Growth of vanadium oxides nanostructures by chemical vapour deposition

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**GROWTH OF VANADIUM OXIDES
NANOSTRUCTURES BY CHEMICAL VAPOUR
DEPOSITION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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Abstract

Among the transition metal oxides, vanadium oxide (V_2O_5) has attracted attention in various industrial applications such as electrochromic, optical switching and energy storage devices [1]. However, the commercial application of V_2O_5 in energy storage devices is limited due to its poor cycling stability, Li ion diffusion and electric conductivity. Two-dimensional (2-D) nanostructures have demonstrated better stability, more active sites for lithium insertion/deinsertion than zero-dimensional and one-dimensional (1-D) structure, making them attractive in energy storage devices [2]. The formation of V_2O_5 nanosheets have been challenging because V_2O_5 tends to grow into 1-D structure because of its preference to grow in [010] direction. Although several works have been done on the formation of nanosheets, the synthesis requires long duration (~12-48 hours) [3].

This thesis investigates the growth of 2-D V_2O_5 nanostructures arrays on various current collectors such as aluminium, nickel and stainless steel using chemical vapour deposition process. This includes various approaches to form 2-D V_2O_5 nanostructures arrays on current collectors, namely self-growing and self/wet-etching.

Aluminium foil was wet etched to create a 2-D hierarchical current collector using lithium hydroxide alkaline solution. Al foil etched with 0.15 M LiOH solution shown larger amount of nanosheets and etched surface area among various concentrations tested. V_2O_5 thin film grown on etched Al foil has an average particle size of ~205, ~121, ~70 and ~24 nm when placed with a substrate distance of 7, 10, 13, 25 cm away from the center of the tube furnace. The growth of the nanoparticles thin film follows the island growth mechanism where the adatom adsorbed on the nuclei. Supercapacitor measurements were made suggests that V_2O_5 on hierarchical Al perform better with C_s of ~289 F g⁻¹ and retention of ~91% and V_2O_5 on untreated Al foil with C_s of ~152 F g⁻¹ and retention of ~76% after 1000 cycles at a rate of 5 A g⁻¹ in 1 M LiClO₄ in PC. The capacitance of the electrode is also dependent on the thickness or mass loading of the film. By increasing the amount of V_2O_5 deposition, the C_s is reduced from ~295 to ~189 F g⁻¹.

Catalyst-free growth of nanowires and nanosheets were synthesized directly on Ni foam. V_2O_5 nanowire averages a diameter of ~ 126 nm and a few micrometers in length. The growth is suggested to follow the vapour-solid growth and the formation is due to the anisotropic growth as [010] is the fastest growth direction. Interconnected V_2O_5 nanosheet arrays on Ni foam have an average diameter of ~ 13.5 μm and thickness of ~ 198 nm. The growth of nanosheets arrays on Ni foam is due to the high substrate temperature which leads to fast diffusion of adatoms and crystal growth rate, and allows side deposition, forming the nanosheets structure. V_2O_5 nanosheets on Ni foam perform better with C_s of ~ 1081 F g^{-1} and retention of $\sim 96\%$ and V_2O_5 nanowire on Ni foam with C_s of ~ 833 F g^{-1} and retention of $\sim 75\%$ after 1000 cycles at a rate of 2 A g^{-1} using 2 M KOH .

Vanadium deposition on stainless steel foils results in the formation of amorphous iron vanadate (FeVO_4) nanosheets arrays. The width and thickness of nanosheets are $\sim 100 - 500$ nm and $10 - 40$ nm, respectively. The growth of the FeVO_4 thin film initiates from the oxidation of stainless steel foil forming Fe_2O_3 on the surface and interacting with the vanadium precursor. Annealing the sample to improve crystallinity in Ar atmosphere leads to the collapse of nanosheet arrays and evaporation of vanadium from the as-grown film. The electrochemical property of the as-grown film achieved an initial discharge capacity of 1693 mAh g^{-1} on the initial cycle at a rate of 0.2 A g^{-1} (0.15 C). The Coulombic efficiency is $\sim 73\%$ for the first cycle and shows a reversible capacity of 1237 mAh g^{-1} after 100 cycles.

The formation of two-dimensional nanosheets arrays on various current collectors have shown good performance and improved cyclic stability. Various morphologies such as nanoparticles thin film and nanowires were also synthesized, demonstrating the flexibility of chemical vapour deposition process.

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Chapter 1 : Introduction

1.1 Background and motivation

Among the transition metal oxides, vanadium oxide (V_2O_5) has attracted attention in various industrial applications such as electrochromic, optical switching and energy storage devices [1]. In particular, nanostructured V_2O_5 has shown improvement in performance as compared to their bulk counterpart [4, 5]. For example, two-dimensional (2-D) structures show better structural stability and larger surface area for sufficient electrolyte contact [2]. It is also reported to show better cyclic performance than nanoparticles and rod-like nanoclusters for the application of Li-ion batteries [6]. However, the formation of V_2O_5 nanosheets have been challenging because V_2O_5 tends to grow into 1-D (one-dimensional) structure because of its preference to grow in [010] direction and also slower growth rates at [001] direction due to its weaker bonding [7].

Vanadium oxide has a large theoretical capacity of $\sim 294 \text{ mAh g}^{-1}$ when operating in a voltage range of 4.0 – 2.0 V vs Li/Li^+ . It has been studied as cathode materials for ~ 40 years due to its low cost ($\sim \$12/\text{kg}$), abundance (in earth crust) and a variety of oxidation states (V^{2+} - V^{5+}) [8, 9]. The layered structure of V_2O_5 makes it an attractive material for intercalation of electron-donating cations. For example, lithium ions are able to intercalate reversibly without any major structural change to the crystal structure of the material. However, the commercial application of V_2O_5 is limited by its poor cycling stability as a cathode material due to its poor Li ion diffusion ($\sim 10^{-12} \text{ cm}^2 \text{ s}^{-1}$), low electrical conductivity ($10^{-3} - 10^{-6} \text{ S cm}^{-1}$) and irreversible phase transformation upon high discharge voltage [10, 11]. In order to improve the performance of V_2O_5 , nanostructured electrodes allow shorter Li ion diffusion length and the morphology of the structure can be maintained during cycling [8]. For example, an improved intrinsic conductivity of $0.8 - 3.4 \text{ S cm}^{-1}$ for V_2O_5 nanoribbons as compared to bulk V_2O_5 crystal of 0.02 S cm^{-1} when tested using four-probe measurements [7]. The diffusion length (L) of Li ion will improve when the radius of the particle (r) is reduced since $L = \sqrt{D\tau} \geq r$, where D and τ are diffusion coefficient and time, respectively [12].

Vanadium oxide is not only studied in batteries, but also in electrochromics and supercapacitors [4, 13]. Furthermore, V_2O_5 has also been studied in supercapacitors using aqueous and organic electrolytes. For example, amorphous V_2O_5 shows ideal capacitor behavior with a capacitance of 346.4 F g^{-1} in 2 M KCl aqueous electrolyte between 0.0 and +0.8 V [14]. V_2O_5 aerogels on Hastelloy felt substrate was able to achieve specific energy density of $5 - 10 \text{ W kg}^{-1}$ in LiClO_4 in propylene carbonate organic electrolyte between 2 – 4 V [15]. However, the preparation technique of pasting a slurry mixture that consists of active nanomaterials, conductive acetylene black and a polymeric binder decreases the capacitance and energy density owing to the additional weight caused by the additives. Through 2-D nanostructuring, the capacitance and energy density would improve as more active materials would be exposed to the electrolyte and reduce the reliance of additives. For example, the capacitance of V_2O_5 deposited on AAO template can be increased to 871 F g^{-1} in 1 M KCl aqueous electrolyte [16].

To integrate nanostructuring as active materials, proper structuring to assemble active materials into three dimensional (3-D) networks on the current collector is required. Figure 1-1 shows a typical configuration of a 3-D self-supported nanoarchitected array.

Figure 1-1: Schematic of a three dimensional self-supported nanostructured array on current collector [17].

The design of the 3-D structure can result in a higher energy density due to larger surface area, stable and ordered structure to buffer any volume change during Li

insertion/deinsertion and provide direct electron/charge transport between active materials and current collector. Since the active materials are directly connected to the substrate, there is no reliance on any binder or conductive agents.

The fabrication strategies to form nanoarchitected arrays include self-growing, wet-etching and template-based growth. Self-growing strategy is the growth of nanostructured materials onto the current collector through a growth process like vapour phase or hydro/solvothermal growth. Figure 1-2a shows an example of how nanowires are grown directly to the substrate. For instance, silicon or tin oxide nanowires can be grown directly on stainless steel (SS) substrates through the use of gold catalyst [18, 19].

Figure 1-2: Schematic of the fabrication techniques of (a) self-growing, (b) self-etching and (c) template-based growth [17].

Self-etching strategy involves creating nanostructured arrays by corroding conductive substrates through the process of chemical or electrochemical reaction. Figure 1-2b shows the process of the formation of nanostructured arrays by corroding the substrate. In this example, copper substrates were etched in an alkaline solution that forms CuO nanoribbons array [20].

Figure 1-2c illustrates the process of template-based growth strategy. A template, usually AAO, is utilized to deposit materials into the pores. For example, copper

nanopillars were grown on Cu foil by electrochemical deposition using AAO as the membrane. The AAO is then removed by alkaline solution after the deposition of Cu [21]. Compared to the other two techniques, template-based growth requires complicated synthesis steps and is less likely to be scalable. Table 1-1 summarizes the fabrication strategies for the formation of nanoarchitected arrays.

Table 1-1: Comparison of the different fabrication strategies for the formation of nanoarchitected arrays [17].

Techniques	Growth method	Remark
1. Self-growing	<ul style="list-style-type: none"> • Vapour phase growth • Hydro/solvothermal growth 	<ul style="list-style-type: none"> • High temperature or high pressure
2. Self-etching	<ul style="list-style-type: none"> • Solution-based corrosion • Vapour-phase corrosion 	<ul style="list-style-type: none"> • Simple, low cost and broadly applicable
3. Template-based growth	<ul style="list-style-type: none"> • Electrodeposition • Vapour phase growth 	<ul style="list-style-type: none"> • Sacrificial template needed

For the growth of nanostructured arrays, different deposition techniques have been employed to deposit materials on the substrates. The comparison listed in Table 1-2 are the few common techniques used for energy storage application and step-conformal deposition [22]. Sol-gel deposition is the formation of gel through the evaporation of solvent by the reaction of metal alkoxide precursor. This coating technique could be used in spray, dip or spin coating. However, this technique is always inconsistent due to the formation of gas bubbles which can result in uneven wetting on the substrates. Furthermore, the purity of the product is low due to the added additives to create the sol. Electrochemical deposition is the application of potential between counter electrode and the conductive substrate. Although good step coverage and quantity of materials deposited can be achieved, it is critical to have both the substrates and the materials deposited to be conductive. For physical vapour deposition, it involves the evaporation of the source

materials through resistive heating and the vapour of material is deposited on the substrate. Due to the high energy sputtering (e.g. in pulsed vapour deposition) involved, the surface of the substrate and the deposited materials might be damaged. Furthermore, reactive gases (e.g. oxygen or nitrogen) in the gas phase can be introduced together with the deposited materials.

Atomic layer deposition (ALD) is the growth of materials through cyclic deposition. The major advantage of ALD is its good step coverage needed in substrates of good high-aspect ratio deposition. However, the deposition rate is very slow at 0.05 nm per cycle and inclusive of dosing and purging between each step.

Based on the comparisons and discussion, chemical vapour deposition (CVD) technique is chosen to grow vanadium oxides nanostructures in this project. CVD has demonstrated to grow various metal oxides for energy storage application. Also, CVD utilizes low kinetic energy particles for the deposition of 3-D structures.

Table 1-2: Comparison of different deposition techniques for the applications of energy storage [22].

Techniques	Advantages	Disadvantages
1. Sol-gel deposition	<ul style="list-style-type: none"> • Low cost • Well controlled metal oxide stoichiometric ratio 	<ul style="list-style-type: none"> • Poor purity from added additives • Uneven wetting on substrates due to gas bubbles formation in sol-gel
2. Electrochemical deposition	<ul style="list-style-type: none"> • Well controlled deposition • Well step coverage 	<ul style="list-style-type: none"> • Substrates used for deposition should be conductive • Material deposited should be conductive
3. Physical vapour deposition	<ul style="list-style-type: none"> • Materials, such as metal oxides, with low vapour pressure can be deposited using laser beams 	<ul style="list-style-type: none"> • Alterations to collecting substrates caused from high energy particles • Atoms in gas phase can be reactive to form oxides or nitrides
4. Chemical vapour deposition	<ul style="list-style-type: none"> • Uniform 3-D deposition 	<ul style="list-style-type: none"> • Requires constant supply of material in gas phase • No Lithium based film has been reported
5. Atomic layer deposition	<ul style="list-style-type: none"> • Good step coverage 	<ul style="list-style-type: none"> • Poor growth deposition rate • Time consuming vacuum purging

1.2 Objectives

The design of the 2-D nanostructures can result in a higher energy density due to larger surface area, stable and ordered structure to buffer any volume change during Li insertion/deinsertion and provide direct electron/charge transport between active materials and current collector. Since the active materials are directly connected to the substrate, there is no reliance on any binder or conductive agents.

The electrochemical properties of nanostructured arrays have shown improved performance due to direct contact of electrode material with the current collector. Also, the cyclic retention and rate capability is enhanced due to sufficient interspaces to relieve strain during intercalation/deintercalation of ions. To improve the contact between material and electrode, various alkaline solutions will be used and explored on aluminium foil. The morphology and etching process will be investigated. To determine the effectiveness of the etched foils, V_2O_5 thin film will be deposited on both etched and untreated Al foil to compare.

2-D nanostructures have better structural stability, more active sites for ions insertion/deinsertion than 0-D and 1-D structure, making them attractive in energy storage devices. The second work will be to create V_2O_5 nanosheets array on nickel foam by CVD. The growth process will be investigated by varying the growth conditions. To examine the performance of V_2O_5 nanosheets array on nickel foam, V_2O_5 nanowires will be grown on nickel foam to compare.

The third work will be to create nanostructured arrays on stainless steel (SS) substrates. The direct deposition of electrode material on SS substrate would eliminate the use of conductive acetylene black and polymeric binder, improving the ion diffusion path and increased the exposed area between electrode material and electrolyte. The growth process will be investigated by varying the growth condition. Electrochemical process of the electrode will be evaluated for Li-ion application.

1.3 Organization of thesis

This thesis comprises a total of 7 chapters. Chapter 1 includes the motivation, objectives and organization of this thesis.

Chapter 2 provides introduction to chemical vapour deposition, energy storage application (specifically lithium ion batteries and supercapacitors) and vanadium oxide. The literature review includes various growth processes of CVD, the history of energy storage application and its storage mechanisms. A brief introduction for V_2O_5 will also be presented.

Chapter 3 includes the experimental procedures of CVD growth of V_2O_5 and V_2O_5 -based compounds. The system setup, growth parameters as well as characterization techniques are listed. Electrochemical measurements and techniques will be presented in this chapter as well.

Chapter 4 illustrates the use of self-etching strategy. Different alkaline solutions were used to etch aluminium foil. The etching process is further studied using different concentration and exposure timing of lithium hydroxide solution. V_2O_5 thin film is then used to grow on the hierarchical Al current collector. The size of the V_2O_5 nanoparticles can be adjusted by varying the substrate distance or the substrate temperature. Electrochemical measurements for the application of supercapacitors were also made to compare V_2O_5 on etched Al foil and on untreated Al foil.

Chapter 5 presents the growth of V_2O_5 using nickel foam. Different conditions are used to grow nanowires, nanosheets and thin film on Ni foam. The growth process follows the vapour-solid mechanism since no catalyst were involved. The morphologies and composition of the samples is studied by varying the flowrate and substrate temperature. Electrochemical measurements for the application of supercapacitors were also made to compare V_2O_5 nanosheets and nanowires on Ni foam.

Chapter 6 presents the work of catalyst-free CVD to grow amorphous iron vanadate on stainless steel substrates. The oxidation of stainless steel foil during the growth process results in the formation of small nanosheets that emerges from the substrate. The

vanadium and oxygen vapour reacts with the oxidized substrate to form FeVO_4 . The morphologies of the samples is also investigated by varying the substrate temperature. Electrochemical evaluation of FeVO_4 nanosheets array was tested for the application of Li-ion batteries.

The last chapter, Chapter 7, summarises the entire project and some recommendations for future work based on the present topic.

Chapter 2 : Literature Review

2.1 Chemical vapour deposition

Catalytic growth of V_2O_5 nanowires have been reported using various catalysts (Cu, Ni or Au) [23]. This can be achieved by coating a very thin layer of metal catalyst on Si substrates. The direct approach of using metal substrates will cater to various applications and allow controlled growth on patterned or unpatterned substrates [24].

2.2.1. Introduction of chemical vapour deposition

Chemical vapour deposition involves the deposition of metal films by heating a metal-containing molecule and growth on a heated substrate [25]. The earliest patent to use CVD was reported in 1893 by depositing tungsten by reducing WCl_6 using hydrogen onto a carbon lamp filament [26]. Since then, CVD has been used in areas such as electronics, protective coating for semiconductors, optoelectronics and so on. CVD is therefore considered a manufacturing technique to deposit materials at micro or nano level. Some examples of CVD technique is discussed as listed below.

(1) As CVD is a non-line-of-sight process, it can deposit materials like Cu on micro-trench with aspect ratio of 10:1. Such feature allows deposition onto deep recesses, holes and other uneven or irregular substrates.

(2) The flexibility of CVD allows different specimens to be used as source materials, from metallic, non-metallic, carbides, nitrides, oxides and sulphides. 70% of the elements in the periodic table are applicable with CVD.

(3) Materials with high sublimation point can be substituted with another compound of lower sublimation temperature. For instance, SiC has a sublimation point of 2973 K.

By substituting with CH_3SiCl_3 and reacting with excessive hydrogen, the temperature can be significantly reduced to 1273 K.

(4) By altering the experimental parameters (e.g. flowrate, substrate temperature, pressure), the morphology or crystal structure of the product can be modified. For example, Ge film or nanowires can be grown by changing the substrate temperature or pressure [27]. Ge crystallinity can also be changed into amorphous or crystalline depending on the pressure and temperature.

(5) CVD does not require high vacuum chamber as compared with technique such as physical vapour deposition.

Although CVD technique has some advantages, some limitations are listed as below.

(1) Some precursors possess high hazards such as flammable, corrosive, toxic or explosive. Some examples like B_2H_6 , $\text{Ni}(\text{CO})_4$ and SiCl_4 . The products of these precursors can be in the form of CO, H_2 or HCl. Further treatment to these byproducts are required which can add up costs to the production.

(2) CVD process is rather complex which requires several test runs to reach suitable growth parameters.

An example of the key steps during chemical vapour deposition is illustrated in Figure 2-1. The sequence of the deposition is described with the following steps. (1) Precursor heats and turns volatile to introduce into the system by transport through gases. (2) The gaseous reactants that are transported adsorb and (3) react on the surface. Any supporting ligand is desorbed (6) and removed from the system (7). The metal atom is then grown into a stable nucleus by (4) surface diffusion and subsequent (5) nucleation. (8) Gas phase reaction may occur, which results in the removal of ligand by heat or reactive gases of during precursor transportation.

Figure 2-1: Schematic process in chemical vapour deposition [25].

2.2.2 Variation of chemical vapour deposition

This section introduces various CVD processes, namely the common configurations such as low pressure CVD, metal-organic CVD and plasma-enhanced CVD.

(1) Low pressure CVD (LPCVD)

LPCVD reactor consists of either glass tubes or quartz tubes connected by metal connections and elastomer O-ring. To reduce the pressure of the system, the system is connected to the exhaust by pump as shown in Figure 2-2. As compared to atmospheric pressure CVD (APCVD), LPCVD provides better deposition uniformity due to the high diffusivity of gases and the lower substrate temperature required. Lowering the pressure extends the surface reaction regime to higher temperatures. If APCVD is used, the deposition will be limited by mass transfer, the rate will decrease from the front to the back of the substrates [28].

Although the uniformity of the product is improved, the product production efficiency is low. Also, deposition may occur on the walls of the chamber.

Figure 2-2: Schematic diagram of the exhaust system used in LPCVD [26].

(2) Metal-organic CVD (MOCVD)

Metal-organic CVD involves the reaction of metal-organic and hydride precursors in the vapour phase by heating. For example, gallium arsenide (GaAs) can be formed by reacting gaseous trimethylgallium ((CH₃)₃Ga) and arsine (AsH₃) [26]. Figure 2-3 shows the MOCVD reactor system for the growth of semiconductor thin films. The advantages of using MOCVD are that it is less sensitive to air/moisture, less dependent on vacuum and can be deposited on low temperature region. One major concern of MOCVD is the selection of precursor. The precursors usually have high thermal stability and high toxicity, especially hydrides (e.g. PH₃, AsH₃). In addition, the carrier gas which consists of ~5% - 95% H₂ gas is flammable.

Figure 2-3: Schematic diagram of a MOCVD setup [26].

(3) Plasma-enhanced CVD (PECVD)

Traditional CVD processes involve the use of heat as the main source of energy to allow precursor reaction to occur. As such, defects could be generated at high substrate temperatures. A typical setup for PECVD setup is illustrated in Figure 2-4. PECVD involves the use plasma, which is a form of electric energy, instead of thermal energy via conventional thermal CVD. Plasma is generated through the electrical discharge in the gas phase to produce chemical active ions and radicals through inelastic scattering. The ions is then deposited on the substrate. Some advantages of PECVD include lower substrate temperature, higher film density and chamber is easier to clean as compared to the other CVD processes. However, the disadvantages are the higher amount of defects on the sample surface due to the bombardment from plasma, pinholes and charges can be created due to the plasma and various forms of species can be generated, making the reaction complex (e.g. SiH₄ gas dissociates into SiH₃, SiH₂, SiH, Si and H).

Figure 2-4: Schematic diagram of a PECVD chamber [26].

2.2.3 Surface reaction rate and rate control steps

The film growth rate can be affected by various parameters, namely substrate temperature, reactor pressure and reactants along the gas phase.

The first influence will be the precursor transportation as in step (1) of Figure 2-1. The precursors are carried by the carrier gas and the flow pattern will determine the rate at which reactants reaches the substrates. The Reynolds number (Re) is a dimensionless parameter used to describe the flow pattern:

$$Re = \frac{QD}{\nu A_c} \quad (\text{Equation 2-1})$$

Where Q is the reactor volume flowrate, D is the tube diameter, ν is the kinematic viscosity and A_c is the cross sectional area of the tube. If the Re number is low, the flow is laminar. If the Re number exceeds to turbulent flow, it will affect the growth rate as well as uniformity.

The uniformity of the substrate can be affected by the boundary layer. The boundary layer thickness can affect step (2) in Figure 2-1. In fluid mechanics, the boundary layer is the formation of a thin fluid film on the substrate due to viscous shear. The boundary layer thickness (δ) is expressed with the following equation:

$$\delta = \frac{5.0}{\sqrt{Re}} x \quad (\text{Equation 2-2})$$

Where x is the distance from the edge of the substrate, Re is the Reynolds number.

Due to the boundary layer thickness, thin film thickness can varied on the substrate. In order to reduce δ , approaches like increase Re or having the substrate to be inclined to minimize the effect of δ .

The deposition rate can mainly affect the thickness of the film. This is particularly important to determine if the deposition happens for diffusion-limited or surface-reaction-limited process. It describes step (4) in Figure 2-1. For surface-reaction-limited process, the film growth rate is dependent with the substrate temperature as shown in the equation below:

$$\text{Growth rate} \propto \exp\left(\frac{E_A}{RT}\right) \quad (\text{Equation 2-3})$$

Where E_A is the activation energy, R is the universal gas constant and T is the temperature. Within the temperature region, the deposition rate increases with substrate temperature. Increasing the temperature higher will proceed to diffusion-limited process where the deposition rate is proportional to $\sim T^{3/2}$. In this region, the temperature dependence is almost a flat line when plotting. This is because the transport rate is almost equivalent to the rate of surface reaction. Further increase in temperature will result in the desorption of reactants before they can be even absorbed on the substrates.

2.2.4 Nanowires growth mechanism

(1) Vapour-liquid-solid (VLS)

VLS growth technique was first introduced by R.S. Wagner in 1964 to grow silicon whiskers by using an impurity metal [29]. Figure 2-5 shows the growth process by VLS

mechanism. (1) A layer of Au catalyst coating is deposited on Si wafer (2) Silane precursor reacts with hydrogen gas to form Si vapour (3) As the eutectic point of Au-Si is low (~ 636 K), Au and Si are able to form solid solution as long as the system is above this temperature (4) Au-Si droplet continues to absorb Si from the vapour and reaches saturation (5) Excess Si is precipitated from the droplet and reaches the liquid-solid interface. As the melting point of Si is higher (~ 1687 K), Si nanowire crystal is formed.

Figure 2-5: Schematic diagram of Si nanowire grown by using Au catalyst and Au-Si phase diagram [30].

The nanowires grow in areas only with Au seed and the diameter of the wire is dependent on the size of the seed. It is also worthwhile to mention that the metal catalyst lowers the activation energy of nucleation. Since the activation energy is lowered, preferred growth occurs there. The growth rates are 100 times faster for nanowire growth in the length direction as compared to the rate of thickness growth. For example, the calculated activation energies for silicon nanowires are 11.9 kcal/mole in the length direction and 15.5 kcal/mole in thickness direction [31].

(2) Self catalytic growth

Oxide-assisted growth (OAG) method uses metal suboxides generated from the source material instead of a foreign material like metal catalyst [30]. For example, Si suboxides, Si_nO_m ($n, m = 1 - 8$) clusters are formed (Figure 2-6) by heating a mixture of Si and SiO_2

powder. The role of Si_nO_m acts as a catalyst and usually in the molten state because surface melting point can be lowered due to the nanosizing effect with reference to bulk of the material. These clusters are highly reactive and prefer to form Si-Si bonds. Si nanowire core is reconstructed by diffusion of O from the center to the surface.

Figure 2-6: Mechanism of Oxide-assisted growth [30].

(3) Vapour-solid (VS)

Vapour-solid growth is a self-catalytic process where the nanowires are grown directly from the vapour. The growth of nanowires would require the initialization of an atomic step. The atomic step would involve defects like screw dislocations or twinning that would assist in the growth continuously. The atomic step allows atoms to nucleate without the need to overcome the energy barrier as screw dislocations are mobile and unstable [32].

2.2.5 Thin film growth mechanism

When nucleation occurs on the surface, the surface energy of a crystal can be affected. This can result in changes in the growth mechanisms and can affect the final film morphology [33].

If the materials are homoepitaxy (A – A), the growing layer and the substrate have the same atomic dimensions and lattice structure. If the growing layer and the substrate are different materials (A – B), the lattice constants and the chemical bonding will be different.

The presence of a foreign material on the substrate can cause changes to the surface stress or strain energy [34]. This can generate different characteristics to the material. For example, GeSi bandgap is reduced when deposited on Si substrate as there is an increase in strain energy on the surface.

As a result of the different stress or strain involved, the wetting of the substrate can be expressed using the following formula where σ refers to the epilayer-vacuum, σ_i refers to the epilayer-substrate and σ_s refers to the substrate-vacuum surface energies.

$$\Delta\sigma = \sigma + \sigma_i - \sigma_s \quad (\text{Equation 2-4})$$

Figure 2-7 shows three models that can be used to illustrate the growth of an adsorbate on the substrate.

Figure 2-7: Three models showing the mechanism of growth. (a) Frank-van der Merwe (FM, layer by layer) (b) Stranski-Krastanov (SK, layer plus island) (c) Volmer-Weber (VW, island formation) [34]

(1) Figure 2-7a shows the layer by layer growth model. In this mechanism, the adsorbate grows as a film on the substrate or a smooth layer is formed. The lattice mismatch between the layers and substrate limits to $< 1.5\%$. As $\Delta\sigma < 0$, the chemical potential or Gibbs free energy is lowered. This scenario indicates that material A is favourable to grow on substrate B as they have a complete wetting effect.

(2) Figure 2-7c shows the three dimensional island growth model. In this mechanism, the adsorbate does not wet on the substrate. The lattice mismatch is very large and the adsorbate-adsorbate interaction is far better than adsorbate-substrate interaction. As $\Delta\sigma > 0$, the chemical potential or Gibbs free energy is higher. Material A is favourable to deposit on the same material as compared to material B so as to minimize the Gibbs free energy.

(3) Figure 2-7b shows the layer and island growth model. In this mechanism, the adsorbate growth in 1 – 4 layers and after which, there is an accumulation in strain and caused materials B to form 3-D islands.

In this section, an introduction and the applications of CVD processes are discussed. The potential benefit of the CVD process is that it allows deposition onto deep recesses, holes and other uneven or irregular substrates. Also, the option to choose various precursor materials highlights the versatility of the CVD process. A brief discussion on the growth mechanisms provides the possible growth morphologies between the growth materials and the substrates.

2.2 Application of binary and tertiary vanadium oxides

The element vanadium was first discovered in 1801 within lead vanadate by a Mexican, Andrs Manuel del Rio, who suggested vanadium as a form of chromium. It was then rediscovered in 1830 by a Swedish, Nils Gabriel Seftstrm who named vanadium after Norse goddess mythology Vanadis which represents beauty and fertility [35]. Primary sources of vanadium come from ores, concentrates, slags and petroleum

residues. Vanadium is the 22nd most abundant element on the Earth's crust, which is more than copper or nickel.

Similar to the various transition elements, vanadium can exist in different valence states from V^{2+} to V^{5+} . Among the various vanadium oxides, only V_2O_5 and V_6O_{13} are intercalated compounds [36]. Also, among the various oxidation states, V_2O_5 has the highest oxidation and is the most stable state. It has an orthorhombic unit cell structure with P_{mmm} space group. The lattice parameters for V_2O_5 are $a = 11.510 \text{ \AA}$, $b = 3.563 \text{ \AA}$ and $c = 4.369 \text{ \AA}$. The tip of the VO_5 pyramid is sequence in an up-up-down-down arrangement [4]. As shown in Figure 2-8, the tip consists of a very short vanadyl bond (VO^{2+}) and the four oxygen lies on the base of the pyramid with distance ranging from 1.78 to 2.02 $\text{\AA}$ [1]. It can also be described as a distorted VO_6 octahedral because the 6th oxygen atom lies on the opposite V – O bond with distance of 2.79 $\text{\AA}$. This particular weak bond gives the opportunity to V_2O_5 being a layered material which can be intercalated with a variety of elements such as Li^+ , Na^+ , Ag^+ , Mg^{2+} , Ca^{2+} , Cu^{2+} , Zn^{2+} , Ba^{2+} and Al^{3+} .

Figure 2-8: Crystal structure of V_2O_5 consisting of VO_5 pyramids that shares edges and corners [1].

Since V_2O_5 is able to intercalate with electron-donating cations, it allows the material to be good conductors, performing better in terms of ionic and electronic conductivity. V_2O_5 has been applied to various applications, in areas such as catalysis, electrochromic, optical switching and rechargeable energy storage devices. For electrochromism, colour changes to a material when a potential difference is applied to intercalate ions. For example, when Li ion is inserted into V_2O_5 , it switches from yellow to pale blue when +1 V is applied and reverses if -1 V is used [37]. The cathodic bleaching to pale blue reaction at -0.3 and -0.8 V and anodic coloured reacts at 0.2 V.

V_2O_5 is an intercalation compound and has a large theoretical capacity of $\sim 294 \text{ mAh g}^{-1}$ in a voltage range of 2.0 – 4.0 V [38]. It has been studied since the mid-1970s because of low cost, higher capacity and higher output voltage. It is largely used as a cathode material and has higher capacity than $LiCoO_2$ (140 mAh g^{-1}), $LiMn_2O_4$ (148 mAh g^{-1}) and $LiFePO_4$ (170 mAh g^{-1}). Lithium insertion into V_2O_5 for Li-ion batteries involves a few stages. The Li insertion and extraction process can be evident from the cyclic voltammogram (CV), showing the anodic and cathodic peaks (Figure 2-9). Firstly, 1% of Li is inserted into crystalline V_2O_5 resulting in $\alpha\text{-}Li_xV_2O_5$. Further intercalation of x amount of lithium is also evident, where x ranges from $0.35 < x < 0.7$, which results in the formation $\varepsilon\text{-}Li_{0.5}V_2O_5$. $\delta\text{-}LiV_2O_5$ is produced as the reaction plateau is evident as one Li is inserted. As more Li is inserted, structural changes can be permanently affected. At the third plateau $\sim 2.3 \text{ V}$, $\gamma\text{-}Li_2V_2O_5$ phase is generated as more Li is inserted. At γ -phase, the $Li_xV_2O_5$ can be reversibly cycled, where x ranges from $0 \leq x \leq 2$. In the γ -phase, the VO_5 pyramids are arranged in an up-down-up-down sequence [39]. The electrochemical reactions are summarizes in the following equations:

Upon further reaction at 1.9 V, an irreversible rock-salt structure $\omega\text{-}Li_3V_2O_5$ is formed with a tetragonal structure ($a = 4.1 \text{ \AA}$, $c = 9.2 \text{ \AA}$). The deeper discharge to less than 2 V is

less applicable as a cathode material. For instance, the lithium diffusivity coefficient reduces from $10^{-10} \text{ cm}^2 \text{ s}^{-1}$ for $x = 2$ to $< 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for $x = 3$ intercalation into V_2O_5 .

Figure 2-9: Cyclic voltammogram of Li intercalation from V_2O_5 to $\omega\text{-Li}_3\text{V}_2\text{O}_5$ [39].

V_2O_5 suffers from poor cycling stability as a cathode material due to its poor Li ion diffusion, electric conductivity and irreversible phase transformation upon high discharge voltage. Several strategies have been used to improve the rate and cycleability. For example, carbon-coated V_2O_5 using mesoporous carbon as template produces nanoparticles of 10 – 20 nm with a thin layer of 2 nm carbon layer coating [40]. At a discharge rate of 1.0 A g^{-1} (6.8C), the discharge capacity is $\sim 297 \text{ mAh g}^{-1}$ and cyclic stability maintains at $\sim 97.3\%$ when comparing between the 5th and 50th cycle. From the electrochemical impedance spectra, the author describes the improvement to the lithium insertion/extraction when using carbon-coating V_2O_5 as compared with pure V_2O_5 nanowires and micro-sized particles. The carbon coating on the electrode material can facilitate electron transport, prevents any decomposition reactions between V_2O_5 and electrolyte and restrain the volume change during Li^+ ion insertion/extraction. However, the formation of the template requires complicated synthesis steps and is less likely to be scalable. In another work, $\text{SnO}_2/\text{V}_2\text{O}_5$ core/shell structure utilizes SnO_2 to improve the charge transport of V_2O_5 [19]. At a current density of 0.2 A g^{-1} (1.5C), the discharge

capacity is 138 mAh g⁻¹. In various studies, SnO₂ is utilized as an electron transport materials due to its high conductivity. For example, SnO₂ nanowires grown by CVD method have a conductivity of 5 – 74 S cm⁻¹ [41]. As a comparison, MnO₂ nanowires have a lower conductivity of $\sim 8.6 \times 10^{-4} - 4.2 \times 10^{-2}$ S cm⁻¹ [42].

V₂O₅ can also serve as anode materials for Li-ion batteries. The theoretical capacity for V₂O₅ anode is ~ 1471 mAh g⁻¹ [43, 44]. For example, V₂O₅/SnO₂ double-shelled nanocapsules were able to achieve capacity of 1776 mAh g⁻¹ and 947 mAh g⁻¹ for the initial discharge and charge cycle at a current density of 250 mA g⁻¹ [42]. In another work, V₂O₅ nanorods were synthesized by ball-milling was able to achieve capacity of 1398 mAh g⁻¹ and 608 mAh g⁻¹ for the initial discharge and charge cycle at a current density of 30 mA g⁻¹ [44]. Although the initial capacity is high, the capacity decreases from 947 mAh g⁻¹ on the 1st charge capacity to 673 mAh g⁻¹ on the 50th cycle and capacity retention of $\sim 70\%$ when compared with 1st charge cycle. The key factor to improve the cycling stability would be good adhesion of material to the current collector. The active materials can detach from the current collector during cycling if polymeric binder strength is insufficient to hold onto the material or the active material is not in contact with the polymeric binder during the electrode preparation [45].

Several Li-vanadate-based electrodes have also attracted attention because they are able to reversibly intercalate up to 7 Li, achieving specific capacity of 800 – 900 mAh g⁻¹ [46]. For example, FeVO₄ was able to generate ~ 1300 mAh g⁻¹ and InVO₄ can achieve a capacity of > 1100 mAh g⁻¹ on the initial cycle using a potential range between 0.02 to 3.5 V when used as anode materials for application of Li-ion batteries. Although amorphous FeVO₄ have an initial capacity of ~ 1300 mAh g⁻¹, the capacity decreases to ~ 800 mAh g⁻¹ after 10 cycles. The electrodes are formed by mixing the metal vanadates with polymeric binder and conductive carbon. Similar to the previous discussion, the conventional approach of electrode preparation is likely to have an effect on the cyclic stability.

V₂O₅ is also highlighted in electrochemical supercapacitors because of its different valence states and electrochemical redox reactions on surface/bulk of the material [47]. It can be used in either aqueous or organic electrolytes (e.g KCl, LiClO₄) [13]. However, the key challenge of using V₂O₅ as supercapacitor is its low electrical conductivity. Some

approaches to improve the performance will be discussed in this section. For example, V_2O_5 aerogel with a surface area of $155 \text{ m}^2 \text{ g}^{-1}$ and pore volume of $0.87 \text{ cm}^3 \text{ g}^{-1}$ was able to achieve a specific capacitance (C_s) of 2150 F g^{-1} at a scan rate of 0.1 mV s^{-1} [48]. The author suggests that the gel structure would allow unrestrictive access of the electrolyte to the particles, enhancing the electronic and ionic conductivity. However, no cyclic performance was tested. Similar concept involving porous V_2O_5 achieves C_s of $\sim 214 \text{ F g}^{-1}$ at a rate of 5 mV s^{-1} in 2 M KCl [49]. When different electrolytes were used, the capacitance changes, C_s of 114 F g^{-1} in 2 M NaCl and 122 F g^{-1} in 2 M LiCl were achieved. The capacitance of the electrode faded when cycled for 100 times. The author suggests that the fading maybe due to stress during K^+ ions insertion/deinsertion. Another contributing factor that may affect the cyclic performance is that the electrode was prepared using the powder with acetylene black and binder. In template based approaches, V_2O_5 is coated on templates which assist the ionic transport. For example, V_2O_5 coated on multi-walled carbon nanotubes is able to achieve a capacitance of $\sim 600 \text{ F g}^{-1}$ for composites and $\sim 1550 \text{ F g}^{-1}$ based on V_2O_5 content in 8 M LiCl solution as electrolyte from -0.6 to 0.6 V using a scanrate of 1 A g^{-1} [9]. The author uses ALD deposition technique to deposit the vanadium oxide onto carbon nanotubes (CNT). Currently, ALD tools are too expensive and the deposition rate is very slow at 0.05 nm per cycle. Furthermore, dosing and purging are required between each step. Similarly, a 10 minute V_2O_5 electrodeposition onto 50 nm pore sized AAO was able to achieve a maximum capacitance of 871 F g^{-1} in 1 M KCl solution from -0.2 to 0.6 V at a scanrate of 5 mV s^{-1} [16]. Increasing the deposition time to 90 minutes actually reduces the capacitance to 271 F g^{-1} as only the surface is exposed to the electrolyte. The AAO template is formed by a two-step anodization process where the samples require multiple oxidation stages and long duration. Furthermore, a layer of 300 nm platinum metal is sputtered on the synthesized AAO template to increase the conductivity.

In this section, the history and energy storage applications of V_2O_5 are discussed. Bulk V_2O_5 suffers from poor cyclic stability due to its poor ion diffusion and electrical conductivity when tested for energy storage applications. Several strategies have been discussed to improve the rate and cyclability. For instance, the usage of template to create nanostructured arrays is discussed in this section. However, the templates require

complicated synthesis steps. In this project, self-growing and wet-etching fabrication strategies that do not require templates were used to create 2-D V_2O_5 nanostructured arrays. Through the formation of 2-D nanostructured arrays, the cyclic stability and energy density of V_2O_5 electrode materials can be improved as more active materials are exposed to the electrolyte, stable and ordered structure to buffer any volume change during ion insertion/deinsertion and provide direct electron/charge transport between active materials and current collector.

2.3 Energy storage application

Many renewable sources (e.g. sun, wind or waves) can generate additional energy sources. This involves the conversion of one form of energy to electrical energy. However, they are intermittent which would require energy storage devices like batteries and supercapacitors to store the electrical potential. This energy can be kept and used when required. For instance, in power tools where this electric potential can be converted to mechanical energy [50].

2.3.1 Lithium ion batteries

Batteries consist of electrochemical cells that are connected in series or parallel depending on the output voltage and capacity [51]. The history of batteries can be dated back by the work of Luigi Galvani and Alessandro Volta. Galvani discussed a dead frog's leg kicked when contact with two different metals and Volta built a battery which is also known as "voltaic pile" consisting of two different metals divided by a cloth immersed with sodium chloride solution [52]. The innovation results in many batteries like alkaline-manganese, nickel-cadmium, and lead-acid batteries. With the increasing demand for more portable devices, batteries will need to have higher energy content to weight and volume ratio. The improvement first came about when batteries were based on Li as anode materials. Lithium is the most electropositive (-3.04 V versus standard hydrogen electrode), light (molecular weight = 6.94 g mol⁻¹) and a very low density ($\rho = 0.53 \text{ g cm}^{-3}$) [53]. As a result, Li metal has a large theoretical capacity of $\sim 3860 \text{ mAh g}^{-1}$ [54].

However, Li metal is highly reactive with lithium perchlorate in dioxolane electrolyte. Dendritic growth of Li upon continuous cycling, results in increased reactivity due to generate of new surfaces and thermal instability. As a result, it causes short-circuit and explosion hazard. It took ten years to achieve the success of rechargeable batteries and Li-ion batteries were finally introduced in June 1991. Figure 2-10 shows the schematic diagram of a Li-ion battery. The main setup consists of a working electrode using graphite, a counter electrode of Lithium metal oxide (usually LiCoO_2), LiPF_6 salt electrolyte in an organic solvent and a separator. An example of the equation involving the electrochemical process is as such ($x \leq 0.5$, $y=6$) [55] with a voltage ~ 3.7 V:

As shown in Figure 2-10, lithium is reversibly inserted and extracted during charge and discharge. During discharge, the lithium ions diffuse from the graphite anode (Li_xC_6) back into the delithiated $\text{Li}_{1-x}\text{CoO}_2$ along with the respective oxidation and reduction reactions involved. The process is reversed when charged.

Figure 2-10: Schematic diagram of a Li-ion battery [56].

The high energy content of Li-ion batteries makes it attractive to be used in portable devices like mobile phones, laptops. For example, Li-ion batteries have energy density from 90 – 210 Wh Kg⁻¹, which is much higher than batteries like nickel metal hydride with 50 – 80 Wh Kg⁻¹ [57].

Capacity is expressed as the quantity of electricity that is generated through an electrochemical reaction [58]. The expression of measuring electricity can be expressed in Coulomb (C) or Ampere (A). The relationship between Coulomb and Ampere is expressed in Equation 2-9.

$$1 \text{ Ah} = 1000 \text{ mAh} = 3600 \text{ As} = 3600 \text{ C} \quad (\text{Equation 2-9})$$

Faraday's constant states that the amount of electrical charge to react with one mole of active material to oxidize or reduce is 96485.3 C mol⁻¹. It is expressed in the following equation.

$$m = R_F \frac{M \cdot Q}{n \cdot F} \quad (\text{Equation 2-10})$$

Where m is the mass (g), M is the molecular weight (g mol⁻¹), R_F is the Faradic efficiency which is equal to 1, n is the number of electrons transferred per mole and F is the Faraday's constant. Rearranging Equation 2-10 and Equation 2-9, the theoretical specific capacity of a material is shown in Equation 2-11.

$$\text{Capacity} \left(\frac{\text{mAh}}{\text{g}} \right) = \frac{1000 \times n \times F}{3600 \times M} \quad (\text{Equation 2-11})$$

The capacity of the battery depends on the discharge current rate. As shown in Figure 2-11 by increasing the discharge rate, the discharge voltage decreases faster and hence lower capacity. C rate (C_n) is commonly used to define the charge/discharge current.

$$I = M \times C_n \quad (\text{Equation 2-12})$$

Where I is current in Amperes (A), C is the numerical value of rated capacity of the battery (Ah), n is the time (hour) which rated capacity is mentioned and M is the multiple of C. For example, a current of 200 mA is used to charge a battery with a rated capacity of 1000 mAh will have a 0.2 C rate. Increasing the C rate will result in faster depletion of the charged battery.

Figure 2-11: Discharge profile of a battery with discharge time. Curve 1 shows the theoretical voltage and increasing discharge currents from curve 2 to curve 5 [51].

2.3.2 Supercapacitors

The work of the earliest capacitor can be dated back to the discovery of the Leyden jar by Dean Kleist at Leydan [59]. The jar consists of a glass phial which is connected to a metal foil covering on the outer surface. It is immersed in an aqueous acidic solution which acts as an electrolyte. Initial work by Michael Faraday suggested that polarization effect due to electric field polarized causing induced dipole moment on the molecules which the molecule can be induced from one to another. An example of dielectric polarization by an external applied field is shown in Figure 2-12. The dielectric material is situated in between the plates of opposite charges. The surface charges are generated on the interface contributes to the capacitance, the positive and negative ends of the induced dipole in between the plates are negated. The polarity of the dielectric will depend on (1) Number of polarizable or valence electrons. For example, the electronic polarizability is larger in π than in σ orbital. (2) Bond length and atomic position. (3) Molecules like H_2O , HCl , HF are polar in nature, contributing to larger degree of polarization. This effect is less significant in symmetrical molecules like CH_4 , CCl_4 . (4) Larger polarization and

dielectric constant can occur between molecules that have intermolecular dipole-dipole interaction as the orientation of the polarization is cooperative.

Figure 2-12: An illustration of polarity induction in a dielectric material caused by an external applied field [59].

An example of the distorted polarizability (α) in relation with dielectric constant (ϵ) for a dilute gas is as given below:

$$(\epsilon - 1) \frac{M}{\rho} = 4\pi N_A \alpha \quad (\text{Equation 2-13})$$

Where M/ρ is the molar volume and N_A is Avogadro's constant.

There are two types of electrochemical capacitors (1) accumulation of electrostatic charges on the interface also known as electrical double layer capacitor (EDLC) (2) pseudocapacitor or also known as Faradaic supercapacitor involves Faradaic process where fast and reversible redox process occurs on the electrode surface.

EDLC uses high specific area carbon as electrodes with electrolytes accumulating surface electrode charges on the electrode surface and electrolyte ions charge balancing to allow neutrality. The electrical double layer capacitance does not involve any charge transfer across the electrode/electrolyte interface. Hence, the electrolyte concentration remains unchanged during charging and discharging process. In 1853, von Helmholtz

adopted a double layer model and was later modified to a model with three regions, namely inner Helmholtz layer, outer Helmholtz layer and a diffuse ion distribution region. An example of double layer model is given on Figure 2-13.

Figure 2-13: Schematic diagram of a double layer model showing the adsorption of hydrated cation and less hydrated anion [60].

In extreme polarization, one of the Helmholtz layer dominates with anions or cations, depending on the type of polarization. For example, the amounts of anions are twice of cations on the positively charge electrodes in the inner Helmholtz layer. The calculation for Helmholtz type of total double-layer capacitance (C_{dl}) comprises of a Helmholtz double layer (C_H) and the remaining ionic diffusion layer (C_{diff}).

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (\text{Equation 2-14})$$

The double layer capacitance is dependent on the electrode potential and is expressed in the following equation.

$$C = \frac{Q}{V} = \frac{\epsilon_0 \epsilon_r A}{d} \quad (\text{Equation 2-15})$$

Where Q is the total charges on the electrode, V is the applied voltage, A is the specific area accessible to the electrolyte, d is the thickness of the double layer, ϵ_0 is the permittivity of free space (8.854×10^{-12} F m⁻¹) and ϵ_r is the dielectric constant of the electrolyte.

For pseudocapacitor, it involves the interaction of charges across the double layer, similar to the process of a battery. However, pseudocapacitor differs from batteries which has better thermodynamic changes and reversibility [60]. The capacitance is related to amount of charge acceptance (Δq) with the change in potential (ΔV). This reversibility is assumed to have no phase change and the process is confine to the surface region.

$$C = \frac{\Delta q}{\Delta V} \quad (\text{Equation 2-16})$$

For example, FeS₂ can reversibly reduce with two electrons. The process occurs on the surface of the material forming two sulfide ions. To maintain charge balance, S²⁻ is protonated to SH⁻ with Fe²⁺. The cathodic and anodic peaks show a reversible mirror-image when using cyclic voltammogram. When FeS was used, irreversible peaks occurs when using cyclic voltammogram. This concludes that pseudocapacitance happens on the surface and able to reversibly reducible.

To compare, (1) EDLC stores up to 0.17 – 0.20 electrons per atom on surfaces. (2) pseudocapacitor is able to store 2.5 electrons per atom (basis of 500 $\mu\text{F cm}^{-2}$) on accessible surfaces and (3) batteries stores 1 – 3 electrons with the bulk of the materials (depends on oxidation state). A double layer carbon capacitance may have 1 – 5% faradic capacitance due to the oxygen functionalities from the experimental preparations. Pseudocapacitors will have some electrochemical double layer capacitance about 5 – 10%. A summary of the parameters is given in Table 2-1.

Table 2-1: A summary of the parameters for double layer capacitor, supercapacitors and batteries [60].

Parameters	Electrostatic capacitor	Supercapacitor	Battery
Charge time	$10^{-6} - 10^{-3}$ s	1 – 30 s	0.3 – 3h
Discharge time	$10^{-6} - 10^{-3}$ s	1 – 30 s	1 – 5 h
Energy density (Wh Kg ⁻¹)	< 0.1	1 -10	20 -100
Power density (W Kg ⁻¹)	> 10000	1000 - 2000	50 -200
Cycle life	> 500000	> 100000	500 - 2000
Charge/discharge efficiency	~1.0	0.90 – 0.95	0.7 – 0.85

Capacitance is expressed as charge stored per volt as expressed in Equation 2-17. The units for capacitance are farads, which is different from battery units of Coulombs or Watt-hours. The capacitance obtained from the material is largely dependent on the surface area or pore-size distribution [13].

The average capacitance can be calculated from the cyclic voltammogram and is expressed in Equation 2-17.

$$C = \frac{I}{\left(\frac{dV}{dt}\right)} \quad (\text{Equation 2-17})$$

Where I is the average current in amperes and dV/dt is the scanning rate. Specific capacitance (C_s) can be obtained by dividing with the weight of the active material.

The specific energy (E) and specific power density (P) are crucial parameters in determining how energy is delivered to a load. It can be calculated from the following equations.

$$E = \frac{1}{2} CV^2 \quad (\text{Equation 2-18})$$

$$P = \frac{V^2}{4R} \quad (\text{Equation 2-19})$$

Where V is the nominal voltage and R is the equivalent series resistance in ohms.

Chapter 3 : Experimental procedures

3.1 Introduction

This chapter consists of three parts to the project, namely, V_2O_5 on Al foil, V_2O_5 on Ni foam and $FeVO_4$ on stainless steel. In the first part, Al foil is etched in alkaline solution to create a nanosheets array structure. The etched Al foil is then used for the deposition of V_2O_5 and used for the application of supercapacitors. In the second part, V_2O_5 nanowires and nanosheets are grown on Ni foam. The as-grown films are used to test for the application of supercapacitors. In the last part, amorphous $FeVO_4$ is grown on stainless steel foil. The as-grown film is used directly and test as anode materials for Li-ion battery application.

3.2 Growth of V_2O_5 on hierarchical Al current collector

3.2.1 Materials

Lithium hydroxide (LiOH) (Acros, 98%), sodium hydroxide (NaOH) (Schedelco, 99.9%) and potassium hydroxide (KOH) (Sigma Aldrich, 90%) are used to prepare the alkaline solutions. Vanadium(III) acetylacetonate (Sigma Aldrich, 97%) powder is used as the source materials for deposition. Commercial Al foil is used as the substrates as well as the current collector.

3.2.2 Growth process

Aluminum foils were first treated with 0.15 M of LiOH dissolved in ethanol solution. The solution was drop-casted onto the foils and subsequently left to dry in air. A layer of white precipitate formed was then washed away using deionised water. The Al foil was then dried in oven at 353 K. A small amount of Vanadium(III) acetylacetonate was weighed into an alumina boat and placed inside a quartz tube in the middle of the tube

furnace. A schematic diagram of the setup is shown in Figure 3-1. The treated Al foils (1×1 cm) were placed downstream positioned at 21 – 26 cm away from the center of the alumina boat. The quartz tube was evacuated to a pressure of $\sim 10^{-2}$ mbar and flushed with forming gas (5% H_2/Ar) at a flowrate of 100 sccm before the deposition. The furnace was then heated to 673 K with a heating rate of 20 K min^{-1} and held at the same temperature for 30 minutes. The ambient pressure was ~ 0.72 mbar during the deposition process. The growth substrates were then subjected to air annealing for another 30 min at 623 K. Subsequently, the substrates were removed from the furnace at room temperature.

Figure 3-1: Schematic diagram of a customize-built CVD setup.

3.3 Growth of V_2O_5 nanostructures on Ni foam

3.3.1 Materials

Vanadium (III) chloride (VCl_3) (Merck, 99%) and Vanadium (V) oxide (V_2O_5) (Alfa Aesar, 99.2%) are used as source materials for deposition. Ni foam substrates with a dimension of 1×2 cm are used as substrates for growth and as current collectors.

3.3.2 Growth process

Nickel foam was first washed in ethanol and dried in oven at 353 K. VCl_3 powder was loaded into an alumina boat and placed in the middle of the tube furnace. In a separate experiment, V_2O_5 powder was used as source material by adding into an alumina boat and

placed in the middle of the tube furnace. The prepared substrates were then placed downstream at 12 – 20 cm away from the center of the alumina boat. Before the deposition, the quartz tube was evacuated to a pressure of $\sim 10^{-2}$ mbar and flushed with forming gas (5% H_2/Ar) at a flowrate of 200 sccm. The furnace was then heated to 1273 K with a heating rate of 20 K min^{-1} and held at the same temperature for 1 hour. The ambient pressure was ~ 1.3 mbar during the deposition process. Subsequently, the substrates were removed from the furnace at room temperature.

3.4 Growth of FeVO_4 on stainless steel

3.4.1 Materials

VCl_3 powder is used as the source material for deposition. Stainless steel (SS) foils (SS304) with a thickness of dimension $1 \times 1 \times 0.01$ cm are used as substrates and as current collector.

3.4.2 Growth process

VCl_3 powders were loaded in an alumina boat and placed in the middle of the tube furnace. Stainless steel foils were washed with ethanol and placed in oven to dry. It was then transferred to the furnace and placed downstream at 4 – 15 cm away from the center of the alumina boat. Before the deposition, the quartz tube was evacuated to a pressure of $\sim 10^{-2}$ mbar and compressed air (21% O_2 , 79% N_2) was introduced at a flowrate of 100 sccm using a mass flow meter controller. The furnace was then heated to 723 K at a rate of 20 K min^{-1} and held at 723 K for 1 h. The ambient pressure was ~ 0.82 mbar during the growth process.

3.5 Sample characterization

3.5.1 Materials characterization

The grown samples were directly used for SEM and XRD characterization. Laboratory powder X-ray diffraction (XRD) patterns of the samples were measured at room temperature from $20 - 40^\circ 2\theta$ using a Shimadzu XRD-6000 diffractometer with a $\text{CuK}\alpha$ source radiation, 1° divergence slit, a secondary graphite monochromator and a scintillation counter, a step size of 0.02° was applied and accumulating for 0.6 s per step. The morphology of the samples were investigated by using a field-emission scanning electron microscopy (FESEM) system (JEOL, model JSM-7600F) using a voltage of 5 kV. For cross-section imaging, a half-moon stub was used to mount samples so as the cross sections face up. The cross-section samples were coated with a layer of gold using SPI-module sputter coater before characterized using FESEM. The grain size and phase of the materials were evaluated using a transmission electron microscopy (JEOL, model JEM-2100). TEM specimens were prepared by scratching the growth substrates and drop cast with ethanol onto a copper grid coated with holey carbon film. The thickness of the sample is measured using atomic force microscopy (Bruker, model AFM DI 3100). The specimens were prepared by ultrasonicating samples in ethanol and dropped cast to silicon substrates. Vibrational spectrum of the samples were measured using Fourier transform infrared spectroscopy (Spectrum, Perkin Elmer). Attenuated total reflectance (Golden Gate single reflection diamond ATR) attachment is used to examine the samples directly without further preparation. X-ray photoelectron spectroscopy (VG ESCALAB 220I-XL) was used to determine the elemental composition and chemical state. The base pressure was 10^{-9} Torr during XPS analysis and $\text{MgK}\alpha$ X-ray radiation (1253.6 eV) at a power of 200 watts was used. The quantification of elemental isotopic concentration is measured using inductively coupled plasma mass spectrometer (ELAN DRC-e). A small quantity of HCl solution was used for the dissolution of sample.

3.5.2 Electrochemical measurements for use as supercapacitor

The film electrodes were prepared by first pasting the growth Al substrates onto the graphite paper (1×2 cm) using carbon tape. For electrochemical evaluation, the testing was performed on Solartron analytical equipment (Model 1470E) using a fully symmetrical two-electrode configuration via a beaker-type cell. Cyclic voltammetry (CV) and galvanostatic charge/discharge were carried out using 1 M Lithium perchlorate (LiClO_4) in propylene carbonate as electrolyte in ambient condition.

The as-prepared film on Ni foam was used directly as the working electrode. The electrochemical evaluation of the electrodes was investigated in a three-electrode half-cell system using 2 M KOH as electrolyte on Solartron analytical equipment (Model 1470E) in ambient condition. A platinum wire and a Ag/AgCl electrode was used as counter and reference electrode respectively.

3.5.3 Electrochemical measurements for use in Li ion battery

The samples were grown directly on the stainless steel substrates testing through CVD method and used as current collector for battery assembly and testing without the traditional electrode preparation step. The coin-cell type battery was assembled in an argon filled glove box with a concentration of less than 1 ppm oxygen and moisture. The Li foil, polyethylene separator, as-prepared anode material, spacer and spring was stacked accordingly in the coin cell case. Lithium foil was used as both the counter and reference electrode, and the electrolyte solution comprises of 1 M LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). The cyclic performance of the cells were tested using a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage window of 0.005-3.5 V (vs. Li/Li^+).

Chapter 4 : Growth of V_2O_5 on hierarchical Al current collector

4.1 Introduction

V_2O_5 has been studied for energy storage applications due to low cost, ease of synthesis, high capacity or capacitance and its Li-intercalating nature [16]. However, it suffers from poor Li ion diffusion and electric conductivity. Several conducting materials have been studied to improve the conductivity.

Firstly, metal oxides (e.g. SnO_2) nanostructures grown on current collector have been used as a substrate to facilitate the electronic transport of V_2O_5 . Due to the core/shell structure, it provides better conductivity and a direct path for fast transport of electrons. However, the growth of SnO_2 nanowires on stainless steel substrate is dependent on the surface chemistry with the current collector. For instance, a layer of gold catalyst film is required to initiate the growth of the SnO_2 nanowires on the current collector [19]. In another work, vanadium oxide is deposited onto CNT by ALD. The composite material is able to achieve a capacitance of 600 F g^{-1} per composite electrode mass [9]. However, CNT lacked surface sites for chemical bonding with metal oxide coatings and has lower electrical conductivity as compared with Cu, Al, Au or Ag [61].

One of the simpler approaches is by etching the substrates using alkaline solution. For example, copper foils were first immersed in a mixture of alkaline solution to produce $Cu(OH)_2$ nanotubes [62]. Post-treatment on $Cu(OH)_2$ nanotubes was then done by heat treatment to convert it to CuO film. The CuO nanotube film was able to achieve an initial discharge capacity of 911 mAh g^{-1} and was able to maintain at 417 mAh g^{-1} for 30 cycles.

One of the commonly used substrates as a current collector for energy storage application is aluminium. Aluminium, like many current collectors, is attractive as a

substrate because of its low cost, lightweight and good conductivity. The most common approach to use aluminium is the formation of a porous alumina template. For example, V_2O_5 was grown on two different pore size AAO templates, 50 nm and 200 nm [16]. V_2O_5 on 50 nm AAO achieves a capacitance of 871 F g^{-1} and V_2O_5 on 200 nm AAO achieves a capacitance of 398 F g^{-1} in 1 M KCl electrolyte solution at a scan rate of 5 mV s^{-1} in a voltage range of -0.2 to 0.6 for the application of supercapacitors. The higher specific capacitance is largely affected by the effective surface area, since only the surface of the materials is exposed to the electrolyte. The AAO template is formed by a two-step anodization process where the samples require multiple oxidation stages and long duration. Furthermore, a layer of 300 nm platinum metal is sputtered on the synthesized AAO template to increase the conductivity. In another work, Al nanowires were grown on Cu substrates using CVD technique [61]. A 50 nm vanadium oxide coating on the Al nanowires achieve a capacitance 964 F g^{-1} using a scan rate of 0.01 mV s^{-1} . However, the formation of the Al nanowires uses trimethylamine alane as organometallic CVD precursor which is highly flammable and corrosive.

Aluminium is widely studied for metal/air batteries where Al is the anode metal. It is well known that aluminium oxide acts as a scale on the surface to protect against corrosion. However, it can be dissolved in acidic or alkaline solution forming species like Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$ and $Al(OH)_4^-$. Similarly to Cu substrates, Al substrates can be etched in various alkaline solutions to form nanostructures. Herein, Al foil is etched using alkaline solution to create nanostructured arrays. The treated Al foil is used for the growth of V_2O_5 thin film using CVD technique.

4.2 Morphology characterization and phase analysis

The etching of the Al foil was initiated by drop-casting the foil with 0.15 M LiOH dissolved in ethanol solution. Figure 4-1a shows the SEM image of the Al foil treated with 0.15 M LiOH solution for a hour. From the SEM image, the etched Al foil forms nanosheets that are interconnected with the neighbouring nanosheets. A total of thirty measurements were made on the two samples to determine the average dimensions of the

sheets. The average thickness and length of the sheets are measured to be ~ 17 nm and ~ 557 nm, respectively. The thickness ranges from 7 – 32 nm and the length ranges from 344 – 860 nm. Different concentrations of the alkaline solutions were also mixed and drop-casted on the Al foil. Figure 4-1b and Figure 4-1c shows the Al foils that were etched using 0.50 M and 1.00 M of LiOH dissolved in ethanol solution, respectively. The measured average dimensions of sheets formed are ~ 29 nm and ~ 549 nm in thickness and length for 0.50 M LiOH and ~ 27 nm and ~ 695 nm for 1.00 M LiOH concentration. The thickness ranges from 10 – 54 nm and the length ranges from 279 – 887 nm for 0.50 M LiOH solution etched Al foil. The thickness ranges from 11 – 41 nm and the length ranges from 314 – 1056 nm for 1.00 M LiOH solution etched Al foil. It is also noted that by increasing the concentration of the LiOH solution, the distance or the gap between each nanosheet increases. The average gap distances in between the sheets were measured to be ~ 310 nm, ~ 376 nm and ~ 593 nm for samples prepared with LiOH solutions of 0.15 M, 0.50 M and 1.00 M, respectively.

The amount of nanosheets per Al foil can be estimated using a simple formula, $S_{Al} = (A_{sheet} + A_{void}) \times N$ where S_{Al} is the area of the Al foil, A_{sheet} refers to the horizontal area of the nanosheet, A_{void} refers to the area of the hole or the gap in between the sheets and N is the amount of nanosheets available for the area S_{Al} . The calculation is simplified with one nanosheet assigned to a spherical hole and the area of the foil used is ~ 1 cm². The calculated amounts of nanosheets (N) per foil are $\sim 1.18 \times 10^9$, $\sim 7.88 \times 10^8$ and $\sim 3.39 \times 10^8$ per centimeters for Al foil etched using LiOH solutions of 0.15 M, 0.50 M and 1.00 M, respectively.

Using the estimated amount of nanosheets, the approximated surface area of etched Al foils (considering the area of etched sidewalls and hole) can be estimated by $S_{etched} = (2A_{depth} + A_{void}) \times N$ where S_{etched} is the area after etching, A_{depth} is determined using the height of the nanosheet. A_{depth} can be determined from the SEM image of the cross section SEM of the foils, and the cross sectional area of the sheet is simply a semicircle. The height of the Al nanosheets can be determined from the SEM images (Figure 4-2). The measured heights are ~ 197 nm, ~ 210 nm and ~ 230 nm for Al foils etched using LiOH solutions of 0.15 M, 0.50 M and 1.00 M, respectively. The calculated areas of the etched

Al foils using 0.15 M, 0.50 M and 1.00 M are approximately $\sim 1.24 \text{ cm}^2$, $\sim 1.14 \text{ cm}^2$ and $\sim 1.07 \text{ cm}^2$, respectively. The results suggest that the Al foil etched with 0.15 M LiOH has the largest amount of nanosheets and etched surface area.

Figure 4-1: SEM images of Al foils etched in various concentrations of LiOH (a) 0.15 M (b) 0.50 M (c) 1.00 M.

Figure 4-2: Measured heights of Al foils etched in various concentrations of LiOH (a) 0.15 M (b) 0.50 M (c) 1.00 M.

XRD characterization was carried out to determine if there is any detectable phase change before and after etching. Figure 4-3 shows the XRD patterns obtained between 20° – 40° for commercially available Al foil that were used for etching and the treated Al foil which was etched with 0.15 M LiOH solution. The Al peaks can be seen consistently at

38° for the two samples (ICSD-43423). There are no detectable phase differences between the two samples.

Figure 4-3: XRD patterns collected for (a) Commercial available Al foil (b) Etched Al foil (c) V₂O₅ thin film grown on commercial available Al foil (d) V₂O₅ deposited on etched Al foil. (e) Standard XRD pattern for crystalline V₂O₅ drawn for reference.

Fourier transform infrared spectroscopy (FTIR) was used to investigate the absorption bands for untreated and treated Al foils (Figure 4-4). The FTIR spectra for both samples show similar pattern, indicating both substrates are Al foils. No peaks of $\text{Al}(\text{OH})_3$ (969 , 589 and 351 cm^{-1}) [63] and AlOOH (3090 , 2090 and 1920 cm^{-1}) was observed [64]. Absorption band of Al-OH stretching was also absent ($3670\text{--}56\text{ cm}^{-1}$). Absorption around ~ 3787 , ~ 3726 and 3427 cm^{-1} belongs to OH groups, which are distinctive peaks of alumina. For example, absorbance peaks of ~ 3790 and $\sim 3730\text{ cm}^{-1}$ remains despite heat treatment at 723 K in vacuum [65]. The two minor peaks around ~ 1521 and 1433 cm^{-1} belongs to impurities such as CO_2 . The adsorbed species reported to retain despite heat treatment at 1073 K [65]. The peaks around ~ 1020 , 753 and 659 cm^{-1} indicates the absorbance band relates to Al-O [66, 67].

Figure 4-4: FTIR spectra of untreated and treated aluminium foils.

The treated Al foil and the untreated Al foil were then used for the growth of V_2O_5 thin film using CVD technique. From the XRD patterns in Figure 4-3, the peaks from V_2O_5 on both substrates can be indexed to orthorhombic V_2O_5 (ICSD-653926). To estimate the thickness of the V_2O_5 layer deposited, untreated Al was used as substrate as control samples. The substrates were subjected to annealing and the final product is

yellowish-orange in colour. Figure 4-5 shows the SEM images of V_2O_5 on both untreated and treated Al foil. It is observed that a thin layer of V_2O_5 was deposited on both the substrates and the morphology of nanostructure arrays were maintained after V_2O_5 deposition on treated Al foil as shown in Figure 4-5b. Using atomic force microscopy, the thin film is measured to have an average thickness of $\sim 20 - 47$ nm (Figure 4-5c).

Figure 4-5: SEM images of (a) V_2O_5 on untreated Al (b) V_2O_5 deposition on etched Al foil (c) Tapping-mode AFM image of V_2O_5 sample.

Treated Al foils were placed downstream from substrate distance (d_{sub}) from 21 – 26 cm away from the center of the source material. The morphology observed shows similar thin film deposition as shown in Figure 4-6. Although some agglomerated particles were observed, it is sparse.

Figure 4-6: SEM images of as-grown film onto treated Al foil with substrate distance (a) $d_{\text{sub}} = 21$ cm, (b) $d_{\text{sub}} = 23$ cm and (c) $d_{\text{sub}} = 25$ cm.

As shown in Figure 4-7a, sheet-like morphology was observed from the low magnification TEM image. The selected area electron diffraction (SAED) pattern shown in Figure 4-7b matches the d-spacing of orthorhombic V_2O_5 . From Figure 4-7c, the high resolution TEM (HRTEM) image of the sample can be indexed to V_2O_5 (001) and (110) planes, which correspond well to the SAED pattern. Electron energy loss spectroscopy (EELS) is used to detect any impurities that might be incorporated in the samples. It is evident from the spectrum obtained that vanadium is present in the samples and no lithium impurities were detected. From Figure 4-7d, vanadium has two peaks at ~ 25 eV and ~ 50 eV. A reference material using lithium carbonate was used to detect the peaks from lithium. Figure 4-7e shows four peaks at ~ 16 eV, ~ 30 eV, ~ 59 eV and ~ 64 eV.

Figure 4-7: (a) Low magnification TEM image of V_2O_5 film (b) SAED pattern of V_2O_5 film (c) High-resolution TEM image of V_2O_5 film (d) EELS of V_2O_5 on treated Al (e) EELS of lithium from lithium carbonate.

4.3 Study of the growth process

4.3.1 Growth of Al nanosheets array

To identify the process of the growth of the Al nanosheets array, the Al foil was soaked in 0.15 M LiOH solution for different timings (one minute to one hour). The SEM images of the different Al foils are shown in Figure 4-8. When the Al foil is soaked for one minute, the foil is rougher with many fine particles of ~65 nm. The foil shows a different morphology as compared to the Al foil which is untreated. For the Al foil soaked for five minutes, small amount of nanosheets starts to form. The nanosheets have a dimension of ~20 nm in thickness and ~148 nm in length. The nanosheet arrays start to form after fifteen minutes of etching. After one hour of etching, the nanosheets arrays formed are similar to those shown in Figure 4-1a.

Figure 4-8: SEM images of (a) commercially available Al foil and treated Al foil using LiOH solution for different timings (b) 1 min (c) 5 min (d) 15 min.

The Al foil was also soaked in pure ethanol solution. No nanosheet was formed as shown from SEM image in Figure 4-9a. LiOH solution was also used to drop-cast onto Si substrates. Only particles were observed, showing that LiOH was not formed and there were no sheet-like structures.

Figure 4-9: SEM images of (a) Ethanol soaked Al foil (b) Silicon substrate drop-casted with LiOH solution.

Aluminium is highly reactive under atmospheric condition and tends to form a layer of oxide [68]. However, the dissolution of the film is possible by exposing to alkaline solution through the hydroxide, and the reaction is expressed with the following equation.

Alkaline solution will diffuse and the oxide layer will gradually react to form hydroxide. After the oxide layer is etched away, aluminium exposed to alkaline solution will go through two sub-step reactions [69] as shown with the following equations.

Al^{3+} is not thermodynamically stable in the alkaline solution. Al(OH)_3 undergoes further corrosion to form Al(OH)_4^- as show in Equation 4-2 and Equation 4-3. The equilibrium solubility shows that Al(OH)_4^- is the more stable species in alkaline solution as compared to aluminium ions [69].

To explore the effects of different types of alkaline solutions with aluminium foil, various alkaline solutions (LiOH, NaOH and KOH). were used to etch Al foil. Figure

4-10 shows the SEM images of the samples after etching with the various alkaline solutions. From the observations, only Al foil etched with LiOH forms nanosheet arrays (Figure 4-10a). Both NaOH and KOH etched Al foils form films with particles (Figure 4-10b, c). The difference of using Li, Na or K hydroxide shows difference in morphology during etching. The nature of the cation has an effect on the chemical activity of hydroxide ions [70]. Lithium, being the smaller alkali-metal ions, has stronger electric field. As such, Li and hydroxide ions are “trapped” together much more easily, reducing the effectiveness of hydroxide ions to react with Al. The attractive force is lesser with Na ions and does not occur for K ions. This phenomenon relates well with the observed SEM images.

Figure 4-10: SEM images of treated Al foils using (a) LiOH (b) NaOH (c) KOH.

4.3.2 Growth of V_2O_5 thin film

The growth of V_2O_5 nanoparticle thin films using the CVD process involves the evaporation of precursors, transportation of precursor through gases and deposition of precursor vapour to the substrate. To allow adequate coverage of V_2O_5 particles on the substrate, the precursor selection would require sufficient deposition rates. Metal-organic precursors have bulky ligands surrounding the metal, which improves the vapour pressure and allow better growth rates. For example, Ge thin film can be deposited using metal-organic precursors such as $Ge(C_2H_5)_4$ or ethylmethyaminogermane [27]. To understand the growth, untreated Al foils were placed from d_{sub} of 7 – 26 cm to grow V_2O_5 thin film

using vanadium(III) acetylacetonate as the precursor material. Figure 4-11 shows the SEM images of the V_2O_5 thin film at various substrate distance. The temperature profile of the furnace is shown in Figure 4-12 at 673K. Figure 4-11a shows the substrate at $d_{\text{sub}} = 7$ cm with a substrate temperature of ~ 649 K. The nanoparticles grown has an average diameter of ~ 205 nm, ranging from ~ 142 to 317 nm. The nanoparticles were reduced to an average diameter of ~ 121 nm, ranging from ~ 93 to 141 nm when placed at $d_{\text{sub}} = 10$ cm with a substrate temperature of ~ 623 K (Figure 4-11b). Figure 4-11c shows the substrate at $d_{\text{sub}} = 13$ cm with a substrate temperature of ~ 568 K. The nanoparticles have an average diameter of ~ 70 nm, ranging from ~ 46 to 102 nm. Substrate placed at $d_{\text{sub}} = 25$ cm is measured having an average diameter of ~ 24 nm, ranging from ~ 11 to 43 nm. No deposition was observed when the substrates are placed after $d_{\text{sub}} = 26$ cm. The formation of the nanoparticles thin film can be suggested to the island growth mode (Stranski-Krastanov growth model). As illustrated in Figure 2-7b, the growth requires a lattice mismatch between the adatoms and the substrate. The lattice parameters for orthorhombic V_2O_5 are $a = 11.510$ Å, $b = 3.563$ Å and $c = 4.369$ Å and cubic Al is $a = 4.05$ Å. Hence, the vanadium vapour tends to deposit on the adatom, forming nanoparticle islands. It is also observed that the size of the nanoparticles decreases as the substrate distance increases. The smaller particle sizes can be due to the faster nucleation process and lower precursor vapour at lower substrate temperature [71]. The crystal growth of thin film involves various stages, namely nucleation, crystal growth and coalescence into single or polycrystalline film and the substrate temperature affects the quality of the film [72]. At low substrate temperature, a continuous film tend to develop as the sticking coefficient is uniform and the surface diffusion is low. At moderate substrate temperature, surface diffusion increases and results in crystal growth as the adatoms diffuse to form larger particles. By increasing the substrate temperature, the diffusivity increases Equation 4-4 [73]. At high temperature, surface diffusion and various mechanisms such as surface vacancies and coarsening are involve in crystal growth of thin film.

$$L = L_0 \exp \left(-\frac{Q}{kT} \right) \quad (\text{Equation 4-4})$$

Where L is the diffusion coefficient, L_0 is the pre-exponential factor, Q is the activation energy, k is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV K}^{-1}$) and T is the temperature.

Figure 4-11: SEM images of as-grown film onto untreated Al foil with substrate distance (a) $d_{\text{sub}} = 7 \text{ cm}$, (b) $d_{\text{sub}} = 10 \text{ cm}$ and (c) $d_{\text{sub}} = 13 \text{ cm}$.

Figure 4-12: Temperature profile of the tube furnace at 673 K.

Figure 4-13 shows the Arrhenius plot for particle size - temperature obtained from the SEM images measurement. The data is fitted to a linear relationship by taking the natural logarithm of the particle size of the samples versus the inverse in temperature. The average activation energy of the sample can be obtained by natural logarithm of Equation 4-4. The calculated activation energy for vanadium oxide nanoparticles on treated aluminium foil is ~ 0.40 eV. A low activation energy enables the adatoms to overcome the potential energy of the nucleation sites on the substrate, forming larger particles.

Figure 4-13: Arrhenius plot of nanoparticle size for vanadium oxide on untreated aluminium foil.

4.4 Electrochemical evaluation of V_2O_5 on treated Al current collector

The CV of the V_2O_5 on treated Al foil was tested between 0 – 3 V using a rate of 5 $mV s^{-1}$. From Figure 4-14, the sample shows obvious anodic and cathodic peaks [61, 74].

The redox reduction peaks for Li insertion into V_2O_5 from cyclic voltammogram are at ~ 2.54 V and ~ 1.89 V. The reaction peaks correspond well with the formation of $Li_xV_2O_5$ during the charging process [43].

Figure 4-14: Cyclic voltammogram of V_2O_5 on treated Al using a scan rate of 5 mV s^{-1} .

V_2O_5 thin films grown on untreated and treated Al foil (etched with 0.15 M LiOH solution for 1 hour and dried overnight) were tested as supercapacitor using a fully symmetrical two-electrode configuration via a beaker-type cell in 1 M $LiClO_4$ in PC. Figure 4-15a shows the comparison of the galvanostatic charge/discharge curves for V_2O_5 on both substrates. The C_s is calculated using the galvanostatic charge/discharge curves with the following equation:

$$C_s = (I \times \Delta t) / (m \times \Delta V) \quad (\text{Equation 4-5})$$

Where I is the discharge current, Δt is the discharge time, m is the active mass and ΔV is the voltage difference after iR drop [75]. The calculated initial cycle C_s for V_2O_5 on untreated and etched Al are $\sim 152 \text{ F g}^{-1}$ and $\sim 289 \text{ F g}^{-1}$ at a rate of 5 A g^{-1} , respectively. The C_s value of V_2O_5 on etched Al is comparable to V_2O_5 in AAO template and electrospun V_2O_5 [16, 74]. For example, a capacitance of 271 F g^{-1} was achieved using V_2O_5 on AAO template in 1 M KCl solution between -0.2 to 0.6 V. The AAO template is formed by a two-step anodization process where the samples require multiple oxidation

stages and long duration. The high capacitance is contributed from a thin layer of ~ 10 nm amorphous V_2O_5 which shorten the diffusion path for electrolyte and a low mass loading of 2.84 Wt% on AAO which increases the capacitance (Equation 4–5). Furthermore, no cyclic measurements were tested. In another example, V_2O_5 /MWCNT film formed using electrophoretic deposition achieved a capacitance of 240 F g^{-1} in LiClO_4 electrolyte between 0 to 1.4 V [76]. From Figure 4-15b and Figure 4-15c, different current densities were used to measure the C_s of the electrodes. The C_s calculated are $\sim 258 \text{ F g}^{-1}$ (5 A g^{-1}), $\sim 148 \text{ F g}^{-1}$ (10 A g^{-1}) and $\sim 30 \text{ F g}^{-1}$ (20 A g^{-1}) for V_2O_5 on etched Al. For V_2O_5 on untreated Al foil, C_s calculated are $\sim 141 \text{ F g}^{-1}$ (5 A g^{-1}), $\sim 27 \text{ F g}^{-1}$ (10 A g^{-1}) and $\sim 15 \text{ F g}^{-1}$ (20 A g^{-1}).

The cyclability of the electrodes was tested via continuous charge/discharge measurements from 0 – 2 V. From Figure 4-15d, V_2O_5 on etched Al shows an initial C_s of $\sim 289 \text{ F g}^{-1}$ and retention of $\sim 91\%$, whereas V_2O_5 on untreated Al shows an initial C_s of $\sim 152 \text{ F g}^{-1}$ and retention of only $\sim 76\%$ after 1000 cycles.

The etched nanostructures performed better in terms of capacitance and cycling stability than the untreated ones. As suggested earlier, such nanostructures permit better electronic contact and shorter ion transport distance, which is similar to the Al or Cu nanowires current collector reported in the literature [61, 77]. Furthermore, interconnected nanosheets from the etched Al would provide better structural integrity as mentioned in materials like TiSi_2 or FeVO_4 . [78, 79] For example, the TiSi_2 nanonets allow multiple ionic or electronic paths. For TiSi_2 nanowires, it has only single ionic or electronic path. When stress or heat generated during cycling, the nanowires may breakdown and detach from the current collector. As a result, the performance of the electrode is much drastic in nanowires than nanonets. For example, Si on TiSi_2 nanonets and nanowires showed a cyclic retention of $\sim 70\%$ and $\sim 65\%$ after 100 cycles, respectively [78]. The decline in capacitance can be due to the high electrical resistivity of the non-aqueous electrolyte used, the sluggish kinetics of the metal oxides and also the thickness of the film which result in limited access to the bulk of the material [9, 80, 81].

The energy and power densities for the metal oxides on etched Al were calculated based on the following equation:

$$E = C_s V^2 / 2 \quad (\text{Equation 4-6}) \quad \text{and}$$

$$P = E / \Delta t \quad (\text{Equation 4-7})$$

Where V is the applied voltage and Δt is the discharge time.

For V_2O_5 on etched Al, at a low power density of $\sim 2 \text{ kW kg}^{-1}$, the energy density reaches $\sim 160 \text{ Wh kg}^{-1}$. The V_2O_5 on etched Al electrodes perform similar or better than similar oxides mixed with carbon nanotubes [75, 82]. For example, V_2O_5 nanosheets mixed with multiwalled CNT and PVDF binder was able to obtain a power density of 1.1 kW kg^{-1} and an energy density of 122 Wh kg^{-1} . In another example, Fe_2O_3 on multiwalled CNT provided a power density of 1 kW kg^{-1} and an energy density of $\sim 50 \text{ Wh kg}^{-1}$.

Figure 4-15: (a) Galvanostatic charge/discharge behavior of supercapacitors for V₂O₅ on untreated and treated Al at rate of 5 A g⁻¹. Galvanostatic charge/discharge curves for different scan rates (b) V₂O₅ on etched Al (c) V₂O₅ on untreated Al. (d) Cyclic performance of samples at rate of 5 A g⁻¹ for V₂O₅ on untreated and treated Al.

A thicker V₂O₅ film is also grown on treated Al for comparison. The mass of the deposited films was varied to ~0.0315 mg and ~0.0625 mg. Figure 4-16 shows the cyclic performance of the deposited film on treated Al foils for 1000 cycles at a rate of 5 A g⁻¹. For ~0.0315 mg of V₂O₅ on treated Al foil, an initial C_s of ~295 F g⁻¹ and retention of ~89% was achieved. For ~0.0625 mg of V₂O₅ on treated Al, the initial C_s is ~189 F g⁻¹ and the capacitance retention is ~57% after 1000 cycles. Since the capacitance is dependent on the redox sites on the top layer of electrodes, increasing the thickness of the film impedes the electronic and ionic transport, resulting in a lower capacitance and cyclic

performance. Since most intercalation compound materials have poor lithium diffusion coefficient, shortening the diffusion path by utilizing a thinner solid film allows the improvement in electrochemical performance [15]. For example, it is reported that increasing the vanadium oxide layers decreases the capacitance, where a C_s of 600 F g^{-1} was reached with a 10 nm thin layer, and by increasing the thickness to $\sim 30 \text{ nm}$ and $\sim 50 \text{ nm}$, it resulted in a reduction in C_s of ~ 200 and $\sim 50 \text{ F g}^{-1}$, respectively [9].

Figure 4-16: Cyclic performance of samples at rate of 5 A g^{-1} for V_2O_5 on treated Al foils using mass of $\sim 0.0315 \text{ mg}$ and $\sim 0.0625 \text{ mg}$, respectively.

4.5 Concluding remarks

In this chapter, Al foil was etched in different alkaline solutions to create various nanostructures. When 0.15 M LiOH solution was used, nanosheets arrays of average thickness and length of $\sim 17 \text{ nm}$ and $\sim 557 \text{ nm}$ were obtained. Al foils were suggested to be reactive with alkaline solution to form $\text{Al}(\text{OH})_4^-$. Different concentrations of LiOH solutions (0.15 , 0.50 and 1.00 M) were also used. The calculated surface area of the Al foil etched with 0.15 M LiOH is highest surface area among the etched Al foils. The treated Al foils were also used to deposit V_2O_5 thin film. The formation of V_2O_5

nanoparticles on Al foil suggest the growth model to the island growth mechanism. The growth of smaller nanoparticles at low substrate temperature can be attributed to the slow diffusion and fast nucleation rate. The size of the nanoparticles can be tuned with the average particle size from ~ 205 nm to ~ 24 nm by adjusting the substrate distance. V_2O_5 on etched Al perform better with an initial C_s of $\sim 289 \text{ F g}^{-1}$ and retention of $\sim 91\%$, whereas V_2O_5 on untreated Al shows an initial C_s of $\sim 152 \text{ F g}^{-1}$ and retention of only $\sim 76\%$ after 1000 cycles.

The 2-D V_2O_5 thin film grown on hierarchical Al foil show good performance and cyclic stability. In this chapter, wet-etching of the Al foil by alkaline solution was used to create 2-D nanostructured arrays. The direct formation of 2-D V_2O_5 nanostructured arrays on conducting substrates such as Ni foam or stainless steel would reduce the need to etch the substrate before deposition of V_2O_5 .

Chapter 5 : Growth of V_2O_5 nanostructures on Ni foam

5.1 Introduction

The performance of electrochemical capacitors depends on its electrochemical activity and kinetics of the electrodes. The conventional binder electrodes using traditional slurry paste have certain disadvantages such as unexposed electrode materials surface which are unable to interact with the electrolyte. As such, the electrochemical performance of the electrodes is reduced. To allow better electrolyte-electrode interaction, binder-free and self-supporting electrodes on conductive current collector is one of the main approaches. The construction of such electrodes that have been mostly studied includes 1-D or 2-D nanostructured materials directly grown on current collector. Such architecture design favours good electrical conductivity as it allows better electrolyte exposure, lower diffusion resistance of the ionic species in the electrolyte and also providing more effective area for active materials to interact with the electrolyte [83].

In particular, 2-D nanostructures have better stability, more active sites for lithium insertion/deinsertion than 0-D and 1-D structure, making them attractive in energy storage devices [2]. For example, 2-D macroporous platelets show good cyclic stability (~71% after 1st discharge cycle) after 30 cycles, whereas Co_3O_4 nanoparticles and rod-like nanoclusters have capacity retention of 21.7% and 37%, respectively for the application of anode materials for Li-ion batteries after 30 cycles [6]. The macroporous platelets also have a better rate performance than nanowire. The capacity for macroporous platelet was 746 mAh g^{-1} at a rate of 4450 mA g^{-1} and nanowire was 593 mAh g^{-1} at a rate 2220 mA g^{-1} . The author suggests that the improvement in cyclability can be attributed to the porous structure of macroporous platelet. The porous structure enables space for volumetric expansion during Li insertion/desertion.

The formation of V_2O_5 nanosheets have been challenging because V_2O_5 tends to grow into 1-D structure because of its preference to grow in [010] direction. Several works have been done on the formation of nanosheets [3]. For example, V_2O_5 powder is mixed with ammonium persulfate to form $(NH_4)_2V_6O_{16}$ nanosheets for 48 hours. It is then converted to V_2O_5 nanosheets through annealing [3, 84]. The V_2O_5 nanosheets achieve capacity of 180 mAh g^{-1} after 50 cycles when tested at a current density of 300 mA g^{-1} . When bulk V_2O_5 crystal is tested for cathode materials for Li-ion batteries, it achieves a lower capacity of 138 mAh g^{-1} after 50 cycles.

Based on previous studies, 2-D V_2O_5 nanosheets structures have shown good performance and cyclic stability when compared with thin film. Furthermore, interconnected nanosheets array allow multiple ionic or electronic paths and structural integrity as mentioned previously in Chapter 4. Hence, in this work, various morphologies of V_2O_5 will be investigated by direct deposition of V_2O_5 using CVD on Ni foam.

5.2 Morphology characterization and phase analysis

Vanadium (V) oxide powder was used as the source material and Ni foams were placed downstream at 10 – 18 cm away from the center of the source material. Figure 5-1a and Figure 5-1b are SEM images showing that free-standing nanowires were grown on the Ni foam. The measured nanowires have an average diameter of ~126 nm and a few micrometers in length. Figure 5-1c shows the HRTEM image of the V_2O_5 nanowire taken along [020] zone axis. The sample can be indexed to orthorhombic V_2O_5 (101) and (200) plane, which corresponds well with the two-dimensional fast Fourier transform image shown in Figure 5-1d [85].

Figure 5-1: SEM images of (a) V_2O_5 nanowires on Ni foam (b) Side-view of V_2O_5 nanowires. (c) High-resolution TEM image of V_2O_5 nanowire (d) Corresponding two-dimensional Fourier transform along the $[020]$ zone axis.

Figure 5-2a shows the XRD pattern that was carried out between $15 - 60^\circ$ for V_2O_5 nanowire array grown on Ni foam. The peaks at 44.5° and 51.8° corresponds to cubic Ni (JCPDS 04-0850). Orthorhombic V_2O_5 peaks were also observed, indicating its well crystalline.

Figure 5-2: (a) XRD pattern for V_2O_5 nanosheets array on Ni foam. (b) Standard XRD pattern for crystalline Ni drawn for reference.

Vanadium (III) chloride powder was used as the source material for the growth V_2O_5 nanosheets array. V_2O_5 nanosheets arrays were synthesized instead when the Ni foams were placed downstream at 12 – 20 cm away from the center of the source material. Figure 5-3a shows the low magnification SEM image of the as-grown sample with $d_{\text{sub}} = 16$ cm ($T_s = \sim 824$ K). The measured average diameter of the sheets is ~ 13.5 μm , with the

smallest diameter of $\sim 5\ \mu\text{m}$ to largest of $\sim 21\ \mu\text{m}$. The measured average thickness of the nanosheets is $\sim 198\ \text{nm}$, ranging from $71 - 527\ \text{nm}$. Sheet-like morphology was observed from the low magnification TEM image shown in Figure 5-3b. It is observed that the nanosheet is formed by nanoparticles with an average measured nanoparticles size is $\sim 19\ \text{nm}$. The high resolution TEM (HRTEM) image of the sample shown in Figure 5-3c can be indexed to V_2O_5 (110) and (011) planes, which correspond well to the SAED pattern. The selected area electron diffraction (SAED) pattern (Figure 5-3d) matches the d-spacing of orthorhombic V_2O_5 .

Figure 5-3: (a) Low magnification SEM image of V_2O_5 nanosheet array grown at $d_{\text{sub}} = 16\ \text{cm}$ (b) Low magnification TEM image of V_2O_5 nanosheet (c) High-resolution TEM image of V_2O_5 nanosheet (d) SAED pattern of V_2O_5 nanosheet.

Figure 5-4a shows the XRD pattern that was carried out between $10 - 60^\circ$ for V_2O_5 nanosheets array grown on Ni foam. Other than Ni and orthorhombic V_2O_5 phases, additional peaks at 37° and 43° corresponding to cubic NiO (JCPDS 44-1159) phase was also detected. It is reported that NiO can be formed easily on Ni foam with thermal treatment of temperature as low as 673 K [86].

Figure 5-4: (a) XRD pattern for V_2O_5 nanosheets array on Ni foam. (b) Standard XRD pattern for crystalline Ni drawn for reference.

5.3 Study of growth process

5.3.1 Growth process of V_2O_5 nanowire

Since no foreign materials or catalysts were involved in the growth process, the initiation of V_2O_5 nanowires follow the vapour-solid growth. Such self-catalytic processes can be sub-categorized into anisotropic growth, defect-induced growth and self-catalytic growth [30]. For V_2O_5 , the formation of nanowires can be attributed to the anisotropic growth as [010] is the fastest growth direction and [001] is slower due to the weak bonding. This phenomenon is observed in 1-D V_2O_5 nanostructures from CVD, electrospinning, and hydrothermal [7, 87].

Figure 5-5 shows the phase diagram of the Oxygen – Vanadium system. From the figure, the melting point of V_2O_5 is 943 K. Since the T_s ($d_{sub} = 17$ cm) of the nanowire growth is ~ 764 K, the vapour from the source material is able to condense on the substrate, forming the nanostructure. Figure 5-6a shows the Ni substrate placed on $d_{sub} = 16$ cm ($T_s = \sim 824$ K), vanadium oxide thin film is observed. The nanoparticles grown have an average diameter of ~ 367 nm, ranging from ~ 263 to 579 nm. Figure 5-6b shows the substrate at $d_{sub} = 18$ cm with a substrate temperature of ~ 705 K. Small nanoparticles were scarcely and randomly deposited on the substrate. The nanoparticles grown has an average diameter of ~ 81 nm, ranging from ~ 31 to 160 nm.

Figure 5-7 shows the Arrhenius plot for particle size - temperature obtained from the SEM images measurement from Figure 5-1 and Figure 5-6. The calculated activation energy (Equation 4-4) for vanadium oxide nanowires on Ni foam is ~ 0.65 eV. A large activation energy indicates a higher substrate temperature is needed for nucleation and growth. The larger nanoparticles at $d_{sub} = 16$ cm can be suggested to the faster nucleation process due to the enhanced diffusion rate with the increased substrate temperature (Equation 4-4) with comparison with d_{sub} at 18 cm. The increased mobility allows the adatoms to overcome the activation barrier of the nucleate, growing into larger nanoparticles. For substrates at $d_{sub} = 17$ cm, the substrate temperature is still relatively

large enough for V_2O_5 to promote vapour-solid nanowire growth. The lower substrate temperature at $d_{\text{sub}} = 18$ cm reduces the amount of adatoms that is able to overcome the activation energy.

Figure 5-5: Phase diagram of Oxygen – Vanadium system [88].

Figure 5-6: SEM images of as-grown film onto Ni foam with substrate distance (a) $d_{\text{sub}} = 16$ cm, (b) $d_{\text{sub}} = 18$ cm.

Figure 5-7: Arrhenius plot of nanoparticle size for vanadium oxide nanowires on Ni foam.

5.3.2 Growth process of V₂O₅ nanosheets array

For the growth of V₂O₅ nanosheets array, Ni foams were placed downstream from d_{sub} from 12 – 20 cm away from the center of the source material. Vanadium chloride is used as precursor material for deposition as it has higher vapour pressure and melting point compares to vanadium oxide. Furthermore, metal chlorides have been used in CVD and successfully grown nanosheets [89]. Substrates that were placed 12 – 15 cm shows nanowall-like structures that are interwoven to each other (Figure 5-8a). No vanadium vapour was detected from the substrates showing that nanostructured NiO were synthesized as a result of the high temperature (~ 1145 to ~ 933 K). Substrates at $d_{\text{sub}} = 16$ and 17 cm indicates the formation of the nanostructured arrays, showing the deposition of vanadium on Ni foam (Figure 5-8b). From the Ni foam substrate at 16 cm, some nanosheets were formed from the stacking of nanoparticles. Sheets with small nanocrystals were also observed for various metal compounds such as SnO₂ [90] when metal chlorides were used as source material [89]. The growth of the V₂O₅ nanosheets can be explained using the island growth model. The adsorbate does not wet on the substrate as the V₂O₅ vapour prefers to deposit on the same material rather than on Ni foam so as to minimize the Gibbs free energy. Since there is a lattice mismatch between the materials, the adsorbate-adsorbate interaction is far better than adsorbate-substrate interaction. The lattice parameters for orthorhombic V₂O₅ are $a = 11.510$ Å, $b = 3.563$ Å and $c = 4.369$ Å and cubic Ni is $a = 3.516$ Å. Another factor to consider is that the high substrate temperature leads to fast diffusion and crystal growth rate. For example, ZnO nanosheets were synthesized at a T_s above 1073 K [91]. The ZnO nanosheets growth is the result of larger precursor concentration which results in side growth/deposition, forming nanosheets instead of nanowires. Similarly, Co₃O₄ nanosheets were synthesized by increasing the substrate temperature as the accumulation of precursor vapour is faster on the edges or corners due to longer molecular diffusion length [92]. Figure 5-8d shows small nanosheets emerging from the Ni foam when the substrate is placed at $d_{\text{sub}} = 17$ cm with a T_s of ~ 765 K. The high precursor vapour of substrates at $d_{\text{sub}} = 16$ cm allows the side deposition, formation of nanosheets larger than substrates at $d_{\text{sub}} = 17$ cm. Figure 5-8e shows the nucleation of nanoparticles when the $d_{\text{sub}} = 18$ cm with a T_s of ~ 705 K. The particles grown have an average diameter of ~ 121 nm, ranging from ~ 40 to 546 nm.

Figure 5-8: SEM images of as-grown film onto Ni foam with substrate distance (a) $d_{\text{sub}} = 12$ cm, (b) $d_{\text{sub}} = 16$ cm. (c) nanosheets showing initialization of growth at $d_{\text{sub}} = 16$ cm (d) $d_{\text{sub}} = 17$ cm with small nanosheets and (e) $d_{\text{sub}} = 18$ cm with nanoparticles.

Figure 5-9 shows the Arrhenius plot for particle size - temperature obtained from the SEM images measurement from Figure 5-8. The calculated activation energy (Equation 4-4) for vanadium oxide nanosheets on Ni foam is ~ 0.13 eV. The lower activation energy would enhance the diffusion of the adatoms, allowing nanosheets growth.

Figure 5-9: Arrhenius plot of nanoparticle size for vanadium oxide nanosheets on Ni foam.

Additional experiments were also carried out to understand the influence of flowrate on the morphology of V_2O_5 grown on Ni foam placed at $d_{\text{sub}} = 16$ cm. Figure 5-10a and Figure 5-10b show the thin films grown on Ni foam using a flowrate of 50 and 400 sccm, respectively. The precursor reactor residence time can be used to explain the deposition process. The residence time (t_s) is expressed using the following equation [26]:

$$t_{\text{res}} = \frac{VPn_m}{Q_{m_i}} \quad (\text{Equation 5-1})$$

Where P is the pressure in the reaction chamber, V is the volume in the reaction chamber, n_m is the molar concentration of the precursor vapour and Q is the flowrate of the carrier gas. During the experiments, the pressure is fixed at 1.3 mbar and the volume of the quartz tube is constant. The residence time is inversely proportional to the gas flowrate. The residence time for the reactant vapour to interact with the substrates is

longer for smaller flowrate and shorter for larger flowrate. Figure 5-10a shows the nanosheets array is synthesized which is similar to the V_2O_5 nanosheets array. The nanosheets grown were thinner with a thickness of ~ 48 nm, ranging from ~ 29 to 64 nm. Since the vapour residence time increases, the nanosheets array formed in Figure 5-10a consists of chlorine residue deposited along with the vanadium vapour as shown in the EDX spectroscopy (Figure 5-10c). Increasing the flowrate, the residence time for reactant to interact with the substrate is reduced. This resulted in a sparse amount of V_2O_5 particles formed on the Ni substrate (Figure 5-10b). Figure 5-10d shows the elemental analysis from energy dispersive X-ray spectroscopy (EDX) for d_{sub} at 16 cm using 400 sccm. No chlorine peaks were observed when the flowrate increases.

Figure 5-10: SEM images of as-grown film onto Ni foam using different flowrate for $d_{\text{sub}} = 16\text{cm}$ (a) 50 sccm (b) 400 sccm. EDX spectroscopy for $d_{\text{sub}} = 16\text{ cm}$ (c) 50 sccm (d) 400 sccm

5.4 Electrochemical evaluation of V_2O_5 on Ni foam current collector

Nickel foam is used as current collector due to its unique three dimensional microstructure which allows larger electrochemical sites and better charge transport due to its interconnected structure [93]. For instance, 3-D Ni foam has a lower internal resistance of 0.008 V as compared to 2-D Ni plate of 0.021 V and improved electrochemical performance [94].

The CV of the V_2O_5 nanostructure on Ni foil was tested from 0 – 0.5 V using KOH as the electrolyte at various scan rates of 1, 5, 10, 50 and 80 mV s^{-1} , and the results are shown in Figure 5-11. The sample shows obvious anodic and cathodic peaks. The pair of peaks is an indication of redox supercapacitor where there is charge transfer as a result of Faradaic reactions occurring at the surface of the electrode [95]. When a potential difference is applied, the redox transition of a metal oxide happens and there is an accumulation of charges on the surface. The ions in the solution will then counter-balance the charges as proton ions are transferred on the surface. Electrons are also transferred to external load, resulting in observable peaks in the cyclic voltammogram. The electrochemical reaction for potassium ions with V_2O_5 is expressed with the following equation [96]:

Where x is the mole fraction of K^+ ions.

Figure 5-11: Cyclic voltammogram of V_2O_5 on Ni foam using various scan rates.

Figure 5-12 shows the CV of V_2O_5 on Ni foam and annealed Ni foam substrate at a scan rate of 1 mV s^{-1} . The response current is weaker for Ni foam substrate than the

grown V_2O_5 sample. The calculated areal capacitance per area is $\sim 113 \text{ mF cm}^{-2}$ and $\sim 715 \text{ mF cm}^{-2}$ for Ni foam and V_2O_5 on Ni foam, respectively. The areal capacitance is calculated by dividing the electrode capacitance by area of the electrode. It is reported that annealed Ni foam has lower areal capacitance when comparing with untreated and cleaned Ni foam (18.2 mF cm^{-2} as compared to 82.7 and 145.6 mF cm^{-2}) [94]. The lower current response is suggested to be the passivation of nickel oxide on Ni foam through heat treatment at 1273 K for 2 hours, where the chemical activity between the electrode and electrolyte is reduced. The higher areal capacitance as compared to the reported values can be due to the shorter reaction time (30 min) and lower substrate temperature ($\sim 824 \text{ K}$) in the course of deposition. In another example, by increasing the heat treatment temperature of NiO, decreases the capacitance [97]. It is suggested that the decrease in capacitance is due to the improved crystallinity of NiO through heat treatment. For instance, the capacitance for NiO decreases from 377 mA cm^{-2} to 88.8 mA cm^{-2} when annealed from 383 K to 723 K . From Figure 5-12, a sharp increase the current response at the end of the positive potential is suggested to the oxygen evolution reaction (OER). The overall reaction for OER on Ni using alkaline solution is expressed with the following equation [98]:

The oxidation of oxygen ions on the surface of Ni substrate causes by an electrocatalytic process which appears as a sharp increase in the CV curve.

Figure 5-12: Cyclic voltammogram of V_2O_5 on Ni foam and annealed Ni foam.

V_2O_5 nanosheets and nanowires were grown on Ni foam, and were tested for supercapacitor. The measurement conducted using three-electrode cell, which consists of the as-grown sample as the working electrode, platinum wire as the counter electrode and Ag/AgCl as the reference electrode.

The mass of the deposited films was ~ 0.558 mg for V_2O_5 nanosheets and ~ 0.149 mg for V_2O_5 nanowires on Ni foam. Figure 5-13a shows the initial cycle C_s for V_2O_5 nanowires and nanosheets on Ni foam are ~ 833 F g^{-1} and ~ 1081 F g^{-1} at a rate of 2 A g^{-1} , respectively. From Figure 5-13b and Figure 5-13c, different current densities were used to measure the C_s of the electrodes. The C_s calculated are ~ 1081 F g^{-1} (2 A g^{-1}), ~ 838 F g^{-1} (5 A g^{-1}) and ~ 709 F g^{-1} (10 A g^{-1}) for V_2O_5 nanosheets on Ni foam. For V_2O_5 nanowires on Ni foam, C_s calculated are ~ 833 F g^{-1} (2 A g^{-1}), ~ 346 F g^{-1} (5 A g^{-1}) and ~ 244 F g^{-1} (10 A g^{-1}).

The cyclability of the electrodes was tested via continuous charge/discharge measurements from 0 – 0.5 V. From Figure 5-13d, V_2O_5 nanosheets on Ni foam shows an initial C_s of ~ 1081 F g^{-1} and retention of $\sim 96\%$, whereas V_2O_5 nanowires on Ni foam

shows an initial C_s of $\sim 833 \text{ F g}^{-1}$ and retention of only $\sim 75\%$ after 1000 cycles.

The V_2O_5 nanosheets arrays performed better than the nanowires on Ni foam. The arrays structure allow multiple electronic paths for electrons to transfer to external load, improving the overall capacitance and its retention [78]. As discussed previously from Figure 5-3b and Figure 5-8c, the gaps in between the interconnected nanoparticles provide access for electrolyte to interact with more surfaces of the V_2O_5 nanosheets array. The morphology of nanosheets array were more preferred as it allows more surface area for the interaction with the electrolyte as mentioned in previous studies [48, 49]. For example, nanoporous V_2O_5 network was able to achieve a C_s of $\sim 304 \text{ F g}^{-1}$ as compared to a C_s of $\sim 92 \text{ F g}^{-1}$ for V_2O_5 nanoparticles [96]. The energy and power densities are calculated using Equation 4-6 and Equation 4-7, respectively. For V_2O_5 nanowires on Ni foam, the energy density reaches $\sim 28.9 \text{ Wh kg}^{-1}$. a low power density of $\sim 0.86 \text{ kW kg}^{-1}$ can be obtained. For a similar energy density of $\sim 31.2 \text{ Wh kg}^{-1}$, a higher power density of $\sim 1.53 \text{ kW kg}^{-1}$ can be achieved for V_2O_5 nanosheets array on Ni foam. In terms of power density, V_2O_5 nanowires on Ni foam achieve $\sim 2.59 \text{ kW kg}^{-1}$, but a low energy density of $\sim 8.47 \text{ Wh kg}^{-1}$. V_2O_5 nanosheets array on Ni foam achieves better power and energy density of $\sim 3.12 \text{ kW kg}^{-1}$ and $\sim 24.6 \text{ Wh kg}^{-1}$, respectively.

Figure 5-13: (a) Galvanostatic charge/discharge behavior of supercapacitors for V₂O₅ nanosheets and nanowires on Ni foam at rate of 2 A g⁻¹. Galvanostatic charge/discharge curves for different scan rates (b) V₂O₅ nanosheets on Ni foam (c) V₂O₅ nanowires on Ni foam. (d) Cyclic performance of samples at rate of 2 A g⁻¹ for V₂O₅ nanosheets and nanowires.

Table 5-1 shows the comparison between V₂O₅ electrodes using various aqueous electrolytes. The reported capacitance in literature were calculated based on V₂O₅ as the active mass. In this work, the calculation is based on the total mass of deposited film which includes V₂O₅ and NiO as the active mass of the samples.

In this work, the calculated C_s for V₂O₅ nanosheets on Ni foam is ~31.2 Wh kg⁻¹. The capacitance is comparable to V₂O₅ electrodes fabricated by mixing with conductive agents and binder. For example, α -V₂O₅ mixed with 25 wt% acetylene black and 5 wt% PTFE

binder achieved a capacitance of 346.6 F g^{-1} between $0 - 0.8 \text{ V}$ using 2 M KCl and the energy density calculated is $\sim 30.8 \text{ Wh kg}^{-1}$ [14]. Although the energy density is similar, the polymeric binder and conductive agents were not included in the calculation of C_s for $\alpha\text{-V}_2\text{O}_5$.

Although interconnected nanoporous V_2O_5 shows higher energy density of 43.8 Wh kg^{-1} than V_2O_5 nanosheets on Ni foam, the cyclic retention loss is $\sim 24\%$ [96]. The decline in capacitance was suggested to the mechanical stress induced during insertion/deinsertion of electrolyte ions to electrode. V_2O_5 nanosheets on Ni foam have better cyclic retention as the electrolyte conductivity of KOH (508 mS cm^{-1}) is higher than K_2SO_4 (104 mS cm^{-1}), allowing better ionic mobility, insertion/deinsertion of ions to electrode [99].

Interconnected mesoporous carbon nanofiber composites with $20\% \text{ V}_2\text{O}_5$ loading shows a lower energy density of 18.8 Wh kg^{-1} and a high power density of 20 kW kg^{-1} in KOH electrolyte [100]. The energy density ($\sim 13 \text{ Wh kg}^{-1}$) decreases when the mass loading of V_2O_5 reduces to 5% . The enhanced power density was attributed to the small mesopores with sizes $3 - 5 \text{ nm}$ that allows fast adsorption/desorption of ions during electrolyte transportation.

The calculated C_s for V_2O_5 nanosheets on Ni foam based on the electrode mass is $\sim 9.46 \text{ F g}^{-1}$. The capacitance is comparable to electrospun V_2O_5 nanofibers with a C_s of 8 F g^{-1} in 2 M KOH electrolyte [74].

Table 5-1: Comparison of various V₂O₅ electrodes using different techniques.

Electrodes	Method	Electrolyte	Specific capacitance (F g ⁻¹)	Energy density (Wh kg ⁻¹)	Reference
V ₂ O ₅ nanosheets	CVD	2 M KOH	1081	31.2	This work
a-V ₂ O ₅	Heat treatment via quenching	2 M KCl	350	30.8	[14]
nanoporous V ₂ O ₅	Sol-gel	2 M KCl	214	19.0	[49]
nanoporous V ₂ O ₅	Capping-agent-assisted precipitation	0.5 M K ₂ SO ₄	316	43.8	[96]
V ₂ O ₅ nanofibers	Electrospinning	2 M KOH	8	0.9	[74]
V ₂ O ₅ / carbon nanofibers	Electrospinning	6 M KOH	150	18.8	[100]

Figure 5-14 shows the galvanostatic charge/discharge curve for V₂O₅ nanosheets on Ni foam using 1 M LiClO₄ in PC as electrolyte at a rate of 1 A g⁻¹. The mass of the deposited films was ~0.8 mg for V₂O₅ nanosheets on Ni foam Using Equation 4-5, the calculated C_s is ~87 F g⁻¹. However, the electrode breaks into pieces during cycling. It is known that the electrolyte is a strong oxidant due to its high oxidation state [101].

Figure 5-14: Galvanostatic charge/discharge behavior of supercapacitor for V_2O_5 nanosheets on Ni foam at rate of 1 A g^{-1} using 1 M LiClO_4 in PC as electrolyte.

5.5 Concluding remarks

In this chapter, V_2O_5 nanowires and nanosheets were successfully synthesized on Ni foam. The formation of nanowires is likely to be vapour-solid growth process and is due to the anisotropic growth as the b-axis is the fastest growth direction and c-axis is a slower growth direction due to its weak van der Waals forces which results in a 1-D growth. The formation of nanosheets is due to the high substrate temperature which allows fast diffusion and crystal growth rate. There is a lattice mismatch between the adsorbate and substrate. As the source vapour reaches the surface, it is adsorbed on the initially-formed V_2O_5 nanoparticles rather than on the substrate. The V_2O_5 nanosheets arrays achieve an initial C_s of $\sim 1081 \text{ F g}^{-1}$ and retention of $\sim 96\%$, whereas V_2O_5 nanowires on Ni foam shows an initial C_s of $\sim 833 \text{ F g}^{-1}$ and retention of only $\sim 75\%$ after 1000 cycles. The larger capacitance can be attributed to the gaps in between interconnected nanoparticles of the nanosheets which provide access for electrolyte and the interconnected nanosheets structure which allow multiple electronic paths for electrons transfer to external load.

The V_2O_5 nanosheets arrays on Ni foam shows good cyclic stability similar to the 2-D V_2O_5 thin film grown on hierarchical Al foil in Chapter 4 as compared to thin films or

nanowires structures. Thus, it is motivating to investigate V_2O_5 nanostructured arrays on stainless steel substrates since it is commonly used as current collector for energy storage applications.

Chapter 6 : Direct growth of FeVO₄ on stainless steel

6.1 Introduction

Transition metal oxides are mostly identified as anode materials for Li-ion batteries anodes as they are relatively stable in atmospheric environment, environment friendly and lower material cost. Among the various metal oxides, metal-vanadates are less studied but show relatively high capacity. For example, InVO₄ can achieve a capacity of > 1000 mAh g⁻¹ and FeVO₄ have an initial capacity of ~1300 mAh g⁻¹ [102]. The capacities of these metal-vanadates show larger capacity than other metal oxides. For example, FeVO₄ is able to reversibly react with about eight Li ions per unit formula. A transitional metal oxide, Fe₂O₃ can reversibly react with six Li ions per unit formula, resulting in theoretical capacity of ~1007 mAh g⁻¹. An interesting phenomenon was also observed for iron vanadate, where amorphous FeVO₄ has a larger capacity as compared with crystalline FeVO₄. Any attempt to anneal amorphous FeVO₄ to temperature above 673 K will reduce the capacity.

Currently, the main issue of FeVO₄ has been the capacity fading upon charge – discharge cycling. For example, amorphous FeVO₄ have an initial capacity of ~1300 mAh g⁻¹, but decreases in capacity to ~800 mAh g⁻¹ after 10 cycles. In order to improve the capacity stability of the materials, downsizing the material to nanoscale is an effective approach. By using one-dimensional or two-dimensional nanostructures on current collector, better improvement in performance and stability of the material has been reported for one dimensional nanorods array like SnO₂ on Ni foil or Co₃O₄ on Ti foil [103, 104]. Hierarchical Co₃O₄ shows a capacity of 700 mAh g⁻¹, whereas carbon black and polymer binder mixed Co₃O₄ nanowires and commercial Co₃O₄ shows a capacity of 350 mAh g⁻¹ and 80 mAh g⁻¹ after 20 cycles. The hierarchical morphology of the samples allow more materials to be exposed to the electrolyte solution, to have better ion diffusion and better distribution of space for volume change. The stability of the materials can be enhanced through the multiconnectivity of two-dimensional interconnected sample. One-

dimensional nanowires have the possibility of breaking off by mechanical stress or lithium-induced stress. When breaking off, the nanowires loss contact with the current collector and the material will not contribute to any capacity. The result of the interconnected nanostructures provides multiple current paths which any breaking off has limited influence on the capacity. For example, a two-dimensional silicon nanonets structure anode achieved a Coulombic efficiency of ~70%, whereas a one-dimensional Si nanowires anode shows a Coulombic efficiency of ~65% after 100 cycles [78].

In this work, amorphous FeVO₄ nanosheets arrays are grown on stainless steel foils using CVD process. The formation of FeVO₄ nanosheets array would eliminate the use of conductive acetylene black and a polymeric binder, improving the ion diffusion path and increase the exposed area between electrode material and electrolyte. Hence, the cyclic stability can be improved by downsizing the material to nanoscale.

6.2 Morphology characterization and phase analysis

Stainless-steel foils were placed downstream at 4 – 15 cm away from the center of the source material. As shown in Figure 6-1a, the stainless steel (SS) substrate collected from a substrate distance (d_{sub}) at 10 cm away have a substrate temperature of $T_S = 673$ K. and the final product of the samples was yellowish-brown in colour. As shown in Figure 6-1b, interconnected nanosheets with voids in between were formed and are aligned with the substrate. The measured width and thickness of the nanosheets range from 100 – 500 nm and 10 – 40 nm, respectively. From the cross sectional view of the sample, the thickness of the sample is ~4 μm .

Figure 6-1: (a) Low magnification SEM image of as-grown film on SS foil. Inset in (a) shows the optical image of the as-grown sample. (b) High magnification SEM image of the as-grown film. (c) cross-sectional view of as-grown sample.

The TEM image of the sample is shown in Figure 6-2 and its corresponding SAED pattern. As shown in the inset, the SAED pattern shows that the sample is amorphous as indicated by the diffused rings. Elemental analysis from EDX using TEM indicates the presence of Fe, V and O from the sample. The Cu and C peaks are from the grid used to hold the sample. The elements were uniformly dispersed in the nanosheet as shown in the elemental mappings (Figure 6-2c).

Figure 6-2: (a) TEM image and the SAED pattern of a single nanosheet (inset). (b) EDX spectrum of the nanosheet (c) Elemental mapping of nanosheet showing Fe, V and O.

XRD characterization was tested between 10° to 70° and used to examine the crystallinity of the sample. From Figure 6-3, no obvious peaks were observed for the FeVO_4 thin film grown on SS foil except for the initial peaks indicated from the SS foil. The as-grown sample did not include any evident diffraction peaks from iron oxides (Fe_2O_3 , Fe_3O_4) and iron vanates (FeVO_4 , $\text{Fe}_2\text{V}_4\text{O}_{13}$), which suggests that the sample has poor crystallinity.

Figure 6-3: XRD pattern of CVD-grown film on SS and SS foil. Standard XRD patterns for crystalline $\text{Fe}_2\text{V}_4\text{O}_{13}$, FeVO_4 , Fe_3O_4 and Fe_2O_3 drawn for reference.

Since the powder pattern of the FeVO_4 thin film is amorphous, the quantification and crystal structure cannot be determined using XRD method alone. Hence, alternative methods such as inductively coupled plasma (ICP) and X-ray photoelectron spectroscopy (XPS) methods were used. ICP is a type of mass spectroscopy which is able to detect the metal concentrations and quantify the sample. XPS is a quantitative method that analyzes the surface chemistry of the sample to determine the elemental composition and chemical state. ICP was used to test the Fe:V ratio in the film grown. The result shows an atomic ratio of 1:1, which match the atomic ratio of Fe: V in FeVO_4 . Analysis depth technique such as XPS was also used to determine the oxidation state of the sample. From Figure 6-4a, the Fe 2p spectrum indicates Fe oxidation state to be Fe^{3+} as exhibit by two binding energies at 711.0 eV and 724.8 eV belonging to Fe $2p_{3/2}$ and Fe $2p_{1/2}$, respectively [105]. From Figure 6-4b, the V 2p spectrum indicates V oxidation state to be V^{5+} as explain by

two binding energies at 516.9 eV and 524.5 eV belonging to V 2p_{3/2} and V 2p_{1/2}, respectively [106]. Hence, these results suggested that the thin film is amorphous FeVO₄.

Figure 6-4: XPS spectra of (a) Fe (b) V 2p spectra obtained from the as-grown sample

6.3 Study of growth process

The initial attempt of the growth process was to create V₂O₅ nanostructures on stainless steel foil. However, during the heating process, the iron oxidizes at the surface and reacts with the vanadium and oxygen vapour from the precursor materials to form amorphous FeVO₄.

Figure 6-5a shows the SEM image of the non-treated SS foil. The SS foil has an initial smooth and unidirectional surface. The stainless steel foil was then annealed at 673 K for 30 minutes in air. It resulted in a rough surface and some emergence of nanosheets can be seen as shown in Figure 6-5b. The particles from annealed SS foil were characterized using TEM. The small particle matches α -Fe₂O₃ (JCPDS no. 33-0644) from the SAED pattern (inset of Figure 6-5c), which can act as a catalyst seed for the growth of FeVO₄ nanosheets. The SS foil provides continuous Fe source to react with the vanadium and

oxygen reactants in the gas phase. It is reported that the iron concentration on the surface of the SS foil increases with heat treatment [107]. For example, the atom percent of iron at the surface increases from 28% to 34% when annealed to 673 K in 6×10^{-6} Torr air. The evaporation and deposition process can be described as follow:

Figure 6-5: FESEM of (a) non-treated (b) annealed stainless steel foil. The arrows indicate the formation of nanosheets. (c) TEM image of the nanosheet obtained from annealed SS foil and the corresponding SAED pattern (inset).

The substrate temperatures and the relationship with the morphologies grown were also investigated. Stainless steel substrates were placed 4 – 15 cm away from the center of the tube furnace. The temperature profile of tube furnace at 723 K is shown in Figure 6-6.

Figure 6-6: Temperature profile of the tube furnace at 723 K.

Figure 6-7 shows the FESEM images of the different morphologies grown at various substrate distances. Figure 6-7a shows the substrate at $d_{\text{sub}} = 4$ cm with a substrate temperature of ~ 713 K. Irregular-shaped particles of 100 – 400 nm were formed and can be attributed to the fast nucleation rate along the substrate surface. It can also be pointed out as the increase in surface roughness from heat treatment as discussed previously. Figure 6-7b shows the substrate at $d_{\text{sub}} = 7$ cm with a substrate temperature of ~ 696 K. Mixed nanoparticles and nanosheets structure was observed and magnified as shown in Figure 6-7c and Figure 6-7d, respectively. The nanosheets density is drastically reduced when the substrate is placed at $d_{\text{sub}} = 15$ cm as shown in Figure 6-7e. No growth on the substrates was observed beyond $d_{\text{sub}} > 15$ cm.

Figure 6-7: SEM images of as-grown film onto SS foil with substrate distance (a) $d_{\text{sub}} = 4$ cm, (b-d) $d_{\text{sub}} = 7$ cm and (e) $d_{\text{sub}} = 15$ cm.

Figure 6-8 shows the Arrhenius plot of FeVO_4 nanoparticles on stainless steel foil. Using Equation 4-4, the calculated activation energy of FeVO_4 on stainless steel foil is ~ 1.75 eV. The activation energy is higher on stainless steel as compared on aluminium foil (~ 0.40 eV) (Figure 4-13). Since the activation energy is higher, it can be suggested

that chemisorption process is involved where there is a reaction between the substrate and adatom.

Figure 6-8: Arrhenius plot of nanoparticle size for iron vanadate on stainless steel foil.

It is worth to mention that it is difficult to convert the amorphous FeVO_4 to crystalline sample without degrading the whole structures through annealing. To crystallize the sample, it may require heat treating the sample at ~ 873 K in air according to previous report on FeVO_4 [102]. However, this process will cause the oxidation of the SS substrate/current collectors. On the other hand, annealing in Ar atmosphere at 873 K leads to the collapse of nanosheet arrays (Figure 6-9a) and loss of vanadium source, which is indicated by the reduced atomic ratio of Fe : V = 5 : 1 according to EDX analysis (Figure 6-9b) and no obvious peaks relating to vanadium compounds in the XRD pattern (Figure 6-9c).

Figure 6-9: (a) FESEM image of as-grown film on a SS substrate calcined at 873 K. (b) Corresponding EDX spectroscopy. For EDX analysis, the film on SS foil as shown in (a) was peeled off by adhesive tape, and then dispersed in acetone solution by ultrasonication. The suspension was finally dripped on the Si substrate for observation. (c) Corresponding XRD pattern of film on SS foil.

6.4 Electrochemical evaluation of FeVO_4 on SS current collector

Figure 6-10 shows a schematic drawing of the 2-D FeVO_4 nanosheets array. The nanosheets array would allow fast Li^+ ion diffusion and good electron transport during lithium insertion/desertion. Due to the reduced dimensions, it reduces the path of the electronic and ionic species to travel from the nanomaterials to the current collector, improving the rate performance. Also, the open spaces between the nanosheets allow more materials to be exposed to the electrolyte and space to accommodate strain during volumetric expansion that associates with Li insertion, contributing to larger capacity.

Figure 6-10: A schematic diagram illustrating the fast lithium ion diffusion and good electronic transport

The mass of the deposited films is ~ 0.6 mg. The CV plots (Figure 6-11a) of amorphous FeVO_4 were tested from 0.005 – 3.5 V using a rate of 0.2 mV s^{-1} for the first three cycles. Two cathodic peaks at ~ 1.4 and ~ 0.7 V were observed, and an anodic peak at ~ 1.7 V. The peaks match closely to the sloping voltage curves shown in Figure 6-11b. The voltage profile shows a typical partly reversible conversion reaction. The conversion

reaction involves the transition metal oxide to first reduce into metal and lithium binary compound (Li_nO). Due to the large interfacial surfaces, the matrix decomposes when reverse polarization is used. From Figure 6-11b, during the first cycle Li^+ intercalation, a capacity of $\sim 465 \text{ mAh g}^{-1}$ is achieved as the voltage decreases to $\sim 0.85 \text{ V}$. This corresponds to approximately 3.0 Li intercalation per formula unit of FeVO_4 . As the voltage decreases, a gradual slope is shown in the figure and a specific capacity of 1228 mAh g^{-1} is achieved (10.8 Li per formula unit of FeVO_4). The total-first discharge capacity achieved is 1693 mAh g^{-1} . The large capacity achieved can be subjected to the formation of a solid electrolyte interface (SEI) and a gel-like polymeric layer surrounding the surface of the material due to the decomposition of solvent in the electrolyte [108, 109]. The electrochemical reaction is different from the reported discharge curves obtained from references, two plateau at $\sim 1.2 \text{ V}$ and $\sim 0.75 \text{ V}$ were observed for Fe_2O_3 and four plateau at 3.14, 2.51, 2.30 and 1.88 V were observed for V_2O_5 [38, 43, 110]. The first charge curve produces a capacity of 1232 mAh g^{-1} , which corresponds to the deintercalation of 7.9 Li per formula unit of FeVO_4 . The 1st cycle results in a capacity loss of 461 mAh g^{-1} which can be attributed to the formation of the SEI layer. The 2nd cycle produces a discharge and charge capacity of 1316 and 1215 mAh g^{-1} , respectively. From Figure 6-11c, the cyclic performance of the electrodes was tested for 100 cycles. The electrodes can achieve a reversible capacity of 1237 mAh g^{-1} after 100 cycles, corresponding to 94% Coulombic efficiency with respect to the 2nd discharge capacity. The Coulombic efficiency of the electrode is 73% on the first cycle and increases close to 100% upon progressive cycling. The cyclic rate performance for FeVO_4 nanosheets array is shown in Figure 6-11d. The electrode shows a capacity of 1237, 1054, 961, 878, 764 and 601 mAh g^{-1} for current densities of 0.5 (0.4C), 1 (0.8C), 2 (1.5C), 3 (2.3C), 5 (3.8C) and 10 A g^{-1} (8C), respectively. At even higher current density of 20 A g^{-1} (15C), the FeVO_4 electrode can still achieve 453 mAh g^{-1} , which is larger than the theoretical capacity of graphite anode electrode of 372 mAh g^{-1} . The specific capacity is able to recover about 1120 mAh g^{-1} when the current density is reduced back to 0.5 A g^{-1} .

Figure 6-11: (a) Cyclic voltammogram of the FeVO₄ nanosheets array at a scan rate of 0.2 mV s⁻¹. (b) Galvanostatic charge/discharge voltage profile (c) Cyclic performance of FeVO₄ nanosheets array (d) Charge/discharge capacities at multiple current densities from 0.5 to 20 A g⁻¹.

The first cycle electrochemical process is analyzed using ex-situ XPS for the FeVO₄ nanosheets array. From Figure 6-12a, the Fe 2p spectrum indicates the Fe oxidation state to be Fe⁰ as exhibited by the two binding energies at 707.1 eV and 720.0 eV belonging to Fe 2p_{3/2} and Fe 2p_{1/2}, respectively [111]. This implies that the Fe is reduced to metallic state from the initial Fe³⁺ as mentioned previously in Figure 6-4a. From Figure 6-12b, the V 2p spectrum can be fitted into two components V²⁺ and V³⁺. The ratio between V²⁺ and V³⁺ is estimated to be 32:68, where the average oxidation state of V being 2.3. During the delithiation or charging process, Fe is oxidized to +3 at 3.5 V (Figure 6-12c). From Figure

6-12d, the V 2p spectrum can be fitted into two components V^{4+} and V^{5+} . The ratio between V^{4+} and V^{5+} is estimated to be 34:66, where the average oxidation state of V being 4.7. The XPS result calculated is similar to the XANES data reported in the literature using triclinic $FeVO_4$ [112]. From the first cycle, a reversible amount of 5.4 Li per formula unit of $FeVO_4$ is reached. By using Equation 2-11, the calculated capacity for the $FeVO_4$ sample is $\sim 847 \text{ mAh g}^{-1}$. However, the calculated capacity is lower than the capacity achieved from the experiment of 1237 mAh g^{-1} . The larger capacity suggests that the oxygen anion acts as redox center where there is Fe-“O-Li” and V-“O-Li” phase interaction. The formation of “O-Li” can result in an increased in capacity.

Figure 6-12: Ex-situ XPS data of Fe 2p and V 2p spectra for FeVO₄ nanosheets array electrode during (a) Fe 2p, 1st discharge (b) V 2p, 1st discharge (c) Fe 2p, 1st charge and (d) V 2p, 1st charge.

6.5 Concluding remarks

Stainless steel foils were placed 4 – 15 cm downstream away from the source material. SEM characterization shows the relationship of the morphology of the sample with substrate temperature. With a substrate temperature of ~673 K, iron vanadate nanosheets array were successfully grown on SS foil using CVD method. When bare SS foil was

annealed in air, the surface of the foils turned rough and revealed some nanosheets structure. TEM characterization reveals that these nanosheets were α -Fe₂O₃, which can act as a catalyst seed for the growth of FeVO₄ nanosheets. The voltage profile from cyclic voltammogram reveals a typical partly reversible conversion reaction. The peaks observed is different from those observed in Fe₂O₃ and V₂O₅. During the first discharge, a high capacity of 1693 mAh g⁻¹ was achieved. The electrode is able to sustain a reversible capacity of 1237 mAh g⁻¹ after 100 cycles, corresponding to 94% columbic efficiency with respect to the 2nd discharge capacity. Also, the 2-D FeVO₄ nanosheets array show good rate performances. At a high current density of 20 A g⁻¹ (15C), a discharge capacity of 453 mAh g⁻¹ can be achieved.

Chapter 7 : Conclusion and future work

7.1 Conclusion

This thesis investigates the formation of 2-D nanostructures arrays through fabrication strategies such as self-growing and wet-etching. Chemical vapour deposition process technique was used to create 2-D nanostructured arrays on various current collectors such as aluminium, nickel and stainless steel. Electrochemical evaluation of the as grown films were fabricated and tested for energy storage applications without any reliance on binders or conductive agents. The growth process of the thin films using CVD were also studied through the formation of nanoparticles thin films, nanowires and nanosheets arrays.

For the growth of V_2O_5 on aluminium substrate, aluminium foil was wet etched to create a 2-D hierarchical current collector using alkaline solution. Various types of alkaline solutions (LiOH, NaOH and KOH) of similar concentrations were used to etch the foil. Al foil etched with LiOH forms nanosheet arrays, whereas NaOH and KOH solutions forms nanoparticles film. Different concentrations of LiOH solutions (0.15, 0.50 and 1.00 M) were also used to estimate the surface area. Al foil etched in 0.15 M LiOH have a larger area of $\sim 1.24 \text{ cm}^2$ as compared to 0.50 M ($\sim 1.14 \text{ cm}^2$) and 1.00 M LiOH ($\sim 1.07 \text{ cm}^2$). FTIR and XRD measurement reveals that no byproduct such as $Al(OH)_3$ or $AlOOH$ were produced during etching. The hierarchical structure remains after V_2O_5 deposition. V_2O_5 thin film grown on Al foil has an average particle size of ~ 205 , ~ 121 , ~ 70 and $\sim 24 \text{ nm}$ when placed with a substrate distance of 7, 10, 13, 25 cm away from the center of the tube furnace. The growth of the nanoparticles thin film follows the island growth mechanism where the adatoms adsorbed on the nuclei. The smaller particle size can be due to the faster nucleation process and lower precursor vapour at lower substrate temperature. From the Arrhenius plot, the calculated activation energy is $\sim 0.09 \text{ eV}$. A low activation energy indicates more nucleation and particles growth. Supercapacitor

measurements were made suggests that V_2O_5 on hierarchical Al perform better with C_s of $\sim 289 \text{ F g}^{-1}$ and retention of $\sim 91\%$ and V_2O_5 on untreated Al foil with C_s of $\sim 152 \text{ F g}^{-1}$ and retention of $\sim 76\%$ after 1000 cycles at a rate of 5 A g^{-1} in 1 M LiClO_4 in PC. The hierarchical structure improves the electronic contact, shorter ion transport distance between V_2O_5 and Al foil electrode and increases the material/electrolyte contact. The arrays structure allow multiple electronic paths for electrons to transfer to external load, improving the overall capacitance and its retention.

Catalyst-free growth of V_2O_5 nanowires and nanosheets were synthesized directly on Ni foam. V_2O_5 nanowires were grown on Ni foam using V_2O_5 powder at d_{sub} of 17 cm and thin film morphologies were observed for substrates placed at 16 and 18 cm. The measured nanowires have an average diameter of $\sim 126 \text{ nm}$ and the nanoparticles thin films grown have an average diameter of $\sim 367 \text{ nm}$ ($d_{\text{sub}} = 16 \text{ cm}$) and $\sim 81 \text{ nm}$ ($d_{\text{sub}} = 18 \text{ cm}$), respectively. From the Arrhenius plot, the calculated activation energy is $\sim 0.65 \text{ eV}$. A large activation energy indicates a higher substrate temperature is needed for effective nucleation and growth of nanoparticles. V_2O_5 nanowires growth is suggested to follow the vapour-solid growth and the formation is due to the anisotropic growth as $[010]$ is the fastest growth direction. In a separate experiment, V_2O_5 nanosheets arrays were synthesized using VCl_3 powder ($d_{\text{sub}} = 16 \text{ cm}$). The nanosheets averages with a diameter of $\sim 13.5 \text{ }\mu\text{m}$ and thickness of $\sim 198 \text{ nm}$. The nanosheet is formed by interconnected nanoparticles with an average size of $\sim 19 \text{ nm}$. Small V_2O_5 nanosheets and nanoparticles were observed when the substrates is placed at 17 and 18 cm, respectively. The growth of nanosheets arrays on Ni foam is due to the high substrate temperature which leads to longer diffusion length and crystal growth rate. The calculated activation energy is $\sim 0.13 \text{ eV}$ from the Arrhenius plot. The low activation energy allows large mobility of the adatoms on the substrate at high temperatures. Supercapacitor measurements reveal that V_2O_5 nanosheets on Ni foam perform better with C_s of $\sim 1081 \text{ F g}^{-1}$ and retention of $\sim 96\%$ and V_2O_5 nanowire on Ni foam with C_s of $\sim 833 \text{ F g}^{-1}$ and retention of $\sim 75\%$ after 1000 cycles at a rate of 2 A g^{-1} using 2 M KOH . The interconnected nanoparticles structure of the V_2O_5 nanosheets provide access for electrolyte to interact with more surfaces of the V_2O_5 nanosheets array. The V_2O_5 nanosheets array on Ni foam (31.2 Wh kg^{-1}) has better energy density than reported V_2O_5 electrode on Ni foil (18.8 Wh kg^{-1}). Also, the V_2O_5

nanosheets array on Ni foam based on total electrode mass have a C_s of $\sim 9.46 \text{ F g}^{-1}$, which is comparable to reported V_2O_5 electrodes of 8 F g^{-1} . The energy and power density of V_2O_5 nanosheets array on Ni foam (31.2 Wh kg^{-1} , 1.53 kW kg^{-1}) is lower than V_2O_5 on etched Al (160 Wh kg^{-1} , 2 kW kg^{-1}). The hierarchical structure of the etched Al foil perform better as it permit better electronic contact and shorter ion transport distance between the material and the electrode.

Lastly, amorphous FeVO_4 nanosheets arrays were grown on stainless steel foils. Interconnected nanosheets with width of 100 - 500 nm and thickness of 10 - 40 nm were synthesized when the substrate is placed at $d_{\text{sub}} = 10 \text{ cm}$. Nanoparticles and mixed morphologies of nanoparticles and nanosheets were observed when the substrate is placed at $d_{\text{sub}} = 4 \text{ cm}$ and $d_{\text{sub}} = 7 \text{ cm}$, respectively. XRD and SAED pattern reveal the sample to be amorphous. Annealing the sample at 873 K to improve its crystallinity in Ar atmosphere leads to the collapse of nanosheet arrays and evaporation of vanadium from the as-grown film. The growth of the FeVO_4 thin film initiates from the oxidation of stainless steel foil forming Fe_2O_3 on the surface and interacting with the vanadium precursor. The calculated activation energy is $\sim 0.27 \text{ eV}$ from the Arrhenius plot. The higher activation energy may impede the growth of FeVO_4 nanostructures on stainless steel foil as compared on aluminium foil as the SS foil is mostly amorphous. Amorphous substrates have less or no nucleation centers where the adatoms might desorb before landing on a nuclei. Cyclic voltammogram was tested between 0.005 - 3.5 V shows two peaks at ~ 1.4 and $\sim 0.7 \text{ V}$ on the first cycle. The plateau observed is different from peaks from Fe_2O_3 and V_2O_5 . The electrochemical property of the as-grown film achieved an initial discharge capacity of 1693 mAh g^{-1} on the initial cycle at a rate of 0.2 A g^{-1} (0.15 C). The Coulombic efficiency is $\sim 73\%$ for the first cycle and shows a reversible capacity of 1237 mAh g^{-1} after 100 cycles. At a current density of 20 A g^{-1} (15C), the FeVO_4 electrode can still achieve 453 mAh g^{-1} , which is larger than the theoretical capacity of graphite anode electrode of 372 mAh g^{-1} . The 2-D nanosheets array structure allows fast Li^+ ion diffusion and good electron transport as it reduces the path of the electronic and ionic species to travel from the nanomaterials to the current collector, improving the rate performance. Also, the open spaces between the nanosheets allow more materials to be

exposed to the electrolyte and accommodating the strain during Li insertion, improving the capacity and cyclic retention.

7.2 Novel contributions from this thesis

The first approach is via wet-etching of current collector such as aluminium foil to create a 2-D hierarchical current collector. In this work, the formation of two-dimensional aluminium nanosheets arrays is simplified via drop-casting of LiOH solution. Only Al foil etched with LiOH forms nanosheet arrays. Both NaOH and KOH solutions results in formation of particles. The growth process of Al nanosheets array also reveals that small amount of nanosheets start to appear when exposed with LiOH solution for five minute. V_2O_5 thin film deposited on the Al nanosheets arrays shows good cyclic stability (~91%) and capacitance ($\sim 289 \text{ F g}^{-1}$) as compared to V_2O_5 thin film on untreated Al (~76%, $\sim 152 \text{ F g}^{-1}$). This result suggests that the hierarchical structure improves the electronic contact and shorten the ionic transport distance.

The second approach is by direct growth of vanadium oxides nanostructures on Ni foam. Interconnected V_2O_5 nanosheets array were successfully synthesized on Ni foam. From the SEM and TEM images, the nanosheets is formed from the stacking of nanoparticles. The low calculated activation energy ($\sim 0.13 \text{ eV}$) also indicates that the adatoms have high diffusion rates resulting in the formation of nanosheets. V_2O_5 nanosheets array on Ni foam shows good cyclic retention (~96%) and higher energy density ($\sim 31.2 \text{ Wh kg}^{-1}$) than V_2O_5 electrodes tested in KOH electrolyte.

Amorphous $FeVO_4$ nanosheets arrays were synthesized directly on stainless steel foil. XRD and SAED pattern shows that the film grown is amorphous. Annealed SS foil results in the iron oxidation and emergence of small nanosheets. This indicates that the SS foil provides Fe source and reacts with V and O from the gas phase to form $FeVO_4$ nanosheets. The 2-D $FeVO_4$ nanosheets array on SS foil achieved a reversible capacity of 1237 mAh g^{-1} after 100 cycles and Columbic efficiency of 94% with respect to the 2nd discharge capacity. It is previously reported that $FeVO_4$ is able to achieve good initial capacity (1300 mAh g^{-1}) but fades drastically in capacity after 10 cycles (800 mAh g^{-1}) synthesized by a pH-controlled dissolution-reprecipitation process [102]. The improved capacity can

be attributed to fast Li^+ ion diffusion and good electron transport. Also, the open spaces in between nanosheets allow more materials to be exposed to the electrolyte and improves the strain accommodation during Li insertion/deinsertion.

7.3 Future work

Based on the results of the current work, vanadium oxides nanostructure arrays show good performance and cyclic stability when tested for energy storage applications. The nanostructured arrays provide higher energy density due to larger exposed area and direct contact of the active materials with the electrolyte. Hence, the motivations to investigate vanadium based electrodes are discussed in this chapter.

7.3.1 Continuation work for V_2O_5 nanostructures for energy storage applications

Although 2-D nanostructured arrays vanadium oxides electrodes show good energy density and cyclic stability, the thickness of the thin film grown is still relatively large. For supercapacitors, the presence of active redox sites is on the top layer of the active materials coating. The electrolyte has limited access to the bulk of the coating. Hence, a thicker thin film coating would decrease the electron transport and decreases the energy densities.

To be able to control the thickness of the deposited thin film, approaches such as electrodeposition and ALD can be used. For example, V_2O_5 is deposited on AAO template using electrodeposition [16]. Figure 7-1 shows the deposition time of V_2O_5 coating onto CNT. The capacitance obtained reaches 871 F g^{-1} with 10 minutes deposition and decreases to 271 F g^{-1} with deposition time of 90 minutes. Similarly, ALD is another vapour deposition technique that allows precise and uniform deposition of coatings. A $\sim 10 \text{ nm}$ V_2O_5 coating on electrode can be obtained by performing 100 ALD cycles. The V_2O_5 electrode is able to achieve capacitance of $\sim 1400 \text{ F g}^{-1}$ at a rate of 5 mV s^{-1} in aqueous electrolyte [9]. Thus, various thickness of V_2O_5 thin film can be deposited on Al

foils that are etched with LiOH solution to create 2-D nanostructured arrays and investigate as an electrode for supercapacitors application.

Figure 7-1: Specific capacitance of V₂O₅ deposited on AAO template with various deposition time [16].

V₂O₅ is one of the attractive materials for Li ion batteries due to its high capacity (~294 mAh g⁻¹) when used as cathode material. However, one of the drawbacks of V₂O₅ is its poor cyclic stability due to its poor ion diffusion and electrical conductivity. Several approaches have been suggested to improve the capacity of the materials. For example, V₂O₅ grown on TiSi₂ nanonets obtained a high initial capacity of 461 mAh g⁻¹ and decreases to 334 mAh g⁻¹ after 40 cycles [115]. The TiSi₂ nanonets are grown directly onto the Ti foil which improves the electron transport as well as the interconnected structure improves the structural stability during cycling [78]. Similarly, interconnected V₂O₅ nanosheets grown on CNT obtained an initial capacity of 285 mAh g⁻¹ and decreases to 190 mAh g⁻¹ after 100 cycles whereas V₂O₅ microflowers obtained an initial capacity of 230 mAh g⁻¹ and decreases to 118 mAh g⁻¹ after 100 cycles [84]. The conductive CNT improves the electronic transport and diffusion length of Li ions. Thus, it is worthwhile to investigate V₂O₅ on the treated Al foils since interconnected V₂O₅ structures show improved capacity and cyclic performance.

7.3.2 Growth of various iron vanadates for energy storage applications

From the current work of amorphous FeVO_4 thin film, it shows low discharge plateau (~ 0.7 V) and good columbic efficiency ($\sim 94\%$) with respect to the 2nd discharge capacity.

Vanadates-based electrodes have reported to show good capacity performance (800 mAh g^{-1}) and low potential (~ 0.2 vs Li^+/Li^0) when used as anode materials for the application of Li-ion batteries [116]. This is approximately intercalation of 7 Li ions per formula unit of vanadates-based electrodes, which is twice the amount of Li intercalation as compared to conventional graphite electrodes.

For example, spinel structured Fe_2VO_4 have a low discharge plateau below 0.6 V and a reversible capacity of $\sim 225 \text{ mAh g}^{-1}$ at a rate of 1C for 30 cycles [117]. Another vanadate material that is studied for Li-ion batteries is $\text{Fe}_2\text{V}_4\text{O}_{13}$ [118]. $\text{Fe}_2\text{V}_4\text{O}_{13}$ has a higher energy density of $\sim 738 \text{ Wh kg}^{-1}$, which is higher than various common cathode materials like LiCoO_2 ($\sim 518 \text{ Wh kg}^{-1}$), LiMn_2O_4 ($\sim 500 \text{ Wh kg}^{-1}$) and LiFePO_4 ($\sim 500 \text{ Wh kg}^{-1}$).

Thus, it is worthwhile to investigate the various oxidation states of iron vanadates for the application of Li-ion batteries. Figure 7-2 shows the binary diagram of various oxidation states of iron vanadates, which can be synthesized and tested.

Figure 7-2: Binary diagram of V_2O_5 - Fe_2O_3 system [118].

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