Biotemplate approach for synthesizing nanomaterials for energy storage applications

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**BIOTEMPLATE APPROACH FOR SYNTHESIZING
NANOMATERIALS FOR ENERGY STORAGE APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2019

BIOTEMPLATE APPROACH FOR SYNTHESIZING NANOMATERIALS FOR ENERGY STORAGE APPLICATIONS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

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Abstract

Biotemplating utilizes a bottom-up approach to synthesize functional nanomaterials with tunable physical and chemical properties. Many naturally available biological materials have been investigated for their unique architectures, and have been successfully used as templates for nanomaterial synthesis. For example, DNA, viruses, proteins and botanical matter have been reported as bio-templates for the preparation of hybrid inorganic nanomaterials. In these reports, only nanomaterials with relatively simple stoichiometric chemistries have been successfully prepared. Preparation of nanomaterials with more complex chemical composition using biotemplating has yet to be investigated.

In this thesis, botanical biotemplates are hypothesized to be useful in synthesizing nanomaterials with complex stoichiometric chemistries. Plants are not only generally abundant in nature, but can also offer unique surface chemistries and 3D porous architectures that could influence nanomaterial synthesis. To investigate this, a simple, facile biotemplating method was developed to prepare a variety of functional nanomaterials. Several land and aquatic botanical species which are known to be hydrophilic were examined. Of the species examined, moss was identified to be the most promising; moss is exceptionally hydrophilic and is able to take up a large amount of metallic precursors. The moss plant also provides a 3D interconnecting pore network which could be preserved after annealing.

The 3D interconnected framework conferred by moss was found to be beneficial to electrode materials in metal-ion battery technologies. In particular, the monoclinic lithium vanadium phosphate $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) is known to be an outstanding cathode material due to its high energy storage capabilities, cycling rates and good thermal stability. Here, the moss plant was successfully utilized as a template to prepare pure, crystalline and mesoporous LVP nanomaterials. The investigation of the formation mechanism of LVP on moss was carried out, and found that the negatively-charged surface of moss was in fact

critical for the molecular recruitment of LVP precursors. Finally, the electrochemical performance of the as-annealed LVP nanomaterials was also examined.

Next, the same synthesis strategy was extended to prepare $\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_4$ (LNMO). The LNMO is also a promising cathode material, widely pursued for metal-ion battery applications to increase energy density with high operational voltages. A pure phase of non-stoichiometric disordered cubic spinel ($Fd3m$) of $\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_{4-\delta}$ using moss as a biotemplate was obtained. After examining the electrochemical performance of the as-synthesized LNMO, it was found to exhibit superior charging capabilities, comparable to other LNMO nanomaterials prepared using conventional chemical methods.

In summary, plants are demonstrated to be promising materials of use in biotemplating approaches. In particular, the moss plant provides a suitable surface chemistry that can be used to recruit metallic precursors. Utilizing this capability of the moss plant, successful functional nanomaterials were synthesized with complex compositions (LVP and LNMO). Both nanomaterials were found to exhibit good electrochemical properties, demonstrating the promise of biotemplating as a green and sustainable nanomaterial synthesis strategy.

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Abbreviations

FTIR	Fourier Transform Infrared Spectroscopy
TEM/HRTEM	High Resolution Transmission Electron Microscopy
XRD/PXRD	Powder X-ray Diffraction
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
BET	Brunauer-Emmett-Teller (for specific surface area in porosity measurements)
CV	Cyclic Voltammetry
LVP	$\text{Li}_3\text{V}_2(\text{PO}_4)_3$
LNMO	$\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_4$ for ordered stoichiometric and $\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_{4-\delta}$ for disordered non-stoichiometric
ED/DMC	ethylene carbonate/diethyl carbonate

Chapter 1

Introduction

Bio-templating is considered a green and sustainable alternative to synthesize nanostructures with 3D hierarchical structures. This strategy is a bottom-up approach that exploits molecular self-assembly to form physiochemical interactions on the template surface, which is necessary for subsequent nucleation of inorganic materials. In this thesis, the hypothesis that plants are suitable biotemplates, and can be used to synthesize nanomaterials with complex chemical compositions, is investigated and addressed.

1.1 Hypothesis/Novelty

Templating is one of the popular strategies used widely to create hierarchical structures in nanomaterial synthesis. Recently, biological materials have emerged as potential candidates for templating. Since then, a variety of biological molecules found in nature have been used to synthesize a range of hybrid inorganic materials; these as-prepared materials have advanced functionalities in a variety of engineering applications.

There is also a growing interest to seek bio-inspired synthesis strategies, as a greener alternative to traditional chemical methods such as lithographic methods to synthesize a substrate template for synthesizing nanomaterials, which are thought to be highly energy-intensive. Biotemplating has emerged as a promising approach due to their environmentally friendly synthesis conditions. In particular, botanical matter constitute a potential class of biotemplates given their natural abundance in nature. However, nanomaterials prepared using plant-based biotemplates have either been simple metals (such as Ag, Au), or basic metal oxides. Preparation of nanomaterials with a more complex chemistry or composition using plants as templates has been relatively unexplored.

In this thesis, botanical templates are hypothesized to be useful in synthesizing complex stoichiometric nanomaterials. Given that the importance of nanotechnology in a variety of engineering applications such as energy storage, catalysis, drug delivery, biotemplating could offer a general, green and sustainable approach to prepare nanomaterials.

1.2 Objectives and Scope

Examination of the various botanical species is first executed, and identification of those botanical templates which can demonstrate promise for use in biotemplating. To investigate the hypothesis, lithium vanadium phosphate (LVP) and lithium nickel manganese oxide (LNMO) were prepared using the botanical template selected; both materials have promising applications as cathode materials in metal-ion batteries which are of complex stoichiometric compositions. The as-prepared nanomaterials will be studied in

understanding their physical and chemical properties. The final as-synthesized products will also be subsequently evaluated as electrode materials in metal-ion batteries to evaluate their electrochemical properties.

In order to provide a mechanistic understanding on how the plant templates influence nanomaterial synthesis, a systematic attempt to determine the manner in which molecular interactions occur between the metallic precursors and the template surface will be investigated.

1.3 Dissertation Overview

The thesis summarizes the study to investigate the hypothesis outlined in the introduction section. In *Chapter 1*, the rationale for the research, the hypothesis and novelty, and the objectives and scope of this project were outlined. *Chapter 2* is a review of the literature concerning the bio-templates used for the synthesis of nanomaterials, the current state-of-art and challenges in nanomaterial synthesis methods, as well as an introduction to LVP and LNMO nanomaterials and their current applications in energy storage. *Chapter 3* is a summary of the experimental methods and materials used in this thesis. In *Chapter 4*, the effort to evaluate various botanical matter as biotemplates is provided. An explanation for the choice of botanical template in subsequent studies can also be found. *Chapter 5* is a study where moss was utilized as a biotemplate to synthesize of lithium vanadium phosphate (LVP). In this chapter, the formation mechanism of LVP utilizing moss was proposed and validated. In *Chapter 6*, the biotemplating synthesis approach was extended in the preparation of lithium nickel manganese oxide (LNMO). The formation of LNMO with the aid of moss was also discussed. Finally, *Chapter 7* is a summary of the key findings of the thesis with the recommendations for future work.

1.4 Findings and Outcomes/Originality

This research led to the development of a general and green synthesis method for the preparation of nanomaterials using plant-based templates. In particular, both LVP and

LNMO were successfully prepared, demonstrating for the first time, that biotemplating approaches could be used to synthesize complex stoichiometric chemistries of the final nanomaterial. The formation mechanism proposed and discussed in this work also further shed insights on the importance of molecular assembly, where utilizing such interactions could be exploited to prepare nanomaterials of complex stoichiometric compositions.

Chapter 2

Literature Review

Templating has been explored as an alternative to create 3D hierarchical structures via a bottom-up approach. By applying with a suitable template, nanomaterials with multi-dimensional structures could be synthesized, which were otherwise challenging using conventional chemical methods. In this chapter, natural materials that have been used in the templating approach will be discussed, in particular, attention will be devoted to nanomaterials prepared using biotemplating. A detailed discussion on the existing synthesis strategies used for the preparation of nanomaterials can also be found. Finally, an introduction to lithium vanadium phosphate and lithium nickel manganese oxides will also be provided, to allow a better understanding of their properties and applications in energy storage.

2.1 Biotemplated materials for the synthesis of nanomaterials

The advent of templating has led to a continuous exploration for new template materials that can influence the manner in which nanomaterials form and nucleate. Naturally available materials have emerged as a promising class of templates, due to their natural abundance. To date, researchers have attempted to exploit the hierarchical structures found in nature, and to devise strategies to guide the formation of nanomaterials using these well-defined architectures. Hence, biotemplating has been recognized as an alternative approach to create novel types of micro/nanostructured materials.

2.1.1 Hierarchical architecture of natural materials

Natural organisms can exist as zero, one, two or three dimensional (0D, 1D, 2D and 3D) architectures as presented in Figure 2.1. Biomolecules and microorganisms are excellent 0D/1D templates due to their nanoscale dimensions, while plants and animals can be used to prepare 2D/3D hierarchical structures materials with macro/micro-features [1-3]. Hence, by selecting an appropriate template, the biotemplating approach can be understood as a versatile strategy to tailor the physiochemical properties and dimensions of the inorganic material.

Figure 2.1 Overview of biological templates placed on a length scale according to their critical dimensions, *reprinted with permission from [3]. Copyright 2011, Wiley.*

2.1.2 Biomolecules and microorganisms

Biological substrates have interesting and unique morphological nano-scaled features, making them useful for nanomaterial synthesis. Some examples of prominent biomolecules are DNA, lipids and peptides, some of which can be engineered to pre-determined self-assembled configurations [1]. Likewise, microorganisms such as viruses, bacteria, fungi, yeasts and algae have been used successfully to create nanostructures with periodic porous

structures [4, 5]. The use of biotemplates was to control the self-assembly of inorganic precursors which are shown to enable the synthesis of higher-order supramolecular structures.

Despite the promise of the biotemplating strategy to fabricate nanomaterials with exciting properties, the approach also have some limitations that remained unresolved. A major drawback of bio-inspired synthesis which use biomolecules and microorganisms as templates is the difficulty to produce sufficient amounts of these templates for large scale nanomaterial production, hence making it a challenge for biotemplating to be viewed as an economical competitor to traditional chemical methods [2].

2.1.3 Plants

In view of the existing limitations of biotemplating strategies, researchers have begun seeking alternative sources of biotemplates that are innately abundant in nature. Of which, plants and their parts, such as stems, leaves or stalks have been explored as potential templates for nanomaterial synthesis [6]. In particular, wood stems have been found to provide a hierarchical, yet porous structure with high mechanical integrity. Various reports on different plant species as well as crude plant materials such as fruit peels and aquatic/land plants have been successfully used to prepare hierarchical porous carbon structures with good mesoporosity [7, 8].

2.1.4 Hierarchical porous structures

The preparation of hierarchical structures with intricate pore systems of different scale range have been a challenge in the synthetic area of research [9]. Hierarchical porous materials provide excellent interconnected frameworks, which can promote the rapid diffusion of ions and electrons due to their large surface areas. One of the most popular hierarchical porous material used in templating is zeolite, where their periodic pore structures have been exploited to fabricate highly ordered mesoporous nanomaterials [7]. Similarly, diatoms are also heavily explored as a mesoporus template due to their unique

open-pore structures [5]. Given that wood is a natural composite, it is a 3D porous architecture with relatively high surface area such as the Paulownia wood shown in Figure 2.2 [3, 10]. As such, wood has been proposed as an alternative carbon-based material for anodes in energy storage applications [11-14].

Figure 2.2 SEM images of cross sections of a) carbonized Paulownia, b) Paulownia-templated Fe_2O_3 , c) pine-templated NiO , e) Paulownia-templated Mn_2O_3 and f) Paulownia-templated Cr_2O_3 , *reprinted with permission from [3]. Copyright 2011, Wiley.*

Of the many plant species reported, moss has emerged as one of the most promising bio-templates. This is due to its widespread abundance which could grow rapidly in damp and shady climates. It also has a unique 3D open-pore macrostructure made up of hyaline cells that are capable of holding water up to 20 times of its dry mass [15-19]. Moss is extensively researched to contain functionally-rich fatty acids [20] acting as a surfactant agent for metal salts, which has been thought to be useful for nanomaterials synthesis. Recently, moss was demonstrated and evaluated as a carbon-based anode in lithium-ion and sodium-ion battery applications [15, 21].

2.2 Current status and challenges for the synthesis of sustainable nanomaterials

2.2.1 Solid-state method

Solid-state method is the most traditional and common method to prepare crystalline inorganic materials. In a typical solid-state synthesis, a grinded mixture of the required inorganic compounds with a source is annealed at an elevated temperature under inert argon or hydrogen reducing atmosphere to generate inorganic materials. The major drawback is the presence of impurities [22]. Another limitation to the solid state method is the uncontrollable particle growth at the elevated temperature during annealing. In some cases where hydrogen is required, the synthesis conditions can be regarded as high cost and potentially hazardous.

2.2.2 Carbon thermal reduction method

As a modified solid-state synthesis method, carbon thermal reduction method is comparatively safer with the use of an inert gas. In this process, carbon sources are introduced to effectively reduce the material particle size, and to improve the overall electrochemical performance of the final products. The carbon sources introduced during the synthesis process also serve as a reducing agent during annealing. Carbon thermal reduction is considered a highly sought-after synthesis method due to its relative low cost and ability to prepare a wide variety of nanomaterials. This modified solid-state synthesis method is also scalable and have been successfully applied to the industrial production of LiFePO_4 cathode materials [22-25]. Nonetheless, the large energy consumption of the carbon thermal reduction method is a significant drawback. Hence, there is a need to optimize reaction temperature and time so as to increase the energy efficiency of this method.

2.2.3 Hydrothermal/Solvothermal method

The hydrothermal technique has been the most popular due to its ability to synthesize

nanomaterials with good crystallinity. It also provides uniformly monodispersed particles with tunable sizes and shapes. As such, the hydrothermal method is recognized as one of the most popular one-pot synthesis techniques to prepare a wide range of inorganic nanomaterials. In a typical reaction, precursors of metal oxides are subjected to a series of chemical reactions in an enclosed Teflon-lined stainless steel autoclave. Chemical solvents are often added to dissolve and recrystallize the materials under high temperature and pressure. Although this method is able to produce high purity with highly uniform dispersed particles with tunable sizes and morphologies, there are serious concerns with safety due to the use of high pressures and temperatures. In addition, the large equipment costs also increases the production cost of the material, limiting the application of this technique for large-scale material production [26].

2.2.4 Sol-gel thermal method

The sol-gel synthesis route offers an attractive advantage of low annealing temperature, while retaining the capability of producing materials with uniform particle size and purities. In a typical sol-gel synthesis process shown in Figure 2.3 (a), both chelating reagents and precursors are mixed. Evaporation at high temperature was then conducted to obtain a gel, which is subsequently annealed to obtain the final inorganic nanomaterial. Compared to the solid state method, the raw materials are allowed to mix homogeneously at the molecular level to form the intermediate sol-gel state. This method is relatively low cost, although in some cases, multiple steps are involved in the entire procedure. The disadvantages are that the required time of sol-gel process is relatively longer compared to other processes. In addition, there is a need to optimize the process to achieve the right viscosity and density in the sol-gel films, making this process challenging for large-scale production [22, 26].

2.2.5 Spray Pyrolysis/Electrospinning

Spray pyrolysis technique is a well-known method to produce highly pure and homogeneous powders with desirable fine and spherical morphology. This method combines the advantages of the traditional method using liquid phase and gas phase. As it is widely used

in the synthesis of inorganic materials such as catalytic and ceramic materials, it is considered suitable for large-scale and continuous production using only simple equipment. However, it remains a challenge to control particle morphology, especially for the preparation of nanomaterials with a more complex stoichiometric chemistries [14, 22, 26].

On the other hand, electrospinning is another method to produce continuous nanofibers of functional inorganic materials shown in Figure 2.3 (b). The electro-spun product are then annealed to form crystalline nanomaterials with high porosity. While this method is considered a novel route for the synthesis of nanomaterials, it is also limited by the need to fine-tune and optimize process parameters to achieve stable nanofibers of the right dimensions and porosities [27].

2.2.6 Freeze-drying

Freeze-drying is a cryo-chemical route for producing fine particles and porous structures. Basically shown in a schematic diagram in Figure 2.3 (c), the precursor solution is prepared and frozen, which is later freeze-dried in a vacuum freeze-dryer. The resultant product will be followed with an annealing step under inert gas flow to synthesize the crystalline inorganic material. As a result of the quick sublimation removal of solvent during this process, porous structure can be retained and contributed to uniform size distribution [28, 29].

2.2.7 Microwave-assisted method

Microwave-assisted chemistry has been explored as a sustainable, rapid and green method to prepare nanomaterials. In this method, microwave radiation is used to assist chemical reactions and to accelerate the reactions which typically reduce the temperatures and significant reduction in reaction time. The rapid reaction times make this method desirable [30]. However, the safety of proper dedicated instrumentation (instead of domestic household microwave ovens) remains a concern since it is possible to overheat sealed vessels which can be a potential hazard. In addition, studies have shown that microwave

heating may not be reproducible in larger reactors due to the inability of microwave irradiation to penetrate through the reactors [31].

Despite many established chemical methods to produce nanomaterials, there is still a push to seek safer and more environmentally friendly synthesis methods [13, 14]. When designing a green and sustainable approach to synthesize nanomaterials, its potential for large-scale production will also have to be considered [32, 33].

(a) Sol-gel thermal

(b) Electrospinning

(c) Freeze-drying

Figure 2.3 Schematic diagrams of various synthesis methods for nanomaterials (a) Sol-gel thermal, (b) Electrospinning and (c) Freeze-drying, *reprinted with permission from [22]. Copyright 2017, Springer Nature.*

2.3 Complex stoichiometric nanomaterials for the energy storage application in lithium-ion battery

Given the rising demands in energy and electricity [34-36], there is a strong demand to improve the current energy storage capacity of electrode materials. Established technologies such as metal-ion batteries and supercapacitors are used in a wide range of applications, such as portable batteries, electronics, electric vehicles and energy grids. In particular, the lithium-ion (Li-ion) battery technology is the most popular and versatile in devices requiring high energy density, power rate and longer cycling lifespans.

2.3.1 Operating principle of Li-ion battery

As the use of Li-ion batteries become increasing widespread, research efforts are geared towards identifying materials which have higher operating voltage and higher theoretical capacities. In a typical Li-ion battery, a cathode (e.g. lithium cobalt oxide), an anode (e.g. graphite), a separator which prevents contact between the cathode and the anode but allows lithium ions (Li^+) to diffuse through (see Figure 2.3). The assembled Li-ion battery will be filled with an electrolyte to conduct lithium (e.g. LiPF_6 in ethylene carbonate/diethyl carbonate).

As charging begins, Li^+ ions intercalated in the cathode pass through the electrolyte to the anode where they receive an electron, and are reduced to lithium metal (Li^0) in the anode. In the discharging process, lithium metal stored in the anode in turn loses an electron to transform to Li^+ , and the Li^+ ions pass through the electrolyte to the cathode. The chemical equations for the mechanism for a typical rechargeable Li-ion battery is presented in Figure 2.4.

Chemical equations for the mechanism:

Figure 2.4 Schematic principle of a typical rechargeable Li-ion battery and the chemical equations for the mechanism, *reprinted with permission from [37]. Copyright 2011, Royal Society of Chemistry.*

The charge and discharging rates of the Li-ion battery is limited largely by the properties of the cathode material. Hence, there is tremendous amount of research devoted to developing new cathode materials, as well as to improve the electrochemical performances of existing cathode materials. These efforts include attempts to decrease the particle size of the active materials, and to host active materials within 3D inter-connected porous carbon networks to facilitate the high Li^+ flux.

2.3.2 Lithium Vanadium Phosphate as cathode material

Among the candidates for cathode materials, monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (LVP) attracted a lot of attention due to its high average potential of 4.0 V and high theoretical specific capacities of 197 mAhg^{-1} based on the extraction of three Li^+ (3.0 V – 4.8 V) or 133 mAhg^{-1} of two Li^+ (3.0 V – 4.3 V). Due to its favorable good thermal stability, LVP has been regarded as a promising cathode material as it can provide rapid ionic diffusion and the raw materials needed are abundant. However, the low electronic conductivity ($2.4 \times 10^{-7} \text{ Scm}^{-1}$) of LVP still greatly limits its use for practical applications. In order to overcome the limitation of low electron conductivity, nano-sized LVP materials are often coated with a thin layer of carbon to enhance their electrochemical performance. For this purpose, many carbon-based templates have been actively explored to synthesize carbon-coated $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ particles [38-46].

Figure 2.5 shows the crystal structure of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$. As shown in the schematic, each VO_6 octahedron is surrounded by six PO_4 tetrahedra whereas each PO_4 tetrahedron is surrounded by four VO_6 octahedra in a three-dimensional configuration. There are three different Li sites with Li1 coordinated by four oxygens whereas Li2 and Li3 has an extra oxygen in their coordination environments. These Li ions are all mobile and conferred to several phase transitions in the potential window 3.0 V – 4.8 V [43].

Figure 2.5 The crystal structure of monoclinic $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, (a) Lattice structure and (b) Li atomic coordination environments, *reprinted with permission from [43] Copyright 2016, Elsevier.*

Recently, bio-templates used to synthesize LVP have been reported. Recombinant proteins using elastin-like polypeptides [47], yeast cells [48], beer waste [49] and recycled tea leaves [50] have been successfully used to produce LVP nanomaterials with good electrochemical properties.

Elastin-like polypeptides were prepared by recombinant engineering where an amino acid sequence was designed to direct the growth of LVP particles. The lysine residues were periodically incorporated within the elastin backbone to provide amine side groups for the interactions of the LVP precursor solution through hydrogen bonding and/or dative bonding. The as-synthesized 3D LVP nanostructures displayed ultrahigh capacities with ultrafast electrochemical properties, realizing the potential of LVP at high rate cycling, reported as 79 mA h g^{-1} at 100°C in the region of $3.0 \text{ V} - 4.3 \text{ V}$ [47]. The as-prepared LVP nanoparticles were found to be 100-200 nm in diameter, with a thick carbon coating of 5 nm in a 3D foam left over due to pyrolysis of the recombinant proteins. A high specific surface area of $106.3 \text{ m}^2 \text{ g}^{-1}$ and narrow pore size distribution centered at 4 nm were reported and attributed to have enhanced the electrochemical performance.

In a separate study, yeast cells were used as mesoporous biotemplates for LVP synthesis using a sol-gel approach. The presence of negatively-charged hydrophilic groups on the surfaces of yeast cells interact with vanadium cations via electrostatic interactions. Annealing the mixture led to the formation of LVP-C microspheres with diameters of 1-8 μm , which contains densely aggregated nanoparticles of 20-40 nm with interconnected 2-15 nm nanopores. The electrochemical performance was found to be $100.5 \text{ mA h g}^{-1}$ at 5C in the region of 3.0 V – 4.3 V [48, 49].

Similarly, used tea leaves were also used as a carbon source in the preparation of LVP nanoparticles via a sol-gel method. When annealed in the presence of tea leaves, the LVP nanoparticles were coated with a layer of amorphous carbon of thickness 10-20nm. The as-prepared LVP-C nanocomposite was evaluated to greatly enhance the electrochemical properties, where an enhanced rate capability and cycling performance could be achieved. An electrochemical performance of 110 mA h g^{-1} at 10 C was reported, which could be retained up to 80 cycles [50].

2.3.3 Lithium Nickel Manganese Oxide as cathode material

Another family of cathode materials that promises higher energy densities is the lithium manganese oxides [51]. In particular, spinel LiMn_2O_4 (LMO) has been widely used in batteries of both electric vehicle and plug-in hybrid electric vehicles. However, this class of materials is limited by its low energy density and poor thermal stability at high temperatures.

To improve the electrochemical properties of LiMn_2O_4 , nickel is incorporated (i.e., spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, LNMO) [52]. In comparison to pristine LMOs, nickel-doped LNMO has a higher operating voltage at 4.7 V vs Li/Li^+ with high rate performance and good cycling behavior [53]. The theoretical specific capacity of LNMO is 147 mA h g^{-1} . Another advantage of LNMO is its high operational voltage, which is 30% higher than the energy density of pristine lithium manganese spinel [36].

Figure 2.6 shows the spinel structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The diffusion paths of lithium and nickel ions are indicated. The Mn, Li and O atoms occupy the 16d octahedral sites, 8a tetrahedral sites and 32e sites, respectively. There are two different crystal structures of the space groups for this spinel material. The first is the $Fd3m$, which is a non-stoichiometric disordered form of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$, where Mn ions are present in mainly Mn^{4+} and little Mn^{3+} . The second is the $P4_332$ stoichiometric ordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ form, where only Mn^{4+} but not Mn^{3+} ions exist. The non-stoichiometric disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ has been found to exhibit better electrochemical properties than the ordered spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [54]. The main challenge for this spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ material is that the redox reaction ($\text{Ni}^{\text{III}}/\text{Ni}^{\text{IV}}$) is close to the potential where the conventional battery electrolyte (1.0 M LiPF_6 in EC/DMC) decomposes. As the formation of a secondary phase such as $\text{Li}_x\text{Ni}_{1-x}\text{O}$ will decrease the electrochemical performance of the spinel material, it is extremely challenging to prepare pure spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [51, 55].

Figure 2.6 The spinel structure of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showing diffusion path of lithium, reprinted with permission from [51], Copyright 2010, Elsevier.

Many synthesis routes have been explored for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The most popular approach to prepare LNMO is currently via using the solid state method, where stoichiometric mixture of the precursor chemicals are ball-milled and subsequently annealed. This method however, produces inhomogenous particle size and distribution, due to uncontrollable

particle growth and agglomeration at elevated temperatures [56].

The sol-gel method uses a lower processing temperature where the mixture is dispersed in a polymeric matrix. The resultant product is then dried and grounded for calcination in air [57]. Using this process, there is improved chemical homogeneity, and smaller LNMO particle sizes can be achieved. Nano-rod porous structures and hollow structures of LNMO have also been successfully prepared using the sol-gel method. These as-prepared particles were found to exhibit exceptional good electrochemical properties [58, 59].

In a separate report, co-precipitation was utilized to generate uniform dispersed precipitates by carefully adding sodium hydroxide to the precursor solution. In this approach, multiple steps of filtering, washing and vacuum-drying were performed before mixing with lithium hydroxide and calcined at elevated temperatures to get $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [60].

In most of the studies reported, there is often unwanted LNMO particle growth due to annealing the product at elevated temperatures. Hence, care must be taken to control particle growth during the synthesis of pure crystalline $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ to avoid affecting the electrochemical performance.

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Chapter 3

Experimental Methodology

This chapter provides a summary of the various methodologies used in the synthesis and characterization of the products prepared using this biotemplating route. X-ray diffraction and electron microscopy were used to study the phases and morphologies of the as-synthesized nanomaterials. Fourier-transform infrared spectroscopy was performed to investigate the mechanisms for the formation of nanomaterials on the biotemplate surface. Brunauer-Emmett-Teller surface area analysis and thermogravimetric analysis were used for further investigation of the porosities of the final product. Finally, the as-prepared materials were evaluated as electrodes in lithium-ion batteries, where their cyclic voltammetry and galvanostatic cycling charge-discharge performances were examined.

In this chapter, the materials and experimental techniques used in this thesis will be outlined.

3.1 Materials

Leucobryum glaucum (moss), *Ceratophyllum demersum* L (CDL), *Rotala rotundifolia* (RR), *Salvinia Minima* (SM), *Sedum x rubrotinctum* (SR), *Catapodium Rigidum* (FG), and *Dracaena Sanderiana* (DS) were examined in this study. All plants were either purchased from a local florist or an aquarium shop.

All plants were first manually cleaned by separating the impurities such as small wood sticks and debris. The cleaned plants were then washed rigorously in water to remove the soil, before freezing at -80°C and lyophilized. All plants were cleaned before using them for nanomaterial syntheses.

All other chemicals were purchased from Sigma-Aldrich (Singapore).

3.2 Synthesis of nanomaterials using plant templates

To prepare iron oxides, the botanical templates were immersed in 50 mM iron (III) chloride hexahydrate (CAS#10025-77-1) solution overnight at 25 mL per gram. Subsequently, the plant templates were rinsed with water to remove the excess solution, then subjected to freeze-drying and a two-step annealing process. The lyophilized samples were first annealed in 800°C for 1 h in argon atmosphere (at a heating rate of 5 °C/min), followed by 400°C for 1 h in air (at a heating rate of 2 °C/min).

For the synthesis of LVP using moss biotemplates, lithium di-hydrogen phosphate (CAS# 13453-80-0) and ammonium metavanadate (CAS#7803-55-6) were dissolved in 60°C dH₂O to achieve a concentration of 1.2 M and 0.8 M respectively. The precursor solution of LVP was first prepared before the addition of the moss template.

In the case of LNMO, lithium acetate dehydrate (CAS#6108-17-4), nickel (II) acetate

tetrahydrate (CAS#6018-89-9) and manganese (II) acetate tetrahydrate (CAS#6156-78-1) were dissolved in dH₂O at 0.1M, 0.05M and 0.15M concentrations respectively. The precursor solution of LNMO was first prepared before the addition of the moss template.

In all syntheses with LVP and LNMO, lyophilized moss plants were immersed overnight in the respective chemical precursor solutions at 25 mL per gram. The following day, the treated moss plants were first dapped to remove the excess of solution using filter paper, before freezing at -80 °C and lyophilized. In experiments where the treated moss were subjected to a washing step, the moss plants were washed in water several times to remove the excess precursor solutions, before they were freeze-dried and lyophilized.

Finally, the lyophilized moss samples were subjected to an annealing step. In order to form crystalline materials, annealing is essential and critical in forming pure crystalline oxides. In the preparation of LVP, samples were annealed at various temperatures ranging from 850°C for 5 h in argon atmosphere at a heating rate of 2 °C per min. In the case of LNMO, samples were annealed in air at 700°C for 1 h at a heating rate of 2 °C per min. Alumina cylindrical crucibles were used for both samples, with the addition of an alumina lid for Moss-LNMO to limit oxidation. Control samples were prepared with lyophilized moss. Control sample was prepared with lyophilized moss (Moss), Moss was also immersed in ammonium metavanadate (Moss-NH₄VO₃) and lithium di-hydrogenphosphate (Moss-LiH₂PO₄) separately and freeze-dried for testing in FTIR.

Schematics illustrating the syntheses of Moss-LVP and Moss-LNMO are shown in Figure 3.1.

Figure 3.1 Schematic of synthesis for Moss-LVP and Moss-LNMO. The differences between the two syntheses are highlighted in red.

3.3 Materials Characterization

3.3.1 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) was performed to obtain phase and crystal structural information of the as-synthesized nanomaterials. All spectra were acquired using the Powder Shimadzu XRD-6000 diffractometer (theta-2theta scan mode), using Cu-K α radiation at 40 kV/30 mA. The as-synthesized nanomaterials are grinded as powder for the characterization and a software such as Match! is used to identify the phase and crystal structural information. X-rays are used to interact with the atoms and diffraction stated as Bragg's law ($2d\sin(\theta) = n\lambda$), where d is the spacing between two diffracting planes, θ is the incident angle, n is an integer and λ is the wavelength of the beam is used to translate the measured data collected by the detector. As PXRD is non-destructive, the small amount required for analysis can be reused for other characterization. Moreover, this technique is quick and accurate in the determination of the phase and purity of the samples.

3.3.2 Electron Microscopy

High resolution transmission electron microscopy (HRTEM) (JEOL-2010UHR) was performed at an accelerating voltage of 200 kV to study the particle morphologies. The point resolution for JEOL-2010UHR is ~ 1.9 Å. This enables the investigation of the crystallinity of the as-synthesized nanomaterial by examine the lattice fringes to confirm the phase of the material. The information is obtained by introducing the electron beam and transmitted through the prepared specimen on the copper grid. An image is formed from the interaction of electrons with the specimen,. Lattice fringes information can be obtained by the interferences between the transmitted electron beam and the diffracted beam. Samples were dispersed in absolute ethanol and dropped onto copper grids for visualization.

For field emission scanning electron microscope (FESEM, JEOL 7600F) studies, the nanomaterial sample was placed on a carbon tape mounted on a sample stub, and subsequently visualized with at an accelerating voltage of 15 kV. It uses the electron beam (produced by the emission of electrons induced by an electrostatic field) to investigate the surface topography which in turn gives insights of the morphological information of the nanomaterials. The focused beam of electrons is scanned on the sample and meanwhile the electrons interact with the atoms on the sample at various depths, the types of signals produced such as secondary electrons, back-scattered electrons etc. are then collected to produce an image according to the position of the beam. This equipment has a resolution of 1.0 nm at an accelerating voltage of 15 kV, and is fast and prompt to investigate the relative morphology and positions of the nanostructures.

3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were acquired on a fourier transform infrared spectrometer (PerkinElmer). Samples were subjected to infrared radiation of wavenumbers between 4000 cm^{-1} and 400 cm^{-1} . This fast analytical technique is favored to identify chemical bonds of the material. Infrared radiation is exposed for the interaction with the sample, and the transmitted

radiation is measured. The interaction of the sample takes place with the absorption of the infrared radiation between 4000 cm^{-1} and 400 cm^{-1} . The data collected represents the different vibrational states of the chemical bonds within the molecule of the sample. FTIR provides a unique fingerprint which is useful to compare the as-prepared samples for analysis to identify functional groups and to analyze the interaction when compared.

3.3.4 Porosity measurement - Brunauer-Emmett-Teller specific surface analysis (BET)

The nitrogen adsorption-desorption isotherms were acquired using an Accelerated Surface Area and Porosimetry System (ASAP Tri-star II 3020 analyzer). The samples were degassed at $120\text{ }^{\circ}\text{C}$ for 4 h under vacuum prior to measurement in the presence of nitrogen. During the measurement, nitrogen gas is typically used as the probing molecule. The principle of nitrogen adsorption as the sample gains exposure of the nitrogen gas at $-196\text{ }^{\circ}\text{C}$ (the boiling point of nitrogen), and the measurement of the adsorption and desorption isotherms will be calculated regarding the surface area of the material and analysis of the pore size and pore volume distributions can be tabulated. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method to obtain the surface areas of the material as well as the pore size and pore volume distributions for each sample.

3.3.5 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed on a TA Instrument Q500. Samples were subjected to a constant heating rate of up to $1000\text{ }^{\circ}\text{C}$. This thermal analysis method measures the change in the physical and chemical properties of materials as a function of increasing temperature with constant heating rate and measuring the loss of the sample's mass. This gives insights to the thermal stability and composition of material. The sample mass was plotted as a function of increasing temperature and the overall carbon content in the sample was estimated from the sample weight loss at $400 - 500\text{ }^{\circ}\text{C}$.

3.4 Electrochemical Characterization

3.4.1 CR2032 Coin Cell Fabrication

The coin-type CR2032 cells were assembled based on the half-cell configuration in an argon-filled glovebox (both moisture and oxygen levels are less than 1 ppm). Coin cells were fabricated using and a solution of 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1 : 1, in wt%) as the electrolyte for Lithium-ion battery.

In the study involving iron oxides, the electrode slurry was composed of various botanical templates incorporated with iron oxides (70wt%), 20% carbon black (acetylene black) and polyvinylidene fluoride (PVDF) (10wt%) in n-methyl-2-pyrrolidone solvent (NMP, 99+%, Alfa Aesar). The mixture was stirred overnight before pasting onto the copper foils as anodes. Lithium foils were used as the counter electrode and reference electrode, and Celgard 2400 was used as the separator. The testing of the half-cells for these anode materials was done within a potential window of 0.01 – 3.0 V

For studies involving LVP and LNMO, the electrode slurry consisted of either Moss-LVP or Moss-LNMO (70wt%), carbon nanotubes (20wt%) and polyvinylidene fluoride (PVDF) (10wt%) in n-methyl-2-pyrrolidone solvent (NMP, 99+%, Alfa Aesar). The mixtures were stirred overnight before pasting onto the aluminium foils as cathodes. The mass loadings in electrodes in all studies were calculated to be 1.0 mg cm^{-2} . Lithium foils were used as anodes. The evaluation of the half-cells for these cathode materials were performed within a potential window of 3.0-4.3 V and 3.5-5.0 V for Moss-LVP and Moss-LNMO respectively.

3.4.2 Cyclic Voltammetry

Cyclic voltammograms were tested using Solartron analytical equipment (Model 1470E) in a voltage range of 3.0-4.3 V for LVP at a scanning rate of 0.2 mV s^{-1} .

3.4.3 Galvanostatic cycling

The assembled half-cells were subjected to galvanostatic cycling in a pre-defined voltage range to determine their lithium storage performances. All cells were tested on a NEWARE multichannel battery test system with galvanostatic charge and discharge in the voltage range of 3.0-4.3 V *vs* Li⁺/Li for LVP and 3.5-5.0 V *vs* Li⁺/Li for LNMO at various current densities.

Chapter 4

Evaluation and selection of suitable botanical templates

In this chapter, the attempt to evaluate various botanical templates for their feasibility for nanomaterial syntheses is discussed. Various land and aquatic plant species were used as biotemplates to prepare iron oxide. The as-prepared products were first characterized using XRD and electron microscopy to understand the effect of the template on the particle morphology. Finally, the electrochemical properties of the as-prepared samples were tested as anodes in lithium-ion batteries were also evaluated. Based on the crystallinities and purities of the particles as well as their respective electrochemical performance data, the most suitable botanical template was selected and used in subsequent studies.

4.1 Introduction

Among the vast number of abundant natural raw materials, polysaccharides and biologically active products from plant extracts are the most popular for use in nanomaterial synthesis [1]. Amongst which, lemongrass plant, mulberry leaves, aloe vera, tea and coffee extract have been used to synthesize gold and silver nanoparticles, or simple transition metal oxides of various morphologies and sizes. Specifically, coriandrum sativum extract which is a herb commonly known as coriander or cilantro was also shown to have the ability to nucleate ZnO nanoparticles [2]. Likewise, others have also demonstrated successful preparation of Co_3O_4 using tea leaves [3] and Fe_3O_4 nanoparticles using glucose [4].

Separately, there are also reports using pyrolyzed botanical templates directly as carbon-based porous anodes [5, 6]. Recently, mesoporous activated carbon from corn stalk core (natural sponge-like porous channel structure) was tested as anode in lithium-ion battery and was found to have excellent reversible capacity of 504 mAh g^{-1} after 100 cycles at 0.2C (compared to the un-activated carbon at 252 mAh g^{-1}). The enhancement in the performance was attributed to the mesoporous structure of the annealed sample [7].

Given the potential for botanical templates to offer interesting structural or functional properties that can influence material synthesis, both land and aquatic plant species were examined in this work. Here, iron oxide was prepared using various plants as templates. The morphologies and electrochemical properties as anodes in lithium-ion batteries of the as-prepared nanomaterials were evaluated.

4.2 Criteria for the selection of botanical templates

To begin the selection for suitable botanical templates, a list of factors have to be considered. The plant templates should ideally have (a) hierarchical porous structures, (b) reported ability to nucleate or reduce metal precursors, and (c) abundantly available in nature.

Based on this selection criteria, several potential botanical templates were shortlisted. Table 4.1 is a list of plant templates examined in this chapter and their respective characteristics.

Table 4.1 List of botanical templates explored.

Name of botanical template	Characteristics
<i>Ceratophyllum demersum</i> L (CDL)	Aquatic plant, weed, no roots with filamentous leaves, bioabsorption studies and water monitoring applications.
<i>Rotala rotundifolia</i> (RR)	Aquatic plant, weed in rice paddies.
<i>Salvinia Minima</i> (SM)	Fern floating aquatic plant, no roots, exposed hair on leave to repel water, invasive species, bioabsorption studies and water monitoring applications.
<i>Sedum x Rubrotinctum</i> (SR)	Succulent plant, water-storing (vacuoles) leaves.
<i>Catapodium Rigidum</i> (Fern Grass) (FG)	Water uptake via the leaves, no plant cuticle for protection.
<i>Dracaena Sanderiana</i> (DS)	Air-purifying plant, multi-stem (shrub), hardy indoor plant.
<i>Leucobryum glaucum</i> (moss)	75% of leaf volume is water-storing hyaline cells surrounding photosynthetic cells, uptake of water to 20 times of its dry mass.

Ceratophyllum demersum L (CDL) has been explored as a plant extract to reduce graphite oxide to graphene. The authors found that the properties of these graphene nanosheets were comparable to those prepared by conventional chemical means [8]. *Rotala rotundifolia* (RR) has been explored for its antibacterial and antioxidant activities to synthesis silver nanoparticles [9]. *Salvinia Minima* (SM) has been explored for bioabsorption studies of various metals such as chromium [10].

Sedum x rubrotinctum (SR) has been explored for phytoextraction of heavy metals due to the vacuoles of succulent species [11]. *Catapodium Rigidum* (Fern Grass or FG) is relatively less investigated, but have been shown to respond to potassium availability in

soils [12]. *Dracaena Sanderiana* (DS) is established as an indoor plant which has air purifying properties, it is reported to be able to remove benzene from contaminated air and water [13]. Lastly, *Leucobryum glaucum* (moss) is an abundant weed, which has well-known hydrophilic properties due to their high fatty acid contents [14, 15].

4.3 Characterization of as-annealed products prepared using various botanical templates

As iron oxides are prominently used in energy storage applications due to their high theoretical capacity, low toxicity and cost with well-studied crystalline phases and morphologies [5, 6, 16, 17], all of the above botanical matter were separately immersed in $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ solution as previously mentioned in Section 3.2. The annealed products were analyzed using XRD and electron microscopy. Table 4.2 provides a summary of the preliminary evaluation of all the samples tested.

Table 4.2 Examination of the as-synthesized botanical templates with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

Name	XRD results	SEM observations	Concluding remarks
CDL	No crystallinity	Showed presence of diatoms	Marine fouling impurities in aquatic plants, difficult to get rid
RR	Fe_2O_3	Inherent pore structures of about 10 μm , 100nm particles	Examined with TEM to have hollow nanoparticles of 80-200 nm
SM	No crystallinity	Disintegrate easily, no observed porous structure.	Immersion of this floating aquatic plant was improvised by changing the volume of bottle.
SR	Fe_2O_3	Pore size of inner leaf 100 μm	Examined with TEM to have agglomerated nanoparticles of 20-50 nm
FG	Fe_2O_3	Lamellar porous structure, disintegrate easily	After two-step annealing, sample weight decreased drastically, low yield.
DS	Fe_2O_3 , with impurity	Hierarchical porous structure	Impurity peak limits the potential.
Moss	Fe_2O_3	Hierarchical porous structure, 300 nm particles	Examined with TEM to have nanoparticles of 100-300nm rhombohedral shape

Of all the samples tested and presented in Table 4.2, only *Rotala rotundifolia* (RR), *Sedum x rubroinctum* (SR) and *Leucobryum glaucum* (moss) appeared to be promising. The remaining botanical samples either failed to produce crystalline iron oxides, or yielded significant amounts of impurities. In the case of *Catapodium Rigidum* (FG), despite successful synthesis of Fe_2O_3 , there was sufficient end products obtained despite repeated experiments due to rapid disintegration of the sample during annealing.

From the XRD spectra presented in Figure 4.1, mixtures of iron oxide in the phases of rhombohedral hematite $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS no. 00-033-0664) or cubic maghemite $\gamma\text{-Fe}_2\text{O}_3$ (JCPDS no. 00-039-1346) were observed for RR (Figure 4.1a) and moss (Figure 4.1c). In the case of SR (Figure 4.1b), only the rhombohedral hematite $\alpha\text{-Fe}_2\text{O}_3$ phase was observed.

The characteristic peaks of α -Fe₂O₃ were also of lower intensities compared to the peaks found in the other two samples (i.e., RR and moss).

Figure 4.1 shows the XRD spectra synthesized with the aid of (a) *Rotala rotundifolia* (RR), (b) *Sedum x rubrotinctum* (SR) and (c) *Leucobryum glaucum* (MOSS). JCPDS no. 00-039-1346 and 00-033-0664 represent cubic maghemite and rhombohedral hematite respectively are included for comparison.

Figure 4.2 SEM and TEM images of botanical templates. (a and d) *Rotala rotundifolia* – RR, (b and e) *Sedum x rubrotinctum* – SR and (c and f) *Leucobryum glaucum* – moss were synthesized with iron oxide nanoparticles.

Figure 4.2 shows the SEM and TEM images for RR, SR and moss. For RR, a macroporous structure was observed (Figure 4.2a). Iron oxide particles of sizes ranging 80 – 200 nm was also obtained, as shown in the corresponding TEM image (Figure 4.2d). Interestingly, the particles appeared to have a hollow profile, with significant agglomeration of nanosized particles on their surfaces. For the SR sample, the structure contained larger pores of about 100 μm , which corresponded to the typical size of the vacuoles found in the inner leaf of SR (Figure 4.2a). From the TEM image, iron oxide nanoparticles of less than 50 nm were observed. However, these particles were highly agglomerated (Figure 4.2e). Lastly, the moss sample were found to have an open-pore structure, where the surfaces were decorated with nanoparticles (Figure 4.2c). The particles were rhombohedral (pictured in the bottom) and cubic in shapes, with dimensions of about 200 nm, which were intrinsic of hematite $\alpha\text{-Fe}_2\text{O}_3$ and maghemite $\gamma\text{-Fe}_2\text{O}_3$ (Figure 4.2f).

4.4 Electrochemical properties of iron oxides prepared using botanical templates

Based on these XRD results, the botanical templates which could produce iron oxides were identified to be *Rotala rotundifolia* (RR), *Sedum x rubrotinctum* (SR) and *Leucobryum glaucum* (moss). Hence, these samples were subsequently evaluated as anodes in lithium-ion batteries.

When iron oxides synthesized using *Rotala rotundifolia* (RR) was tested, the electrochemical properties were disappointing with a charge capacity of 19.2 mAh g^{-1} . This value was significantly low, compared to the charge capacity of 372 mAh g^{-1} of conventional graphite anodes [5]. Figure 4.3a shows the first three discharge-charge voltage capacity profiles of RR. The initial discharge capacity was 70 mAh g^{-1} and initial charge capacity was 19.2 mAh g^{-1} , with an initial coulombic efficiency of only 27.4%.

Despite attempts to assemble the half-cell containing iron oxide prepared using *Sedum x rubrotinctum* (SR), a satisfactory slurry under the same conditions for coating the foils could not be obtained. The assembled half-cells were tested regardless, but reliable data was not obtained.

Finally, Figure 4.3b shows the first three discharge-charge voltage capacity profiles of *Leucobryum glaucum* (moss) sample. The initial discharge/charge capacities was found to be $749/435 \text{ mAh g}^{-1}$. The coulombic efficiency was calculated to be 58.1% due to the irreversible capacity at the first cycle predicted to be largely due to the formation of solid-electrolyte interphase (SEI) which is one of the most common attributors for decrease in charge capacity [18].

Figure 4.3 Electrochemical measurement as anode in lithium-ion battery, the first three discharge-charge voltage capacity profiles of (a) *Rotala rotundifolia* – RR and (b) *Leucobryum glaucum* – moss) with iron oxide nanoparticles at 0.1 A g^{-1} , with a cut-off potential window of 0.01–3.0 V and respective color corresponding to the voltage capacity profiles (Charge : 1st – dark blue, 2nd – purple, 3rd – red and Discharge : 1st – black, 2nd – blue, 3rd green).

Despite the presence of both hematite and maghemite hollow particles, the RR sample failed to exhibit good electrochemical performance. It is likely that there was insufficient porosity present in the macrostructure to allow for efficient ion transport. In the case of SR, a homogenous slurry for the half-cell experiments could not be prepared. It is possible that the large agglomerated clusters of iron oxides observed in the SR samples could not be readily dispersed within the slurry mixture. As such, the electrochemical properties of the

iron oxides prepared using SR could not be determined.

Finally, iron oxides synthesized using *Leucobryum glaucum* (moss) were also evaluated as anodes. The electrodes were able to deliver a first charge capacity of 435 mAh g⁻¹ which is higher than conventional graphite anode. The superior electrochemical properties of the iron oxides prepared using moss could be attributed to the presence of an open-pore network as well as the high surface areas of the shaped iron oxide nanoparticles.

4.5 Summary

In this chapter, a variety of botanical templates was evaluated as biotemplates for the synthesis of iron oxides. The as-annealed products obtained in each case was analyzed using XRD to confirm the presence of crystalline iron oxides. Of which, only RR, SR and moss yielded pure crystalline particles, which were indexed to either α -Fe₂O₃ or γ -Fe₂O₃ as well as mixtures containing both of these oxides. TEM images of RR showed hollow nanoparticles while moss yielded iron oxide nanoparticles that were rhombohedral and cubic in shape.

When the samples were evaluated as anodes in lithium-ion batteries, only iron oxides prepared using moss exhibited good electrochemical properties. It is likely that the large surface areas attributed by the open-pore network, as well as the shape of the iron oxide particles, played a critical role in enhancing electron transport and efficient diffusion of Li⁺ ions.

Taken together, the findings in this chapter suggests that moss appears to be a suitable biotemplate for nanomaterial synthesis. In the subsequent chapters 5 and 6, the moss plant will be explored as a biotemplate for the preparation of LVP and LNMO. The formation mechanism responsible for the interactions between the metallic precursors and the moss surface will also be investigated.

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Chapter 5

Biotemplating approach for the synthesis of LVP

Elaboration on the synthesis parameters (washing step, annealing temperature, annealing duration and the starting precursor concentrations) to synthesize Lithium Vanadium Phosphate successfully by utilizing the selected botanical template – Moss will be explained in this chapter. Characterization of the nanomaterial will be correlated to the change made in the reaction parameters. From the findings of synthesizing this nanomaterial, the working mechanism of Moss was investigated. The evaluation of the electrochemical performance of Moss-LVP as a cathode material in Lithium-ion battery was carried out.

5.1 Introduction

In the previous chapter, the iron oxides prepared using moss gave the most promising electrochemical properties. To investigate the hypothesis of this thesis, further investigation of the use of moss as a template for the synthesis of nanomaterials with a more complex stoichiometry was conducted.

As reviewed in Chapter 2, the monoclinic lithium vanadium phosphate ($\text{Li}_3\text{V}_2(\text{PO}_4)_3$, LVP) is a well-known cathode material researched widely for lithium-ion batteries. LVP possess superior thermal stabilities, high theoretical capabilities (197 mAhg^{-1} based on the extraction of three Li^+ (3.0 V – 4.8 V) or 133 mAhg^{-1} of two Li^+ (3.0 V – 4.3 V)) as well as high operating potentials; these characteristics make LVP highly favorable for applications such as electric vehicles. Despite the excellent electrochemical properties of LVP, this cathode material suffers from an intrinsic low electrical conductivity. Since the overall performance of lithium-ion batteries are largely limited by the electrochemical capabilities of the cathode, a lot of effort is devoted to improve the electronic conductivity of LVP. These efforts include coating LVP nanoparticles with carbon [1-5], and/or attempting to disperse LVP within a conductive carbon matrix.

Although many methods exist for the synthesis of LVP, using a botanical template to synthesize LVP have been relatively unexplored. Hence, in this work, attempts to prepare LVP using moss plants as templates will be reported. The physical and electrochemical properties of the annealed products as cathodes in lithium-ion batteries will also be examined.

5.2 Optimization of LVP synthesis parameters

Since there were no prior reports involving the use of moss to prepare LVP, key experimental parameters that were thought to be critical to the formation of LVP were first identified [3, 4, 6-14]. Amongst which, the effects of annealing temperature and duration as well as the starting precursor concentrations were of interest. Table 5.1 shows the series

of LVP samples (#1 to #5) that were prepared under different synthesis conditions. All samples were analyzed using XRD to confirm the presence of LVP (Figure 5.1). Samples were also visualized using FESEM to observe the macrostructures and particle morphologies of each sample (Figure 5.2).

Table 5.1 A list of LVP samples prepared under different synthesis conditions.

LVP sample #	Washing step	LiH ₂ PO ₄ conc	NH ₄ VO ₃ conc	Annealing Temp	Annealing duration
1	Yes	0.6M	0.4M	850 °C	10h
2	No	0.6M	0.4M	850 °C	10h
3	No	0.6M	0.4M	750 °C	10h
4	No	0.6M	0.4M	850 °C	5h
5	No	1.2M	0.8M	850 °C	5h

In the initial attempts to synthesize LVP, the treated moss plants were washed in water immediately after immersing overnight. The washed moss plants were then freeze-dried and annealed at 850 °C for 10 h. This initial annealing temperature was selected based on previous reports, where annealing temperatures of between 600 and 1000 °C are found to yield LVP of good crystallinities [4, 15-17]. However, when the end products were analyzed using XRD, characteristic peaks of LVP could not be observed (refer to LVP sample #1 in Table 5.1 and its corresponding XRD spectrum in Figure 5.1a).

This results suggested that the washing step could have in fact removed most of the precursors present. Hence, the synthesis procedure was modified to eliminate the washing step. Subsequently, dapping of the excess solution from the treated moss plants was performed and the sample was directly freeze-dried. Under the same annealing conditions (i.e., 850 °C for 10 h), the characteristic LVP peaks in the XRD spectrum was observed (refer to LVP sample #2 in Table 5.1 and corresponding XRD spectrum in Figure 5.1a), indicating a pure crystalline phase of monoclinic Li₃V₂(PO₄)₃ was obtained.

Figure 5.1 Effect of the synthesis parameters and their resulting XRD spectra. The effects of (a) washing and dapping excess, (b) annealing temperature, (c) annealing duration, (d) XRD data of LVP sample #5 showing sharp peaks characteristic of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (JCPDF no. 04-012-2044).

When LVP sample #2 was visualized under SEM and TEM, the LVP particles were observed to be about 150-200 nm in size. However, the particles existed mainly as agglomerated clusters (Figures 5.2a and d). More importantly, the macroporous structure was noted to have partially collapsed, likely due to the long annealing duration of 10 hours.

Figure 5.2 SEM and TEM images of LVP sample #2 (a and c) and #3 (b and d).

These observations prompted the examination of the effect of the annealing temperature in the synthesis procedure. While a sufficiently high annealing temperature is necessary to obtain a good degree of crystallinity in LVP, elevated temperatures promote particle growth and agglomeration. Since smaller LVP particle sizes are known to exhibit superior electrochemical properties, the annealing temperature was reduced from 850 °C to 750 °C (while maintaining the annealing duration at 10 h). At a lower annealing temperature (refer to LVP sample #3), a pure sample of crystalline LVP could still be achieved despite lower intensities of the crystallinity peaks (Figure 5.1b). More importantly, the open-pore framework was retained, decorated with LVP nanoparticles of 100-200 nm (Figure 5.2 b and d). In this sample, it was noted that there was significantly less particle agglomeration.

To examine if the LVP particle size can be reduced further, the annealing duration was decreased from 10 h to 5 h. Comparing LVP samples #2 and #4 in Figure 5.1c, a significant reduction in LVP peak intensities was observed with a decrease in the annealing duration while both showed the presence of pure crystalline LVP. Lesser particle agglomeration was

observed for LVP sample #4 when compared to LVP sample #2, this observation is similar to that of LVP sample #3 with a lower annealing temperature of 750 °C. Hence, it was determined that with the reduction of annealing duration to 5 h at a higher temperature of 850 °C could also achieve pure crystalline LVP with lesser agglomerated nanoparticles.

Next, the starting precursor concentrations were increased by two-folds (i.e., LVP sample #5). Consequently, an XRD spectrum showing characteristic XRD peaks of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ (JCPDF no. 04-012-2044) was obtained and presented in Figure 5.1d. The strong and sharp intensities of the diffraction peaks suggested that a pure crystalline $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ was present.

LVP sample #5 was next visualized using electron microscopy (Figure 5.3). The typical open-pore structure resembling that of known moss structure could be clearly observed, with macropores of about 10 μm in diameter in Figures 5.3 (a and b). At higher magnifications, the surfaces of the material were observed to be covered with LVP nanoparticles, with diameters ranging from 100nm to 200nm in Figures 5.3 (c and d). While most of the LVP particles had spherical morphologies, rod-like LVP particles could also be found in the sample (Figure 5.3d). The elongation of LVP particles were likely due to particle growth at elevated temperatures [11].

TEM images of LVP sample #5 further confirmed that the LVP particles were indeed crystalline. The lattice spacing was measured to be 0.3664 nm, coinciding with plane (211) of LVP in Figures 5.3 (e and f). The TEM result was also in good agreement with the XRD data presented in Figure 5.1d.

Figure 5.3 Morphology of LVP sample #5 examined using FESEM (a-d) and TEM (e-f). (a-d) 3D network consisting of the open-pore network of the moss plant decorated with LVP nanoparticles. The diameter of the pores were measured to be about 10μm. LVP particles with diameters ranging from 100 – 200nm were found to cover the entire surface of the carbon framework (e-f) TEM images showing LVP nanoparticles, with lattice spacing of 0.3664nm, which corresponded to the (211) plane of $\text{Li}_3\text{V}_2(\text{PO}_4)_3$.

5.3 TGA and BET analysis

Of the samples synthesized, LVP sample #5 was found to contain LVP particles of the highest crystallinity. The 3D macroporous network on which LVP particles were well-dispersed, making this sample ideal for battery applications. As such, LVP sample #5 was subjected to further evaluation. For the rest of the study, LVP sample #5 will be referred to as moss-LVP.

Figure 5.4 (a) shows the TGA results of moss-LVP. The overall carbon content of moss-LVP was also measured to be about 1.44% using TGA performed in air. This data is in good agreement with the XRD results (Figure 5.1 (d)), where no observable diffraction peaks from carbon were observed. The Brunauer-Emmett-Teller (BET) data of moss-LVP is shown in Figure 5.4 (b) where the specific surface area of Moss-LVP was found to be $16.65 \text{ m}^2\text{g}^{-1}$, with the pore size distribution presented in Figure 5.4 (c). This result confirmed that both micropores (1nm) and mesopores (20nm) were present in moss-LVP.

Figure 5.4 (a) TGA curve measures the carbon content of moss-LVP to be about 1.44%, based on the weight % change between 120 – 450°C. (b) Nitrogen adsorption and desorption isotherms at 77 K for Moss-LVP with (c) the pore size distribution for moss-LVP, centering around 1nm (nanopores) and 20nm (mesopores).

5.4 Electrochemical measurements

Finally, moss-LVP was evaluated as a cathode in lithium-ion batteries. The capacity contribution from the carbon is negligible in the voltage 3.0 - 4.3 V, and hence only the mass of active material is included in the calculation of the specific capacities. Figure 5.5a shows the cyclic voltammograms (CV) curves measured at 0.2 mV s^{-1} . The three anodic peaks observed around 3.64, 3.71, 4.11 V as well as the three cathodic peaks at 3.55, 3.64 and 4.02 V were characteristic of the two-phase transitions during lithium extraction and insertion for $\text{Li}_3\text{V}_2(\text{PO}_4)_3$ at 3.0 – 4.3 V [17].

The initial charge and discharge capacities were found to be 118.8 mAhg^{-1} and 103.7 mAhg^{-1} respectively in Figure 5.5b. This corresponded to the first columbic efficiency of 87%. The theoretical discharge capacity of LVP is 133 mAhg^{-1} at 1C for the voltage range of 3.0 – 4.3 V. An irreversible capacity loss after the first discharge was noted, likely due to the decomposition of the electrolyte to form solid electrolyte interphases (SEI) layers. At high electrochemical potential zone above 4.3 V, the solvents in the electrolyte begins to be oxidized by the cathode to form CO_2 gas and the corresponding SEI layer, which resulted in SEI layers on the surface of the cathode. Nonetheless, a discharge capacity of 95.7 mAhg^{-1} after 100 cycles at 1C (Figure 5.5b) was still able to be obtained, retaining almost 92.2% of its initial discharge capacity.

The rate cycling performance of moss-LVP was also evaluated and presented in Figure 5.5c. A discharge capacity of at least 80 mAhg^{-1} for currents of up to 5C was obtained. While a reduction of discharge capacity at higher current densities was observed, recovery of its initial discharge capacity at 1C was still obtained after cycling at the higher current densities. The high-rate capacity and good cycling performance of moss-LVP could be attributed to the well-crystallized nano-sized LVP particles, intercalated with the open-pore 3D hierarchical carbon matrix conferred by the moss template.

Figure 5.5 Electrochemical performance of moss-LVP as cathodes in Lithium-ion batteries. (a) CV curves at 0.2 mVs^{-1} . (b) Initial charge-discharge voltage capacity profiles at 1C (left). The discharge capacities for 100 cycles (right) (c) Rate cycling performance for various current densities.

5.5 Attempt to improve the electrochemical properties of moss-LVP

By comparing moss-LVP prepared in this work with those synthesized using other biotemplates [18-20], the electrochemical performance of moss-LVP was found to be comparable at 1C, but was significantly poorer at higher currents presented in Table 5.2.

Table 5.2 A comparison of the electrochemical performance of moss-LVP with LVP prepared using other templates in the literature.

Bio-templates reported	1 st discharge capacities at the various current densities/mAh g ⁻¹		
	1C	5C	10C
Moss-LVP	104	80	55
Elastin-LVP^a	129	121	112
Yeast-LVP^b	112	100	-
Tea-LVP+oxalic acid^c	131	121	110
^a Y. Zhou <i>et al.</i> , "Biochemistry-Enabled 3D Foams for Ultrafast Battery Cathodes," <i>ACS Nano</i> , vol. 9, no. 4, pp. 4628-4635, 2015/04/28 2015. ^b X. Du <i>et al.</i> , "Enhancing the electrochemical performance of lithium ion batteries using mesoporous Li ₃ V ₂ (PO ₄) ₃ /C microspheres," <i>Journal of materials chemistry</i> , vol. 22, no. 13, pp. 5960-5969, 2012. ^c C. Wei <i>et al.</i> , "Synthesis of biocarbon coated Li ₃ V ₂ (PO ₄) ₃ /C cathode material for lithium ion batteries using recycled tea," <i>RSC Advances</i> , 10.1039/C4RA15592K vol. 5, no. 36, pp. 28662-28669, 2015			

One possible explanation for the poor electrochemical performance could be the intrinsically low carbon content in moss-LVP (i.e., 1.44%). There were no detectable carbon coatings on the LVP particles (Figure 5.3e); the carbon layer on the LVP particles was found to be necessary for superior electrochemical performance [18].

To see if an improvement of the overall electrochemical properties for moss-LVP could be achieved, an addition carbon source was introduced during the synthesis process. Oxalic acid is a carbon source which is widely used and serves to reduce and chelate metals. It is commonly used to enhance the electron conductivity of LVP nanomaterials. By utilizing

the identical synthesis conditions for the preparation of moss-LVP, 1.68 M of oxalic acid in 2:1 w/w ratio of OA:V was added to the LVP precursor solution [20].

Figure 5.6a shows the XRD results of moss-LVP with and without the addition of oxalic acid. There were no significant differences for both XRD spectra, suggesting that addition of oxalic acid did not affect the formation and crystallinity of LVP. However, FESEM images of moss-LVP containing oxalic acid shows a largely collapsed macrostructure (Figure 5.6b), where the LVP particles were also seen to be severely agglomerated (Figure 5.6c).

When the electrochemical properties of moss-LVP containing oxalic acid was evaluated, a modest increase in the discharge capacity was observed. At 10C, a discharge capacity of 60 mAh g⁻¹ was achieved and maintained for up to 12 cycles. In comparison, the discharge capacity of moss-LVP was found to decrease drastically after the 8th cycle.

Despite an improvement in the electrochemical performance of moss-LVP due to the addition of oxalic acid, the overall electrochemical properties of moss-LVP could still be further improved.

Figure 5.6 Effect of oxalic acid on moss-LVP. (a) XRD spectra of moss-LVP with and without oxalic acid (OA). (b) FESEM and (c) TEM images of moss-LVP containing oxalic acid. (d) Discharge capacities of moss-LVP with oxalic acid (circles) and without oxalic acid (squares) for 12 cycles at 10 C in 3.0 – 4.3 V.

5.6 Investigation of the working mechanism of Moss to synthesize LVP

To provide a working mechanism for the formation of moss-LVP, moss was subjected to different treatments before annealing and surface was analyzed using FTIR presented in Figure 5.7a. Untreated moss was used as a control in this study. In the untreated moss control (labeled Moss in Figure 5.7a), the FTIR spectrum contained signature peaks of hydroxyl groups (O-H stretching) and a distinct region of carbonyl groups (C=O stretching) [21]. These bands are consistent with the known characteristics of high fatty acid content of moss as a plant [22, 23].

When ammonium metavanadate (NH_4VO_3) was added to moss (labeled as Moss- NH_4VO_3 in Figure 5.7a), the FTIR spectrum was observed to consist of intrinsic ammonium metavanadate peaks only. Specifically, the characteristic V=O band at 913 cm^{-1} , the NH_4^+ deformation at 1413 cm^{-1} as well as the bands of N-H stretching at 3193 cm^{-1} were observed [24]. No sharp bands of a higher frequency above the inherent vibration at 913 cm^{-1} due to the change in the coordination of vanadium ions could be observed [24]. Hence, it was concluded that ammonium metavanadate did not interact with moss. This result was largely expected since the moss surface and VO_3^- are both negatively-charged.

When lithium dihydrogen phosphate (LiH_2PO_4) was added to moss (labeled Moss- LiH_2PO_4 in Figure 5.7a), four distinct peaks of deprotonated phosphate (H_2PO_4^-) at 1146 cm^{-1} , 1041 cm^{-1} , 940 cm^{-1} , 870 cm^{-1} were observed. There was also a slight shift in the first two peaks corresponding to the bending vibrations of H_2PO_4 (1160 cm^{-1} and 1074 cm^{-1}) [25]. A slight shift of the O-H stretching vibration was also observed, indicating possible metal-carboxylate interaction with the presence of Li^+ . The bands at 1438 cm^{-1} and 1361 cm^{-1} suggested stretching of COO^- group [26, 27]. Taken together, the FTIR data suggests that moss has interacted with lithium ions by undergoing deprotonation of carboxyl groups in the presence of LiH_2PO_4 .

Figure 5.7 (a) FTIR of various moss samples: untreated moss (Moss), moss treated with NH₄VO₃ (Moss-NH₄VO₃), moss treated with LiH₂PO₄ (Moss-LiH₂PO₄) and moss treated with both NH₄VO₃ and LiH₂PO₄ (Moss-LVP). (b) A proposed working mechanism for the formation of Moss-LVP.

Finally, in the presence of both precursors of NH_4VO_3 and LiH_2PO_4 (labeled Moss-LVP in Figure 5.7a), V-O-V band was found to have shifted to 952 cm^{-1} , indicating a likely coordination of vanadium(V) ions with the presence of Li^+ ions via electrostatic interactions [24]. The P-O band of a singular vibration at 1069 cm^{-1} was attributed to the presence of PO_4^{3-} . A strong peak at 1405 cm^{-1} represents the bending vibration of O-H of the $-\text{COOH}$ group. Also the broad and large band due to O-H stretching was found to have shifted slightly to lower wavenumbers, while the C=O band region showed weaker and multiple bands.

Based on the FTIR data, the formation mechanism by which LVP is recruited to the surface of moss was proposed (Figure 5.7b). Here, Li^+ ions were first recruited by the negatively charged surface of moss via electrostatic interactions. The collective adsorption of the Li^+ cations then further facilitated the assembly of VO_3^- and H_2PO_4^- ions onto the surface. The lyophilisation step before annealing retained the physical porous structure of moss which could have aided to eventually yield LVP particles.

5.7 Summary

In this chapter, a green and sustainable approach was developed for the preparation of lithium vanadium phosphates. By systematically examining the effect of the experimental parameters on the formation of LVP, a biotemplating strategy was optimized to produce highly crystalline LVP dispersed within a 3D hierarchical macroporous network. When the as-annealed moss-LVP was evaluated as cathodes in lithium-ion batteries, good rate cycling stability and electrochemical performances were obtained and were comparable to those reported in the literature. The superior electrochemical properties were suggested to be accredited to the well-crystallized LVP nanoparticles presented within a mesoporous 3D carbon network. The FTIR analysis confirmed that the negatively-charged surface of moss was critical for the molecular recruitment of LVP precursors. The close proximity of LVP ions was also necessary for the subsequent nucleation of LVP during the annealing process. These findings demonstrate that plant-based biotemplates can indeed be used to prepare nanomaterials beyond simple chemistries.

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Chapter 6

Biotemplating of lithium nickel manganese oxide (LNMO)

In this chapter, the biotemplating approach from the previous chapter with the understanding of working mechanism, was extended for the preparation of Lithium Nickel Manganese Oxide (LNMO) which is another important class of cathode materials used in lithium-ion batteries. Here, material characterization of the morphology and crystal structures were carried out and electrochemical properties of the as-annealed LNMO were evaluated.

6.1 Introduction

In the previous chapter, it was demonstrated that LVP could be synthesized using moss plants via a biotemplating approach. In this chapter, the same approach was extended to prepare lithium nickel manganese oxides (LNMO), a class of manganese oxides currently investigated heavily as the next-generation cathode materials.

Manganese-based oxides are predominantly attractive as cathode materials given their low cost and non-toxic characteristics. In particular, the spinel structure of LiMn_2O_4 provides a three-dimensional environment favorable for the intercalation for lithium-ion diffusion. However, these materials suffer from poor cycling behavior at elevated temperatures [1]. To overcome this limitation, Mn is often replaced with other transition metals. Of which, nickel has been identified to be the most promising [2].

In particular, spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) has one of the highest operating voltages and can achieve up to 4.7 V (vs Li/Li^+) compared to other transition metal doped oxides. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also has a high theoretical capacity at 147 mAhg^{-1} , while maintaining other advantages such as low cost and are safer compared to commercial NMC (LiNiMnCoO_2) and NCA (LiNiCoAlO_2) [3, 4]. A disordered stoichiometric spinel ($Fd3m$) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is more favourable than the ordered stoichiometric spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($P4_332$) presenting better electrochemical performance, and distinguished by a difference in the voltage plateau in a small step around 4 V representing the $\text{Mn}^{3+/4+}$ redox couple [5].

The main challenge associated with this spinel material is that the redox reaction ($\text{Ni}^{\text{III}}/\text{Ni}^{\text{IV}}$) is close to the potential where the conventional battery electrolyte (1.0 M LiPF_6 in EC/DMC) decomposes. It is also difficult to prepare pure spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ without contamination of a secondary phase such as lithium nickel oxide [6]. From the reported studies thus far, a pure crystalline $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ synthesized using a single annealing step is thought to be challenging. Nonetheless, in this chapter, an attempt to prepare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) using moss via the biotemplating approach was reported.

6.2 Optimization of LNMO synthesis parameters

Similar to the work in chapter 5, parameters used in the synthesis of LNMO were first optimized to prepare a pure, crystalline phase of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In particular, the annealing temperatures and durations in air as well as the concentration of the precursors were varied. Table 6.1 is the list of the as-synthesized LNMO samples prepared under different conditions.

Table 6.1 A list of the as-synthesized LNMO samples #1- #7 prepared under different conditions

LNMO Sample #	Li acetate conc	Ni acetate conc	Mn acetate conc	Annealing Temperature	Annealing duration
1	0.2 M	0.1 M	0.3 M	700°C	5h
2	0.2 M	0.1 M	0.3 M	800°C	5h
3	0.2 M	0.1 M	0.3 M	900°C	5h
4	0.2 M	0.1 M	0.3 M	700°C	1h
5	0.2 M	0.1 M	0.3 M	700°C	5h
6	0.2 M	0.1 M	0.3 M	700°C	10h
7	0.1 M	0.05 M	0.15 M	700°C	1h

In the initial efforts to prepare LNMO, the treated moss samples were annealed in argon. However, contaminating compounds such as Manganese Oxide and Lithium Nickel Oxide (e.g., $\text{Li}_{0.5}\text{Ni}_{1.25}\text{Mn}_{1.25}\text{O}_4$ and $\text{Li}_{0.4}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$) were commonly observed. Instead, when the samples were annealed in air atmosphere, the purities of LNMO was found to have improved. The introduction of the lid to the crucible limits the oxidation during annealing in air, and also contributed to a more consistent and more pure as-synthesized LNMO samples.

Next, the samples were subjected to different annealing temperatures to identify the optimal temperature for LNMO formation. Figure 6.1a shows the XRD spectra for the LNMO samples #1 – 3, all of which corresponded to the characteristic spectrum for LNMO

(JCPDF no 01-080-2162). With increasing temperatures, the intensities of the characteristic LNMO peaks were also increased, indicating higher crystallinity of the LNMO phase. However, there were still smaller peaks which are not characteristic of LNMO, indicating impurity phases for these samples. At the highest annealing temperature of 900 °C, larger particle sizes were observed (Figure 6.2a). In favor of smaller LNMO particles, the lowest annealing temperature of 700 °C was selected.

Figure 6.1 The effects of the reaction parameters on the LNMO samples as mentioned in Table 6.1. (a) Annealing temperature, (b) Annealing duration, (c) Concentration of precursors.

To see if the particle growth could be reduced further, the annealing duration at 700 °C

was also optimized. LNMO samples #4 - #6 were prepared with different annealing durations ranging from 1, 5 and 10 hours. As shown in Figure 6.1b, there were no significant differences in purities and crystallinities of the LNMO in the three samples. All three samples also yielded similar sizes of LNMO nanoparticles of ~100nm (Figure 6.2b).

Figure 6.2 SEM images for the as-synthesized LNMO samples mentioned in Table 6.1 as according to the effects of the reaction parameters (a) Annealing temperature, (b) Annealing duration and (c) Concentration of precursors.

Next, the effect of precursor concentrations on the purity of LNMO crystalline phase was examined. At a lower concentration of lithium acetate (0.1M), nickel acetate (0.05M) and manganese acetate (0.15M) (refer to LNMO sample #7), a pure phase of crystalline LNMO could be obtained without any smaller secondary peaks indicating impurity (Figure 6.1c and Figure 6.2c). Based on the optimization results, LNMO sample #7 was selected for further evaluation. From here on, LNMO sample #7 is referred as Moss-LNMO.

Moss-LNMO was visualized using field-emission scanning electron microscopy (FESEM) as shown in Figures 6.3a and b, where uniform LNMO nanoparticles of ~50 nm were

observed. TEM images of Moss-LNMO also confirmed that the LNMO particles were indeed crystalline. The lattice spacing was measured to be 0.403 nm, which coincided with (002) plane of the cubic spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (see Figures 6.3c and d) [7]. The TEM observation was also consistent with the XRD data, where peaks of well-crystallized $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (JCPDF no.01-080-2162) could be clearly observed in Figure 6.4a. The strong and sharp intensities of the diffraction peaks with no detectable impurity phases, suggested that a pure crystalline $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was obtained successfully. The Brunauer-Emmett-Teller (BET) data of Moss-LNMO is shown in Figure 6.4b where the specific surface area of Moss-LVP was found to be $9.32 \text{ m}^2\text{g}^{-1}$. There were also mesopores of ~ 20 nm present in Moss-LNMO.

Figure 6.3 SEM (a - b) and TEM (c - d) images of Moss-LNMO of crystallized nanoparticles.

Figure 6.4 Material characterization of Moss-LNMO with (a) XRD diffraction pattern of a pure crystalline phase of LNMO and reference pattern JCPDS# 01-080-2162, (b) BET porosity measurements which gives a surface area of $9.32 \text{ m}^2\text{g}^{-1}$ (left), and presence of mesoporous of predominantly 20 nm was observed in the pore size distribution (right).

6.3 Evaluation of the electrochemical performance of Moss-LNMO

The as-annealed Moss-LNMO were evaluated as cathodes in lithium-ion batteries. Moss-LNMO was evaluated with 1C equating to the current density of 147 mAhg^{-1} which is the theoretical capacity for the voltage range of 3.5 – 5.0 V. The capacity contribution from the carbon is negligible in the voltage 3.5 – 5.0 V, and hence only the mass of active material is included in the calculation of the specific capacities.

The initial charge and discharge capacities were found to be 147 mAhg^{-1} and 120.4 mAhg^{-1} respectively in Figure 6.5a. This corresponded to the first columbic efficiency of 82%. An irreversible capacity loss after the first discharge was noted, likely due to the decomposition of the electrolyte to form SEI layers. The dominant plateau at about 4.7 V and a minor plateau at about 4.0 V in the discharge cycle represents the Ni phase transition and the Mn phase transition in $\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_4$ respectively. This minor plateau at about 4.0V substantiated the successful synthesis of the favourable non-stoichiometric disordered spinel crystal structure ($Fd3m$) [5]. A discharge capacity of 100 mAhg^{-1} after 100 cycles at 1C were still obtained in Figure 6.5b, demonstrating good charging stability by retaining 83% of its initial discharge capacity. The rate cycling performance of moss-LNMO was also evaluated and presented in Figure 6.5c. A discharge capacity of at least 100 mAhg^{-1} for currents of up to 5C was still obtained. Although a reduction of discharge capacity at higher current densities was observed, recovery of its initial discharge capacity at 1C was still retained. The high-rate capacity and good cycling performance of Moss-LNMO could be attributed to the well-crystallized nano-sized particles.

As seen in Table 6.2, the electrochemical performance of Moss-LNMO was found to be superior to the solid-state and conventional co-precipitation synthesis methods of LNMO [8]. But for the hollow nanostructures synthesized by the precipitation method [9], it has better discharge capacities than Moss-LNMO at the higher current densities. The superior electrochemical performance of Moss-LNMO compared to the conventional synthesis methods was attributed to the three-dimensional interconnected network of hierarchical porous structures, which served as an ideal template to synthesize pure crystalline of less than 100 nm uniform particles of the favourable non-stoichiometric disordered $Fd3m$ spinel crystal structure of $\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_{4-\delta}$ cathode material.

Figure 6.5 Electrochemical performance of Moss-LNMO. (a) Initial charge-discharge cycle at 1C between 3.5-5.0 V, (b) Cycling performance of 100 cycles at 1C, (c) Rate performance at various current densities (1C-2C-3C-4C-5C-10C-1C).

Table 6.2 Comparison of the electrochemical performances of LNMO prepared in this work as well as by various methods.

Synthesis method and nanostructure type	1 st discharge capacities at the various current densities / mAhg ⁻¹		
	1C	5C	10C
Moss-LNMO	120	100	50
Solid-state LNMO ^a	100	60	40
Conventional Coprecipitation LNMO ^a	106	75	55
Hollow LNMO ^c	118	115	111.5
^a C. Yin, H. Zhou, Z. Yang, and J. Li, "Synthesis and Electrochemical Properties of LiNi _{0.5} Mn _{1.5} O ₄ for Li-Ion Batteries by the Metal–Organic Framework Method," <i>ACS applied materials & interfaces</i> , vol. 10, no. 16, pp. 13625-13634, 2018. ^b L. Zhou, D. Zhao, and X. Lou, "LiNi _{0.5} Mn _{1.5} O ₄ Hollow Structures as High-Performance Cathodes for Lithium-Ion Batteries," <i>Angewandte Chemie International Edition</i> , vol. 51, no. 1, pp. 239-241, 2012.			

6.4 Formation mechanism of Moss-LNMO

Based on the FTIR data as discussed in section 5.7, the surface of moss was found to be highly negatively-charged due to its high fatty acid content. In the presence of LMNO precursors, the positively-charged cations were readily recruited onto the moss surface. Given careful control of the precursor concentrations and their relative ratios, LNMO crystals could be readily nucleated via a self-assembly mechanism.

In order to stabilize the oxidation of the LNMO, a lid was introduced to the crucible which was necessary to limit the amount of oxygen surrounding the material during annealing, and to allow time for Mn³⁺ to be oxidized to Mn⁴⁺ [10]. Without the use of a closed crucible, a pure phase of LNMO could be harder to be obtained.

6.5 Summary

In this chapter, synthesis of the non-stoichiometric disordered cubic spinel ($Fd3m$) of $\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_{4-\delta}$ using moss was successfully demonstrated. By extending a facile biotemplating approach, well-crystallized and pure LNMO particles of less than 100 nm in size could be readily prepared. The LNMO particles were well-dispersed within a 3D interconnected, hierarchical carbon structure conferred by the moss template.

The electrochemical performance of Moss-LNMO was also found to be comparable to other reports of LNMO prepared by solid-state and conventional co-precipitation methods. The moss-LNMO reported in this work had an initial discharge capacity of 120.4 mAhg^{-1} , 100 mAhg^{-1} and 50 mAhg^{-1} at the various current densities of 1C, 5C and 10C respectively. A discharge capacity of 100 mAhg^{-1} after 100 cycles at 1C could still be achieved; the high-rate capacity and good cycling performance of Moss-LNMO could be attributed to the well-crystallized and uniform nanosized particles, as well as the large surface areas provided by the 3D hierarchical carbon framework.

Given the known negatively-charged nature surface of moss, it was likely that the cations were recruited onto the template surface via electrostatic interactions. However, careful control of the precursor oxidation during annealing was critical to obtain the correct cubic spinel phase of $\text{LiNi}_{0.5}\text{M}_{1.5}\text{O}_4$. In conclusion, biotemplating have been shown to be a promising strategy to synthesis of inorganic oxides with complex stoichiometric compositions.

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Chapter 7

Conclusions and future work

This study was focused on the design and development of a green and sustainable approach for nanomaterial synthesis. In particular, a readily abundant botanical template (i.e., moss) was identified. The unique hierarchical porous structure and functional surface chemistry were found to influence the recruitment of metallic precursors. Using a biotemplating strategy, new avenues to synthesize nanomaterials of a more complex stoichiometric compositions was investigated. These findings demonstrate the feasibility of using moss to prepare lithium vanadium phosphate (LVP) and lithium nickel manganese oxides (LNMO). Both nanomaterials demonstrate promising use as cathodes in lithium-ion batteries.

7.1 Conclusions

This thesis work aimed to investigate the hypothesis on whether plant-based templates could be used for the preparation of nanomaterials with complex stoichiometric compositions. The study began by exploring various botanical matters which are abundantly available in nature.

Selected plant species were used for the preparation of iron oxide, and the physical and electrochemical properties of the as-annealed products were evaluated. Of which, iron oxides prepared using moss was found to be the most promising. The annealed product was found to retain the unique 3D hierarchical porous structure of the parent moss plant. Iron oxide particles were also found to be uniformly dispersed onto the surfaces of the porous network. The electrochemical properties of the iron oxides were also found to be encouraging, although further optimization of the synthesis parameters could be performed to improve the overall performance of the material.

Given the success of the preliminary screening, moss was next used to prepare lithium vanadium phosphate (LVP). Various synthesis parameters were examined to optimize the procedures necessary to yield pure crystalline phases of LVP. Samples prepared under different annealing temperatures and durations as well as various concentrations of the precursor solutions were examined.

Materials were first characterized with X-ray diffraction (XRD) to understand the effect of varying parameters on the purity and crystallinity of the end products. Characterization techniques such as Electron microscopy (FESEM and HRTEM) were used to visualize the overall macrostructure as well as particle morphologies obtained for each sample, and correlated to the changes made in the synthesis parameters. Porosity measurement tabulated by BET method and a thermogravimetric (TGA) analysis were also performed to determine the porosity and residual carbon content in the successful sample. Finally, the as-prepared materials were assembled into half-cells and their electrochemical properties were evaluated as cathodes in lithium-ion batteries.

It was found that LVP-treated moss annealed at 850 °C for 5 h yielded pure LVP with the highest crystallinity (referred as moss-LVP). The electrochemical properties of this sample was also found to be the most promising. Although there was an improvement in the rate cycling stabilities with the addition of oxalic acid, the electronic properties of moss-LVP could be further improved.

Finally, in order to provide a mechanistic understanding of how moss interacted with the metallic precursors, FTIR was performed. It was found that moss was able to recruit the metallic cations via electrostatic interactions using its negatively-charged surface areas. The self-assembled ions further served as a nucleating center for subsequent growth of LVP nanoparticles.

It was shown that moss plants could be used to successfully synthesize lithium vanadium phosphate. A similar biotemplating approach was extended to prepare another class of cathode materials, lithium nickel manganese oxide (LNMO). The key synthesis parameters were examined to optimize the process necessary to yield pure, crystalline phases of cubic spinel (*Fd3m*) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$. It was found that annealing treated moss in air at 700 °C in 1 hour successfully yielded LNMO without observing any contaminating phases. A covered crucible was also found to be critical in limiting the oxygen flow and to ensure complete oxidation of Mn^{3+} to Mn^{4+} . The electrochemical properties of the LNMO prepared in this work was also found to be superior, and comparable to other LNMO reported in the literature. The working mechanism for the recruitment of LNMO precursors onto the surface of moss was also discussed.

In summary, the thesis addressed the hypothesis, and successfully demonstrated the feasibility of using plant-based templates to prepare nanomaterials with complex stoichiometry. In the process, a simple yet general approach for nanomaterial synthesis was developed, which could be readily applicable for the preparation of a variety of inorganic materials. Taken together, findings of this thesis shed insights on the role of synthesis parameters in the formation of LVP and LMNO, as well as provide a mechanistic

understanding of the molecular assembly of metallic precursors on the moss surface. The biotemplating approach used in this work can be readily extended to prepare a variety of nanomaterials not limited to simple stoichiometry for a spectrum of engineering applications.

7.2 Future work

It will be meaningful to conduct full cell studies of the cathode materials synthesized in this study (Moss-LVP and Moss-LNMO) with a commercial anode such as Lithium Titanium Oxide (LTO) or Moss-iron oxide, to evaluate the feasibility of incorporating this the as-annealed materials in lithium-ion batteries. The full cell battery performance however, may require the optimization of the cathodes, which can be enhanced with a systematic study of different carbon sources to initiate carbon coating or introduce other transition metals as dopants [1-4].

The synthesis strategy developed in this work is simple, yet generalized. Hence, it is also possible to further extend the biotemplating approach to prepare nanomaterials for other engineering applications. For example, other materials with complex stoichiometric nanomaterial such as NiCo_2S_4 could also be prepared for applications as electrocatalysts in water-splitting and supercapacitors [5, 6]. Likewise, given the high water absorption ability of moss, one can also explore using the material as a form of bioremediation. On one hand, the moss plant could be used to absorb toxic metallic ions from waste, while converting the metallic ions into useful nanomaterials such as oxides and phosphates.

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Appendix

Figure A.1 The moss species examined in this study – *Leucobryum glaucum*, which is also generally regarded as cushion moss or white moss. *Copyright 2003, J.K. Lindsey [1]*

Figure A.2 Fern grass examined in the exploration of botanical templates in chapter 4.

Figure A.3 *Sedum x Rubrotinctum* was examined in the exploration of botanical templates in chapter 4.

Figure A.4 *Rotala rotundifolia* was examined in the exploration of botanical templates in chapter 4. Copyright 2019, Springer Nature [2]

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