the layered anisotropic structure (Figure 6.1). Adjacent layers stack via

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weak van der Waals interactions, which open up an opportunity to exfoliate the ultrathin flakes away from its bulk materials. Liquid-phase exfoliation is considered to be the most practical approach to produce high-quality single or multilayer nanosheets due to its simplicity, high throughput, and no requirement of a third phase dispersant (*i.e.*, a surfactant).²¹⁶⁻²¹⁸ Although interesting works have been carried out on different material systems (*e.g.* the solvent exfoliation of layered crystals like graphite,²¹⁹ boron nitride,²²⁰ perovskite,²²¹ and more recently, transition metal chalcogenides^{218, 222-224}), liquid-phase exfoliation of layered V₂O₅ has not been explored.

Herein, we present the first preparation of few-layer V₂O₅ nanosheets with thickness of 2.1-3.8 nm through direct exfoliation of bulk V₂O₅ crystals in formamide solvent. This process is carried out under ambient conditions and can be scaled up to yield large quantities of nanosheets. Lithium insertion in these ultrathin nanosheets is mainly surface lithium storage with extremely short Li insertion paths, thus meets the requirement of ultrafast charge/discharge process (*e.g.*, delivering reversible capacities of 117 mAh g⁻¹ at 50 C).

6.2 Material Preparation

All the starting materials were of analytically pure grade and used as received. In a typical procedure, bulk V₂O₅ powder (50 mg, Alfa Aesar) was added into a 100 mL glass bottle containing a formamide solution (50 mL, Sigma-Aldrich) and the whole mixture was shaken to suspend the powder and kept overnight. The resulting suspension was then sonicated at room temperature for 3 days. After ultrasonic treatment, the exfoliated V₂O₅ nanosheets were isolated from the upper solution of glass bottle via centrifugation and

washed with ethanol for several times to remove residual formamide, and then dried in oven (70 °C) overnight for further characterization. The yield of V₂O₅ nanosheets is around 60%, which is determined by the weight percentage of exfoliated V₂O₅ nanosheets to the bulk V₂O₅ reactants.

6.3 Results and Discussion

Figure 6.1 shows the schematic illustration of the liquid-exfoliation process. Firstly, bulk V₂O₅ was swelled by intercalation of formamide molecules into the interlayer space (Figure 6.2), resulting in significantly weakened interlayer attraction. Subsequently, mechanical shaking (*i.e.*, ultrasonication) was introduced to impose a transverse sliding force on the swollen phase, leading to the exfoliation of the V₂O₅ layers. Formamide has been confirmed as an effective delaminating agent for various layered materials due to its high capability of entering the interlayer gallery.²²⁵⁻²²⁸ As shown by the X-ray diffraction

Figure 6.1 Exfoliation of layered bulk V₂O₅ into {001}-oriented few-layer V₂O₅ nanosheets.²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

Figure 6.2 XRD patterns of bulk V_2O_5 before (a) and after (b) immersing in the formamide solution for overnight. It can be clearly seen that the bulk V_2O_5 after immersing in the formamide solution for overnight shows a new peak at a 2θ value of around 6.5° (d -spacing = 1.4 nm), indicating the intercalation of formamide molecules into the interlayer space of crystal V_2O_5 .²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

pattern (XRD) in Figure 6.3a (upper), the strong diffraction peak for the exfoliated products could be assigned to the $\{001\}$ facet of orthogonal V_2O_5 (space group: Pmmn (59); JCPDS card 41-1426), and another small diffraction peak could be indexed to the $\{002\}$ facet. This phenomenon indicates that the $\{001\}$ orientation is highly preferred. The layer-to-layer distance (d -spacing) is calculated to be 0.43 nm according to the $\{001\}$ reflection.

The field-emission scanning electron microscopy (FESEM) image of bulk V_2O_5 shows irregular shaped particles with sizes of 1–4 μm (Figure 6.4). In contrast, the transmission

Figure 6.3 Characterizations for {001}-oriented few-layer V_2O_5 nanosheets. (a) XRD patterns. (b) TEM image and the corresponding colloidal acetone dispersion. (c) HRTEM and (d) the corresponding selected-area electron diffraction. (e) AFM image and (f) the corresponding height profiles.²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

Figure 6.4 FESEM image of bulk V_2O_5 .²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

electron microscopy (TEM) image of the exfoliated products (Figure 6.3b) exhibits 2D thin sheet structure with lateral dimensions of 100-400 nm. The colloidal dispersions of exfoliated products (inset in Figure 6.3b) are highly stable without any aggregations over a period of several weeks. The high-resolution (HR) TEM image shows clear lattice fringes with interfringe spacing of 0.34 nm (Figure 6.3c), corresponding to the d -spacing of $\{110\}$ planes of V_2O_5 . The selected area electron diffraction (SAED) pattern (Figure 6.3d) taken from an individual nanosheet exhibits well arranged spots, and can be indexed to the $\langle 001 \rangle$ zone-axis diffraction of lamellar V_2O_5 , which further confirms that the as-obtained V_2O_5 nanosheets are highly $\{001\}$ -oriented. Furthermore, as depicted in Figure 6.3e and f, the atomic force microscopic (AFM) image and the corresponding height profiles display smooth sheet-like morphology with height of only about 2.1-3.8 nm. Based on a d -spacing of 0.43 nm along the $\{001\}$ planes as indicated by the XRD

Figure 6.5 Nitrogen adsorption/desorption isotherms of bulk V₂O₅ and ultrathin V₂O₅ nanosheets.²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

pattern, it is concluded that the O-V-O atomic layer number for these sheets is in the range of 6-10. The specific surface area of V₂O₅ nanosheets was measured by nitrogen adsorption/desorption isotherms (Figure 6.5) and was estimated to be 147.5 m² g⁻¹ using the Brunauer-Emmett-Teller (BET) method. This value is much higher than that of bulk V₂O₅ (e.g. 3.2 m² g⁻¹).

Motivated by the unique ultrathin thickness of the exfoliated V₂O₅ nanosheets, the as-obtained V₂O₅ nanosheets were tested for their lithium storage performance as a cathode material. Coin cells with a metallic Li counter electrode were assembled and galvanostatic charge/discharge technique was employed to evaluate the electrochemical properties of V₂O₅ nanosheets at room temperature. For comparison, bulk V₂O₅ powders

were also tested. Figure 6.6a shows their initial charge-discharge voltage profiles at a current density of 59 mA g^{-1} (0.2 C) between 4.0 and 2.05 V. For V_2O_5 nanosheet electrode, the first discharge capacity achieves 292 mAh g^{-1} , corresponding to the insertion of $\sim 2 \text{ Li}$ per formula. This value is much higher than the gravimetric capacity of

Figure 6.6 Cathode performance of {001}-oriented few-layer V_2O_5 nanosheets and bulk V_2O_5 in the voltage range of 4.0–2.05 V. (a) Initial galvanostatic charge-discharge voltage profiles at a current density of 59 mA g^{-1} (0.2 C). Here, $1 \text{ C} = 294 \text{ mA g}^{-1}$. (b) Cycling performance at 0.2 C . (c) Rate capability at various charge and discharge rates. (d) Ragone plot of V_2O_5 nanosheets, in comparison with some advanced energy storage and conversion devices.²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

the state-of-the-art cathode materials (normally less than 200 mAh g⁻¹).²³⁰ Additionally, three typical plateaus at around 3.4, 3.2 and 2.3 V are also observed in the discharge profile, which correspond to a series of phase transitions of crystalline V₂O₅. Lithium intercalation into the interlayer space of V₂O₅ along the *a-b* plane follows the equation of $V_2O_5 + xLi^+ + xe^- \rightarrow Li_xV_2O_5$.²⁰⁴ The first two plateaus correspond to the phase transition of $V_2O_5 \rightarrow Li_{0.5}V_2O_5 \rightarrow Li_{1.0}V_2O_5$. The third one located at 2.3 V is ascribed to an additional lithium insertion ($Li_{1.0}V_2O_5 \rightarrow Li_{2.0}V_2O_5$). These electrochemical activities are highly reversible in the subsequent charge process, which give a charge capacity of 290 mAh g⁻¹ and Coulombic efficiency as high as 99%. Moreover, the V₂O₅ nanosheets exhibit good cycling stability (Figure 6.6b). During the 50th cycle under a rate of 0.2 C, the nanosheets still retain a reversible capacity of about 274 mAh g⁻¹, corresponding to 93.8% of the initial capacity. By contrast, a much lower initial discharge capacity of 189 mAh g⁻¹ can only be achieved for bulk V₂O₅ electrode with a large polarization (Figure 6.6a), which is mainly related to the much longer diffusion distance for Li ion and electron transportation. The bulk V₂O₅ also suffers from an abrupt capacity fading with capacity retention of only 46% during the 50th cycle (Figure 6.6b).

Superior rate capability is highly desirable for high-power LIB applications such as hybrid electric vehicles (HEVs) and electric vehicles (EVs). The cycling responses of the V₂O₅ nanosheet electrode at different C rates were evaluated and shown in Figure 6.6c. The V₂O₅ nanosheets exhibit a high 2nd-cycle discharge capacity of 266 mAh g⁻¹ at a current density of 1 C (294 mA g⁻¹) and reduces to 251, 233, 192, 156, and 137 mAh g⁻¹ at 3, 5, 10, 20, and 30 C, respectively, whereas the bulk V₂O₅ electrode is not able to show any electrochemical responses at 20 C (Figure 6.6c). The above results are

consistent with the impedance measurements. A larger radius of semi-circle is obtained for bulk V_2O_5 electrode in the electrochemical impedance spectra (Figure 6.7), which indicates a lower kinetics of charge transfer. More interestingly, even under very high charge and discharge rate of 50 C, the V_2O_5 nanosheets still show a high specific capacity of 117 mAh g^{-1} during the 200th cycle, indicating its excellent energy storage performance at high power rate and good cyclability. Few studies have ever demonstrated

Figure 6.7 Electrochemical impedance spectra of bulk V_2O_5 and ultrathin V_2O_5 nanosheet electrodes measured at the 4th fully discharged state. The high-middle frequency semicircle represents the charge-transfer process and a straight slopping line at low frequencies corresponds to Li^+ diffusion in solid electrode known as Warburg impedance.²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

charge/discharge capabilities at such high rates. Such C-rate performance is significantly better than some of the state-of-art V₂O₅ and other cathodes,^{138, 198, 211, 231-235} such as V₂O₅ thin-film electrode²³² (thickness: 150-170 nm; prepared by cathodic deposition; delivering a capacity of 120 mAh g⁻¹ at ~36 C), reduced graphene oxide (46 wt%) supported porous V₂O₅ spheres²³³ (showing a capacity of 102 mAh g⁻¹ at 19 C), Na_{1.08}V₃O₈ nanosheets²¹¹ (exhibiting a capacity of 73 mAh g⁻¹ at 50 C), and nanoporous LiMn₂O₄ nanosheets²³⁵ (displaying a capacity of 69 mAh g⁻¹ at 25 C). Furthermore, the power and energy performance of ultrathin V₂O₅ nanosheets were evaluated with a Ragone plot (Figure 6.6d), which was calculated based on the weight of both positive and negative electrodes, the cell voltage, and the capacities at various rates from 1 to 50 C. For comparison purpose, the Ragone plot also includes some advanced energy storage systems.^{8, 236-238} Remarkably, the V₂O₅ nanosheet electrode exhibits a gravimetric energy of 158 Wh kg⁻¹ at a power rate of 20 kW kg⁻¹. In comparison, the pseudocapacitors show low energy densities of only 1-70 Wh kg⁻¹ at power rate of 1-20 kW kg⁻¹.²³⁹⁻²⁴¹ This indicates that the V₂O₅ nanosheets can be used to build superior electrochemical energy-storage devices with both high-power and high-energy densities.

The ultrathin V₂O₅ nanosheet electrode in this research shows high lithium intercalation capacity, good cycling stability and excellent rate performance. This is believed to result from several factors related to its unique nanostructure as shown in Figure 6.8: (1) the nanosheet structure offers large specific surface area with effective electrolyte penetration and interface reactions; (2) the ultrathin thickness of 2.1-3.8 nm provides short diffusion paths for charge carriers; (3) the free-standing sheets allows effective strain relaxation upon electrochemical cycling.

Figure 6.8 A schematic of lithiation processes for bulk V_2O_5 versus $\{001\}$ -oriented few-layer V_2O_5 nanosheets. Facile lithium storage is observed for laterally confined ultrathin V_2O_5 nanosheets.²²⁹ Reprinted with permission from ref. 229. Copyright 2012, Royal Society of Chemistry.

6.4 Conclusions

Few-layer V_2O_5 nanosheets with thickness of 2.1–3.8 nm has been successfully synthesized through a simple and scalable liquid exfoliation technique. As a potential cathode material for LIBs, these ultrathin V_2O_5 nanosheets display large reversible capacity, high Coulombic efficiency, and stable cyclability. More importantly, it shows ultra high rate capability with a capacity of 117 mAh g^{-1} (energy density: 158 Wh kg^{-1}) at a charge and discharge rate of 50 C (power density: 20 kW kg^{-1}). These excellent electrochemical properties are highly attractive for fast charging, high-power batteries for EVs applications.

Chapter 7: Reduced Graphene Oxide Supported Highly Porous V₂O₅ Spheres as a High-Power Cathode Material for Lithium Ion Batteries †

7.1 Introduction

Lithium ion battery (LIB) is widely used as the power source for portable electronics. The ever-growing demands for portable power source, especially for high-energy and high-power applications such as electrical vehicles (EVs) and hybrid electrical vehicles (HEVs), have prompted numerous research efforts towards cost-effective and high-performance electrode materials.^{4, 72, 238, 242-244} Among them, vanadium pentoxide (V₂O₅) has attracted much attention as a cathode material due to the advantages of low cost, easy synthesis, high energy density and better safety compared to commercial cathodes, e.g. LiCoO₂ and LiNiO₂.^{4, 245} It is a typical intercalation compound with a layered crystal structure and a large theoretical capacity of 294 mAh g⁻¹ between 4.0 and 2.0 V, which is higher than those of LiMn₂O₄ (148 mAh g⁻¹) and LiFePO₄ (170 mAh g⁻¹). However, the practical application of V₂O₅ is limited by sluggish kinetics of electron and lithium-ion transport,^{186,187} which leads to low specific capacities at high current densities and poor cyclability.

To develop high-performance V₂O₅ based cathode, especially at high current densities, nanostructures are the most favourable as they can offer a range of unique advantages

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over their bulk counterparts including short Li⁺ diffusion distance and large interfacial contact area between the electrode and electrolyte. For example, nano-sized V₂O₅ prepared by thermal-decomposition of vanadyl oxalate could deliver an initial discharge capacity of 274 mAh g⁻¹ at a low current density of C/20 (15 mA g⁻¹) while commercial micro-sized V₂O₅ only attained a capacity of ~100 mAh g⁻¹.²⁰² Similar enhanced Li storage capacities could also be obtained in V₂O₅ nanorod arrays, nanobelts and fibrillar-structured films.¹⁸⁹ With regard to the rate capabilities of V₂O₅, V₂O₅/carbon tube-in-tube nanocomposites²⁰⁴ exhibits a good retention of the rate capacity, giving 89% (2 C), 80% (4 C), 72% (6 C) and 56% (10 C) retentions, respectively, on the basis of capacity value of 250 mAh g⁻¹ at 0.5 C. However, such performance is still inferior to other reported high-performance cathodes such as flower-shaped LiFePO₄/C/polypyrrole microspheres,¹⁵⁸ displaying 92% (2 C), 81% (5 C) and 63% (10 C) retentions, respectively, based on the capacity of 136 mAh g⁻¹ at 0.5 C. Therefore, further performance improvement of the V₂O₅ based cathode is required.

The charge transfer is reported to be greatly improved by hybridizing V₂O₅ with carbonaceous materials, e.g. porous carbon¹⁸¹ or carbon tube-in-tube.²⁰⁴ Among these carbonaceous materials, graphene (a monolayer of sp²-bonded carbon atoms), has attracted great attention due to its extraordinary electrical/thermal conductivities, ultrahigh specific surface area, good mechanical strength and chemical stability.^{52, 246-249} Low cost graphene can be produced in bulk efficiently through chemical oxidation of graphite to hydrophilic graphite oxide, which can then be exfoliated as individual graphene oxide (GO) sheets by ultrasonication. The graphene oxide is then converted to conducting graphene by chemical reduction process using either hydrazine (electrical

conductivity: $8.28 \times 10^3 \text{ S m}^{-1}$)⁵² or solvothermal reduction process (electrical conductivity: $3.74 \times 10^2 \text{ S m}^{-1}$).²⁵⁰ Generally, these graphene sheets obtained by chemical reduction method is also known as reduced graphene oxide (rGO). Incorporation of rGO with M_xO_y (M=Fe, Co, Mn, Sn, etc.),^{89, 130, 208, 251-254} silicon²⁵⁵ or alloys²⁵⁶ as anodes have been successfully developed and are reported to have superior performance for LIB. Except for LiFePO₄,²⁵⁷ there are only few reports on combining cathode materials with rGO and no report on V₂O₅/rGO cathode.

Herein, we introduce a facile solvothermal approach to synthesize reduced graphene oxide (rGO) supported highly porous V₂O₅ spheres consisting of nanoparticles (hereafter abbreviated as V₂O₅/rGO). The process is driven by the heterogeneous nucleation of vanadium oxide on graphene oxide (GO) sheets and a subsequent thermal pyrolysis in air to yield the V₂O₅/rGO composite. As a cathode material for LIB, the V₂O₅/rGO nanocomposite can deliver high specific capacity with stable cycling performance, especially at high C rates. For example, the V₂O₅/rGO cathode with 46 wt% rGO showed reversible capacities of 128 and 102 mAh g⁻¹ at current densities of 13 C and 19 C, respectively.

7.2 Material Preparation

Preparation of Graphite Oxide. Graphite oxide was prepared from natural graphite (SP-1) by a modified Hummers method.^{258,259} Briefly, 1.5 g graphite powder was added into a solution of concentrated H₂SO₄ (10 mL, 98 wt%, Fisher Scientific), K₂S₂O₈ (1.25 g, Alfa Aesar) and P₂O₅ (1.25 g, Alfa Aesar), and the mixture was kept at 80 °C for 4.5 h under vigorous stirring. The mixture was then cooled to room temperature and the pre-

oxidized graphite was obtained by washing with de-ionized (DI) water and drying in a vacuum oven at 50 °C. Successively, pretreated graphite was put into 60 mL concentrated H_2SO_4 with an ice bath, and then 7.5 g $KMnO_4$ (Alfa Aesar) was added gradually under stirring. The reaction temperature was kept below 20 °C. After adding all of $KMnO_4$, the mixture was stirred at 35 °C for 2 h and then slowly diluted with 125 mL DI water. During the diluting process, large amount of heat was released and hence water should be added in an ice bath to maintain the temperature below 50 °C. The mixture was stirred for 2 h and further diluted with additional 200 mL DI water. After that, 30 wt% H_2O_2 (10 mL, Fisher Scientific) was slowly added into the mixture to completely react with the excess $KMnO_4$, and the color of mixture changed into brilliant yellow along with bubbling. The resulting mixture was washed with diluted HCl aqueous (1/10, v/v) solution and DI water. The graphite oxide was finally obtained after drying in a vacuum oven at 30 °C.

Preparation of rGO Supported Highly Porous V_2O_5 Spheres. 40 mg graphite oxide was put into 40 mL N-methylpyrrolidone (NMP, Merck) solution and ultrasonicated at room temperature for 2 h to form a stable graphene oxide (GO) dispersion. Then, 500 μ L vanadium isopropoxide ($VO(OiPr)_3$, Aldrich) and 100 mg of 25 wt% ammonia (Fisher Scientific) were sequentially added into the above GO dispersion under ultrasonication for another 30 min. The mixture was put into a 50 mL Teflon-lined autoclave and maintained at 180 °C for 12 h, after which it was cooled to room temperature resulting in precipitation. The precipitate was collected and washed with ethanol solution, and dried in an oven at 60 °C for 12 h. Reduced graphene oxide (rGO) supported highly porous V_2O_5 spheres (V_2O_5 /rGO) were obtained by thermal pyrolysis of the as-prepared

precursor at the temperature of $350\text{ }^\circ\text{C}$ for 30 min under a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in air. The overall synthetic procedure of $\text{V}_2\text{O}_5/\text{rGO}$ is illustrated in Figure 7.1. The weight percentage of the vanadium oxides in the products of the solvothermal process was adjusted by changing the amount of ammonia added, which reacted with excess vanadium isopropoxide ($\text{VO}(\text{OiPr})_3$) through hydrolysis and condensation process. That in turn would change the weight ratio between rGO and vanadium oxides.

Figure 7.1 Schematic diagram of growing highly porous V_2O_5 spheres on the surface of rGO sheets. Scale bar in FESEM and TEM images is 100 nm.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

7.3 Results and Discussion

GO and the product from the solvothermal process with ammonia precursor at a weight ratio of GO to ammonia ($R_{\text{GO}} : \text{ammonia}$) at 2 : 5 were characterized by X-ray diffraction (XRD) (Figure 7.2a). The XRD pattern of GO exhibits a broad peak at $2\theta = \sim 24^\circ$,

Figure 7.2 (a) XRD patterns of GO and the rVO/rGO sample prepared by the solvothermal process with $R_{\text{GO}} : \text{ammonia} = 2 : 5$. (b) Raman spectra of GO, pure rGO, rVO/rGO and corresponding V₂O₅/rGO composite.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

corresponding to the (002) Bragg reflection (Figure 7.2a, bottom). The XRD pattern of rGO shows broad diffraction peaks at 2θ of around 24° and 43° , which are indexed as the (002) and (100) peaks of the disorderedly stacked rGO sheets, respectively. In addition, the formation of rGO after such solvothermal process is confirmed by the Raman spectrum (Figure 7.2b). The Raman spectroscopy results show an increase in the intensity ratio ($I_{\text{D/G}}$) between the D band (located at 1360 cm^{-1}) and G band (located at 1590 cm^{-1}), e.g. $I_{\text{D/G}} = 0.83$ for GO increased to $I_{\text{D/G}} = 1.11$ for both pure rGO and rVO/rGO composite. Moreover, the four-point-probe measurement depicts high electrical conductivity of pure rGO ($\sim 3.5 \times 10^2 \text{ S m}^{-1}$). There are no obvious peaks related to vanadium oxides in XRD pattern, which suggest that the vanadium oxide is amorphous.

Figure 7.3 XRD pattern of the rVO sample prepared without GO in the solvothermal process. A broad hump at 2θ of about 30° is attributed to the signal from the sample holder.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

Figure 7.4 Representative FESEM images of the rVO/rGO samples prepared by the solvothermal process with $R_{\text{GO}} : \text{ammonia} = 2 : 5$.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

Similar amorphous nature is also observed for the sample prepared without addition of GO in the precursors (Figure 7.3). Meanwhile, the V⁵⁺ is likely reduced during the solvothermal process and is denoted as reduced vanadium oxide (rVO). The low magnification field emission scanning electron microscopy (FESEM) image clearly shows the existence of rGO sheets (Figure 7.4a). The high magnification FESEM image (Figure 7.4b) shows that these rVO particles with sizes of 10-50 nm are uniformly anchored onto the surface of rGO sheets. In the absent of GO in the precursors, rVO form clusters with size of 1-3 μm (Figure 7.5).

Figure 7.5 FESEM image of the rVO sample prepared in the absent of GO.²³³ *Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.*

After the solvothermal process, the products were annealed in air at 350 °C for 30 minutes to convert rVO to crystalline V₂O₅. The annealed sample with R_{GO} : ammonia = 2 : 5 was characterized by XRD. As shown in Figure 7.6a, besides the well recognized diffraction peaks of orthogonal V₂O₅ (space group: Pmmn (59); JCPDS card 41-1426), an

Figure 7.6 (a) XRD pattern of the V₂O₅/rGO composite prepared with R_{GO} : ammonia = 2 : 5.

(b) TGA curves of V₂O₅/rGO composites prepared with different R_{GO} : ammonia values.²³³

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additional diffraction shoulder peak partially overlapping the V₂O₅ (110) peak is observed. This peak originates from the stacked rGO sheets in V₂O₅/rGO. There is no detectable peak from impurity phase. A broad hump at 2θ of about 30 ° is attributed to the signal from the sample holder. The Raman spectrum (Figure 7.2b) indicates that the rGO sheets remain without obvious oxidation, e.g. I_{D:G} = 1.09. To determine the weight percentage of rGO in the samples prepared at different R_{GO} : ammonia values, thermal gravimetric analysis (TGA) was carried out in air (Figure 7.6b). For the sample prepared with R_{GO} : ammonia = 2 : 5, the weight loss of 3.5% below the temperature of 150 °C is attributed to the evaporation of moisture. The thermal decomposition of rGO mainly occurs at around 450 °C leading to a weight loss of 44.2%. Excluding the weight of moisture in the sample, the weight percentage of rGO is determined to be ~46 wt%, herewith the sample is named as V₂O₅/rGO(46 wt%). Similarly, for sample prepared with

$R_{\text{GO}} : \text{ammonia} = 1 : 5$, the TGA result (Figure 7.6b) indicates that the weight percentage of rGO is ~ 18 wt%. Thus, the sample is named as $\text{V}_2\text{O}_5/\text{rGO}(18 \text{ wt}\%)$.

The morphology of the $\text{V}_2\text{O}_5/\text{rGO}(46 \text{ wt}\%)$ sample was elucidated by FESEM and TEM (Figure 7.7). The FESEM image (Figure 7.7a) clearly shows that V_2O_5 spheres are attached onto the rGO sheets. The diameters of the V_2O_5 spheres are in the range of 200–800 nm. As seen from the high magnification FESEM image (Figure 7.7b), there are many pores on the spheres with sizes of around 50 nm. Some broken spheres can also be

Figure 7.7 Representative (a-c) FESEM and (d-e) TEM images of the as-prepared $\text{V}_2\text{O}_5/\text{rGO}(46 \text{ wt}\%)$ sample, which show that these V_2O_5 spheres are highly porous. The SEM image in (c) shows the some broken V_2O_5 spheres, which indicate that they may be hollow structures. (f) HRTEM image of V_2O_5 in the $\text{V}_2\text{O}_5/\text{rGO}(46 \text{ wt}\%)$ sample.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

observed (Figure 7.7c), which indicates that these V₂O₅ spheres may be hollow structure. The TEM images (Figure 7.7d-e) confirm that these V₂O₅ spheres are highly porous and composed of interconnected small grains of ~50 nm. The high resolution (HR) TEM image of the small grains (Figure 7.7f) displays clear lattice fringes with a spacing of 0.34 nm and is indexed to the (110) planes of orthogonal V₂O₅ (JCPDS card 41-1426). It is suggested that the rVO nanoparticles as observed in Figure 7.4b grew and assembled into the highly porous (or pseudohollow) spheres during the annealing process. The driving force for the assembly of the porous sphere is possibly to reduce the total surface energy of V₂O₅ nanocrystals. The V₂O₅ spheres were strongly anchored on the surface of rGO sheets even after one-hour sonication process as illustrated by the TEM observation. The strong adhesion between the oxide particles and the rGO sheets may facilitate the fast charge transport through the highly conductive rGO sheets.^{260,241} For the V₂O₅/rGO(18 wt%) sample, the diameters of V₂O₅ spheres increase to 0.5-2 μm (Figure 7.8a-b). The TEM image (Figure 7.8c) reveals that the V₂O₅ spheres are pseudohollow structure with most of the V₂O₅ grains assemble in the shell.

Figure 7.8 Representative (a-b) FESEM and (c) TEM images of the as-prepared V₂O₅/rGO(18 wt%) sample. The TEM image shows that these V₂O₅ spheres are pseudohollow.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

Figure 7.9 Cathode performance of as-prepared V₂O₅/rGO(46 wt%) in the voltage range of 4.0-2.0 V. (a) Galvanostatic charge-discharge voltage profiles at a current density of 90 mA g⁻¹; (b) cycling performance at a current density of 90 mA g⁻¹; (c) charge/discharge capacities at various current densities from 190 to 5700 mA g⁻¹; (d) cycling performance at a high current density of 5700 mA g⁻¹. The first 5 cycles was tested at a current density of 190 mA g⁻¹.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

The Li⁺ insertion/extraction properties of V₂O₅/rGO as a cathode material were investigated by galvanostatic charge-discharge measurements. Figure 7.9a shows the galvanostatic discharge (Li⁺ insertion) and charge (Li⁺ extraction) voltage profiles of the

V₂O₅/rGO(46 wt%) electrode at a current density of 90 mA g⁻¹ (0.3 C) between 4.0 and 2.0 V vs Li⁺/Li. Three typical plateaus at around 3.4, 3.2 and 2.3 V are observed in the discharge curves, which correspond to a series of phase transitions of crystalline V₂O₅.

The electrochemical reactions are written as:^{166, 204}

The first two plateaus correspond to the reactions (7.1) and (7.2). The third plateau at ~2.3 V is ascribed to a further lithium insertion into Li_{1.0}V₂O₅ (Equation (7.3)). These reactions are reversible in the subsequent charge processes. As shown in Figure 7.9a, the V₂O₅/rGO(46 wt%) electrode depicts an initial discharge capacity of 238 mAh g⁻¹ and a subsequent charge capacity of 238 mAh g⁻¹, indicating no irreversible capacity loss. Here, the specific capacity is calculated based on the mass of V₂O₅ alone as the rGO is inactive in the voltage range of 4.0-2.0 V. During the 20th cycle, the multi-step charge/discharge behaviour can still be observed, which suggests the highly reversible phase transition processes without formation of the irreversible rock-salt phase ω-Li₃V₂O₅.¹⁹⁰ Figure 7.9b shows the charge and discharge capacities of the V₂O₅/rGO(46 wt%) electrode for the first 50 cycles at a current density of 90 mA g⁻¹. A discharge capacity of 202 mAh g⁻¹ is delivered during the 50th cycle, corresponds to 85% of the initial capacity and the capacity fading rate is then estimated to be 0.30% per cycle. This value is lower than previous reports, e.g., 0.64% for electrospun ultralong V₂O₅ nanowires at 0.1C during the first 50 cycles¹⁹⁰ and 0.38% for V₂O₅ microspheres prepared by a pyridine-assisted hydrolysis method at 0.2C during the first 20 cycles.²⁶¹ Moreover, the Coulombic

efficiency consistently maintains at ~100% for the first 50 cycles. For comparison purpose, the cycling performance of the mixture of GO (46 wt%) and ~100 nm V₂O₅ spheres at a current density of 90 mA g⁻¹ is also investigated (Figure 7.10). The mixture was synthesized by polyvinyl pyrrolidone (PVP)-assisted hydrolysis method. The specific capacity decreased sharply from 200 mAh g⁻¹ during the 1st cycle to 56 mAh g⁻¹ during the 12th cycle due to GO being electrically insulating.

Figure 7.10 Cycling performance of the mixture of GO (46 wt%) and ~100 nm V₂O₅ spheres at a current density of 90 mA g⁻¹.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

Good high-C-rate performances are desirable in developing high power/fast charging lithium ion battery. The cycling responses of the V₂O₅/rGO(46 wt%) electrode at different C rates were evaluated and shown in Figure 7.9c. The electrode shows discharge capacities of 211, 200, 184, 175 and 167 mAh g⁻¹ during the 2nd cycle at current densities of 190 (0.65 C), 380 (1.3 C), 950 (3.2 C), 1520 (5.2 C) and 1900 mA g⁻¹ (6.5 C),

respectively. Even at very high current densities of 3800 (13 C) and 5700 mA g⁻¹ (19 C), the V₂O₅/rGO(46 wt%) electrode can still deliver high capacities of 127 and 102 mAh g⁻¹ during the 2nd cycle, respectively. The retention of the rate capacity is calculated to be 95% (1.3 C), 87% (3.2 C), 83% (5.2 C), 79% (6.5 C), 60% (13 C) and 48% (19 C) on the basis of the capacity value of 211 mAh g⁻¹ at a current density of 190 mA g⁻¹ (0.65 C). Compared to other reported V₂O₅^{202, 204, 261} and LiFePO₄¹⁵⁸ cathodes, the above performance of V₂O₅/rGO(46 wt%) as cathode for high-rate Li storage is excellent. Furthermore, the V₂O₅/rGO(46 wt%) electrode exhibits an excellent cyclability at a high current density of 5700 mA g⁻¹ (19 C) as shown in Figure 7.9d, delivering a discharge capacity of 93 mAh g⁻¹ during the 200th cycle. Such capacity is also higher than other reported high-performance cathodes such as spinel LiMn₂O₄ nanorods²⁰⁵ with a capacity of 85 mAh g⁻¹ during the 100th cycle at 1 C rate and flower-like LiFePO₄/C/polypyrrole microspheres¹⁵⁸ with a reversible capacity of 85 mAh g⁻¹ during the 400th cycle at 5 C rate. The excellent high-C-rate performance of V₂O₅/rGO(46 wt%) is believed to result from the following aspects: (1) the highly conductive rGO sheets facilitate the fast charge transfer within the electrode and to the current collector; (2) the highly porous structure of V₂O₅ spheres is beneficial for penetration of the electrolyte into the electrode and create short diffusion paths of lithium ions; (3) the well-crystallized nanoparticles ensure the reversible phase transition and the pores in the V₂O₅ spheres provide good buffering effects to maintain the electrode structures during the cycling process.

For practical applications, the content of rGO was reduced from 46 wt% to 18 wt% by changing the R_{GO} : ammonia. The lower rGO content, V₂O₅/rGO(18 wt%), was then combined with 10 wt% carbon black to give ~24 wt% of total electrode. This weight

Figure 7.11 (a) The cycling performance of the V₂O₅/rGO(18 wt%) electrode at a current density of 90 mA g⁻¹ (0.3 C). (b) Charge/discharge capacities of V₂O₅/rGO(18 wt%) electrode at various current densities from 190 to 5700 mA g⁻¹.²³³ Reprinted with permission from ref. 233. Copyright 2011, Royal Society of Chemistry.

percentage is within the range of typical amounts of conductive additive (20-25 wt%) in V₂O₅ based electrodes.^{202, 261,155} The cycling responses of V₂O₅/rGO(18 wt%) electrode at different C rates is also investigated (Figure 7.11). The V₂O₅/rGO(18 wt%) electrode

exhibits an 1st and 50th discharge capacities of 235 and 198 mAh g⁻¹ at a rate of 0.3 C (Figure 7.11a), respectively, showing a capacity retention of 84%. These values are comparable to those of V₂O₅/rGO(46 wt%) electrodes. The high-rate test (Figure 7.11b) reveals that the electrode delivers discharge capacities of 215, 200, 190, 184, 180, 126 and 95 mAh g⁻¹ during the 2nd cycle at C rates of 0.65, 1.3, 3.2, 5.2, 6.5, 13 and 19 C, respectively. A slightly worse Li storage performance at 19 C (e.g. capacity: 95 mAh g⁻¹; rate capacity retention: 64%) as compared to that of V₂O₅/rGO(46 wt%) is mainly attributed to (1) the lower rGO weight percentage, resulting in the reduction of the overall electrical conductivity of the electrode; and (2) the larger diameter of V₂O₅ spheres (Figure 7.8) which in turn may reduce the total contact area between the electrode and electrolyte.

7.4 Conclusions

A facile synthesis approach to prepare rGO supported highly porous V₂O₅ spheres as a high-power cathode material for LIB has been successfully developed. The V₂O₅/rGO electrodes exhibit a significant improvement in electrochemical performance with highly reversible capacities, good cycling stabilities and excellent rate capabilities (e.g. 102 mAh g⁻¹ at 19 C).

Chapter 8: $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ Nanocrystals Embedded in a Nanoporous Carbon Matrix Supported on Reduced Graphene Oxide Sheets: Binder-Free and High-Rate Cathode Material for Lithium-Ion Batteries†

8.1 Introduction

The development of safe, high-energy- and power-density, low-cost and long-lasting lithium-ion batteries (LIBs) is of great technological importance for wide spread applications including electric vehicle (EV), renewable energy storage, aerospace and smart electrical grid.²⁶²⁻²⁶⁴ Most commercial LIBs use lithium cobalt oxides as the positive electrodes, but there are concerns about its high cost and environmental toxicity. Olivine-type LiFePO_4 has emerged as a promising candidate owing to its low price and high safety eventhough it shows a lower Li intercalation voltage (e.g. 3.45 V vs. 4 V) and a lower energy density than that of cobalt-based materials.²⁶⁵ Hence further improvement of such type of cathode materials is encouraged. The higher discharge potential (e.g. 3.6-4.55 V) and higher theoretical capacity (e.g. 197 mAh g⁻¹) of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) have triggered significant research efforts.¹¹⁹ The thermodynamically stable monoclinic LVP phase consists of a three-dimensional (3D) framework of slightly distorted VO_6 octahedra, PO_4 tetrahedra sharing oxygen vertexes,¹¹⁹ corner-shared chains of Li polyhedra and interconnected interstitial space, which leads to a fast ionic transport.

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One of the challenges associated with the use of LVP cathodes for high-power LIBs is how to circumvent the limitation of their intrinsically low electronic conductivity ($\sim 10^{-8} \text{ S cm}^{-1}$).²⁶⁶ Approaches for enhancing electron transport kinetic in batteries include: (1) designing nano-sized electrode materials.^{119, 126-127, 208, 267-269} The nanoscale electrodes require short diffusion paths of charge carriers, resulting in a much enhanced power performance. However, obtaining nanostructured LVP is not easy, especially below 10 nm size, due to the uncontrollable crystal growth during the high-temperature treatment (normally between 700-900 °C).^{121, 270-274} (2) Coating the active material with a conductive layer, typically carbon.^{4, 119, 162, 175, 275} Inspired by this technique, many efforts have been carried out over the past few years to enhance the rate capability of LVP by thermal decomposition of various carbon-containing precursors, such as glucose,^{121, 270-271} citric acid,^{270, 272} starch,²⁷⁰ polyethyleneglycol,²⁷³ and 1,4-dihydroxy-2-butyne,²⁷⁴ to obtain carbon layers to improve the conductivity of the solid phase. However, this type of approaches normally results in LVP with partial carbon coating and large grain size, (e.g. > 50 nm), which leads to a large polarization of the electrode due to un-optimized electron transport process (Figure 8.1). In addition, it should be noted that LVP contains three mobile Li cations, which allows reversible extraction/insertion of 2.0 Li^+ (or a theoretical capacity of 132 mAh g^{-1}) between 3.0 and 4.3 V. However, when the upper cut-off voltage increases to 4.8 V, full extraction of the third Li^+ is difficult due to extremely sluggish kinetics of both Li^+ and e^- transport in $\text{V}_2(\text{PO}_4)_3$. For example, the PVDF-mediated LVP delivers 95 mAh g^{-1} at a discharge rate of 5 C between 3 and 4.3 V (e.g. 72% of the theoretical value) but it only delivers 78 mAh g^{-1} at 5 C between 3 and 4.8 V (e.g. only 40% of theoretical capacity, 197 mAh g^{-1}).²⁷⁰ Thus, it is of technical

Figure 8.1 Electron-transfer pathway for LVP with partial carbon coating and whole electrode prepared with carbon black (conductive additive) and polymer binder. Electrons cannot reach some positions of LVP when Li^+ intercalation/deintercalation takes place. Furthermore, polymer binder would affect e^- transport (an undesirable decrease in the film's electrical conductivity) and block electrolyte permeation paths.¹¹⁸ *Reprinted with permission from ref. 118. Copyright 2012, Elsevier.*

challenge to improve the cathode performance of LVP in a wider voltage window (3.0–4.8 V) with a higher theoretical capacity.

Recently, binder-free electrodes have attracted great attention in the development of rollable batteries, which may show enhanced rate capabilities^{276–279} and open up the possibility of LIB applications at high temperatures, e.g. $> 200^\circ\text{C}$, at which most binders are not stable.¹⁷⁶ However, this concept is mainly demonstrated on anodes. On the other

hand, there are several reports on novel nanostructures of phosphate-based cathode materials for high-performance LIB applications, e.g. LiFePO_4 particles with complete carbon coatings,⁴ LiFePO_4 nanoparticles embedded in a nanoporous carbon matrix²⁶⁵ and $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ nanorods on reduced graphene oxide (rGO) sheets.²⁸⁰ LVP/graphene composites have been prepared²⁸¹ and show promising cathode performance ($\sim 70 \text{ mAh g}^{-1}$ when discharge at 50°C). But the grain size of LVP in the previous study was large ($\sim 50 \text{ nm}$) due to less confinement of the grain growth at high synthesis temperatures, e.g. $\sim 800^\circ\text{C}$. It is understood that the rate capability is directly related to the kinetics of the Li diffusion in the active materials. Thus, confining the grain size and maximizing the contact area between the electrolyte and active components are the keys to further improve such material for high power applications including electric vehicles. The nanoporous carbon can act as an electrolyte container^{265, 282} as well as the template to inhibit the grain growth of inorganic grains during high temperature process. Combination of LVP nanocrystals, nanoporous carbon and rGO to make high performance cathode, as illustrated in Figure 8.2, is therefore promising.

Herein, we present a facile approach to synthesize 5~8-nm LVP nanocrystals embedded in a nanoporous carbon matrix (LVP-NC@NPCM) attached onto rGO sheets, which is hereafter abbreviated as LVP-NC@NPCM@rGO. The rGO sheets not only form the interconnected conducting scaffold to enhance the charge transfer but also act as the heterogeneous nucleation site to facilitate the growth of nanograins of LVP. The nanoporous carbon acts as the nanocontainer to enhance the electrolyte/active material interaction and also inhibit the grain growth of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, which leads to the fast kinetics of the Li ion transfer and the excellent cathode performance in both voltage

Figure 8.2 Designed ideal structure for the composite of LVP nanocrystals embedded in a nanoporous carbon matrix attached onto reduced graphene oxide sheets and its electron-transfer pathways throughout the whole binder-free electrode. Inset: optical image of binder-free LVP-NC@NPCM@rGO electrode.¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

ranges of 3.0-4.3 and 3.0-4.8 V, especially at high current densities. As-prepared LVP-NC@NPCM@rGO composites can be further used to fabricate the binder-free cathode, as illustrated in the insert in Figure 8.2. Such cathode shows high specific capacities, stable cyclabilities and excellent rate capabilities e.g. it can be charged or discharged at a high rate of 50 C between 3.0 and 4.3 V with a reversible capacity of $\sim 90 \text{ mAh g}^{-1}$.

8.2 Material Preparation

In a typical synthesis, 0.6 mM NH_4VO_3 (Alfa Aesar) was first dissolved in 30 mL of distilled water under vigorous stirring at 60 °C to give a yellow solution. Next, stoichiometric amounts of $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$ (Aldrich), $\text{NH}_4\text{H}_2\text{PO}_4$ (Sigma-Aldrich) and 37 mg citric acid (Alfa Aesar) were dissolved in this order into above solution under stirring. This solution was then introduced into 20 mL of graphene oxide (73 mg) dispersion prepared from natural graphite (SP-1) by a modified Hummers method^{258, 283-284} and stirred for 12 h at room temperature. Subsequently, the mixture was stirred at 60 °C to remove the excess water so that black gels were obtained. Afterwards, the gel precursors were first heated at 350 °C for 5 h under Ar, followed by milling and then heating at 750 °C for 8 h under Ar containing 5% H_2 .

8.3 Results and Discussion

The X-ray diffraction (XRD) pattern of the as-obtained LVP-NC@NPCM@rGO sample is shown in Figure 8.3a. Besides the diffraction peaks of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (space group: $P2_1/n$ (14), ICSD #96962),²⁷¹ an additional diffraction shoulder peak at $2\theta = 25^\circ$, partially overlapping with the LVP (121) peak, originates from the stacked graphene

Figure 8.3 (a) XRD pattern of the as-prepared LVP-NC@NPCM@rGO. (b) Raman spectra of LVP-NC@NPCM@rGO, reference GO and LVP/C samples.¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

sheets in LVP-NC@NPCM@rGO. No obvious peaks corresponding to graphite are found in the XRD pattern, indicating the carbon in the sample is not well crystallized. There are no detectable crystalline impurities as indicated by the XRD pattern. Figure 8.3b shows the Raman spectra of LVP-NC@NPCM@rGO, the reference GO sample and the carbon coated LVP (LVP/C) sample prepared in the absent of GO. The Raman spectrum of LVP-NC@NPCM@rGO displays two characteristic bands of carbonaceous materials located at 1361 cm^{-1} (D-band, disorder-induced phonon mode) and at 1595 cm^{-1} (G-band, graphite band), which may be a mixed signals from both amorphous carbon and rGO sheets. Meanwhile, the four-point-probe measurements show that the electrical conductivities of LVP-NC@NPCM@rGO and LVP/C are 330 and 11 S m^{-1} , respectively, while GO is electrically insulating, which indicates that the GO is successfully reduced in

Figure 8.4 TGA curves of (a) LVP-NC@NPCM@rGO and (b) LVP/C carried out in air at a heating rate of 10 K min^{-1} .¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

the annealing process. Based on the thermogravimetric analysis (TGA) result (Figure 8.4), the total content of carbon materials, including both rGO and amorphous carbon, in LVP-NC@NPCM@rGO is calculated to be 29.0 wt% while the content of amorphous carbon in LVP/C sample is 11.9 wt%. The weight loss of 1.0% or 0.6% below 100°C is attributed to the evaporation of moisture. The weight changes in the temperature range of $100\text{--}850^\circ\text{C}$ is ascribed to the burning-out of amorphous carbon and rGO sheets (weight loss) and oxidization of V^{3+} to V^{5+} (weight gain). The possible chemical reactions are written as:

Excluding the weight of moisture in the samples, based on the total weight changes of 23.2% and 5.0%, the carbon+rGO and carbon contents are calculated.

Figure 8.5 (a) FESEM and (b) TEM images of LVP-NC@NPCM@rGO. Inset in (b) is the SAED pattern of rGO sheets. (c) High-magnification TEM and (d) HRTEM images of a single nanoparticle, showing that LVP nanocrystals with sizes of 5–8 nm embedded in a nanoporous carbon matrix. Inset in (c) is the SAED of the amorphous carbon. (e) HRTEM image of a single LVP nanocrystal. (f) Nitrogen adsorption/desorption isotherms of LVP-NC@NPCM@rGO. Inset in (f) is the pore-size distribution plot calculated by the BJH formula based on the desorption branch isotherm.¹¹⁸ *Reprinted with permission from ref. 118. Copyright 2012, Elsevier.*

The morphology of the LVP-NC@NPCM@rGO was investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM), which reveal that quasi-spherical particles with a size of 20–80 nm are anchored onto the surface of nanosheets (Figure 8.5a–b). The selected area electron diffraction (SAED)

Figure 8.6 (a) FESEM, (b and c) TEM, and (d) HRTEM images of LVP/C sample. The results mainly show that the grains are big (100-500 nm) and the carbon layer is not completely coated on LVP.¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

pattern (inset in Figure 8.5b) of the nanosheets shows hexagonal symmetric spots, which confirms the presence of graphene. The high-magnification TEM image (Figure 8.5c) of a single nanoparticle displays that it consists of nanograins with sizes in the range of 5-8 nm embedded in an amorphous matrix, which is indicated by the diffused rings in the corresponding SAED pattern (inset in Figure 8.5c). The amorphous matrix is believed to

be carbon while the high-resolution (HR) TEM image (Figure 8.5d) indicates that the carbon matrix is nanoporous with pore sizes of ~ 4 nm. The HRTEM analysis (Figure 8.5d-e) further confirms that the nanograins in the carbon matrix are monoclinic LVP (ICSD #96962). The observed lattice fringes with a spacing of 0.36 nm (Figure 8.5e) correspond to the (121) planes of monoclinic LVP. In comparison, samples prepared without addition of graphene oxides in the precursors are irregular shaped particles with sizes of 1-2 μm (Figure 8.6a). The TEM images (Figure 8.6b-d) reveal that the samples are composed of large LVP grains of 100-500 nm attached in the carbon matrix. The nitrogen adsorption-desorption isotherms of LVP-NC@NPCM@rGO (Figure 8.5f) and LVP/C (Figure 8.7) samples show a type IV characteristic, which indicates the presence of mesopores and is consistent with the HRTEM observation (Figure 8.5d). Based on the Barrett-Joyner-Halenda (BJH) analysis, the pore size distribution (insets in Figure 8.5f and Figure 8.7) is narrow with an average size of 3.3 nm for both samples. The specific surface area is estimated to be $\sim 156 \text{ m}^2 \text{ g}^{-1}$ for LVP/C@rGO and $\sim 27 \text{ m}^2 \text{ g}^{-1}$ for LVP/C, respectively, using the Brunauer-Emmett-Teller (BET) method. The higher specific surface area of LVP-NC@NPCM@rGO sample than that of LVP/C is due to the extra contribution of rGO sheets.

The proposed formation scheme of hierarchical LVP-NC@NPCM@rGO nanoarchitectures is plotted (Figure 8.8). When added to a solution containing VO_2^+ , Li^+ and H_2PO_4^- ions, the citric acid (denoted as CA) acts as a chelating agent. The CA molecule can easily capsulate VO_2^+ to form $[\text{CAVO}_2^+]$ and further combines with Li^+ and H_2PO_4^- to assemble into the structure $[\text{CAVO}_2^+ \cdot \text{HPO}_4^{2-} \cdot \text{Li}^+]$, which is similar as those reported in preparation of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ using a cationic surfactant²⁸⁵ and CA-mediated

Figure 8.7 Nitrogen adsorption/desorption isotherms of LVP/C. Inset: The pore-size distribution plot calculated by using the BJH formula based on the desorption branch isotherm.¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

Figure 8.8 Schematic illustration of the formation mechanism of LVP-NC@NPCM@rGO.¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

LiFePO_4 .²⁸⁶ When GO aqueous suspension is added, the hydroxyl, epoxide and carboxyl groups on the GO sheets act as the heterogeneous nucleation sites to anchor the $[\text{CAVO}_2^+ \cdot \text{HPO}_4^{2-} \text{Li}^+]$ molecules. The subsequent heat treatments under Ar/H_2 atmosphere led to (1) the formation of LVP nanograins through reduction of VO_2^+ , (2) carbonization of CA and (3) the reduction of GO, which result in the hierarchical LVP-NC@NPCM@rGO nanoarchitectures. The presence of the rGO sheets can also help to separate the LVP grains and prevent the coarsening of LVP@NPCM during the heat treatment process.

The presence of rGO sheets in the LVP-NC@NPCM@rGO sample enable the preparation of binder-free cathode by depositing directly the slurry of LVP-NC@NPCM@rGO in *n*-methyl-2-pyrrolidone (NMP) onto the aluminum current collector with a diameter of 14 mm (inset in Figure 8.2). For comparison purpose, we also prepared the cathode using LVP/C sample with the addition of 10 wt% PVDF as the binder and 10 wt% carbon black as the conductive phase. The Li storage properties of the LVP-NC@NPCM@rGO binder-free cathode and LVP/C normal cathode were tested in coin-type half cells using lithium foils as the anode.²⁸⁷⁻²⁸⁹ Here, it is worth pointing out that the capacity contribution from the carbon matrix or rGO is negligible in the voltage ranges of 3.0-4.3 and 3.0-4.8 V (*vs.* Li^+/Li). Thus, only the mass of LVP was included during the calculation of specific capacities. Figure 8.9a shows the galvanostatic charge (Li^+ extraction) and discharge (Li^+ insertion) voltage profiles of the LVP/C and binder-free LVP-NC@NPCM@rGO electrodes at a current density of 66 mA g^{-1} (0.5 C) between 3.0 and 4.3 V. Three typical plateaus are observed at around 3.6, 3.7 and 4.1 V in the charge curves, which correspond to a series of phase transitions of crystalline LVP.

Figure 8.9 Electrochemical characterization of binder-free LVP-NC@NPCM@rGO and normal LVP/C electrodes. (a) Initial charge-discharge profiles and (b) cycling performance at a charge/discharge rate of 0.5 C between 3.0 and 4.3 V. (c) Comparison of discharge capacities of two electrodes at various current densities between 3.0 and 4.3 V and (d) the corresponding electrochemical impedance spectra measured at the 4th fully discharged state. Inset in (c) is the cycling performance of LVP-NC@NPCM@rGO electrode at 50 C in the voltage windows of 3.0-4.3 V. (e) Cycling performance at 0.2 C (inset in (e): initial charge/discharge profiles) and (f) rate capability of binder-free LVP-NC@NPCM@rGO electrode in a wider voltage window (3.0-4.8 V). Inset in (f) is the cycling performance of LVP-NC@NPCM@rGO electrode at 30 C in the wider voltage window of 3.0-4.8 V.¹¹⁸ Reprinted with permission from ref. 118. Copyright 2012, Elsevier.

The electrochemical reactions are written as:^{119, 290-291}

The two plateaus in the voltage range of 3.6 to 3.7 V correspond to the reactions (8.3) and (8.4). The plateau at 4.1 V is ascribed to a further lithium extraction from $\text{Li}_2\text{V}_2(\text{PO}_4)_3$ (reaction 8.5). These reactions are reversible in the subsequent discharge process. As shown in Figure 8.9a, the LVP-NC@NPCM@rGO and LVP/C electrodes depict initial charge capacities of 130 and 129 mAh g^{-1} and subsequent discharge capacities of 128 and 125 mAh g^{-1} , respectively, which are close to the theoretical capacity of LVP in this voltage window (132 mAh g^{-1}). Both types of electrodes exhibit excellent cycling stabilities with almost no capacity fading during 100 cycles (Figure 8.9b). Relatively higher specific capacities of LVP-NC@NPCM@rGO electrode may be due to the higher activity of fine LVP nanograins (e.g. 5-8 nm).

The cycling responses of the LVP-NC@NPCM@rGO and LVP/C electrodes at different C rates were also evaluated and shown in Figure 8.9c. The binder-free LVP-NC@NPCM@rGO electrode shows discharge capacities of 127, 126, 125, 121, 117, 112, 107 and 102 mAh g^{-1} during the 2nd cycle at current densities of 132 (1 C), 264 (2 C), 660 (5 C), 1056 (8 C), 1320 (10 C), 2640 (20 C), 3960 (30 C) and 5280 mA g^{-1} (40 C), respectively. Even at a very high current density of 6600 mA g^{-1} (50 C), it can still deliver a high capacity of 90 mAh g^{-1} . Such high-C-rate performance of LVP-NC@NPCM@rGO electrode is much better than that of LVP/C electrode, which only achieves low discharge capacities of 52 and 15 mAh g^{-1} at 30 C and 40 C, respectively,

and even cannot be discharged at a high rate of 50 C. The inferior Li storage property of LVP/C is mainly attributed to its low electrical conductivity as verified by the electrochemical impedance spectra (Figure 8.9d). The LVP/C cathode shows a larger radius of semi-circle in the Nyquist plots as compared to that of the LVP-NC@NPCM@rGO cathode, which indicates a higher charge-transfer resistance. Moreover, the LVP-NC@NPCM@rGO electrode exhibits an excellent cyclability at a high rate of 50 C as shown in the inset of Figure 8.9c, delivering a discharge capacity of 88 mAh g^{-1} during the 1000th cycle. Such cyclability is comparable to ever-reported high-performance cathodes, such as binder-free layered $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ electrode composed of 5 wt.% single-walled carbon nanotubes.²⁹²

It is known that there is additional Li^+ extraction, associated with the $\text{V}^{4+}/\text{V}^{5+}$ redox couple, occurring at $\sim 4.6 \text{ V}$ plateau. This increases the voltage range to 3.0–4.8 V, leading to a higher theoretical capacity of 197 mAh g^{-1} for LVP. However, this Li^+ extraction at $\sim 4.6 \text{ V}$ is kinetically difficult to achieve due to the reduced ionic/electronic conductivity of complete delithiation phase $\text{V}_2(\text{PO}_4)_3$.²⁹⁰ Thus, we also evaluated the electrochemical performance of LVP-NC@NPCM@rGO electrode at 3.0 to 4.8 V (Figure 8.9e–f). The plateau at $\sim 4.6 \text{ V}$ (inset in Figure 8.9e) can be clearly observed. Importantly, the lithium reinsertion process gives rise to a solid solution behavior ($\text{V}_2(\text{PO}_4)_3 \rightarrow \text{Li}_2\text{V}_2(\text{PO}_4)_3$) as indicated by the characteristic S-shaped, meaning that Li ions are disordered in the framework. After this point, two-phase transition reappears. The initial discharge capacity of LVP-NC@NPCM@rGO electrode between 3.0 and 4.8 V is as high as 181 mAh g^{-1} with a Coulombic efficiency of 90% at a current density of 40 mA g^{-1} (0.2 C). Although slightly decreased, the reversible discharge capacity still can reach 164 mAh g^{-1}

during the 100th cycle, which is much better than those ever-reported for LVP-based cathodes.^{121, 270-274, 281} Figure 8.9f shows the high-C-rate performance of LVP-NC@NPCM@rGO between 3.0 and 4.8 V, which delivers discharge capacities of 168, 164, 160, 154, 145, 136, 126 and 109 mAh g⁻¹ during the 2nd cycle at current densities of 197 (1 C), 394 (2 C), 591 (3 C), 985 (5 C), 1970 (10 C), 2955 (15 C), 3940 (20 C) and 5910 mA g⁻¹ (30 C), respectively. A superior cycling performance at 30 C can also be achieved in such wider voltage window (inset in Figure 8.9f), showing a discharge capacity of 91 mAh g⁻¹ during the 1000th cycle. The outstanding Li storage performance of LVP-NC@NPCM@rGO is believed to result from the following aspects: (1) ultrafine LVP nanocrystals (5-8 nm) provide short diffusion distances for Li⁺ intercalation/deintercalation; (2) the nanoporous carbon matrix acts as both conducting 3D networks and electrolyte containers to allow fast migration of both Li⁺ and e⁻ to each LVP nanoparticle, which also provides an elastic buffer to maintain structural integrity during repeated charge-discharge processes; (3) highly conductive rGO sheets facilitate the fast charge transfer within the electrode and to the current collector; (4) the binder-free fabrication further improves the electrical conductivity and electrolyte permeation in the LVP-NC@NPCM@rGO electrode.

8.4 Conclusions

In summary, LVP nanocrystals (5~8 nm) embedded in a nanoporous carbon matrix attached onto rGO nanosheets have been successfully synthesized by combining sol-gel process and high-temperature annealing. The rGO sheets not only form the interconnected conducting scaffold to enhance the charge transfer but also act as the

heterogeneous nucleation site to facilitate the growth of nanograins of LVP. The nanoporous carbon acts as the nanocontainer to enhance the electrolyte/active material interaction and also inhibit the grain growth of LVP. Binder-free cathodes can be fabricated based on such LVP-NC@NPCM@rGO sample, which shows high specific capacities, stable cyclabilities and excellent rate capabilities in the voltage ranges of both 3.0-4.3 and 3.0-4.8 V. For example, the composite exhibits a capacity of 90 mAh g^{-1} even at a high rate of 50 C between 3.0 and 4.3 V, which can be remained at 88 mAh g^{-1} after 1000 cycles. For a large voltage window (3.0-4.8 V), the electrode can still deliver high capacities of 168, 145 and 109 mAh g^{-1} at rates of 1, 10 and 30 C, respectively. Combined with a good electrochemical performance and ease of synthesis, LVP-NC@NPCM@rGO can be a very promising cathode material for higher energy density and power demanding lithium-ion batteries.

Chapter 9: Conclusions and Outlook

9.1 Conclusions

This PhD research work mainly focuses on the design of novel synthetic approaches to produce nanostructured vanadium-based cathode materials including VO₂(B), V₂O₅, and Li₃V₂(PO₄)₃ for lithium ion batteries with high-power and high-energy densities. According to the time constant (t) equation for lithium diffusion: $t = L^2/D$ (L : diffusion length, D : diffusion constant), the t for lithium insertion/removal squarely decreases as by replacing micro-sized materials with nano-dimensional electrodes such as nanoparticles, nanobelts, nanosheets, and nanospheres.

Initially, VO₂(B) with a theoretical capacity of 161 mAh g⁻¹ (2.0-4.0 V) and voltage plateau at ~2.5 V were investigated. A facile one-pot hydrothermal reduction method was developed to synthesize the carbon coated VO₂(B) nanobelts using the sucrose as the reducing agent and carbon source. The formation of one-dimensional nanobelts was attributed to the anisotropic structure of VO₂(B) with fast growth along the [010] direction. Additionally, the thicknesses of carbon coating layer could be well controlled from 3.0 to 6.9 nm by the amount of sucrose added. When evaluated as the cathode materials for lithium ion batteries, VO₂(B)@C nanobelts with a carbon layer thickness of ~4.3 nm (carbon content: ~6.6 wt%) exhibited largely reversible lithium storage capacities, superior cycling stabilities and rate capabilities (e.g., 100 mA h g⁻¹ at 12.4 C).

Subsequently, to improve the lithium storage capacity and the working potential, V₂O₅ active materials with the theoretical capacity of 294 mAh g⁻¹ (working voltage range: 2.0-4.0 V) and voltage plateaus at around 3.4, 3.2 and 2.3 V were studied. For nanostructured V₂O₅ materials, hydrated V₂O₅ (V₂O₅ 0.44H₂O) nanobelts were first prepared by a facile

hydrothermal reaction in the assistant of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$). Based on the SEM and TEM observation, the $\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O}$ nanobelts were highly flexible with the length of up to 100-400 μm . These flexible nanobelts could be further used to fabricate the binder-free bulky paper electrode under oven drying. When examined for lithium ion batteries, the flexible binder-free $\text{V}_2\text{O}_5 \cdot 0.44\text{H}_2\text{O}$ nanobelt cathodes exhibited high reversible specific capacities (e.g., 163 mAh g^{-1} at 6.8 C). To further enhance the kinetics of charge transfer, ultrathin V_2O_5 nanosheets and reduced graphene oxide supported highly porous V_2O_5 spheres consisting of nanoparticles ($\text{V}_2\text{O}_5/\text{rGO}$) were also fabricated. Ultrathin V_2O_5 nanosheets (thickness: 2.1-3.8 nm) were prepared by a liquid-phase exfoliation of layer structured bulk V_2O_5 in formamide solution. The ultrathin sheet allowed fast lithium diffusion and electron transportation, resulting in remarkable power and energy densities (e.g., 117 mAh g^{-1} at 50 C). $\text{V}_2\text{O}_5/\text{rGO}$ hybrids were synthesized by a facile solvothermal approach combined with following heat treatment. As cathode materials for LIBs, $\text{V}_2\text{O}_5/\text{rGO}$ (rGO content: 46 wt%) showed a reversible capacity of 128 mAh g^{-1} at 13 C.

Finally, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ active materials with higher potentials (3.6-4.55 V) and acceptant theoretical capacity of 197 mAh g^{-1} were investigated. $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ nanocrystals (5-8 nm) embedded in a nanoporous carbon matrix attached onto rGO sheets (LVP-NC@NPCM@rGO) were fabricated by a sol-gel process combined with the following heat treatment. Such unique nanostructure allowed fast kinetics of the Li ion transfer, leading to a capacity of 109 mAh g^{-1} at a high rate of 30 C between 3.0 and 4.8 V.

The above results indicate that nanostructured $\text{VO}_2(\text{B})$, V_2O_5 , and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes can be used to build superior LIBs with high-power and high-energy densities.

9.2 Outlook

Nanostructured vanadium-based cathode materials including $\text{VO}_2(\text{B})$, V_2O_5 , and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ have demonstrated high reversible specific capacities, good cycling stabilities, and high-C-rate performances, which could serve as promising cathode candidates for high-power and high-energy lithium-ion batteries. The future research work is recommended in the following aspects:

- (1) As the Chapter 6 demonstrated, nanosheet structure is significant benefit for the fast lithium diffusion and electron transportation. It is thus encourage to develop a novel synthetic route to synthesize ultrathin nanosheets of high-voltage $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ cathodes for high-power lithium-ion batteries.
- (2) It is known that all of these vanadium-based cathodes suffer from the low electrical conductivities. In addition to fabrication of nanomaterials and introduction of carbonaceous materials, it is suggested to carry out the systematic doping research (e.g., doping Fe to the V-site) on $\text{VO}_2(\text{B})$, V_2O_5 , and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.
- (3) Kinetic studies of $\text{VO}_2(\text{B})$, V_2O_5 , and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ are also necessary. It is encouraged to using the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) technologies to identify the redox reactions, to evaluate the charge transfer resistances, and to calculate the diffusion coefficients of Li^+ .
- (4) It is suggested to conduct full cell studies of $\text{VO}_2(\text{B})$, V_2O_5 , and $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. By varying anode materials such as graphite, iron oxide, lithium titanium oxide, and silicon to yield optimized specific capacities, working voltage, and cycling stabilities.

- (5) The hydrothermal method in Chapter 4 and 5, and sol-gel process in Chapter 8 are very simple, and the cost of inorganic reactants is relatively cheap. It is highly encouraged to scale up the synthetic processes with larger reaction vessels and more amounts of reactants, and to assembly large-scale LIBs with higher energy, which are of great significance in the viewpoint of practical applications.

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