

ABSTRACT

Title of Dissertation: ELECTROCHEMISTRY OF PRECISION
NANOSTRUCTURES FOR HIGH
PERFORMANCE ENERGY STORAGE
DEVICES

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With the increase in the demand for high performing energy storage devices, the energy storage community has explored ways to improve Li-ion battery chemistry. Previous research has demonstrated that nanostructuring of Li-ion electrodes enables significant improvements in their power and energy densities. However, a systematic study is needed to quantify the impact of specific structural properties on the electrochemical behavior of the nanostructured electrode and to develop a guideline for high performance energy storage devices. In the first study of this dissertation, we investigate the impact of pore diameter, dynamic conductivity and interconnected structures on the electrochemistry of V_2O_5 , cathode material for Li ion batteries. We determined that there were positive and negative effects of the interconnected structure depending on the material properties. When V_2O_5 's electronic conductivity increased with the degree of lithiation, a higher power density was measured with more

interconnections. When the material's electronic conductivity decreased with lithiation, a lower power density was measured with more interconnections. In the second study, we employ microfabrication techniques and atomic layer deposition to fabricate well defined nanochannels to study the effect of electrolyte nanoconfinement on the electrochemistry of anatase TiO_2 . Surprisingly, nanoconfinement resulted in high energy and power densities when compared to the bulk material. Simulations showed that the improvement in the electrode behavior was due to the negative surface charges of TiO_2 which resulted high local concentration of Li ions within the nanochannel and minimal loss in the driving potential was observed at the stern layer. In the third study, we fabricate a platform for high performance 3D solid state batteries on a Si wafer to study the effect of high aspect ratio nanostructures on the electrochemical behavior of thin film solid state batteries. The V_2O_5 electrode in 3D scaffold showed 113 times higher capacity than the planar electrode at $2\mu\text{A}/\text{cm}^2$ and 1333 times higher capacity at $0.5\text{mA}/\text{cm}^2$. These studies can help to understand key structural parameters for improved Li-ion batteries, and the test platforms we developed in these studies can be applied to increase understanding of structural impacts on other ion battery chemistries as well.

ELECTROCHEMISTRY OF PRECISION NANOSTRUCTURES FOR HIGH
PERFORMANCE ENERGY STORAGE DEVICES

by

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Dedication

I dedicate this to my dad, Yung Jin Kim, my mom, Ok Mi Kim, my sister, April Kim, and our dog, Cookie Kim.

I would like to specially thank our dog, Cookie, who recently passed away on the 22nd of October, 2019. He was a family member and I will miss him greatly. He was with me since I started by studies as an undergraduate here at UMD. All the troubles and problems I faced, he was able to make me forget about them with just a wag of his tail. He will be missed greatly.



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List of Abbreviations

AAO – Anodized Aluminum Oxide

ALD – Atomic Layer Deposition

BSE – Backscattered Electrons

CV – Cyclic Voltammetry

CVD – Chemical Vapor Deposition

EDL – Electrical Double Layer

EDS – Energy Dispersive X-ray Spectroscopy

FFT – Fast Fourier Transform

PC – Propylene Carbonate

SE – Secondary Electrons

SEM – Scanning Electron Microscopy

TEM – Transmission Electron Microscopy

1 Towards High Performing Energy Storage Devices

1.1 Background and Motivation

The current century will be the turning point in the way energy is harvested. Previously, especially since the industrial evolution, the main source of energy was fossil fuel. Modern society is built on the utilization of fossil fuels from transportation to generation of electricity. With the growing population and increase in the quality of life comes an increased demand for electricity.¹ With the increased demand for electricity, more non-renewable fossil fuel will be burnt. With the usage of fossil fuels, more greenhouse gases will be released into the atmosphere leading to global warming. It is projected that the average global surface temperature will be at or above the 1.5C° by 2100. Many areas are already seeing increased average temperature above 1.5C°.² This increase in the average surface temperatures will lead to hotter heatwaves in land, increase in frequency and intensity of precipitations in some areas whereas other areas will see increased droughts. With higher CO₂ levels will lead to acidification of the ocean. All of these changes within couple of decades will cause massive disruption to the food and water sources.³

In order to minimize the usage of fossil fuels and try to reduce the amount of greenhouse gases released into the atmosphere, the energy source needs to be clean and renewable. One of the promising renewable energy source is solar energy.⁴ With the advancements in the photovoltaic cells and higher efficiency rates and lower manufacturing costs, solar power has become more affordable. However, it does have

a weak point in that it requires the sun, more specifically the sun light. When the photovoltaic cells are not in direct sunlight, their efficiency significantly drops. Without sun light, it cannot produce electricity. Dependence on the environment also is similar to other renewable energies such as wind power. Without wind, the turbines would stay still, not producing energy. There is also another case where too much electricity is generated and is wasted. In order to solve these issues with renewable energy sources, energy storage devices are needed to store excess energy and release them, as a buffer to the fluctuations in the energy demand.⁵⁻⁹ The advancement in energy storage devices, such as batteries, can enable wide spread use of renewable and green energy sources.

Not only are energy storage devices needed to stop and revert climate change, they are also needed to accommodate the ever increasing number of portable electronic devices such as smart phones, wireless sensors, internet of things, and wearable devices.¹⁰⁻¹² As more portable devices are getting smaller with the advancement in technology, the energy storage systems also need to further improve. One method of improving energy storage systems is through nanostructuring. Nanostructured energy storage devices can have vastly different morphologies which can be categorized based on their dimensionality.^{8, 12-14} More detail on this categorization is discussed later in this chapter. These different morphologies may hinder or improve energy storage behavior of the electroactive material. In this dissertation, carefully controlled nanostructured electrodes were fabricated to systematically study the impact of specific structural properties on the electrochemical properties of the nanostructured electrodes.

1.2 Electrical Energy Storage Devices, Batteries

1.2.1 Battery Energy Storage Mechanism

One of the ways to store electricity is to use electrochemistry. There are two major electrochemical energy storage systems, supercapacitors and batteries. The two energy systems differ in their energy storage mechanisms. In supercapacitors, the energy is stored in form of electrostatic interactions between the electrode and the electrolyte whereas in batteries, the energy is stored in forms of electrochemical reactions. The electrodes in the batteries are oxidized and reduced to store electrochemical energy. The performance of energy storage systems are generally characterized by its energy density and power density as well as its cycle life. Energy density relates to how much energy the battery can hold. It is generally expressed as shown in Equation 1.1

$$E = \int VIdt$$

Equation 1.1

where E is the energy density, V is the cell voltage, and I is the current density. The energy density is often expressed either in gravimetric, volumetric, or areal units of Wh/g, Wh/L, or Wh/cm² respectively, where W is in Watts and h is hour. Similar to the energy density, power density is in units of W/g or W/cm². The unit of the energy and power density used are often based on the application of the battery. On applications where the weight of the battery is a concern, such as in transportation where the weight should be minimized to extend the range of the vehicle, W/g are used.

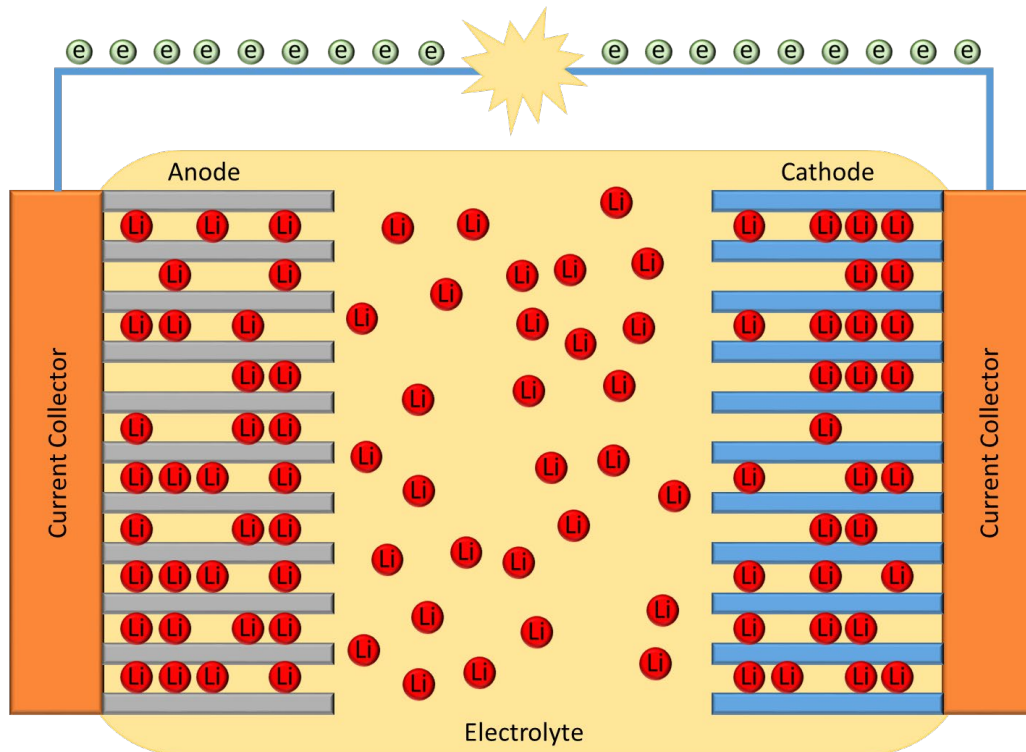


Figure 1.1 – Diagram of a standard Li ion battery

On the other hand, for applications such where the area of the energy storage system is limited, such as on a circuit board for integrated power, large W/cm^2 are used.

Traditional energy storage systems are mainly categorized into two classes based on their energy storage mechanisms, supercapacitors and batteries. Supercapacitors utilize electrostatic, non-faradaic interactions to store electrical energy. These type of interactions are considered fast as there are no electrochemical reactions occurring. Due to the nature of the energy storage mechanism of supercapacitors, they have very good power density but low energy density as energy is stored only near the surface of the electrode. On the other hand, batteries rely on electrochemical reactions where charge is transferred and redox reactions occur. The electrochemical reactions occur

throughout the entire electroactive material, and not just near the surface. In order to utilize all of the active material, ions and electrons have to be transported to the active sites. Due to the rate limiting step from ion and electron transports, these reactions are considered to be slow, leading to low power densities. As batteries involve electrochemical reactions, the energy that can be stored in them are very high compared to that of supercapacitors.

In order to understand the limits of current battery systems, the general storage mechanism of a battery must be first understood. Figure **Error! Reference source not found.** is a representative diagram of the commonly used Li-ion battery. The two electrodes, an anode and a cathode, are separated by the electrolyte and porous membrane called a separator to physically separate the electrodes. The most common cathode material, anode material, and electrolyte is the lithium cobalt oxide (LCO), graphite, and lithium hexafluorophosphate respectively. The purpose of the electrolyte is to electrically isolate the cathode and the anode while still allowing ions to move between them. Each of the electrodes is electrically connected via external circuit.

When a load is applied, the battery is discharged to power devices like a cellphone. The anode is oxidized. The electron released from the oxidation of the anode is transported through the external circuit to the cathode whereas the counter ion, in this case the positively charge Li ion, is released from the active sites of the anode. The released Li ion has to transport through the solid active material then transport through the electrolyte to the cathode. The cathode is then reduced by the electron. To balance the negative charge from the reduction of the cathode, the counter ion then has to transport

through the cathode material to the active site. The reverse occurs when the battery is charged. The cathode is oxidized, the electrons and counter ions are transported to the anode via the external circuit and electrolyte respectively and the anode is reduced. To clarify, the term cathode and anode are used to designate the electrode that is reduced and oxidized respectively during a discharge of a fully assembled battery cell and do not describe the traditional cathode and anode definitions used in electrochemistry.

1.2.2 Electron and Ion Transport and Their Limitations

From the general storage mechanism for battery systems, there are several steps where the energy storage performance can be limited by electron transport and ion transport, and the kinetics of the reduction/oxidation of the material. In traditional Li-ion battery systems, the cathode and anodes are manufacture from larger particle sizes, as large as a tens of micron, mixed with binders and conductive additives which are then spread onto a metal foil which is used as the current collector.¹⁵⁻¹⁷ The major concern with this type of battery structure is the large active particle size and inherent inhomogeneity. As mentioned previously, ions have to travel through the active material to the active sites. With large particle size, the diffusion time through this particle is large. With large charge and discharge time, eventually all the active material can be accessed. However, this is not ideal and leads to poor power performance, low energy density at high power density, because only materials near the electrolyte will be active when the discharge time is short. Thus in a traditional battery system, it is the diffusion of the

ions through the material that causes poor power and energy density. There are two main strategies in improving power and energy density, new materials and electrode architecture.

The first strategy is formulation of new materials that has high energy and power density. For example, Lithium Cobalt Oxide (LCO) has been the staple of Li ion battery cathode for its relatively high energy density and high power density. However, due to the high cost and environmental impact of the cobalt as well as to increase the performance of Li-ion batteries, different cathode materials are synthesized and tested.¹⁸ Some of the newer, high voltage cathodes include Lithium manganese oxide (LMO), Lithium Nickel Cobalt Manganese oxide (NCM), and Lithium Nickel Cobalt Aluminum Oxide (NCA).¹⁸⁻²⁰

The second strategy is to utilize currently available materials and restructure them. As discussed previously, large bulk active materials have poor ion diffusion, leading to low ionic conductance and therefore low energy density and power density, rooted from poor material utilization. While the intensive property of the material, such as the ionic conductivity and electronic conductivity, cannot be changed, the extensive property, such as the ionic conductance and electronic conductance, can be changed with the structure of the material. While conductivity and diffusion have different units, they do generally describe a similar process of ion and charge transport and are related by the Nernst-Einstein equation shown in Equation 1.2 where σ is the ionic conductivity, e is the elementary charge, V is the volume, T is temperature, K_B is the Boltzmann constant, N is number of cations/anions, Z is the charge, and D is the diffusion coefficients.^{21, 22}

$$\sigma = \frac{e^2}{VK_B T} (N_+ z_+^2 D_+ + N_- z_-^2 D_-)$$

Equation 1.2

Therefore, in this dissertation, diffusion and conductance will be used to relate the rate of either ion or electron transport with electrode architectures. As ion diffusion is what is limiting the energy storage performance of bulk electrode designs, the effect of nanostructuring is often expressed in terms of time constant. The time constant for a diffusion time is shown in Equation 1.3 where t is the time constant, L is the diffusion length, and D is the diffusion coefficient.

$$t = \frac{L^2}{D}$$

Equation 1.3

In order to minimize ion diffusion time and maximize ionic conductance, the diffusion length can be minimized in the direction of the ion transport. This is achieved through nanostructuring. There are various nanostructures available and are generally categorized into based on their dimensionalities, from 0D material to 3D materials, and whether the nanostructures are in ordered or random assemblies. A systematic study of the key features of these nanostructures and understanding their impact on the electrochemical behavior can provide important design parameters for high performance energy storage devices.

1.3 Nanostructured Electrodes as Testbed for Understanding key features Towards Higher Performing Batteries

1.3.1 Introduction of Nanostructures

As stated in previous sections, the limiting factor for current Li ion batteries is the ion transport through the bulk of the material which results in low power and energy densities and short cycle life. By manipulating the structure, high power and energy densities and long cycle life can be achieved on currently developed electrode materials.²³⁻²⁵ There are countless nanostructures available. Generally, nanostructured electrodes can be categorized into four structures based on their nanostructured dimensions. Zero dimensions, where all three dimensions are within nanometer scale, usually are nanoparticles. Some examples of 0D nanostructures are fullerenes, a sp² carbon spheres²⁶, and quantum dots²⁷, and silver nanoparticles²⁸. One dimension nanostructures are those with one dimension not in the nanometer range. Such are elongated structures like carbon nanotubes²⁹, PEDOT-MnO₂ coaxial nanowires³⁰, and Ni nanotubes³¹. Two dimension nanostructures are those with only one dimension in the nanoscale range. These structures are usually sheet-like such as graphene³², and MXenes³³. Three-dimensional nanostructures are more diverse than other types of nanostructures where all three dimensions are not in nanoscale such as porous carbon membranes³⁴, porous Ni scaffolds³⁵, and interconnected anodized aluminum oxide porous network³⁶⁻⁴⁰. Interconnected anodized aluminum oxide network provides an unique testbed for understanding the effect of interconnections on the electrochemical

behavior of the 3D electrodes over 1D electrode. More detail on this study will be discussed in Chapter 2.

1.3.2 Ordered nanostructures as test bed

Of the four categories of nanostructures, one-dimensional and three-dimensional nanostructures can be categorized as ordered or disordered structures. An ordered nanostructure have periodicity while disordered do not. An ordered nanostructure is crucial when it is used as a testbeds to systematically study the impact of structure on the electrochemical behavior of 3D vs 1D array of nanostructures. Disordered structures introduce inherent inhomogeneity. This inhomogeneity can cause electrochemical hotspots, degradation, non-uniform material utilization, and uncontrollable ion and electron pathways.^{15, 41}

An example of ordered and disordered 1D nanostructure is carbon nanotubes. Depending on the synthesis technique, carbon nanotube (CNT) based electrodes can be either disordered or ordered. A commonly used technique for the synthesis of CNT is catalyzed chemical vapor deposition (CVD) of carbon nanotube with cobalt catalyst. Traditionally, cobalt is deposited on a substrate first. Then the carbon source, such as methane, is carried into a heated chamber where it is reduced into carbon nanotubes. This creates bundles and randomly organized carbon nanotubes, a disordered 1D array of nanostructures. On the other hand, when the Co catalysts is placed in an ordered porous nanostructure, vertically aligned ordered carbon nanotube arrays are synthesized.⁴²

It is well known that of the same material and same structure, ordered and disordered structured materials behave differently. Huang, Wang, and Wei fabricated and compared three different polypyrrole structures: film, randomly oriented nanowire network, and ordered nanowire arrays. They found that the ordered nanowire arrays performed better because the film structure and the nanowire network hindered the ion transport.⁴³ Similarly, Etacheri et al. compared disordered and interconnected, ordered SnO₂ nanoparticles. They found that the interconnected and ordered SnO₂ nanoparticles performed better due to the larger average porous structures and interconnections providing better connectivity, lowering the charge transfer resistance, and large porous structure, increasing ion diffusion.⁴⁴

The goal of this dissertation is to systematic study the effect of nanostructural parameters on the electrochemical behavior of the electrodes though the utilization of precision nanostructures. In order to systematically study how a specific structural parameter affects the electrochemistry, a highly ordered and tunable nanostructure is needed as the testbed to understand structural parameters on the electrode behavior.

The nanostructured electrodes that are used to study the structural affect also needs to be binder and additive free. Traditional battery electrode synthesis requires four major components: active particles, binders, conductive additives, and solvent. These are mixed in a certain ratio and spread over the metal foil which becomes the current collector. This technique inherently introduces heterogeneity into the electrode sample. The resulting composite electrode will have some areas with higher binder content where other areas may have higher conductive additives. It also introduces random

network of pores in the electrode, and does not guarantee direct electrical contact between the active particles and the current collectors.^{15, 45-47}

In the studies performed here, highly ordered, binder free nanostructures are synthesized to study the structural impacts on the electrochemistry of the resulting electrode to provide guide lines for high performance battery systems.

1.3.3 Template assisted synthesis of additive free ordered nanostructures

One of the most commonly used methods in the synthesis of additive free ordered nanostructures is through the usage of nanotemplates. The basis for this technique is to fabricate nanoscale templates on which the active material can be deposited, forming nanostructured electroactive electrodes. There are various types of templates, generally categorized into two main types, soft and hard templates. Soft templates, as the name suggests, do not have a rigid shape. They are usually formed in solution-based synthesis such as micelles⁴⁸, and block copolymers⁴⁹. Hard templates are rigid structures such as anodized aluminum oxide.^{30, 31, 37, 45, 50-52} The studies in this dissertation utilize anodized aluminum oxide as the hard template for synthesis of ordered nanostructures. More detail on the anodized aluminum oxide template fabrication is discussed in detail in upcoming section 1.4 and in Chapter 2 and Chapter 4.

1.4 Anodized Aluminum Oxide Template

1.4.1 Introduction of Anodized Aluminum Oxide

Anodized aluminum oxide (AAO) is an ideal template for systematic studies due to its structural tunability. The structure of the AAO can be seen in Figure 1.2. AAO is comprised of hexagonally arranged cells. Each cell is separated by the cell boundary and within each cell is a pore. The pores run perpendicularly to the aluminum substrate, in the direction of the electric field during the anodization. The distance between the centers of the two cells is called the interpore distance, D_{int} , and is highly dependent on the anodization voltage.^{53, 54} The pore diameter, D_p , and the barrier layer thickness, t_b , are not only dependent on the anodization temperature but also on the additives in the electrolyte such as polyethylene glycol.^{54, 55}

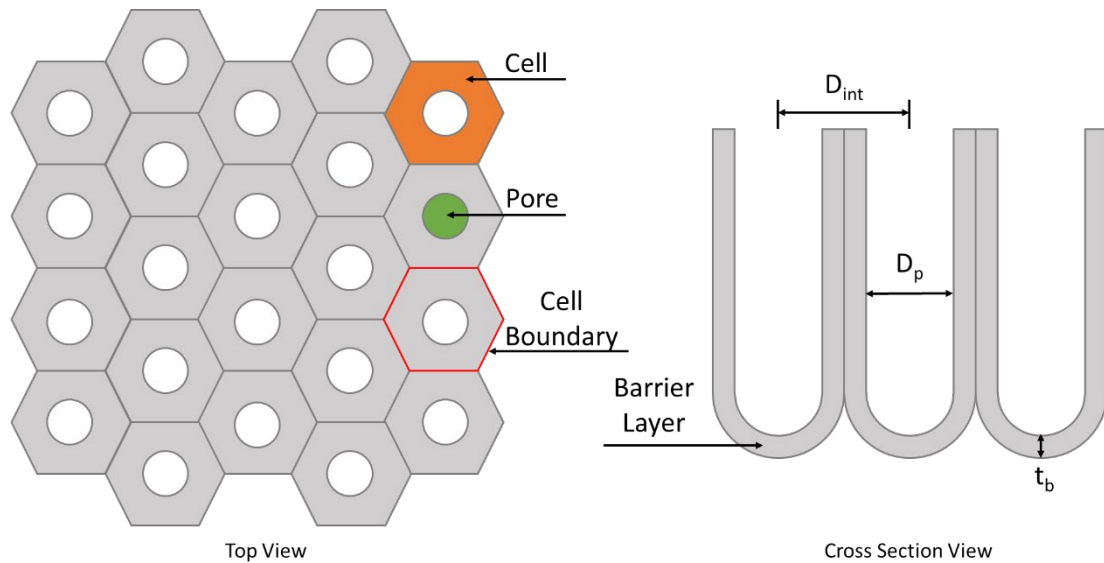


Figure 1.2 - Schematic of AAO structure

1.4.2 AAO formation of Aluminum

1.4.2.1 Pore initiation

Generally, when the surface of a valve metal such as aluminum is oxidized, it forms a non-porous barrier type oxide layer. This occurs in pH neutral electrolytes where the aluminum oxide is not soluble. At the aluminum metal/oxide interface, metallic Al is oxidized to Al^{3+} . At the oxide/electrolyte interface, water is split into protons and anionic oxygen, O^{2-} . For the barrier type oxide layer, Al^{3+} ions migrate towards the electrolyte and O^{2-} ions migrate towards the aluminum metal surface from the applied electric field. This results in formation of the Al_2O_3 at both the metal/oxide interface and electrolyte/oxide interface.⁵⁶ However, for porous type oxide layer, Al^{3+} does not react in the oxide/electrolyte interface with the O^{2-} ions, instead it is directly injected into the electrolyte.^{57, 58} This difference in the anodization mechanism results in the difference in what is called the pilling-bedworth ratio of the initially formed oxides. Pilling-bedworth ratio is the ratio of molar volume of the oxide formed to the molar volume of the metal used. For the barrier type, this ratio is 1.7, while for porous type, it is 0.9.⁵⁹ This means that the porous type oxide layer is under tensile stress and is prone to cracks in the oxide layer. Any imperfections such as cracks in the oxide layer or surface roughness, in the oxide layer will cause local hot spots where the local current density is high. The high current density leads to local heating as well as higher polarization of the Al-O bond in the oxide layer for higher rate of dissolution of the local oxide layer.⁶⁰⁻
⁶² This further perpetuates the non-uniform oxide growth at the metal/oxide interface.

The anodization current increases as the oxide film becomes more porous with the formation of random pores at the metal/oxide interface.^{57, 59, 60}

1.4.2.2 Steady state pore formation

Under the ordered growth regime of a particular electrolyte and voltage, these random pores will combine or branch off depending on the size of the pores until all of the pores are uniform. The average field model explains how these random pores eventually become ordered structures. The migration of the O^{2-} ions across the oxide, and the polarization of the Al-O bond are all dependent on the electric field across the oxide layer at the bottom of the pores, i.e. the barrier layer. With the large distribution of pore sizes, the thickness of the barrier layer will be also different. Smaller pores have thinner barrier layer than that of a larger pore. The electric field will be largest with the smaller pore as the sample voltage is applied across a smaller oxide thickness which would lead to faster anodization of the Al at the metal/oxide interface. The opposite would occur on the larger pores, slowing its growth until both the smaller pore and the larger pore reach similar size, an equilibrium pore dimensions at the given voltage/electrolyte conditions.^{63, 64}

1.4.3 Interpore Distance

The interpore distance is one of the most important parameters when considering the usage of the AAO template. This parameter ultimately determines the limitations of the

pore diameter. From post processing, the pore diameter can be increased but is limited by the interpore distance, i.e. when pore diameter is same as the interpore distance, the iconic AAO structure no longer exists as the adjacent pores are overlapping. Thus for utilization as a template for energy storage materials, the interpore distance is an important factor to consider.

As stated in previous section, during the steady state pore formation, the electric field plays an important role in the formation of ordered, uniform porous structure. Thus the interpore distance is highly dependent on the anodization voltage.⁶⁵⁻⁶⁷ D_{int} is generally governed by the anodization voltage with the relationship as shown in **Eq 2** where V_a is the applied anodization voltage.⁶⁸

$$D_{int}(nm) = 2.5 \times V_a$$

Equation 1.4

The pore diameter is also dependent on the anodization voltage with the relation as shown in Eq 3.⁵⁹

$$D_p(nm) = 1.29 \times V_a$$

Equation 1.5

The above equations also depend on several anodization conditions such as the type of anodization (hard or mild), electrolyte concentration, additives, and temperature.^{54, 59,}

^{69, 70}

1.4.4 Interconnected AAO Template

AAO is traditionally known as a hexagonally arranged porous structure. These pores are formed perpendicular to the applied electric field. While this may be ideal for some applications, an interconnected AAO, where adjacent pores are connected to each other, can be more desirable. Because the interconnections remove additional pore walls, the porosity of the AAO can be maximized. These interconnections also introduce large surface area available for material deposition.^{40, 50} First reported by Li et al., the interconnected AAO was used for Y-branched carbon nanotubes.³⁶ There are several methods in introducing interconnections in an AAO template. Li et al. produced Y- interconnecting AAO film by lowering the anodization voltage from the 50V to 35V. The majority of the anodization is done at 50V. By altering the voltage to 35V, new equilibrium is established. The lower voltage led to rearrangement of the pore sizes, to a smaller pores but also double in the number of pores. The anodization voltage is brought back up to 50V for ordered interconnected AAO templates. Similarly, Martin et al. varied the anodization potential from equilibrium state at 25V to 32V in sulfuric acid. The higher voltage anodization, 32V, is considered to be a hard anodization process where the anodic oxide formed is less chemically stable than the oxide from at 25V, a mild anodization process. Due to this difference in the chemical stability, Martin et al. was able to etch the AAO template to form interconnected AAO templates.³⁹ More detail on the interconnected AAO fabrication will be discussed as part of Chapter 2.

1.5 High aspect ratio, ordered nanostructure enabled by Atomic layer deposition.

There are various deposition techniques available for the fabrication of nanostructures such as electrochemical deposition and physical vapor deposition. In this dissertation, chemical vapor deposition (CVD) is used to deposit electroactive materials on the AAO template, particularly the atomic layer deposition technique. This technique usually involves multiple precursor materials in which it decomposes into the desired material on the substrate surface. This type of deposition is not self-limiting which means that the more the substrate is exposed to the precursor, the thick the material becomes. For high aspect ratio structures, where some portions are more readily exposed to the precursors, for example the opening of a pore verses the bottom of a pore, the material is anisotropically deposited where a thick layer would deposit at the opening of the pore and thin or no material is deposited at the bottom of the pore. Thus for high aspect ratio template such as AAO, a self-limiting and conformal deposition techniques are needed.⁷¹

A special type of chemical vapor deposition technique is the atomic layer deposition (ALD). Similar to the traditional CVD, ALD has two or more precursors but one as the metal precursor and one as the oxidant. The ALD process for aluminum oxide with trimethylaluminum and water is shown in Figure 1.3 in order to describe the ALD process. In ALD, usually only one precursor is introduced to the surface of the substrate at a time in excess amount and is allowed to fully react with the surface, hydroxyl groups in this example. This allows the surface of the substrate evenly saturated with

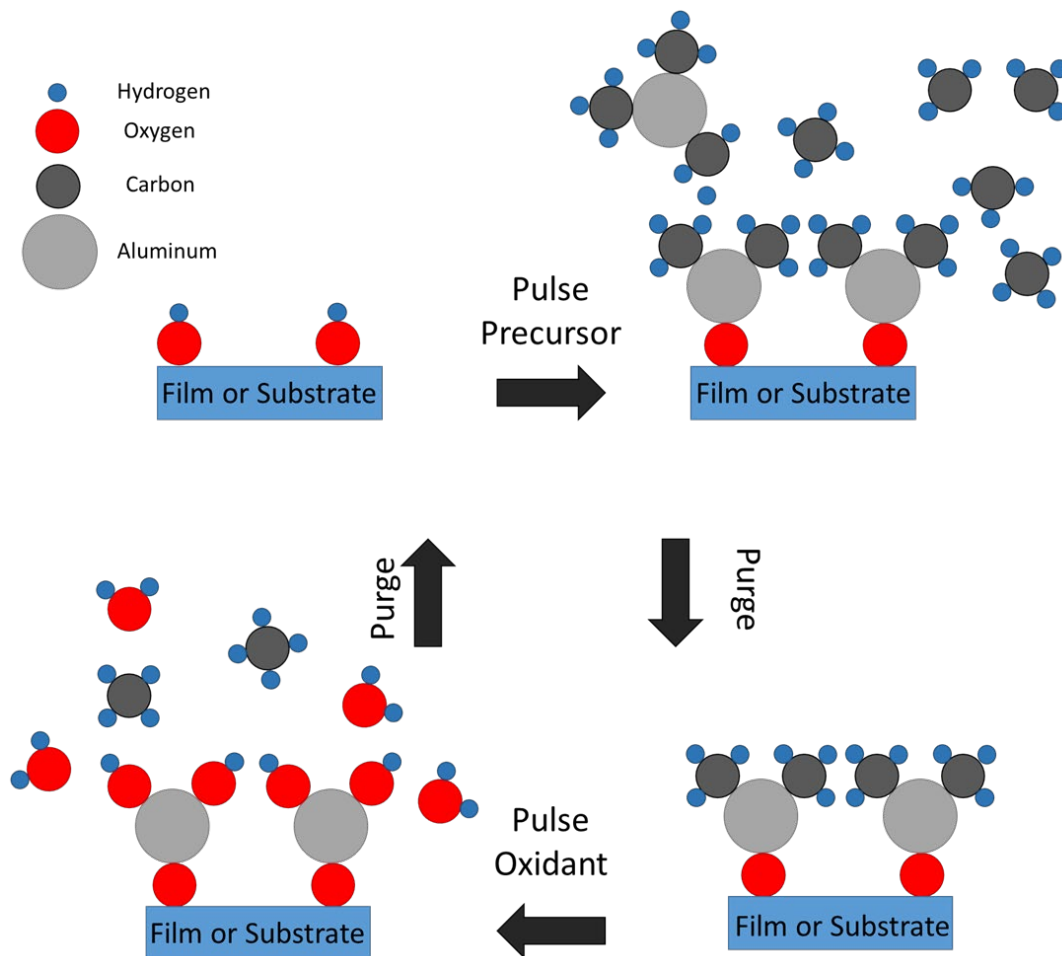


Figure 1.3 – Reaction scheme of ALD Al_2O_3 deposition process.

the precursor. Excess precursor that didn't react with the substrate is removed by purging with inert gas such as Ar. The second precursor is introduced, again in excess, to react with the first precursor. This forms a conformal coating of the material on the surface of the template. Excess precursor is then removed and the first precursor is introduced again. This is repeated to deposit material "atomically" and due to the nature of the technique, the material is deposited conformally in high aspect ratio AAO structure.

1.6 Overall Goal of This Dissertation.

In this dissertation, precision nanostructures are used to understand the impact of specific structural parameters on the electrochemical behavior of the electrode. Traditional Li-ion battery cathode and anode are used as these are well studied materials to isolate the impact of structure on the electrochemistry. The major objective of this dissertation are:

- (1) Utilize atomic layer deposition to deposit conformal thin electroactive layers in highly ordered nanostructures
- (2) Provide guidelines on the key structural parameters for improved electrochemical behaviors
- (3) Develop highly ordered 3D scaffold to explore the effect of high aspect ratio nanostructures for 3D solid state batteries

In Chapter 2, the effect of interconnections on the electrochemical behavior of ALD V_2O_5 Li ion cathode material is studied. In Chapter 3, the effect of nanoconfinement of

liquid electrolyte in highly ordered 20nm nanochannels coated with TiO_2 Li ion anode is studied. These two chapters satisfy the first two objectives of this dissertation. In Chapter 4, high aspect ratio AAO is used as a substrate for the fabrication of 3D solid state Li ion battery and satisfies all three objectives. In the final chapter, the summaries of these studies and outlook are discussed.

2 Impact of Pore Size, Interconnections, and Dynamic Conductivity on the Electrochemistry of Vanadium Pentoxide in Well Defined Porous Structures

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Nam Kim performed the fabrication, electrochemical testing, and analysis of data.

Emily Sahadeo and Chanyuan Liu had significant part in discussion of the data. Oliva

Rose contributed to the sample preparation.

2.1 Introduction

With the increased demand for high performing energy storage devices, researchers all over the world are focusing on improving the energy densities, power densities, and cycle life of various energy storage devices.⁷²⁻⁷⁸ Due to their superior energy storage performance, lithium ion batteries are often chosen for portable devices.⁷⁹⁻⁸² Commercialized lithium ion batteries are traditionally made of composite electrodes using electroactive particle sizes ranging from microns to nanometers mixed with conductive additives and binders. Due to the non-uniformity of the particles and non-uniform mixing of the conductive additives and binders, differences in the local tortuosity, porosity, and conductance within the electrodes are inevitable, which causes differences in ionic and electronic transport.^{16, 41, 46, 47} The electronic conductivity of the electroactive materials are often not static during the lithiation and delithiation steps of battery cycling. For example, lithium cobalt oxide, when fully lithiated, has

electronically insulating properties. However, as it is delithiated the material becomes more electronically conducting.⁸³ In another material, manganese dioxide, as it is lithiated it becomes more electronically conducting.⁸⁴

The randomness of the electrode morphology combined with the dynamic properties of the electrode material makes understanding their impact on the electrochemistry difficult. Initial studies on understanding the origin of battery performance (power density, energy density, and cycle life) was based on the use of homogenous spherical particles such as the Newman model. While this model can predict the energy and power density of the electrode, due to its low-dimensional nature this model would need to be much more complicated to explain the degradation mechanisms in real battery electrodes; the electrode structures used in the model are overly simplified. Using focused ion beam, or X-ray tomography, several studies were carried out using the real electrode structures as the basis for the modelling of the battery performance with a small section (few thousands of cubic μm) of the total battery electrode.^{16, 41, 46, 47, 85} Another approach in understanding how the local electrode structure impacts the electrochemistry is to fabricate well controlled uniform testbed electrodes with controlled structural properties such as tortuosity and porosity.

In order to fabricate well controlled electrode structures, we used anodized aluminum oxide (AAO) as a template. With the right combination of the temperature, anodization voltage, and electrolyte, a uniform, porous aluminum oxide layer can be formed.^{59, 86} In traditional AAO structure, cylindrical pores are formed in a hexagonal pattern perpendicular to the surface. Atomic layer deposition can be used to conformally

deposit electrode materials in these high aspect ratio structures.⁸⁷ This methodology results in nanotubular array electrodes, with each electrode electronically and ionically isolated from one other. The AAO template structure can be varied by introducing interconnections between adjacent pores during the anodization process.^{37, 88, 89} The electrode structure resulting from this interconnected template has additional electronic and ionic pathways between adjacent electrodes. These interconnecting layers can be introduced into the AAO template controllably by simply varying the anodization voltage.

In our previous study, we focused on how different numbers of interconnecting layers, which introduced additional electronic and ionic pathways, as well as structural irregularities had an impact on the electrochemistry of the vanadium pentoxide (V_2O_5).⁹⁰ In this study, the number of interconnecting layers was varied from zero (straight) to three interconnecting layers within about 1.7 μm thick AAO films. These AAO films were used as a scaffold for nanotubular V_2O_5 electrodes. Each electrode was cycled within the one lithium insertion/deinsertion voltage window (2.6V to 3.8V vs Li). An interesting phenomenon was observed where with more interconnecting layers, not only was the mass loading of the electrodes increased due to the increased surface area from the interconnections, but they also had increased capacity retention at high current densities. To understand how the interconnections impacted performance, the three types of transports (bulk ion transport, solid state ion transport, and electron transport) that govern the electrochemical reactions had to be deconvoluted experimentally. It was found that these interconnections allowed more

active material closer to the planar current collector, leading to better material utilization at high current densities where the electron transport was the limiting mechanism.

In the aforementioned study, a more significant degradation of the interconnected electrodes over the straight electrodes was expected due to the increased structural irregularities of the electrodes at the interconnected regions.^{15, 91, 92} However, no significant degradation was seen between the two structures. This result suggests that the interconnecting layers likely did not cause inhomogeneous current distribution.⁹⁰ However, an alternate explanation may be that the ability of V_2O_5 to accommodate up to two lithium ions reversibly enabled the electrodes to be cycled without severe capacity degradation.⁹³⁻⁹⁵ Within the one Li ion insertion voltage window, the high current densities around the localized interconnected regions could result in a second Li ion insertion which is still reversible, resulting in no significant degradation compared to zero interconnecting layer electrodes. However, if a third lithium ion is inserted, that process is irreversible and result in significant degradation of the electrochemical behavior.⁹⁶

We initiated the study in this manuscript to explore whether high current density regions form due to structural irregularities at the interconnections, and if they subsequently drive further lithiation of V_2O_5 up to third lithium ions. In this work, we move beyond the one lithium insertion voltage window and instead cycle V_2O_5 in the two-lithium insertion window. By going into the second Li insertion voltage window, at high current densities it is possible that the structural irregularities from the

interconnecting regions will cause a third Li ion to insert due to the overpotential needed to maintain the reaction current.⁹⁷ This third Li insertion is an irreversible reaction, which could degrade the electrodes with interconnecting regions faster than their straight pore counterparts or otherwise impact the electrode chemistry. Herein, we discuss how the interconnections between AAO pores, the pore size, and the changes in the material conductivity influence the performance of V₂O₅ cathodes in the two-lithium insertion voltage window.

Here we demonstrate that within our test structures, interconnecting regions have different impacts on the electrochemistry of the electrodes depending on the degree of lithiation. With only one Li insertion voltage window, interconnected electrodes can maintain higher capacities at high current densities, as seen from the previous study. Conversely, within the two Li insertion voltage window, interconnected electrodes maintain lower capacities at high current densities. We also demonstrate that the need for diffusion of the additional Li ions into the nanotubular pores does not cause this deviation in the two Li insertion voltage window. By using an integrated current collector, we show that it is due to the synergy, both positive and negative, between the changes in the dynamic electronic conductivity of the V₂O₅ electrode and the properties of the interconnecting structure that impacts the overall conductance of the electrode. This finding suggests that in real commercial battery electrodes, when the active material does not have direct contact with the current collector, the active material usage at high current densities is maximized when there are additional electronic pathways in materials whose electronic conductivities increase with lithiation.

However, material utilization is minimized when active materials have decreased electronic conductivities upon lithiation.

2.2 Experimental Methods

2.2.1 AAO Template preparation

99.99% pure Al foil was purchased from Alfa Aesar. It was degreased in acetone for 10 minutes. It was dried and placed in electropolishing solvent composed of 800 mL of 200 proof ethanol and 160mL of 70% perchloric acid at a temperature of 3°C. The temperature of the solutions were set by a water bath chiller/heater unit. 15V was applied between the Al foil and stainless steel electrode for 5 minutes to electropolish the Al foil. The first anodization was performed in 0.3 M Oxalic acid at 8 °C under 40V for 6 hours. The disordered AAO that formed from the first anodization step was removed by placing it in the mixture of 70 mL of 85% phosphoric acid, 180 mL of 10% chromic acid, and 750 mL of water at 60°C for 4 hours which left a patterned surface on the Al foil. This patterned aluminum was then used to grow ordered AAO films. By disrupting the anodization voltage from 40V to 20V and back to 40V with 2V step every 30 seconds, one interconnecting region can be added into the AAO film. By repeating this voltage disruption process, up to seven interconnecting regions are added in the AAO film. AAO film was left on the native Al foil for structural support. The pores were widened in 5% phosphoric acid at 38 °C at various times for different pore diameters. More detailed AAO preparation is described elsewhere.³⁷

2.2.2 Material deposition and Characterization

Atomic layer deposition was used to conformally coat the walls of high aspect ratio pores. Vanadyl triisopropoxide was pulsed for 2.5 seconds and O_3 was pulsed for 5 seconds alternatively in Beneq TFS 500 ALD system at 170 °C for the deposition of V_2O_5 .⁹⁸ For Ru metal, bis (ethylcyclopentadienyl) ruthenium was pulsed for 5 seconds and O_2 was pulsed for 6 seconds at 300 °C in home-built furnace reactor. Tescan FEG SEM and Hitachi Su-70 were used for morphological characterization. Due to the charging of the insulating nature of AAO, thin layer of carbon was sputtered on the bare AAO samples. After the deposition of V_2O_5 , the electronic conductivity of V_2O_5 was high enough where the sample did not show any charging effect from the electron beam.

2.2.3 Electrochemical cells

$LiClO_4$ ACS reagent grade, anhydrous 99.7%> purity propylene carbonate were purchased from Sigma Aldrich. $LiClO_4$ was dried at 180°C under vacuum for at least 24 hours before it was transferred to the glovebox where the electrolyte, 1 M $LiClO_4$ in PC, was prepared. T-cells were purchased from Swagelok and stainless steel rods

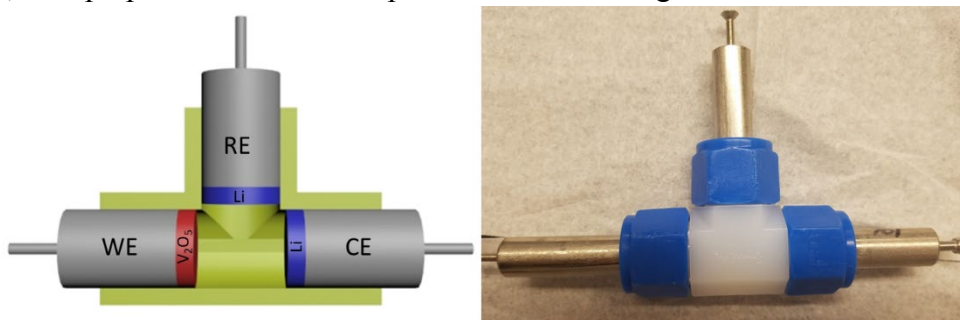


Figure 2.1 – Cross section diagram of the T-cell configuration on the left and image of the fully assembled T-cell on the right.

were used for making contacts to the electrodes. A diagram of the T-cells are shown in Figure 2.1.

The half cells were prepared in these T-cells as three-electrode systems with two separate Li metals as the counter and reference electrodes. The air-tight seals allow these T-cells to be assembled in inert atmosphere of the glovebox and tested outside of the glovebox in air. The active mass was calculated from the change in mass of the AAO template before and after the deposition steps. A Biologic MPG-12 potentiostat was used for all electrochemical measurements.

2.3 Results and Discussion.

2.3.1 Template characterization

AAO templates with zero, four, and seven interconnecting layers were fabricated.

Figure 2.2 shows representative SEM cross section images of AAO films with zero and

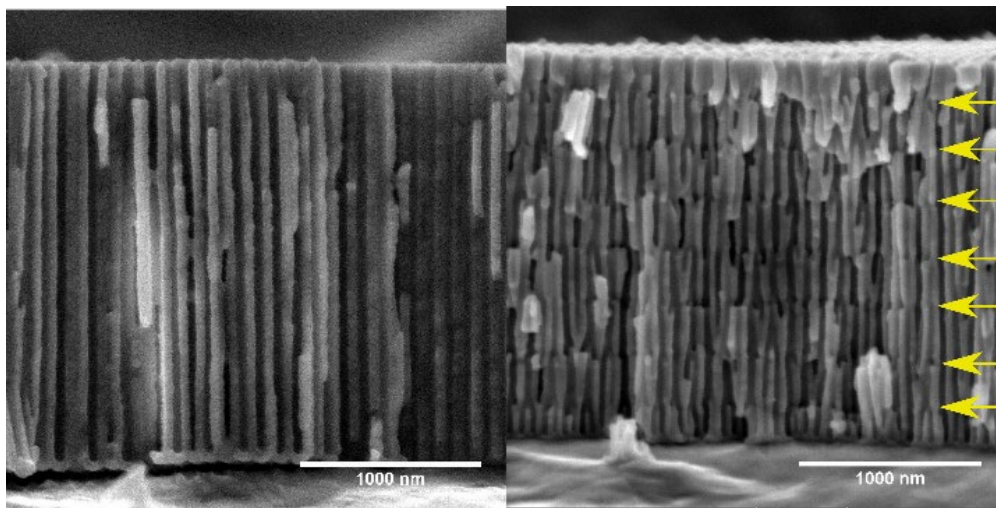


Figure 2.2 - Cross-sectional SEM images of AAO films with zero (left) and seven (right) interconnecting regions. The interconnecting regions are highlighted in yellow. Carbon was sputtered to minimize charging

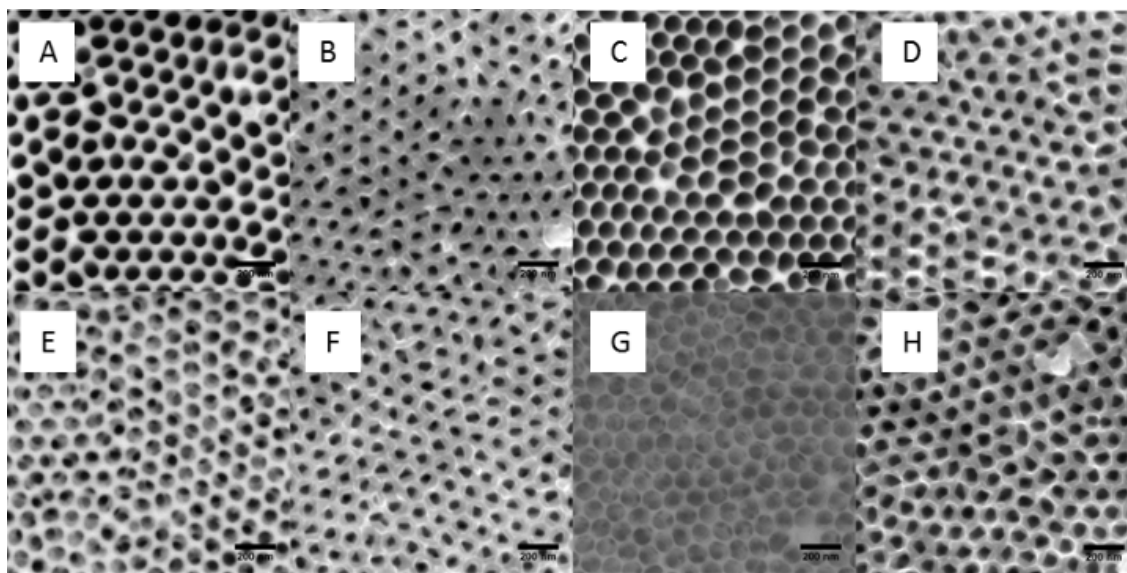


Figure 2.3 - SEM image of the top of AAO templates before and after deposition of 20nm thick V_2O_5 . Before A) and after B) deposition of zero interconnecting layers after 11.5 minutes of pore widening, before C) and after D) deposition of zero interconnecting layers after 15.5 minutes of pore widening, before E) and after F) deposition of seven interconnecting layers after 11.5 minutes of pore widening, and before G) and after H) deposition of seven interconnecting layers after 15.5 minutes of pore widening.

seven interconnecting layers. The seven interconnecting layers are evenly distributed in 2.3 μm thick AAO films, while the straight pores contain no interconnections but are of the same thickness. Due to the insulating nature of the AAO, carbon was sputtered to minimize charging on the surface during SEM imaging. To create the electrodes within the AAO template, a ~ 10 nm thick crystalline V_2O_5 film was deposited in the AAO templates using ALD. The successful deposition and its thickness was confirmed with SEM images of the AAO pore diameter before and after deposition as seen in Figure 2.3. After the second anodization the pores diameters were widened. Figure 2.3A and Figure 2.3E depict pores of zero interconnecting and seven interconnecting layer AAO samples after 11.5 minutes of pore-widening respectively. The images after

V₂O₅ deposition into these pores are shown in Figure 2.3B and F for zero and seven interconnecting layer samples respectively. The pores after deposition were about 50 nm in diameter. This pore size was used for all tests in this study, except where the pores are denoted as being “61 nm” in diameter. The “61 nm”-wide pores are illustrated in Figure 2.3C and Figure 2.3G for zero and seven interconnecting layer samples which underwent total of 15.5 minutes of pore widening prior to V₂O₅ deposition. After V₂O₅ deposition, the pores were about 61 nm. Detailed analysis of the pore diameters can be seen in Table 2.1.

pore widening time (minutes)	# Int. Layer	Before ALD Pore Diameter(nm)	After 200 cycles of Vanadium Oxide Pore Diameter (nm)
11.5	0	75+/-2	48+/-3
11.5	7	70+/-3	51+/-4
15.5	0	83+/-2	61+/-3
15.5	7	80+/-4	63+/-4

Table 2.1 - Average and standard deviation of pore sizes of various AAO templates before and after 200 cycles of vanadium oxide deposition measured by the ImageJ software.

After deposition, gold was sputtered on top of the AAO as a planar current collector. Image of pristine AAO on Al substrate, with Ru integrated current collector, with just V₂O₅, and with gold sputtered planar current collector can be seen in Figure 2.4. Using Swagelok T-cells with two Li foils as separate reference and counter electrodes, V₂O₅ electrodes with varying numbers of interconnecting layers were tested.

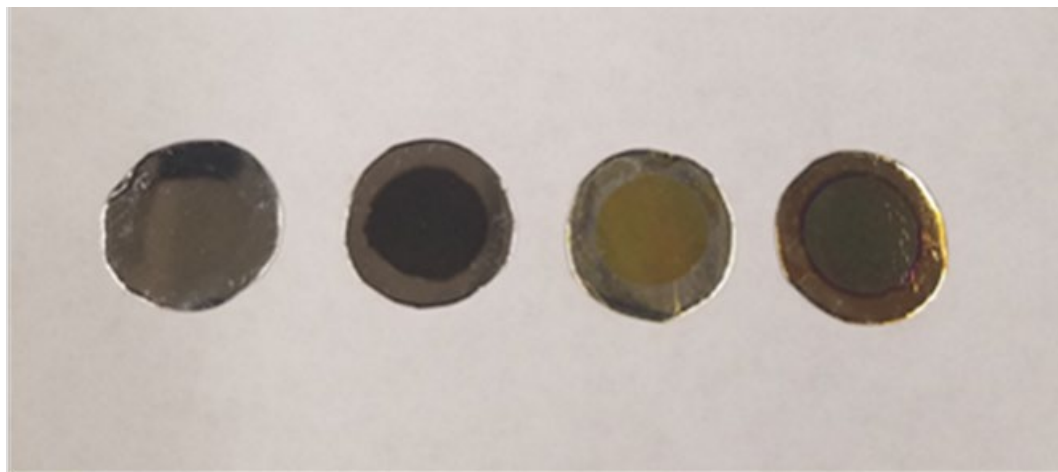


Figure 2.4 - Images of (from left to right) AAO before deposition, AAO with Ru integrated current collector, AAO with V_2O_5 , AAO with V_2O_5 and Au planar current collector. The middle portion is the AAO while the rest is the Al support substrate.

2.3.2 Electrochemical Testing of Interconnected V_2O_5 Electrodes

To confirm the results from our previous study with the different number of interconnections chosen for this paper, V_2O_5 was cycled within the one lithium insertion voltage window in electrodes with four and seven interconnections. From Figure 2.5A, it is apparent that with more interconnecting layers, better capacity retention was seen at higher current densities, which agrees with the previous findings. The current densities were defined by a “C” rate. A 1C rate is the gravimetric current density that needs to be applied to theoretically fully discharge the battery, in this case the cathode V_2O_5 , in one hour. For one-lithium insertion voltage window, a 1C is 147 mA/g and for two-lithium insertion voltage window, a 1C is 294 mA/g.

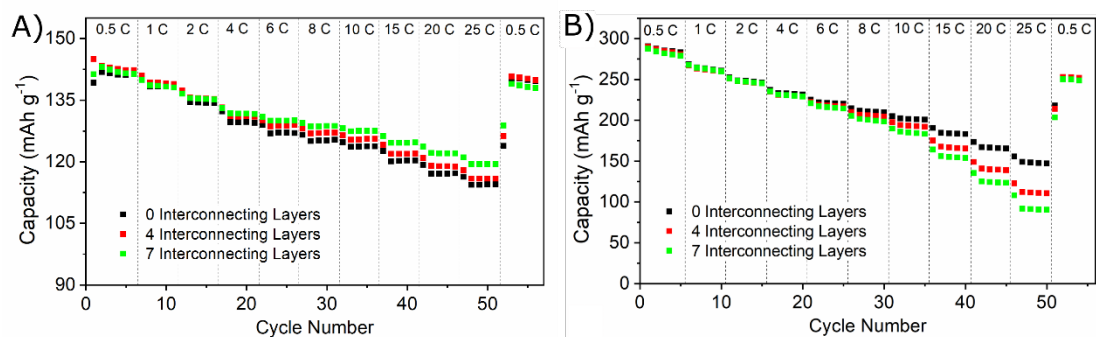


Figure 2.5 – Capacity of V_2O_5 electrodes with varying number of interconnections cycled between A) 2.6V and 4V vs Li and b) 2V and 4V vs Li.

After confirming the one-lithium insertion results, we then tested the impact of additional Li ion insertion into V_2O_5 electrodes with interconnecting layers. The electrochemical window was increased (4V to 2V vs Li), enabling a second electron transfer reaction to occur. As it can be seen in Figure 2.5B, at low current densities, the interconnections had no significant impact on the capacity of the electrode, as seen previously. However, when the current density was increased, the electrode with more interconnecting layers had lower capacity, which is the opposite of what was observed in the one-lithium insertion regime. The capacity, or the total material usage, at high current densities is limited either by the Li ion transport or electron transport, depending on the electrode structure and the active material. There are mainly three types of transports: bulk ion transport which describes the movement of ions from the bulk of the electrolyte to the confined spaces in the porous structure, solid ion transport which describes the movement of ions from the surface of the active material into the bulk of the active material, and finally electron transport which describes the movement of electrons from the current collector through the active material. The diagram which describes these transports is shown in Figure 2.6. To deconvolute the ion and electron

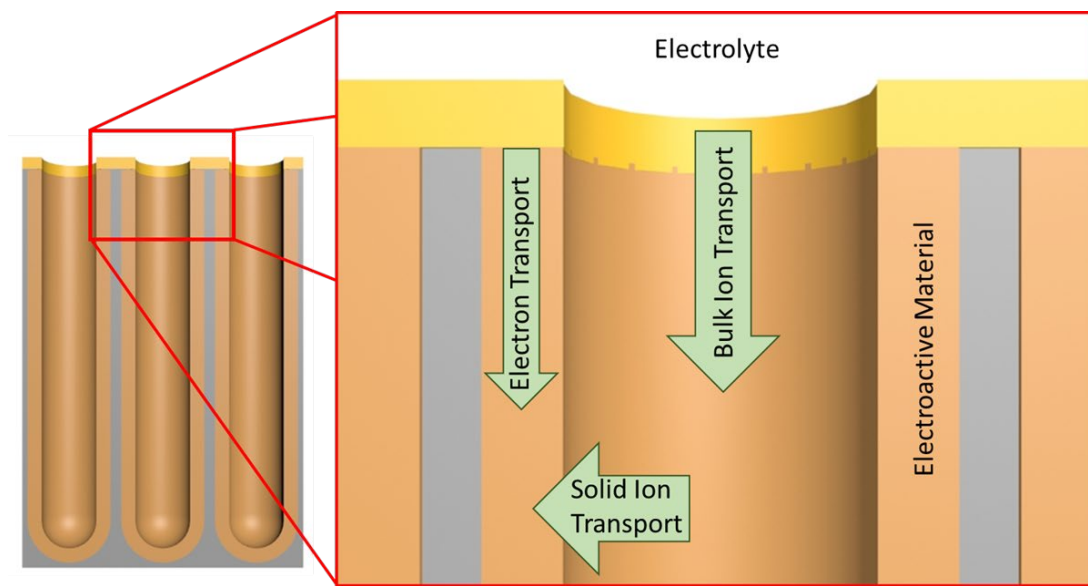


Figure 2.6 – Diagram of the three main transports in the electrode. The diagram depicts the zero interconnecting AAO structure with conformally deposited active material with top current collector.

transport effects, we carefully designed experiments to probe these properties independently. The results of these tests are presented in the following sections

2.3.3 Effect of Pore Size

To determine if the performance of V_2O_5 electrodes in our set-up was limited by Li ion transport into the pores, we considered how the size of the pore opening may affect the results. Using the SEM images of the AAO top-view before and after deposition, pore diameters were analyzed using ImageJ software's Analyze Particle function. Additionally, the cross-section images of the AAO templates and the template thickness were used to determine the dimensions of the pores for the estimation of Li ion concentration in the pores. To estimate the amount of Li ions available in each of

the pores and the amount that need to diffuse from the bulk of the electrolyte into the confined pore spaces within the porous electrode for a two-Li insertion, a few assumptions were made for the calculations. The pores are assumed to be perfectly cylindrical and using the diameter of the AAO pore measured from the SEM images before and after ALD of V_2O_5 , 70 nm and 50 nm respectively, the V_2O_5 thickness was found to be 10 nm. The length of the AAO was 2.3 μm and using these values the nanotubular electrode volume was estimated. Utilizing the bulk density of V_2O_5 , 3.36 g cm^{-3} , the total V_2O_5 in the pore was estimated.⁹⁹ The total number of Li ions in each of the pore was estimated by assuming that the internal volume of the tubular structure was still cylindrical. Utilizing the diameter of the pore opening after ALD, 50nm, and a depth of 2.3 μm from the cross-section images, the total volume of electrolyte was estimated. Assuming the initial concentration within the pore was the same as the bulk, 1M LiClO_4 in PC electrolyte, the total number of Li ions per pore was estimated. The amount of Li ions and V_2O_5 in each pore was estimated to be 8.01×10^{-17} moles of V_2O_5 /pore and 4.52×10^{-18} moles of Li ion/pore at rest. To lithiate the V_2O_5 to $\text{Li}_2V_2O_5$, each V_2O_5 unit requires two Li ions, indicating 1.60×10^{-16} moles of Li ions are needed per pore. With only 4.52×10^{-18} moles of estimated Li ion/pore, which accounts for only 3% of the total required Li ions for two full lithiations of V_2O_5 in each of the pores, 97% of the required Li ions still need to diffuse from the bulk of the electrolyte into the confined pores of the V_2O_5 nanotube electrodes. At low current densities, the rate of depletion of Li ions within the pores and the diffusion of Li ions from the bulk into the pores may be similar, allowing full material usage. As the current density increases, the

rate of Li ion depletion increases as well. However, the rate in which the Li ions can diffuse from the bulk into the pores is limited by the diffusion coefficient and the diffusional cross-sectional area, i.e. the pore diameter, resulting in ion starvation where the ions are not diffusing fast enough to match the reaction rate. Kitada et. al and several other groups have shown that in highly confined electrode systems, it was the ion transport that was limiting the capacity at higher current densities.¹⁰⁰⁻¹⁰² To explore the possibility of ion starvation in this system, the pore diameters were varied by changing the pore widening time of the AAO template. By altering the pore diameter, it is expected that a larger pore will be able to maintain larger ion transport capability than a smaller pore, due to the larger cross-sectional diffusional area.

With increased pore widening time, the final pore diameter was able to be increased from 50 ± 3 nm to 61 ± 4 nm. With the increased pore diameter, not only is the amount

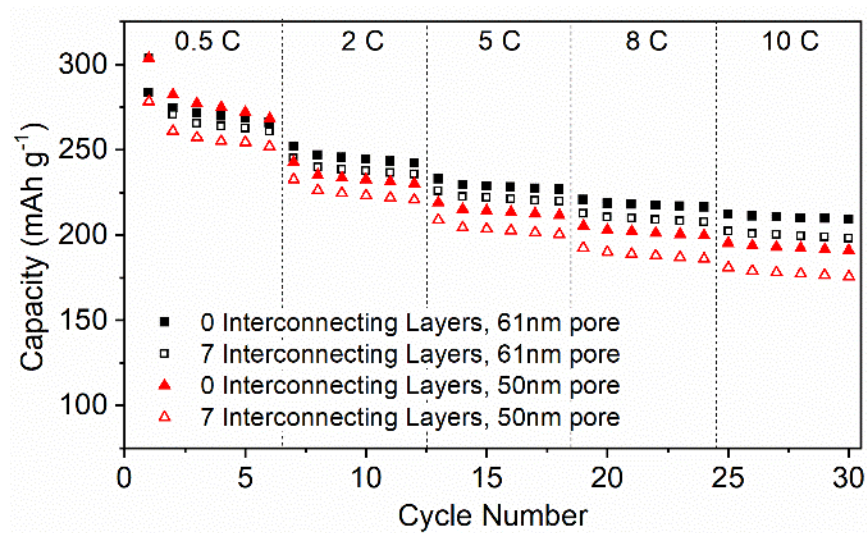


Figure 2.7 - Capacity of V₂O₅ of electrodes with various interconnecting layer with larger, 61nm pore, and smaller, 50nm, pore diameter openings at various current densities.

of Li ions available in the pore greater, but also the pore cross-sectional area is larger which increases the Li ion transport rate for Li ion diffusion from the bulk electrolyte into the pores. Figure 2.7 shows the resulting capacities of electrodes with larger 61 nm pores and smaller 50 nm pores. Current densities up to 10 C were chosen as it was enough to clearly show the difference in the impact of the pore diameters and interconnecting layers on the capacities. There was an increase in the capacity retention at various current densities with larger pore diameters, but the trend observed in Figure 2.5b where more interconnections showed higher capacity loss is maintained even in the electrodes with larger pore openings. Therefore, these results still do not explain the discrepancies between the one-Li and two-Li insertion voltage windows. This suggests that even 50nm pore diameter is enough to support the ion transport needed for high current densities.

2.3.4 Effect of Dynamic V_2O_5 Conductivity

As V_2O_5 is a well-studied cathode material for Li-ion batteries, its electronic conductivity has previously been studied at various levels of lithiation.^{103, 104} The literature shows that the conductivity of V_2O_5 is dynamic with the degree of lithiation. While the absolute number of the electronic conductivity varies from study to study, it is accepted that the conductivity reaches its maximum at about $Li_{0.5}V_2O_5$ and declines upon further lithiation yet remains in the same order of magnitude up to one full Li insertion, $Li_1V_2O_5$. With the second Li insertion, however, the electronic conductivity

drops by two orders of magnitude. Understanding that the electronic conductivity of V_2O_5 is dynamic, both positive and negative synergistic behaviors between the interconnections and the degree of lithiation can be explained.

Pearse et al. used XPS to probe into the mechanism of inhomogeneous lithiation in V_2O_5 thin films with a non-integrated current collector.⁹⁷ The XPS mapping showed, at low current density, there was a uniform distribution of reduced vanadium from +5 state to +4 state over the distance measured from the current collector. At high current density, the vanadium near the current collector showed significantly higher reduced states than the rest of the film. When COMSOL Multiphysics was used to model this observation, the same XPS mapping of the vanadium states could not be fit using constant electronic conductivity values reported for V_2O_5 . The distance over which the reduction occurred indicated by the model was shorter than what was experimentally observed. Using dynamic electronic conductivity, conductivity as a function of lithiation, the model was finally able to reproduce the experimental data. The reason was the increased conductivity of V_2O_5 during lithiation. The improved conductivity of V_2O_5 during lithiation led to a smaller drop in the overpotential throughout the electrode, leading to much better material usage further away from the current collector. This explanation can also be adapted to describe the phenomenon that is observed with interconnections and the difference in the electrochemical properties of V_2O_5 .

The voltage profiles during the charge and discharge processes at 0.5C and 25C in both the one-Li ion (Figure 2.8A and C) and two-Li ion insertion (Figure 2.8B and D)

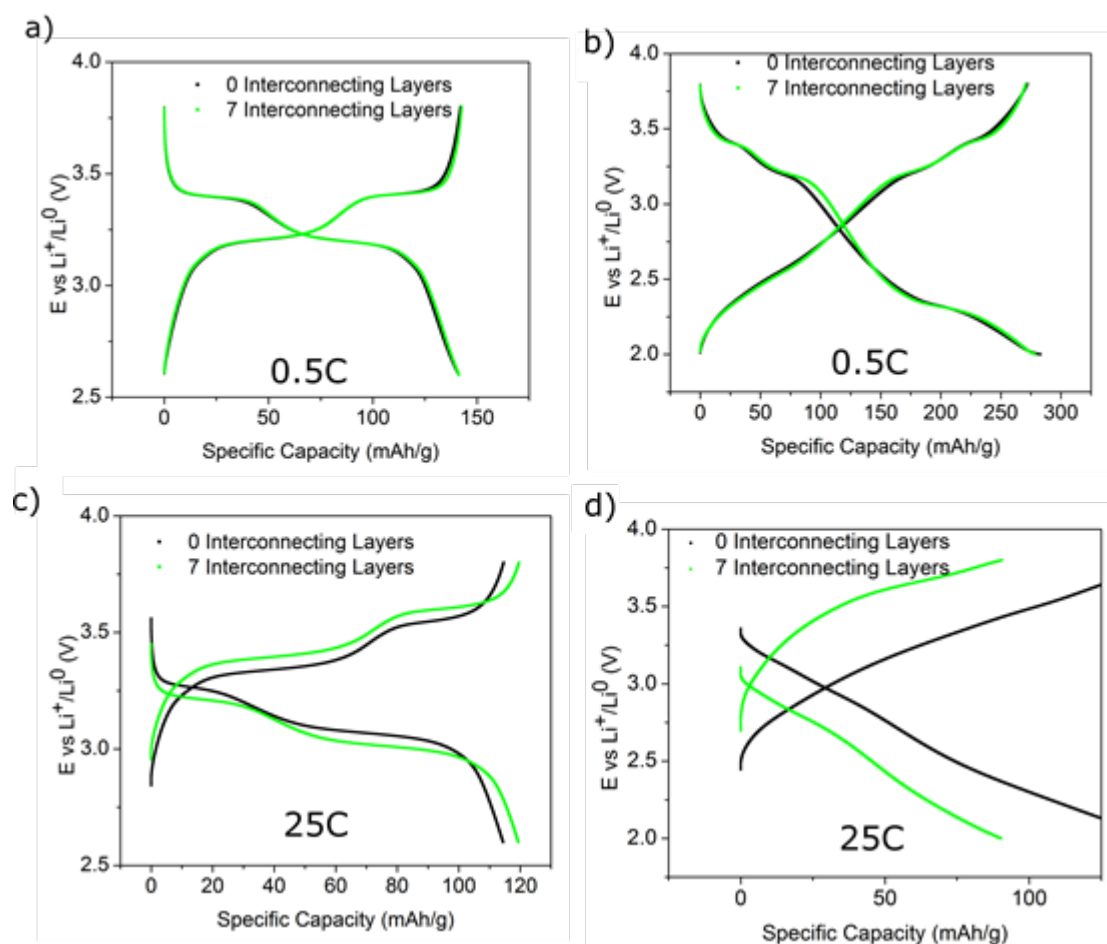


Figure 2.8 - Voltage profiles of 0 interconnecting layer and 7 interconnecting V_2O_5 electrode cycled between one electron window (2.6V-4V vs Li) at 0.5C A) and 25C C), and between two electron window (2V-4V vs Li) at 0.5C B) and 25C D).

regimes were analyzed to further understand the mechanism for the different phenomenon observed between the electrodes with different numbers of interconnections. The voltage profiles show the variances in electrochemical behavior between electrodes with zero and seven interconnecting layers. From the voltage profiles, the plateaus represent voltages where Li insertion and deinsertion and resulting phase transitions occur. To more clearly show these differences, first derivatives of the inverse of the voltage profiles were taken. The differential curve of

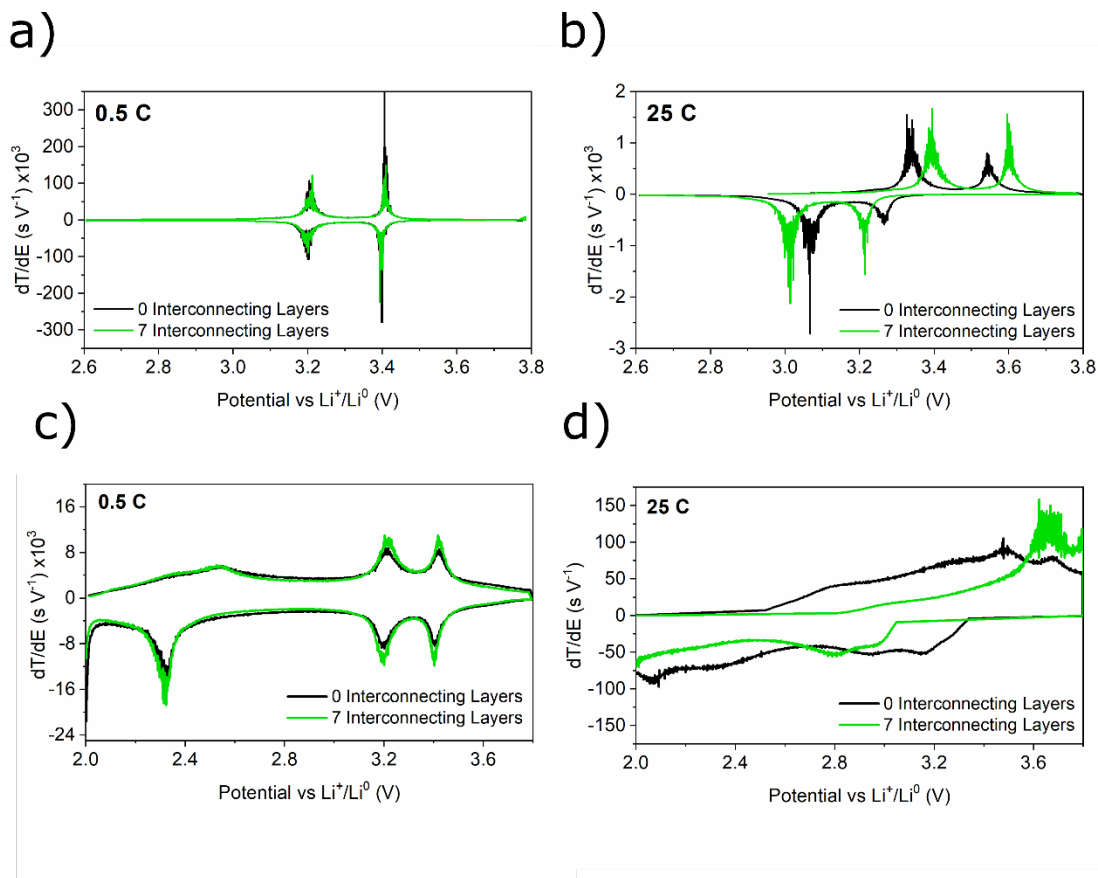


Figure 2.9 - First derivative of the inverse of the voltage profiles of 0 interconnecting layer and 7 interconnecting V_2O_5 electrode cycled between one electron window (2.6V-4V vs Li) at 0.5C A) and 25c C), and between two electron window (2V-4V vs Li) at 0.5C B) and 25C D).

the voltage profile is analogous to a cyclic voltammogram, and the peaks also correspond to the electrochemical reactions.¹⁰⁵ These can be seen in Figure 2.9A,B and Figure 2.9C,D for the one-Li and two-Li regimes respectively.

With one Li ion insertion, initially at low current densities, there is no significant influence of interconnecting layers on the capacity as the time scale is long enough for the electrodes to be lithiated uniformly, utilizing all the active material (Figure 2.9A). The peaks corresponding to each phase transition that occurs during lithiation and

delithiation of V_2O_5 overlap for the electrodes with zero and seven interconnecting layers at 0.5C. However, as current density is increased, the electrodes are polarized due to relatively low electronic conductivity, leading to highly lithiated regions near the planar current collector. Within the one Li ion insertion voltage window, as stated before, the electronic conductivity increases with lithiation up to half Li then drops back to its initial conductivity when fully lithiated. At high current densities, however, as the electrodes are polarized, regions near the current collector are lithiated more than regions further away. With the interconnections, additional electronic pathways are introduced, which increases the overall distance electrons must travel. Due to the minimal conductivity change within the one-Li regime, and the longer electronic pathway from the interconnections, the electrode with seven interconnecting layers shows larger peak separation than the electrode with zero interconnecting layers at 25C in Figure 2.9B. Liu *et. al* also saw a similar effect with templated LiFePO_4 electrodes, where longer electron transport pathways resulted in higher overpotentials.¹⁰² However, in our study the electrodes with seven interconnecting layers showed higher capacities than zero interconnecting layers within a one Li insertion voltage window. This observation could be explained by the full insertion and deinsertion peaks that are present in the differential plot of the electrode with seven interconnecting layers, which still shows a high degree of material utilization. There is more material closer to the planar current collector with more interconnections, which leads to the higher capacity at 25C. This result demonstrates a positive synergistic behavior between the properties

interconnecting layers and the electronic conductivity of the active material with lithiation, leading to better capacities at higher current densities.

A similar explanation can be used for the negative synergistic behavior between the interconnecting layers and the decrease in the electronic conductivity of the active material, which is the case for the two Li insertion voltage window. At lower current densities, there is minimal polarization of the electrode, thus enabling V_2O_5 to be fully lithiated, leading to similar specific capacities with varying numbers of interconnecting layers. The differential plot for the two Li ion insertion voltage window in Figure 2.9C illustrates the three distinct phase transition peaks for a total of two Li ion insertions into V_2O_5 at 0.5C. There is no clear difference between the electrodes with zero and seven interconnecting layers, again supporting this explanation. When the current density is increased, similar to the one Li insertion case, the electrode becomes more polarized. However, instead of having similar electronic conductivity during lithiation of the V_2O_5 , it significantly decreases with lithiation, leading to even higher degree of electrode polarization. As can be seen in Figure 2.9D, there is a significant amount of peak separation at 25C for both electrodes. For the one with zero interconnecting layers, the five phase transition peaks can still be seen even though large electrochemical irreversibility is seen. For the electrode with seven interconnecting layers, not only there are the additional electronic pathways the electrons need to travel but these pathways become further electronically insulating with further lithiation of the V_2O_5 , reducing the amount of active material that can be utilized in the electrode further away from the current collector. In Figure 2.9D, the electrode with seven interconnecting

layers shows only partial phase transitions due the severe peak separations, thus upon reaching the upper and lower voltage limits, the peaks are cut off. **Error! Reference source not found.** Figure 2.10 shows an illustration of the proposed difference in the degree of material utilization these interconnections may have. These images are not the result of calculations or simulations, rather they are presented to give a visual representation of what we propose is causing the changes in the electrode performance. Similar illustrations are provided later in this paper to help represent changes in the electrode under different conditions.

Another explanation for the electrode behavior differences could be that the Li ion diffusivity, the solid ion transport through the active material, changes with degree of lithiation. As shown by McGraw et al., the diffusivity of Li ions in V_2O_5 indeed is also dynamic with lithiation.¹⁰⁶ In order to experimentally resolve the impact of dynamic diffusivity and dynamic electronic conductivity, the structure of the current collector was varied from a planar Au current collector to an integrated Ru current collector. A

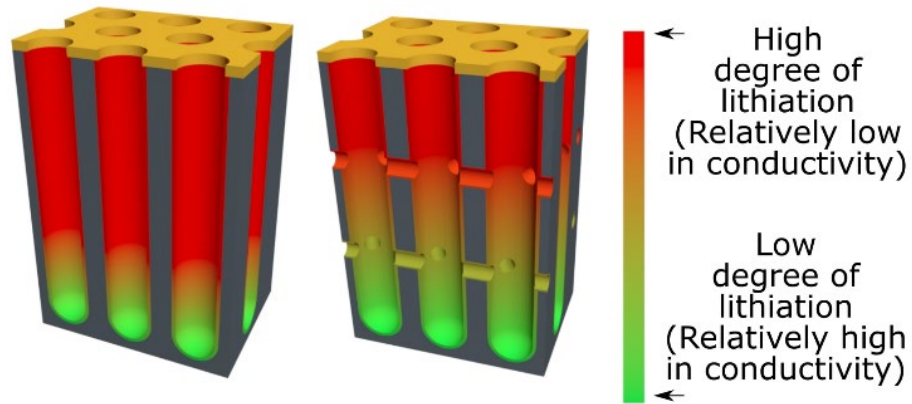


Figure 2.10 - Graphical description of the proposed impact of interconnections on the degree of material utilization due to the electronic conductivity of V_2O_5

thin layer of metallic Ru is deposited in the AAO templates via atomic layer deposition. The Ru coats the walls conformally as shown in a previous work.¹⁰⁷ In the current study, a planar current collector was used meaning the electrons have to be transported along the material as far as 2.3 μm away from the current collector. However, with the integrated current collector, the electrons would travel through only the thickness of the active material, about 10 nm. If the dynamic electronic conductivity of the material plays a key role in the poor behavior of the electrode with the interconnections, with the integrated current collector there should be no difference in the capacities with varying numbers of interconnecting layers because electrons have a high conductivity pathway along the length of the electrode. Therefore, even if the electronic conductivity of the V_2O_5 itself is poor, the integrated current collector will mitigate this negative effect. However, if it is the Li ion diffusivity that has a key role, integrated current collectors should have minimal impact on the electrochemistry and the difference in capacity retention should still be seen upon variation of the interconnecting layers. As shown in Figure 2.11, with an integrated current collector there is no difference between electrodes with zero and seven interconnecting layers. This result demonstrates that the differences in the capacities observed in Figure 2.5 are due to the negative synergistic behavior between the structural properties of interconnecting layers and the dynamic electronic conductivity of the active material. Figure 2.11B shows an illustration of proposed electrode structure with the integrated current collector. This is purely an illustration to show the uniform lithiation that occurs due to the integrated current collector and not a mathematical simulation. These observations

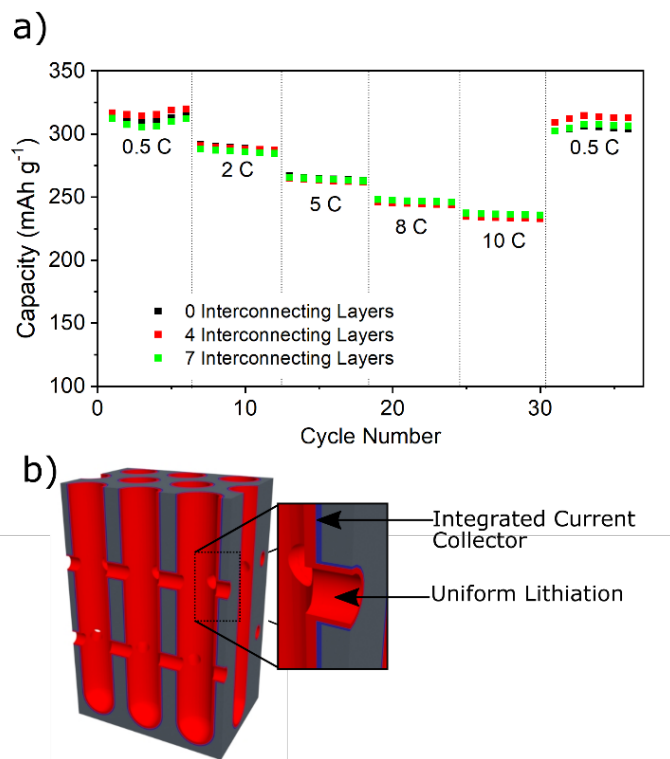


Figure 2.11 - A) Capacity of V_2O_5 of electrodes with various interconnecting layer, cycled between 2 V and 4V vs Li with integrated Ru current collector B) Proposed uniform lithiation with integrated current collector

also suggest that in commercial electrodes with active materials that decrease in electronic conductivity upon lithiation such as LCO, the loss in capacity could be due to the loss in the electronic conductance.

2.3.5 Degradation of the Electrode

The impact of interconnecting layers on the degradation of the electrode was also explored. With a planar current collector, there is a difference in the degradation rate between zero interconnecting layers and seven interconnecting layers. To better

represent the degradation of the electrodes, the capacities were normalized to the first cycle. While this data shows that with more interconnecting layers the capacity degrades at a faster rate, the mechanism for the degradation is unclear. There are two possibilities for the degradation in this system. The first possibility is the structural irregularities due to the interconnections, which may result in sharp edges and corners where electrochemical hotspots could form, leading to irreversible reactions (for V_2O_5 , the 3rd Li insertion is irreversible). To understand the irreversible reactions, it is important to understand the various phase changes of V_2O_5 upon lithiation. Pristine V_2O_5 is in the α phase. From zero Li ion to one Li ion insertion, V_2O_5 goes through reversible phase transitions from α to ϵ , then ϵ to δ phase. From one to two Li ions, the δ phase transforms into γ due to the breaking of some V-O bonds to accommodate the second Li ion. While phase transition to the γ phase is structurally irreversible, all Li ions can still be reversibly removed into the γ' phase. When more than two Li ions are inserted, another phase transition occurs into the ω phase to accommodate additional Li ions. This change to a rock-salt structure is irreversible not only with regard to the crystalline phase transition, but also the large amount of Li ions that cannot be removed after insertion, thus lowering the energy density after three Li ions are inserted.^{93, 108,}

109

The other possible electrode degradation mechanism is due to the electrode polarization where to maintain the required current densities, high overpotentials are applied to the active material closer to the current collector, again resulting in irreversible reactions. The use of the two different current collector structures allows the separation of these

two mechanisms. The electrochemical hotspots are the result of sharp edges where the electric field is the highest. By providing an integrated current collector, the electric field at these sharp edges should be enhanced, thus lead to further irreversible reactions.

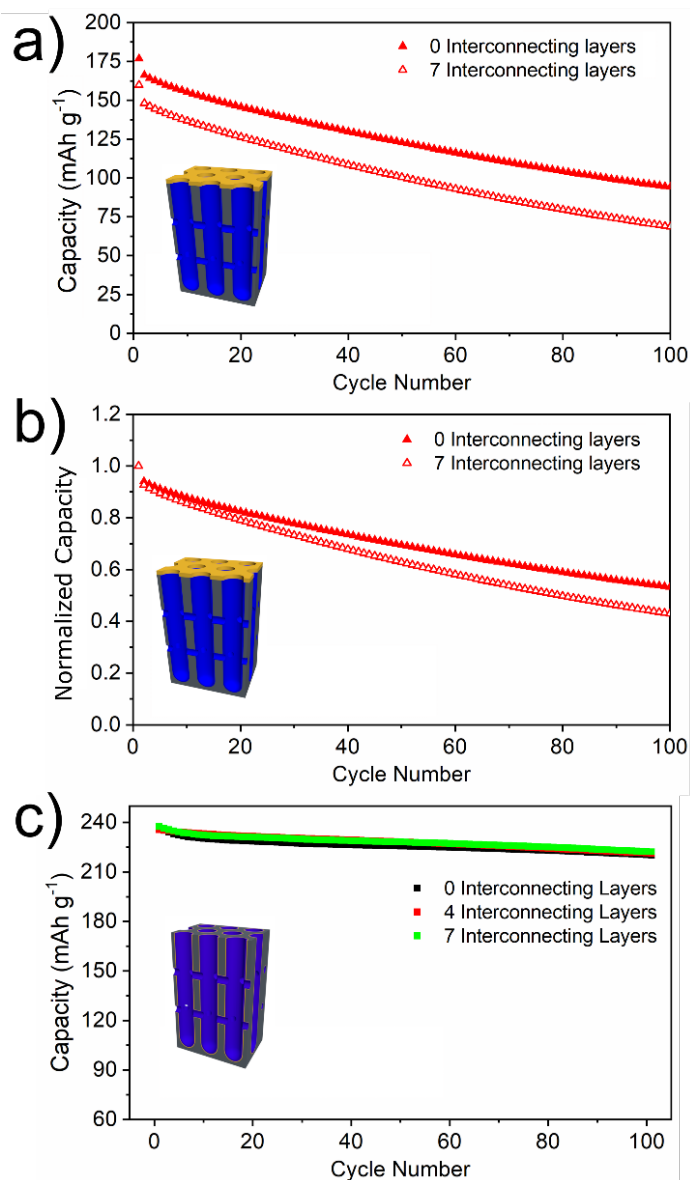


Figure 2.12 - Gravimetric cycling at 10C A) with planar current collector and C) with integrated current collector with different numbers of interconnecting layers B) shows normalized capacity of A) respective to the first cycle.

However, it can be seen in Figure 2.12 that with the integrated current collector no difference in the degradation can be seen. This outcome suggests that the degradation mechanism, despite the structure irregularities of the interconnecting layers, are likely due to the polarization of the electrode.

2.4 Conclusion

In this study, well controlled nanostructured electrodes were fabricated to understand the complex interactions between structure and its impact on the ion and electron pathways which determine the electrochemical behavior of the electrode. Differing behaviors were observed between electrodes with and without interconnecting layers in one and two Li insertion voltage windows. In the one-Li insertion voltage window, electrodes with seven interconnecting layers showed about 5% higher capacity than electrodes with zero interconnections at 25C, whereas in the two-Li insertion voltage window, electrodes with seven interconnecting layers showed about 20% less capacity than those with zero interconnections at 25C. To understand the impact of the interconnections within the different Li insertion voltage windows on the electrode capacity, the pore diameters of the electrodes were first changed. While larger pore diameter showed higher capacities overall, it still showed that in the two- Li insertion regime, fewer interconnections led to higher capacities. To understand whether the capacities were limited by the dynamic electronic conductivity or dynamic Li diffusivity, an integrated current collector was used. With the integrated current collector, no difference in capacity was seen among samples with varying numbers of

interconnections, showing that the difference between the electrodes with interconnecting layers in the two different voltage windows were from the positive and negative synergistic behavior of the electronic conductivity of the material and the structural properties of interconnections. The impact of the structural irregularities from the interconnections on the degradation rate was also investigated. From gravimetric cycling at 25C, the electrodes with seven interconnecting layers lost 10% more capacity than the electrodes without any interconnections. Further, this was supported by experiments with integrated current collectors where these samples demonstrated the same capacities with increased current densities independent of how many interconnections were present, thus that the polarization of the electrode was the source of the increased degradation rate.

This study demonstrates that material properties must be carefully chosen due to the observation that within the same electrode architecture, dynamic materials' properties can either help or harm the electrochemical characteristics of the electrode depending on how the properties change during ion insertion. It was also shown that the irregularities caused by the interconnections did not have a significant impact on the degradation mechanism, whereas the polarization of the electrode was found to be the major contributor to the electrode degradation. This well controlled 3D porous electrode structure can be further used as test bed platform to examine the impact of additional ionic and electronic path ways in different battery material with varying battery chemistries.

3 Nanofluidic Battery, impact of nanoconfined electrolyte on the electrode behavior

This work was a collaboration between Dr. Mark Reed's group at the Yale University, Dr. Henry White's group at the University of Utah, and Dr. Sang Bok Lee's and Dr. Gary Rubloff's group at the University of Maryland. This work was published in ACS Nano, 2019, 13, 7, 8481-8489. This work was initiated by Dr. Sylvia Xin Li from Yale and Dr. Chanyuan Liu from UMD. My contribution is the ALD of TiO_2 , final assembly of nanochannel devices, experimental set up, data collection, and analysis of electrochemical data. Dr. Sylvia Xin Li's contribution is initiation of the project, fabrication of the device, data collection, and analysis of electrochemical data. Dr. Chanyuan Liu's contribution is initiation of the project, development of TiO_2 annealing process and ALD of TiO_2 . Dr. Kim McKelvey's contribution is building of the COMSOL simulations analysis of the simulated data.

3.1 Introduction

In conventional electrical energy storage systems, such as a battery or a capacitor, metal or metal oxide electrodes are in a bath of electrolyte. During charging and discharging of these energy storage devices, the surface of the electrodes become charged.¹¹⁰ The electrode often has functional groups on the surface as well, such as oxide/hydroxide groups for metal oxides that have some inherent surface charges.¹¹¹⁻¹¹³ In order to balance this charge, the ions in the electrolyte will interact in order to minimize that

charge. This formation of counter ions on the surface of the electrolyte is called the electrical double layer (EDL).

There are several models describing the EDL. The first model that describes such layer is the Helmholtz model. Helmholtz described a simple model that when a charged metal surface is placed in electrolyte solution, there will be an opposite charge in the electrolyte that will accumulate at the surface and form a thin layer to counter balance that charge.^{114, 115} This model, however, does not account for the effect of charge density on the metal surface as well as the concentration of the ions in the electrolyte. A more complex model was proposed by Gouy and Chapman where they solve these issues from the Helmholtz model. In the Gouy-Chapman model, instead of a single rigid layer of counter ions, there are two different layers in the EDL, the compact and diffuse layer. The compact layers are similar to what Helmholtz described in that this layer contains strongly bound counter ions near the charged surface. The diffuse layer describes more loosely bound counter ions that decrease in concentration as the charge effect decreases further away from the charged surface.^{116, 117} However, this model also had deficiencies in that it assumed the counter ions were simply point charges and caused significant deviations in fitting with experimental data. The Gouy-Chapman-Stern model takes into account the counter ion size and limits how close the counter ions can be to the charged surface. Stern redefined this compact layer, also called the stern layer, as the maximum distance which a solvated counter ion can approach the charged surface.¹¹⁵

When two charged surfaces, in close proximity to each other, are placed in electrolyte, interesting phenomenon are observed such as ion selectivity¹¹⁸, ionic current rectification^{119, 120}, and desolvation^{121, 122}. Of particular interest in nanostructured energy storage system is that the inherent volumetric energy density is lower because more of the space is taken up by the electrolyte. In order to maximize the energy density, nanostructured electrodes need to be placed as close as possible without sacrificing the ionic transport in nanoconfined electrolytes between two charged surfaces.¹²³⁻¹²⁵ The effects of nanoconfined electrolyte in battery electrodes have yet to be fully explored.

In order to study the effect of nanoconfined electrolyte on the electrode behavior for Li ion battery system, a new test bed is needed. Here, through the utilization of microfabrication techniques and atomic layer deposition, a test device is fabricated with a 20nm gap between two anatase TiO₂ surfaces. Anatase TiO₂ is an anode material for Li ion.^{82, 126-129} One of the TiO₂ surface is electrically connected to an external circuit to be used as the working electrode for electrochemical characterization. It was found that with nanoconfinement, the electrode had better electrochemical reversibility as well has higher capacity at higher scan rates than planar electrodes when the electrolyte concentration was decreased down to 1mM, simulating ion depletion conditions that may be seen in densely packed electrode structures. With the usage of COMSOL Multiphysics simulations, it was found that the charged surface of TiO₂ in the nanochannel inherently increased the ion concentrations due to the overlap of the EDL.

3.2 Experimental Methods

3.1.1 Device fabrication

The overall process of the device fabrication can be seen in Figure 3.1. Three inch wafer with thermal SiO₂ was cleaned and degreased in acetone, methanol, and IPA with sonication for 5 minutes in each solvent. The wafer was air dried and placed into ALD chamber. More detail on the TiO₂ ALD recipe is described later. It was then shipped to Yale University for the following procedures. The sacrificial chromium layer was patterned by photolithography and deposited by e-beam deposition. The wafer was shipped back to UMD where it was cleaned and degreased again before the additional TiO₂ deposition. This sandwiched the sacrificial Cr layer which defines the nanochannel dimensions. Each Cr sacrificial nanowire was 20nm thick, 4μm wide, and 26μm long. This wafer was shipped back to Yale for reactive ion etch (RIE) of excess TiO₂ around the Cr layer to expose TiO₂/Cr/TiO₂ layer. Ti adhesion layer was deposited first, then Pt current collector. In order to ionically isolate the top of the Pt current collector, PECVD SiO₂ was deposited. DRIE etching was performed once again to not only remove excess PECVD SiO₂ but also create micro pillars to support the PDMS microfluidic channel top from collapsing onto the reservoir and the nanochannels. The device was shipped back to UMD for the final time. Before the PDMS top was placed, the device was cleaned. It was annealed according to the recipe described later in this section. PDMS top and device were placed under oxygen plasma in Branson Barrel Resist Stripper at 200W for one minute to activate the PDMS surface for bonding with SiO₂ surface of the device. Once the PDMS was placed on the device, it was placed on

a hot plate at 95°C for five minutes. It was then placed on a hot plate between 110-120 °C for 30 minutes with thick Al plate as weight to press down the PDMS firmly and evenly on the surface of the device. After the 30 minutes, the plate was cooled to 70-80°C and the bonded device was left for eight hours. It was cooled to room temperature afterwards. Silver wire was electrically attached to the Pt current collector on the device via silver paste. It was then covered with EP42HT-2 solvent resistant epoxy purchased from Master Bond to provide mechanical reinforcement. The wired-epoxy device was then placed in the oven at 80°C for 8-12 hours to cure the epoxy and was left out to cool to room temperature before storing it for future use.

3.1.2 Device Preparation

When the device was ready to use, PTFE tubing was inserted into the PDMS top with microfluidic channels that went over the electrolyte reservoir areas on the device. A

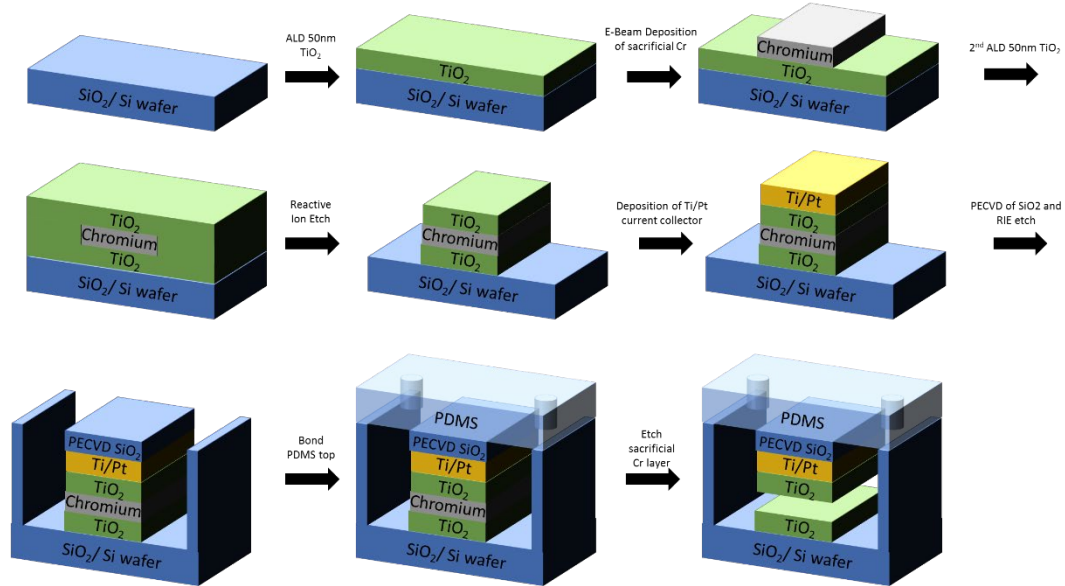


Figure 3.1 – Schematics of the nanochannel device fabrication. ALD deposition and final assembly of PDMS top layer and removal of Cr sacrificial layers were performed at UMD

syringe pump was used to flow solutions through the device at rates between 20 μ L/min to 60 μ L/min. Each syringe had 0.2 μ m filter to minimize the blockage of the microchannels and was replaced w each time a different solution was used. First, DI water was used to fully wet the reservoirs. Once the reservoirs, especially near the Cr sacrificial layers, were fully wet, Cr etchant solution was used to remove the sacrificial Cr layer. Cr etchant was flushed out of the device with about 40 mL of DI water on each side of the nanochannel. Water was then replaced with pure propylene carbonate (PC) solution for about 20mL on each side. This was then replaced by the electrolyte with varying concentration of LiClO₄ in PC. Dry electrolyte was achieved by placing a small piece of Li in the syringe along with the electrolyte to absorb any moisture that may accumulate during the data acquisition. About 20mL of electrolyte was used to fully flush any remaining solution from previous steps. In order to prepare for the electrochemical testing, the PTFE tubing on the outlet on each side was replaced with a pipette tip which was used as a reservoir for the Ag/Ag⁺ electrode to ionically connect the reference electrode (RE) to the device. The remaining outlet on each side was replaced with Pt wire infused PTFE tubing as the counter electrode (CE). Electrolyte was pumped through until the pipette tip reservoir was full and Pt counter electrodes were fully immersed. The diagram of fully assembled device can be seen in Figure 3.2A. An image of the device under a microscope can be seen in Figure 3.2B where the microfluidic channels, the Pt current collector, and the nanochannel area can be seen.

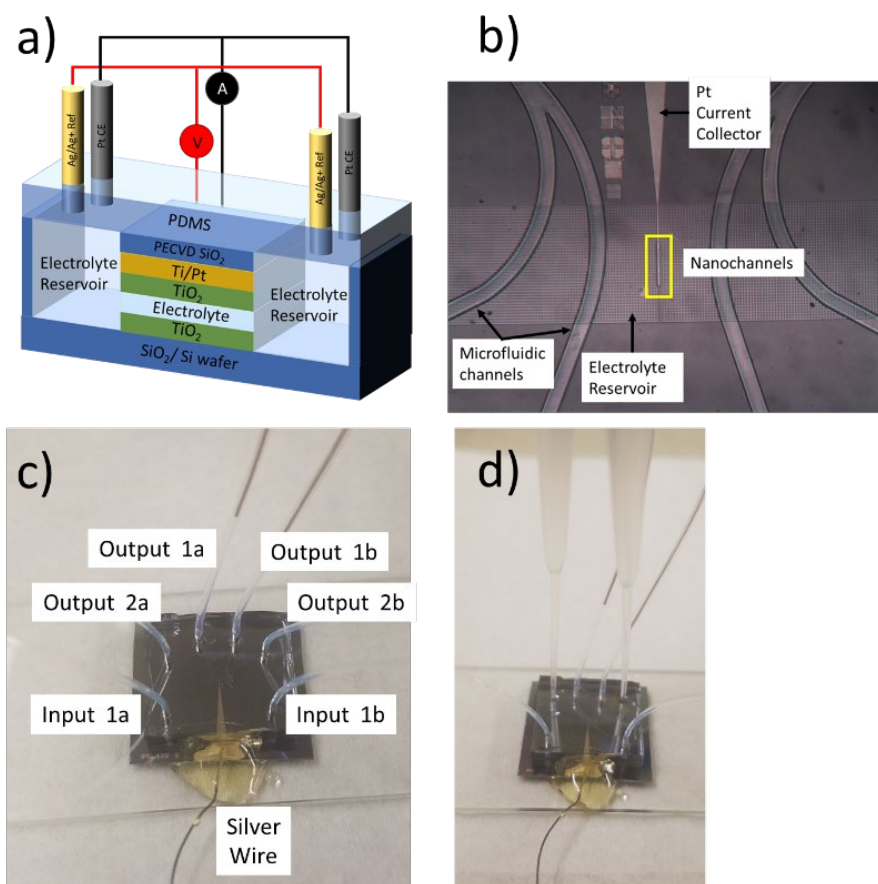


Figure 3.2 – A) Diagram of fully assembled nanochannel device showing how the voltage and currents were measured. B) shows a close image of the nanochannel device with the PDMS top attached. Four microfluidic channels can be clearly seen, with Pt current collector and the nanochannels highlighted in yellow. Image of C) fully connected device and D) device with pipette tip as reservoir for reference electrodes

Figure 3.2C and Figure 3.2D shows how the PTFE tubing and the pipette tips were attached to the nanochannel device.

3.1.3 Pt counter electrode infused PTFE tubing

The PTFE tubing used in this experiment was 28 gauge light wall PTFE tubing purchased from Component Supply Company. 0.25mm Pt wire with 99.9% purity was

purchased from Alfa Aesar. A small cut was made on one of the ends of the PTFE tubing to insert the Pt wire. A thin strip of stretched parafilm was used to wrap around the cut in order to stop the solvent resistant epoxy from blocking the tubing. Solvent resistant epoxy was then used to coat the area to lock in the Pt wire in the PTFE tubing.

3.1.4 Bulk Electrode Fabrication and Preparation

The thin film “bulk” electrode was fabricated similarly to the nanochannel device. Pt was evaporated on to a piece of Si wafer with thermal SiO₂ layer. Using the same ALD process, the TiO₂ layer was deposited with corner of the wafer masked for direct contact to the Pt current collector. Copper tape with electrically conductive adhesive was used to make electrical contact to the underlying Pt current collector. Due to the chemical incompatibility of the adhesive, to minimize a possible impact of the copper tape with the electrolyte, and to remove any sharp edges along the wafer piece from affecting the electrochemical data, the wafer piece was sealed using the solvent resistant epoxy. The prepared bulk electrode was then placed in a beaker cell. A three electrode system was also used for comparability. A large piece of Pt foil, about twelve times larger in area than the exposed TiO₂ WE, was used as the CE.

3.1.5 Electrochemical testing

Propylene carbonate, LiClO₄ and AgClO₄ were purchased from Sigma Aldrich. LiClO₄ was dried at 180°C under vacuum for at least 24 hours before it was loaded into the glovebox. Others were used as received.

A CHI 660A electrochemical workstation with faraday cage and picoamp booster and Biologic VSP was used for electrochemical measurements. An Ag^+ reference kit was purchased from BASI. The reference electrode solution was composed of 0.1M LiClO_4 and 0.01M AgClO_4 in PC. The CHI software was used to smooth the CV data to remove external signal noise. More details on this will be described later in the chapter.

3.1.6 Bulk conductivity Measurement

For measuring unconfined, bulk electrolyte conductivity, a commercial conductivity meter with two Pt electrodes (S216T) from Topac Inc. was used. Electrochemical impedance spectroscopy was used to measure the solution resistance. First, a standard solution with known conductivity of $1413 \mu\text{S cm}^{-1}$ was used to calibrate the conductivity meter. Then the conductivity meter was placed in various concentrations of LiClO_4 in PC and the solutions' conductance values were measured.

3.1.7 ALD Process of TiO_2 and Annealing Process

Amorphous TiO_2 was deposited using Fiji F200 reactor at 150°C with a pulse time of 0.3 seconds of tetrakis (dimethylamino) titanium (TDMAT) and 0.06 sec of water which resulted in the growth rate of $0.43 \text{ \AA/cycle}$ with total thickness of 43nm for all the samples for 1000 cycles. The thickness of each deposition was verified with a test Si wafer piece with N&K spectrophotometer and was also confirmed with SEM cross section.

TiO_2 was annealed under Ar gas. From room temperature, the furnace temperature was ramped to 400°C in 30 minutes. It was then held at 400°C for 30 minutes and was

allowed to cool over several hours before it was removed from the furnace. The crystallinity of the annealed material was tested by Raman spectroscopy.

3.3 Results and Discussion

3.3.1 Morphology Characterization of Nanochannel Device

Before the bonding of the PDMS top, the nanochannel area was checked with optical microscope. The depicted layers in Figure 3.1 and Figure 3.2A can be clearly seen in the SEM image of the cross section of the layers in Figure 3.3B. SEM measurements show that TiO_2 layers are 43nm and the Cr sacrificial layer is 20nm thick. Figure 3.3C

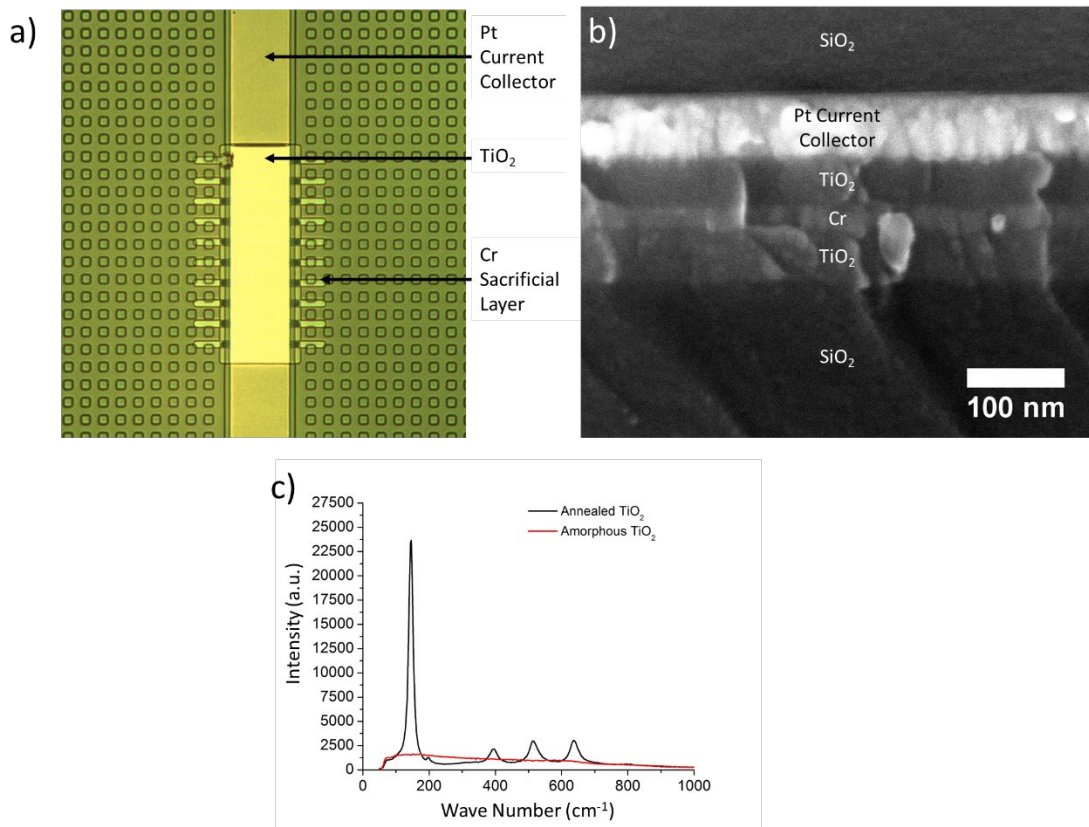


Figure 3.3 – A) Zoomed in area of the nanochannel before the sacrificial Cr is removed. B) SEM image of the cross-section of the nanochannel that shows 45nm of TiO_2 layers around 20nm of Cr layer. C) Raman of as deposited amorphous TiO_2 and annealed TiO_2 .

shows the Raman spectra of as deposited amorphous TiO_2 and annealed TiO_2 . The peaks of the annealed TiO_2 corresponds very closely to the literature values of anatase phase of TiO_2 .

3.3.2 Noise reduction in nanochannel measurements

Once the nanochannel device was ready, cyclic voltammetry was run in order to observe the characteristic Li ion insertion and de-insertion peaks of anatase TiO_2 . As can be seen in Figure 3.4A, the cyclic voltammogram is noisy and it is difficult to observe any peaks. There is almost a repetitive pulse noise over time. This can be even more clearly seen in Figure 3.4B when it is plotted as current over time. In order to address the noise issue, connections to the nanochannel was modified such that the voltage difference between the two reference electrodes across the nanochannel could be recorded. This showed that there was large fluctuation in the voltage across the channel due to the noise in the measurement. In order to minimize the recorded noise, any peripheral devices connected immediately next to the potentiostat were not only turned off but unplugged. These are devices such as ovens, syringe pumps, and fluorescent lighting of the lab. With these devices turned off, the noise dropped significantly. Before these changes, the OCV fluctuated over $\pm 1\text{V}$. With these changes only about $\pm 100\text{mV}$. This improved the CV. As can be seen in Figure 3.5A, CV that

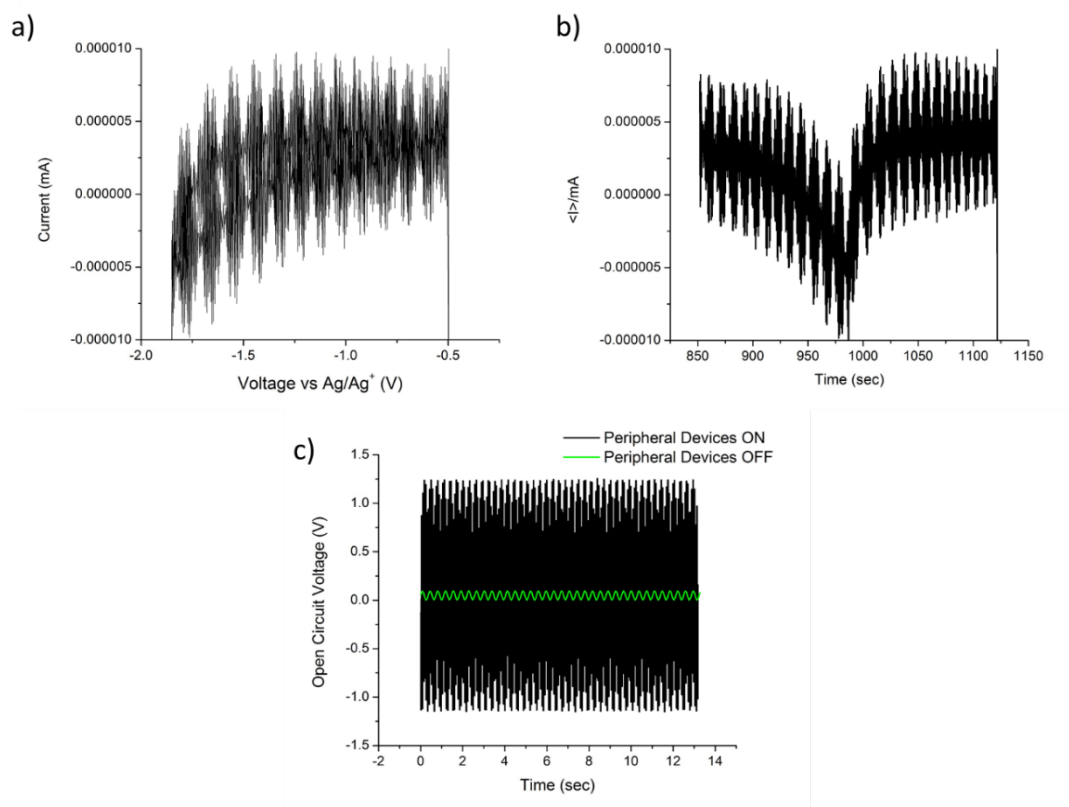


Figure 3.4 – A) Cyclic voltammetry of the nanochannel device. B) I-T curve of A). C) open circuit potential between the two reference electrodes over about 13 seconds with and without peripherals turned on.

resembles a typical Li intercalation into anatase TiO₂ was obtained. However, there were clear fluctuations in the curves and random artificial “peaks” were formed at different cycles. The simple solution was to change the scan rate from 10mV/s to 9mV/s. At 9mV/s, highly reproducible cyclic voltammograms were measured, as seen in Figure 3.5b. It is unclear why such noise was measured at 10mV/s but not at 9mV/s. It could be some electrical noise that interacted with the device and the electrical measurement device to produce such artificial peaks and fluctuations. This also occurred with 20mV/s and 5mV/s (not shown) and so 19mV/s and 4.5mV/s were chosen respectively.

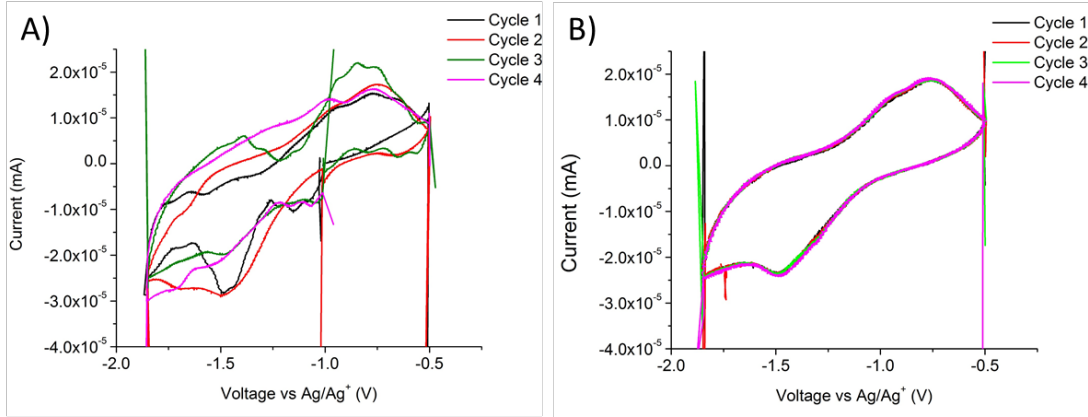


Figure 3.5 – Cyclic voltammogram of TiO₂ in the nanochannel at A) 10mV/s and B) 9mV/s

3.3.3 Electrochemical Measurements of Nanoconfined Electrolyte vs Bulk Electrolyte

While the qualitative description of the EDL was described in the introduction, in order to quantitatively measure the effect of nanoconfinement, and overlap of EDL, the mathematical definition of EDL is shown in Equation 3.1¹³⁰

$$\Psi(B) = \frac{\Psi(0)}{e}$$

Equation 3.1

where $\Psi(0)$ is the potential at the surface of the electrode, $\Psi(B)$ is the potential at the EDL, B is the distance away from the surface of the electrode, and e here is the euler's number which is about 2.72. Notice the potential at the electrical double layer at B is not zero. This means that additional ion accumulation occurs beyond the EDL.

To calculate the EDL thickness, the linearized Poisson-Boltzman equation shown below was used,

$$B = \sqrt{\frac{\epsilon RT}{2F^2 Z^2 C_b}}$$

Equation 3.2

where B is the EDL thickness in meters, ϵ is the permittivity of the medium in $C^2 J^{-1} m^{-1}$, R is the gas constant in $J mol^{-1} K^{-1}$, F is the faraday's constant $C mol^{-1}$, Z is the charge of the ion, and C_b is the bulk electrolyte concentration in mol/m^3 .¹³¹ Based on the literature values, the dielectric constant of propylene carbonate was assumed to be 64.¹³² Z was 1 as both Li^+ and ClO_4^- are singly charged. With these values, the calculated B at 100mM $LiClO_4$ was 0.9 nm, at 10mM $LiClO_4$ was 2.7 nm, and at 1mM $LiClO_4$ was 8.7 nm. From these calculations, in 20nm channel at the 1mM concentration of $LiClO_4$, the EDL does not technically overlap but as discussed earlier, the diffuse layers should still overlap.

Conventional thoughts on the effect confined electrolyte has on the electrode behavior for Li ion insertion is that the Li ion transport will be significantly hindered due to not only lower volume of electrolyte resulting in lower number of Li ions initially available, but also slow ion transport due to the lower cross-sectional area which results in lower flux of ions. However, when the results of CVs of confined electrolyte in nanochannel devices were compared with that of the planar bulk device, the opposite was observed. Figure 3.6A, B, and C shows CVs of the nanochannel device and bulk device at 0.5, 4.5, and 19 mV/s. Most of the CVs of the nanochannel device measured

higher areal capacities than the bulk device as shown in Figure 3.7. Closer analysis of the CVs showed that the nanochannel device had sharper peaks. There was also a change in the overall CV as the scan rate increased. At a low scan rate of 0.5mV/s, in both devices, the insertion and deinsertions peaks are clearly seen. However, starting at a moderate scan rate of 4.5mV/s, the unconfined bulk device lost its insertion peak while the insertion peak in nanochannel device was maintained. At a higher scan rate of 19mV/s, the bulk device lost even the deinsertion peak whereas the nanochannel

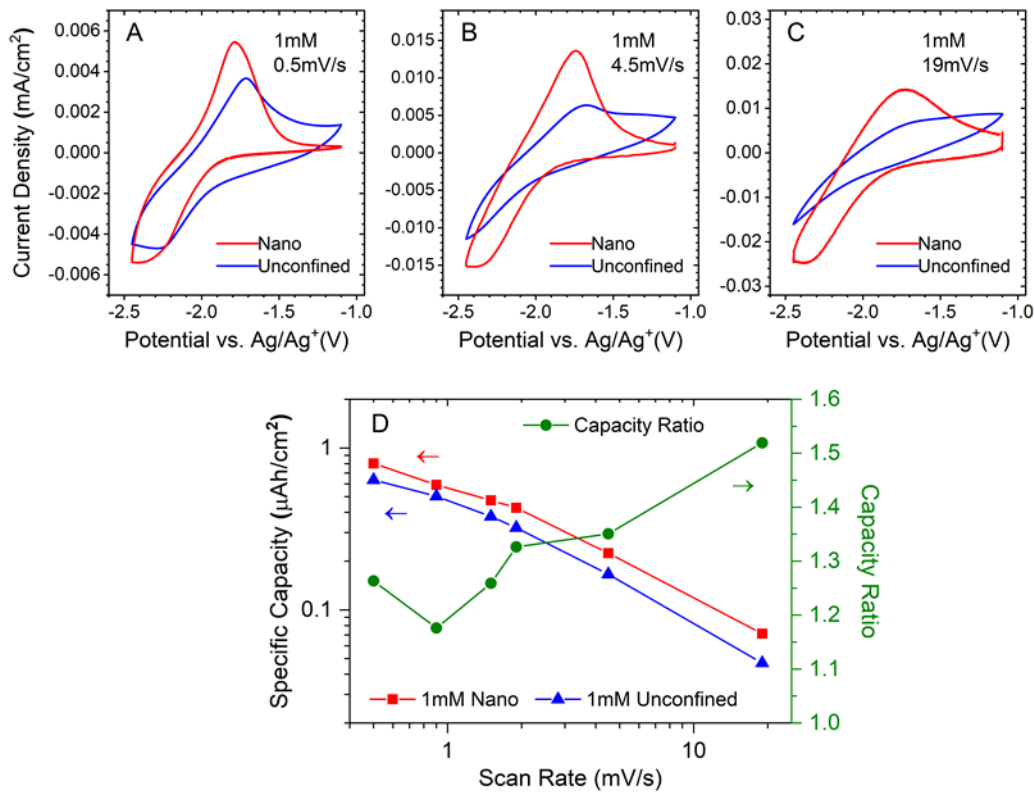


Figure 3.6 – Cyclic voltammograms of nanochannel electrode device and bulk, unconfined electrode device with 1mM LiClO₄ electrolyte at A) 0.5mV/s, B) 4.5mV/s. C) 19mV/s. D) shows specific areal capacities and capacity ratio of nanochannel device and bulk device at various scan rates

device still maintained both peaks.

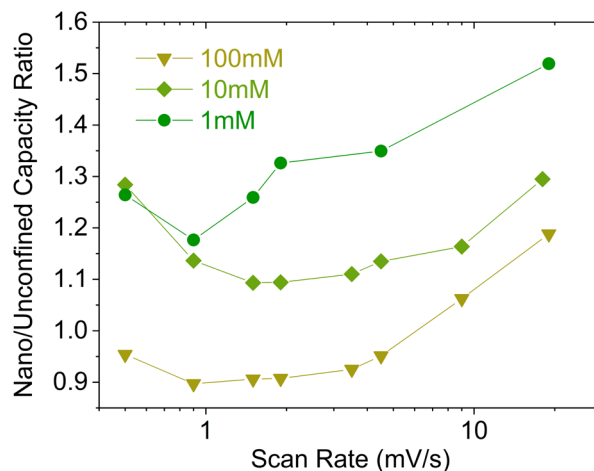


Figure 3.7 – Nanochannel to unconfined bulk device capacity ratios at various concentration and scan rates

Similar results were seen at 10mM and 100mM concentrations and can be seen in Figure 3.8A and C where at high scan rates the insertion peak in the unconfined bulk device disappeared while the nanochannel device maintained it. Peak separations between the insertion and deinsertion peaks were analyzed as function of scan rate at different electrolyte concentrations. The peak separations for 1mM, 10mM, and 100mM can be seen in Figure 3.9, Figure 3.8B, and Figure 3.8D respectively. Figure 3.8D shows that the peak separation between confined and unconfined devices were similar at the concentration of 100mM. At a lower concentration of 10mM, the difference in the peak separation increased more rapidly for bulk device as the scan rate was increased. At 1mM, due to the loss in the insertion peak of the bulk device, such comparison was not possible but the peak separation in the confined device did stabilize to around 0.63V as seen in **Error! Reference source not found.**

The combination both peak maintenance and shaper peaks of the nanochannel device led to higher capacities than the bulk device at various scan rates, and resulted in greater than one nanochannel-to-bulk capacity ratios, especially at higher scan rates as shown in Figure 3.7. In order to understand the mechanism behind such increase in specific areal capacity with nanoconfinement in the nanochannel device, finite element simulation was performed.

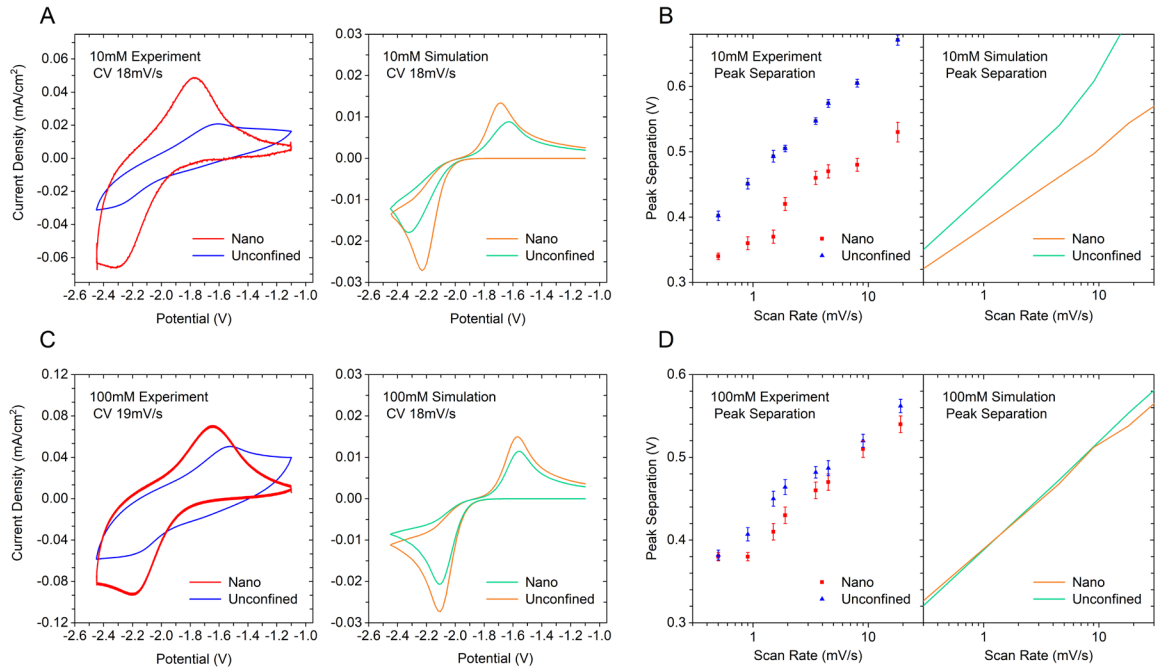


Figure 3.8 - Comparison of the experimental data and simulated data. A) and C) compare the cyclic voltammograms between confined and unconfined device at 10mM and 100mM LiClO₄ concentration respectively while B) and D) compare the peak separations between insertion and deinsertion peak at 10mM and 100mM LiClO₄ at various scan rates.

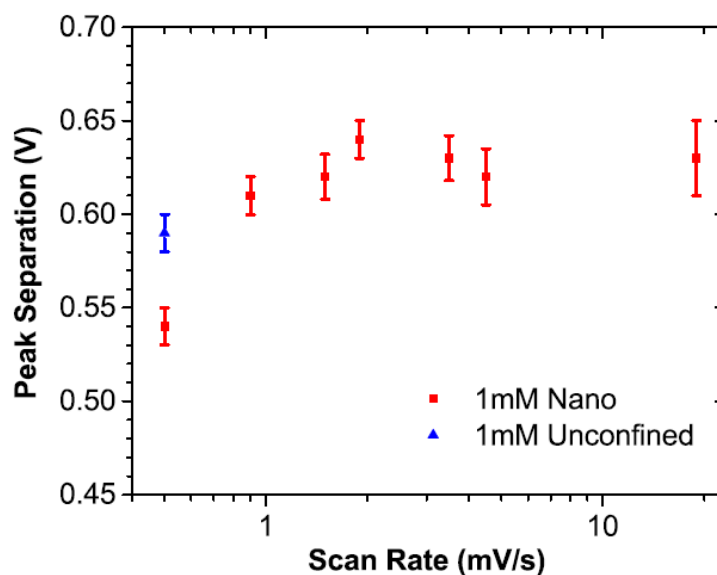


Figure 3.9 - Peak separation analysis of unconfined and confined device. Due the disappearance of the insertion peak, only at 0.5mV was able to be analyzed for the unconfined device

The finite simulation was performed by Dr. Kim McKelvey from the University of Utah in Dr. Henry White's research group. As this portion is crucial in understanding the enhancement effect of nanoconfined electrolyte, it will be discussed here in detail.

3.3.4 Finite Elemental Analysis

For modeling nanochannel device, a two-dimensional model was constructed in COMSOL Multiphysics software along the direction of the nanochannel while for

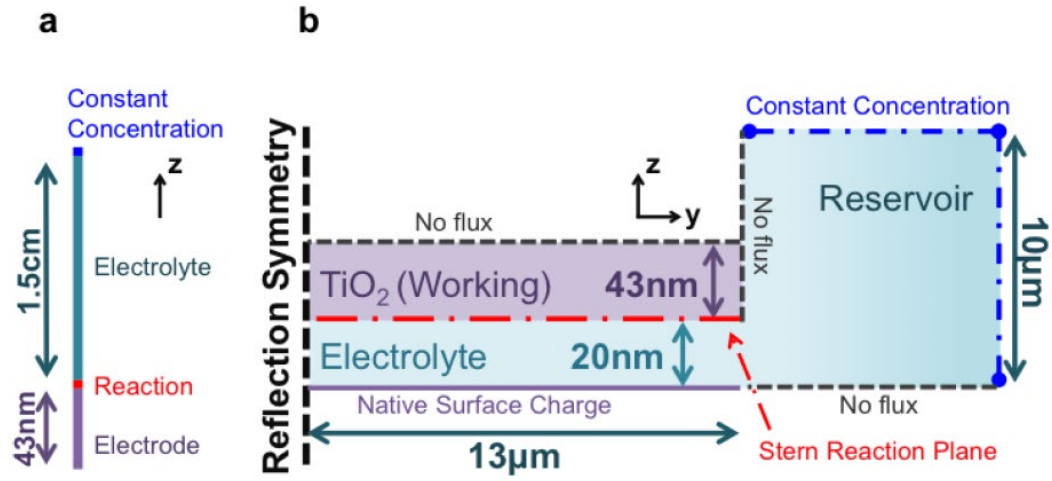


Figure 3.10 – Diagram of the finite element simulations for A) bulk and B) nanochannel devices. The dimensions describe the geometries and boundary conditions that were used in the simulation.

modeling bulk and unconfined device, a one-dimensional model was used. The diagram of the models for the nanochannel device can be seen in Figure 3.10. Poisson's equation and Nernst-Planck equations are used to relate the local ion concentrations to the electric potentials and to describe diffusion and migration ion transports in the model, respectively. Poisson's equation can be seen in Equation 3.3 and Nernst-Planck equation in Equation 3.4 where Φ is the applied potential, c_i is concentration of i ion, z_i is the charge of the i ion, t is time, D_i is diffusion constant of i ion, and T is the temperature.⁹⁷,

131

$$\nabla^2 \phi = -\frac{F}{\varepsilon} \sum_i c_i z_i$$

Equation 3.3

$$\frac{\partial c_i}{\partial t} - D_i \nabla \left(\nabla c_i + \frac{F z_i c_i}{RT} \nabla \phi \right) = 0$$

Equation 3.4

For the Li diffusion in TiO₂ electrode was described by the Fick's second law in Equation 3.5.^{97, 131}

$$\frac{\partial c_{\text{Li}}}{\partial t} - D_{\text{Li}} \nabla^2 c_{\text{Li}} = 0$$

Equation 3.5

Instead of the surface of the TiO₂, the stern layer was defined as the reaction plane. As described in the earlier section, there is a minimum distance in which a solvated ion can approach the surface of the electrode, called the stern layer. For this model, this stern layer is defined as 0.6nm, the radius of solvated Li ion in PC.¹³³ As the reaction plane is in the stern layer, and not at the TiO₂ surface, the applied potential of TiO₂ is not the potential seen at the reaction plane as there is a potential drop across the stern layer. In this model, the actual electrostatic potential at the reaction plane, V_{driving} , is defined by Equation 3.6 where V_{TiO_2} is the applied potential and Φ_{stern} is the potential drop across the stern layer.

$$V_{\text{driving}} = V_{\text{TiO}_2} - \phi_{\text{stern}}$$

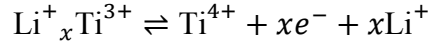
Equation 3.6

With this definition of V_{driving} , a modified Butler-Volmer equation, Frumkin-Butler-Volmer equation shown in Equation 3.7 is used to define the reaction current of Li ion insertion and deinsertion into TiO₂.

$$I = F \left[c(\text{Li}^+)c(\text{Ti}^{4+})ke^{-\alpha F \frac{V_{\text{TiO}_2} - \phi_{\text{Stern}} - V_{\text{Eq}}}{RT}} - c(\text{Li}^+_x\text{Ti}^{3+})ke^{-\alpha F \frac{V_{\text{TiO}_2} - \phi_{\text{Stern}} - V_{\text{Eq}}}{RT}} \right]$$

Equation 3.7

The Li ion insertion and deinsertion reactions were described by Equation 3.8 where x was limited to 0.5.



Equation 3.8

For the scan rates tested, the Li ion diffusion time from the electrolyte reservoir to the center of the nanochannel was about one second and was determined to be not the limiting factor.

With this model, several CVs were simulated to match that of the experimental data. As can be seen in , the simulated CVs showed key features of the corresponding experimental data such as peak separation but did not replicate it perfectly. This could be due to several assumptions used in the simulations. Variables such as the rate constant, k, the charge transfer coefficient α , and the equilibrium potential, V_{eq} , were assumed to be independent of the Li ion concentration and ionic conductivity of the electrolyte.

With the simulation able to produce the key features of the experimental data, the simulation model was determined to be accurate enough to understand the experimental results. Figure 3.10 and Figure 3.11A describes the 2D geometry that was used for the simulation studies. Several assumptions and limitations were placed. First, the TiO_2

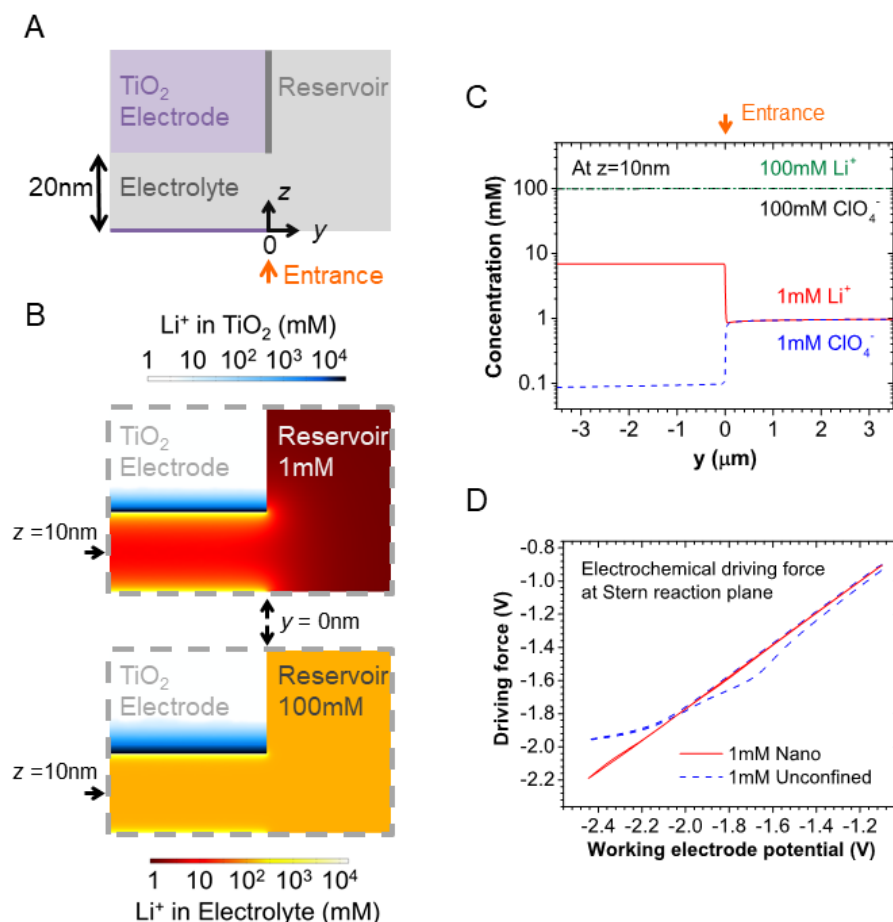


Figure 3.11 - A) diagram of the model geometry with the entrance of the nanochannel highlighted in orange. The origin of the cross-section plane, (yz plane) is at the entrance of the nanochannel. **B)** Li-ion distribution in the electrolyte (red to yellow scale) and in TiO_2 with a potential of -2.45V vs Ag/Ag^+ . The top is for 1mM KCl and the bottom is for 100mM KCl solution. **C)** Li ion concentration in the nanochannel at $z=10\text{nm}$ (middle of the channel) along the y direction of the channel (along the length). **D)** calculated electrochemical driving force at the stern layer at 1mM KCl for the nanochannel and bulk, unconfined TiO_2 .

electrode that is exposed to the reservoir side was determined to be non-active and insignificant due to the large difference in the interface area between the TiO_2 -nanochannel electrolyte interface and TiO_2 -reservoir electrolyte interface. It was also assumed that the bottom TiO_2 was not electrically connected to the top TiO_2 layer.

While the bottom layer TiO_2 was inactive as an electrode, it should have some inherent surface charge as the surface should have functional groups such as $-\text{OH}$ groups from defect sites on the surface of the crystalline TiO_2 .¹¹² In order to measure such inherent surface charge, two Pt wires that were used as counter electrodes on each side of the nanochannels were reconfigured such that the Pt wires used to apply ionic current across the nanochannel. The measured ionic current was used to determine the ionic conductivity of the confined electrolyte in the nanochannel. As a comparison, the ionic conductivity of the unconfined electrolyte was also measured using a commercial conductivity meter as described in the experimental section. Figure 1.1

The conductivity of the confined and unconfined electrolytes at various concentrations are plotted in Figure 3.12. The confined electrolyte conductivity deviates from the expected, unconfined electrolyte especially at lower concentrations where the EDL is thicker. Simulation of the nanochannel conductivity at various native surface charge of TiO_2 was used to estimate the surface charge of TiO_2 . When the surface charge was zero, the ionic conductivity of the channel agreed very well to that of the unconfined electrolyte, further supporting that the enhancement in the electrochemistry of TiO_2 in the nanochannels was from EDL. As the surface charge of the TiO_2 was decreased to a more negative charge, the simulated conductivity deviated further from the unconfined

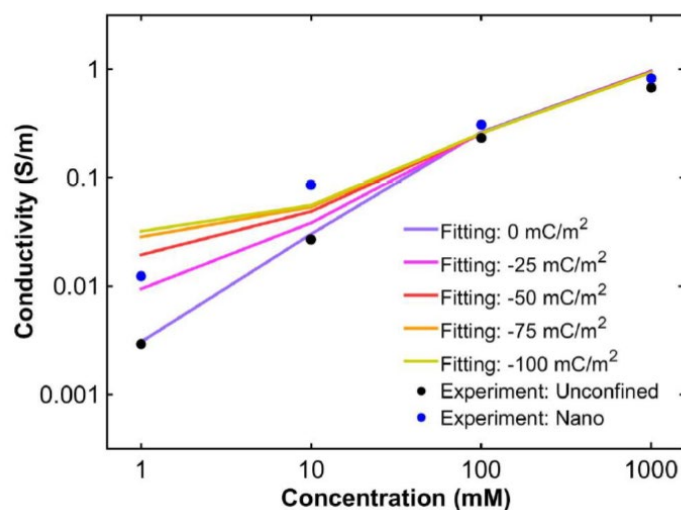


Figure 3.12 – Ionic conductivity of varying concentrations of LiClO₄ in PC for confined and unconfined electrolyte.

electrolyte. After several simulation with varying surface charge density, it was determined that the native surface charge of TiO₂ of -50mC/m² had the best fit to the experimental data of the nanochannel device.

With the native surface charge of TiO₂ determined, this was then used in the final simulation of the ion distribution in the nanochannel. Figure 3.11B shows the snapshot of the nanochannel at -2.45V vs Ag/Ag⁺ electrode at the scan rate of 18mV/s for 100mM and 1mM LiClO₄ electrolyte. The gradient from white to blue in TiO₂ electrode indicates increase in the Li ion concentration, or degree of lithiation of TiO₂ while the gradient from dark red to light yellow indicates increase in the Li ion concentration in the electrolyte. At 100mM, the Li ion concentration in the nanochannel is localized very close to the surface of the TiO₂ electrode and in the majority of the channel, Li ion concentration is at the same concentration as the reservoir at 100mM.

However, at 1mM, significant changes in the Li ion concentration in the channel was observed, compared to the electrolyte reservoir. In order to further observe the concentration differences in the nanochannel, concentration profiles at the center of the channel along the length of the channel are shown in Figure 3.11C. When the reservoir concentration was at 100mM, equal concentrations of Li^+ ions and ClO_4^- are observed from the reservoir through the nanochannels. At 1mM, the electrolyte composition within the channel was almost 10mM Li^+ ions and about 0.1mM ClO_4^- ions, due to the EDL and diffuse layer forming along the both surfaces of TiO_2 nanochannel. The result of Li ion accumulation was that not only there were much higher local concentration of Li ions near the reaction surface for insertion into the TiO_2 material but also the voltage drop at the stern layer was minimized in the nanochannel device compared to the unconfined, bulk device. This led to a much higher V_{driving} as can be seen in Figure 3.11D and **Error! Reference source not found..** With higher V_{driving} , less peak separations, higher current peak current densities, and larger capacities were measured for the nanochannel device over the bulk device.

These results suggests that electrolyte confinement between electrodes should be arranged as close as possible to provide high local ion concentrations and reduce potential drop across the stern layer to reduce peak separations, increase peak current densities, and to increases capacities for higher performance electrodes.

3.4 Conclusion

In this study, microfabrication and ALD were used to fabricate highly ordered and well controlled precise nanochannels to study the effect of confining electrolytes in 20nm

nanochannels on Li ion insertion into anatase TiO_2 . When compared to unconfined bulk device, the confined nanochannel device had 52% higher specific areal capacity at relatively high scan rate of 19mV/s. This improved energy and power capability of the confined nanochannel device were attributed to the 10 fold increase in the Li ion concentration in the nanochannel due to the overlapping of the diffuse layers. With higher Li ion concentration in the nanochannel, the voltage drop across the Stern layer was minimized and led to a higher applied driving potential at the reaction plane. This led to smaller peak separations, higher current densities, and higher specific areal capacities for the nanochannel device. These results suggests that confinement could be used to further increase electrode performance and that confinement does not lead to decrease in performance.

3.5 Towards Sub 5 nm Nanochannel Device

This work was a continuation of exploring the effect of electrolyte confinement on the nanochannel properties and is currently an on-going project.

3.5.1 Methods

Overall, the fabrication method of the nanochannel device was kept the same as the 20nm nanochannel device. However, instead of sacrificial Cr layer that was deposited by E-beam metal deposition, it was replaced with Al_2O_3 that was deposited with ALD as uniform deposition of this sacrificial layer was crucial in determining the dimension of the nanochannel.

With the new sacrificial layer, modified device preparation steps were used. For the removal of Al_2O_3 sacrificial layer, 5% phosphoric acid was used. The device was placed on heated plate at 38°C . Due to the small volume and large surface area of the device, it was assumed that the room temperature 5% phosphoric acid was fully heated by the time it reached the Al_2O_3 layer. Whereas the Cr layer removal process was visible via optical microscope with the disappearance of the metallic layer at the entrances of the nanochannel, the Al_2O_3 layer was transparent and could not be seen. Every 30 minutes of etching of the sacrificial layer, Pt wires were placed in the each side of the channel, and the ionic conductivity across the channel was measured using Keithley power supply. Once the ionic conductivity of the expected value was measured, the device was flushed with DI water for a day. Then various concentrations of KCl were used to characterize the nanochannel dimensions.

It was found that too long of Al_2O_3 etching will slowly etch away at the TiO_2 layer. This resulted in a “10 nm” device based on the ionic conductivity of the device.

For the morphology characterization of the nanochannels, JEM 2100 FEG TEM/STEM was used to take TEM images and EDS mapping.

The electrolytes were prepared in various concentrations of KCl in DI water. The DI water was allowed to equilibrate with the atmosphere at least for one day. pH of the electrolyte was measured just before the electrolyte was used. For pH adjustment, 1M NaOH or 1M HCl was used. For the degassed electrolyte, the salt was first mixed with the DI water. Then it was placed in a vacuum chamber with just before the solution

boiled. It was left under vacuum for 24 hours. The pH was the adjusted and used immediately.

3.5.2 Results and Discussion

Figure 3.13A shows the TEM cross section of the as prepared sub 5 nm nanochannel device. The Al_2O_3 layer is measured to be about 3nm, the TiO_2 layers around 50nm,

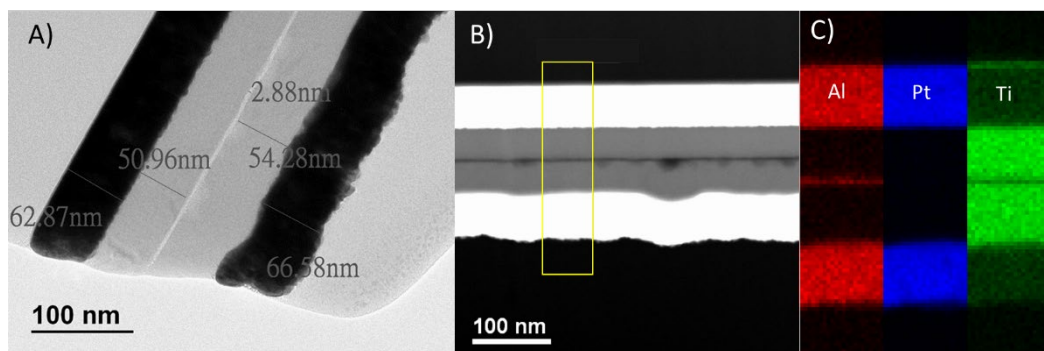


Figure 3.13 – TEM image A) and High Angle Annular Dark Field B) image of the cross section of 3nm nanochannel device. Yellow in B is the EDS mapping area. C) EDS mapping for Al, Pt, and Ti in the nanochannel.

and Pt current collectors around 60nm. The TiO_2 layer is slightly thicker than previous 20nm nanochannel device, most likely due to the change in the growth rate of TiO_2 . This change in TiO_2 thickness should have minimal impact on the electrochemical behavior of the channel. The $\text{Pt/TiO}_2/\text{Al}_2\text{O}_3/\text{TiO}_2/\text{PT}$ layers was clearly seen when high angle annular dark field image is taken. STEM, scanning transmission electron microscope, was used in order to take EDS mapping of the cross section.

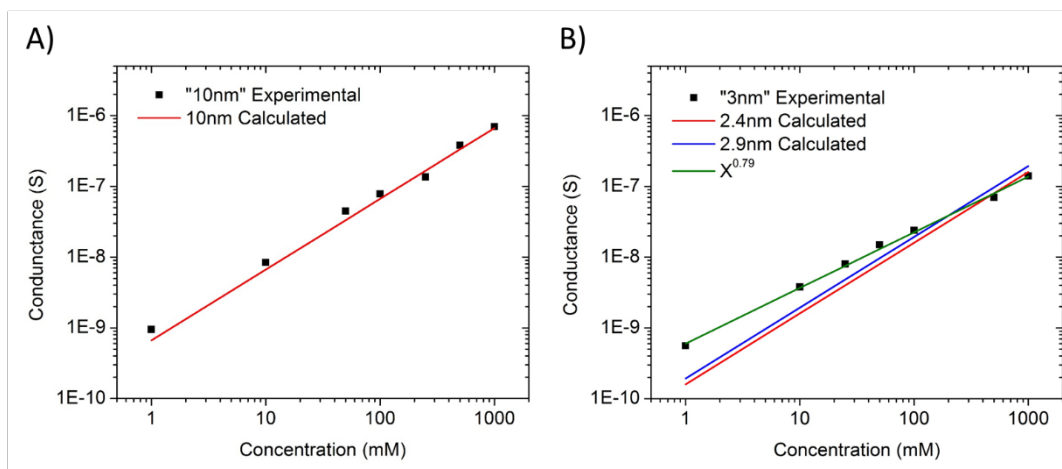


Figure 3.14 – Ionic conductance of A) 10nm channel and B) 3nm channel in various concentration of KCl in DI water. The pH of the solution was measured to be 5.8.

First, the ionic conductivity through the nanochannels were measured at various KCl concentrations in aqueous solution. As stated before, extended etching in phosphoric acid caused the TiO₂ nanochannel to have larger pore dimensions of about 10nm. The ionic conductivity for the 10nm channel is shown in Figure 3.14A. The 10nm channel showed no deviation from the bulk estimated conductance, even at a low electrolyte concentration of 1mM. To reiterate, the bulk estimated conductance assumed that there was no charge accumulation from the formation of EDL and diffuse layer. This can be explained by the inherent property of the anatase TiO₂. The pH at which the surface charge of the TiO₂, also called the point of zero charge, is estimated to be between 5.7 and 5.8.¹¹¹ When the pH of the electrolyte was measured, the pH was 5.8. The DI water was allowed to equilibrate with the atmosphere and the drop in the pH was most likely due to the CO₂ dissolution and buffering the solution to pH 5.8. With no significant native surface charge, EDL and diffuse layer cannot form which results in a 10nm

channel to behave exactly like that of the bulk system. However, the 3nm device deviates from this behavior. Figure 3.14B shows the ionic conductance of the 3nm device in various concentrations of KCl aqueous solutions. Surprisingly, the 3nm device did not fit the calculated bulk conductance. This could be due to small difference between the pH of the solution and the pH of the point zero charge of the TiO_2 . For a larger channel of 10nm, such small difference may not have been enough to cause significant change in the channel ionic conductance, but it was enough for the smaller 3nm channel.

In the 3nm channel, another interesting phenomenon was observed. Figure 3.15 shows the results from linear voltage sweep across the 10nm channel and 3nm channel in 1M KCl. Each of the color plotted represent a “run” and each run represents four voltage sweep cycles. For the 10nm device, a single conductance state was observed for 20 runs, with each runs having four separate cycles. However, for the 3nm channel, three distinct conductance states were observed. This may have to do with the small surface charge effect of the TiO_2 at pH 5.8 on these two different size nanochannels. If the point of zero charge of TiO_2 was 5.7 and the pH was 5.8, the small difference could induce a very small surface charge. In the 10nm such small surface charge has an minimal effect on the channel conductance whereas for the smaller 3nm channel, it was enough to cause the deviation in the channel conductance. In order to induce larger EDL and diffuse layer effects, the salt concentration was changed to 1mM. The resulting I-V profiles can be seen in Figure 3.16A and C for the 10nm and 3nm at pH 5.8 respectively. For the 10nm, even at 1mM electrolyte concentration, only single

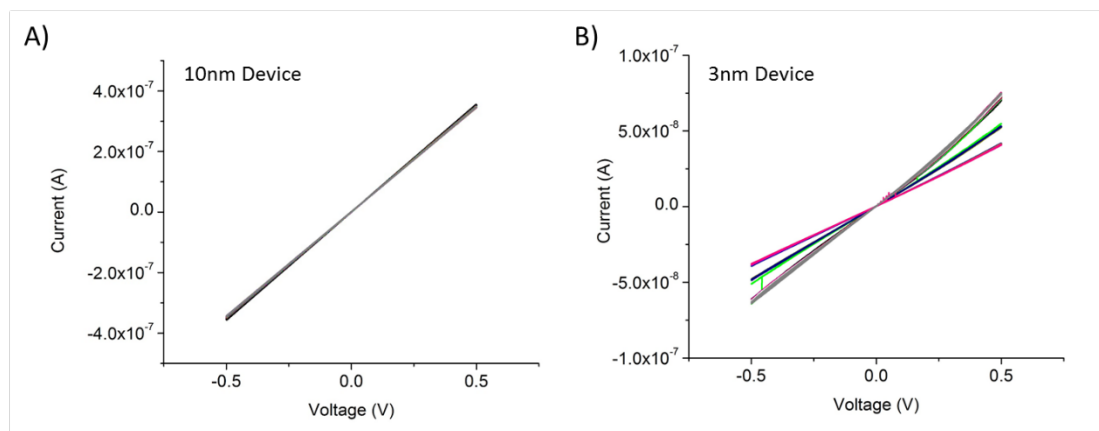


Figure 3.15 – I-V profile of A) 10nm channel and B) 3nm channel device in 1M KCl solution at pH of 5.8. Each graph contains 20 separate runs, with each run consisting of four voltage sweep cycles and is represented by different colors.

conductance state was seen. For the 3nm channel, split conductance was still seen. In order to induce larger surface charge effect, the pH was adjusted to more basic conditions, pH 8 for the 10nm device and pH 10 for the 3nm device. The difference in the pH between the 3nm and the 10nm device was due experimental design error. The I-V profiles at the higher pH can be seen in Figure 3.16B and D for 10nm and 3nm channel respectively. For the 10nm channel, several conductance state was observed at the higher pH levels. Similar results were seen for the 3nm channel. These results indicate that the appearance of different conductance state is dependent on the surface charge of the TiO_2 and distance between the two TiO_2 surfaces. These change in the conductance states resemble that of resist-pulse measurements. In resistive pulse measurements, the conductance across the channel is changed as particles travel or block the entrance of the channel prevent the flow of ionic currents through the channel and results in a drop of the channel conductance.^{119, 134-137} It is highly unlikely contaminants such as dust particles to reach the nanochannel openings. There are

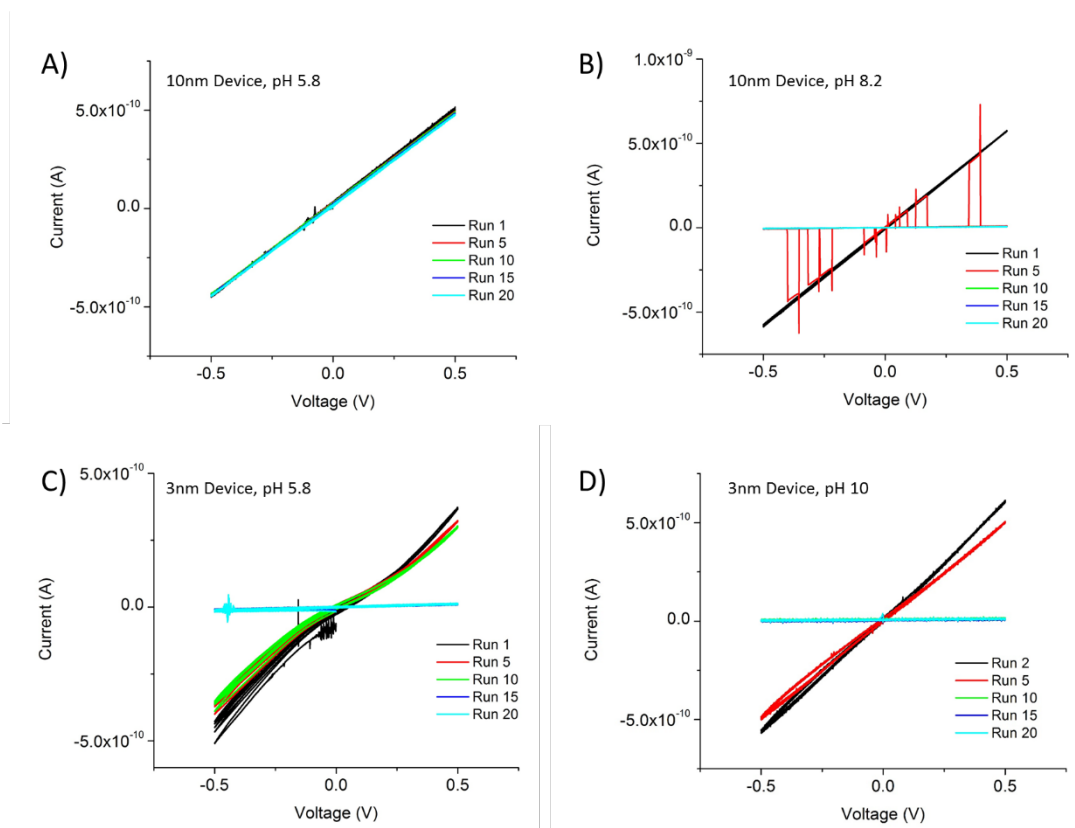


Figure 3.16 - I-V profile of (A, B) 10nm channel and (C, D) 3nm channel device in 1mM KCl solution. A) and C) were measured in pH 5.8 electrolyte while B) was in pH 8.2 and D) was in pH 10.

several other possible explanations. One explanation is nanoprecipitation of the salt. Powell et. al. used conical nanopore ranging from 2 to 6nm with 0.1M KCl with 2mM pH 8 phosphate buffer solution. They added a small amount of Ca^{2+} ions to induce ionic current instabilities leading to high and low conductance states. The phosphate buffer would react with the Ca^{2+} ions to form CaHPO_4 , relatively insoluble salt compared to that of K_2HPO_4 in the phosphate buffer. While in the bulk solution, the calculated concentration of CaHPO_4 is well under the solubility constant, within the nanopore the ion concentration within the nanopores are significantly different than the bulk leading to partial precipitation of the CaHPO_4 and blocking the nanochannel and low ionic

conductance of the pore.¹³⁸ Smeets et. al. used 2.6 to 12.7nm single nanopores on SiN membrane with 1M KCl with 10mM Tris-HCL buffer at pH of 8. They also saw change in the ionic conductance of their nanopore system and concluded that a nano-sized gas bubble traveling through their nanochannel caused the change in the ionic conductance and agrees with their simulated data.¹³⁹

In this system, there were no additional additives such as buffers that may precipitate and block the nanochannels. It may have been nanobubbles that formed and blocked the nanochannels. A possible explanation was the formation of CO₂ nanobubbles in the nanochannels. The DI water, when exposed to the atmosphere, dissolved the atmospheric gas. When CO₂ is dissolved, it reacts with water to form carbonic acid. This acid then further reacts with water to form carbonate ions. Similar to what Powell et. al. observed, in the bulk, the carbonate ions are in equilibrium with water and stay solubilized. However, due to surface charge in the nanopores, the local ion concentrations are significantly different than the bulk. From experiments and analysis of the results from the 20nm channel, it was expected for the nanochannel to accumulate positive counter ions, again assuming that the surface charge of the TiO₂ was negative. For the 10nm channel at pH of 8, the surface charge should be mostly negative. This results in accumulations of protons, from water, and potassium ions, from the salt, within the nanochannel. When the dissolved CO₂, in forms of HCO₃⁻ reaches the entrance of the nanochannel, with the higher local concentration of H⁺ ions, HCO₃⁻ forms H₂CO₃ and degrades into water and CO₂ gas. The bubbles of CO₂ gas that formed could block portions of the nanochannel and cause the observed low ionic

conductance. The CO₂ bubbles could also be re-dissolved into the solution as it moves farther away from the nanochannel. To explore such possibility, the electrolyte was degassed. In order to avoid bubbling additional gases such as Ar or N₂ and risk the possibility of these gas forming bubbles within the nanochannel, slight vacuum was applied, just before the electrolyte started to boil at room temperature to remove the dissolved CO₂. When the pH of the degassed solution was measured, the pH was between 6.6 and 6.8, close to the ideal neutral pH 7 of water. The pH was quickly adjusted to 8.2 and the degassed solution was used to test the conductance of the 10nm channel. The conductance of 10nm channel with 1mM degassed KCl at pH of 8.2 can be seen in Figure 3.17. With the degassed electrolyte, the split conductance was no longer observed supporting the explanation above. Unfortunately, microfluidic channel clogged and the 3nm channel was no longer usable to test the degassed electrolyte.

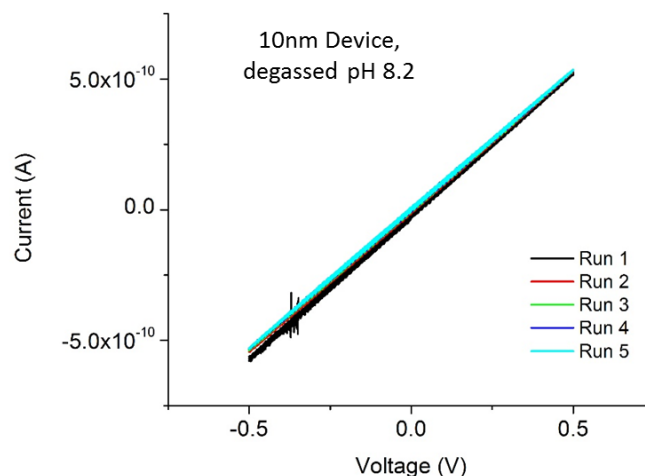


Figure 3.17 – I-V profile of the 10nm channel with 1mM KCl solution that was degassed under vacuum.

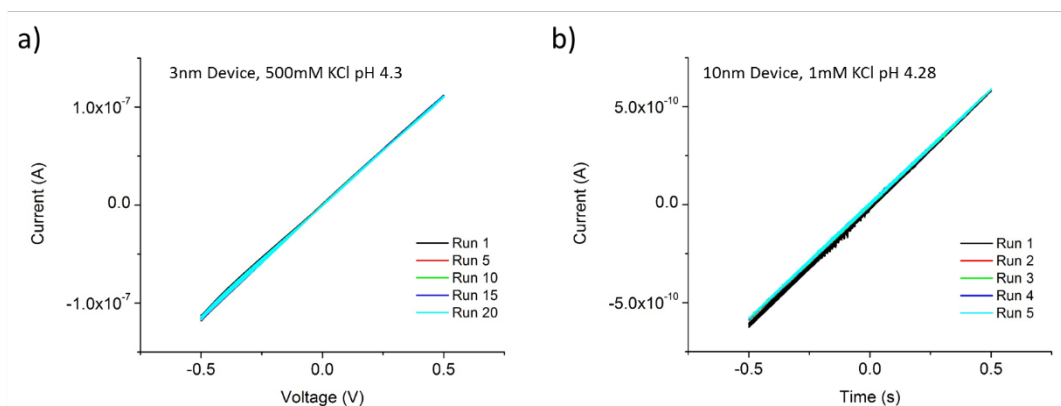


Figure 3.18 – I-V profiles of the 3nm of 10nm channel at lower pH of 4. The 3nm device was ran at 500mM and the 10nm device was ran at 1mM KCl. The pH was adjusted by adding HCl.

To further explore the effect of pH on the split conductance states, lower pH was also used. If the negative surface charge of TiO_2 was causing high accumulation of protons and cations, a positively charged surface of TiO_2 should not cause split conductance states. The I-V profiles of the 3nm and 10nm channel at lower pH of 4 without degassing is shown in Figure 3.18A and B respectively. The 10nm channel shows no split conductance at the lower pH with 1mM KCl. The 3nm device also shows no split conductance at the lower pH at 500mM KCl. Due to the clogging of his device at the microfluidic channels, 1mM KCl could not be run. However, the 3nm channel still had split conductance at 1M and 1mM KCl at pH 5.8 and the results from the 500mM concentration of KCl still supports the above hypothesis that despite using as prepared, as made electrolyte without degassing, the lower pH prevented the different conductance states from appearing.

3.5.3 Conclusion

In this study, sub 5nm nanochannels were successfully fabricated with Al_2O_3 sacrificial layer. It was found that phosphoric acid can etch TiO_2 and requires careful monitoring of the ion conductance of the nanochannel to prevent unwanted etching of TiO_2 . Ion conductance in 3nm and 10nm channels were performed with aqueous KCl solutions. The ion conductance of the 10nm channel followed that of the bulk ionic conductance while the 3nm channel showed deviations and higher ionic conductance than the expected bulk conductance. This was attributed to the pH of the electrolyte close to the point zero charge of the anatase TiO_2 . For the 10nm channel the relatively small surface charge did not have an impact on the channel conductance but for the 3nm channel, the same relatively small surface charge was enough to impact the channel conductance. An interesting phenomenon was observed for the 3nm channel in 1M KCl solution where several distinct conductance states appeared in the I-V profile while 10nm showed just a single conductance state. The change in electrolyte concentration had no effect on the observation of several conductance states for the 3nm channel but only one conductance state for the 10nm channel. It was only when the pH was changed to a higher level both 10nm channel and 3nm channel showed several conductance states. It was hypothesized that the split conductance was due to the formation of CO_2 gas bubbles from the decomposition of carbonates near the nanochannels due to the ion accumulation effect of EDL and diffuse layer. With the electrolyte degassed, even at pH of 8.2, the 10nm channel showed only one conductance state. Unfortunately the 3nm channel device was no longer usable and requires further testing to verify this

hypothesis. For the next 3nm device, similar channel characterization should be performed at a pH of 5.8. Then conductance of the channel should be measured at high and low pH. At the high pH, degassed electrolyte should be used to directly compare the findings to the 10nm device. A 20nm device should also be tested in the same manner to have more complete understanding of the pH effect on the conductance states of nanopore systems. While this study took a different direction and studied aqueous solutions, the findings from this study can be used for aqueous energy storage systems and to minimize interference in random gas bubbles by controlling the pH of the electrolyte.

4 Towards High Performance Solid State 3D Battery on Si Wafer with Porous Aluminum Oxide Template

This work is an ongoing collaboration between Dr. Sang Bok Lee's and Dr. Gary Rubloff's group. This work was first proposed by Dr. Keith Gregorczyk from Dr. Rubloff's group. Jack (John) Hayden initially started exploring the metal deposition rates and morphologies as well as to develop the masking processes. Miles Mowbray updated the masking process and masked the electropolished samples. My contributions are finishing and updating the metal deposition processes, develop a new electroplishing procedure, develop the anodization parameters and procedures, and electrochemical characterization of the half cells as well as prelithiation of the cathode. Keith Gregorczyk developed and optimized all the ALD processes used for the 3D solid state batteries used in this work.

4.1 Introduction

The lithium ion battery has changed the consumer electronics by providing high power and high energy energy storage solutions. Most of the commercially available Li-ion batteries are manufactured with composite electrodes with liquid electrolyte. An inherent property of composite electrodes is that the particle size, tortuosity, and electronic connectivity are inhomogeneous. This leads inhomogeneous charging and discharging of the battery leading to faster degradation and non-uniform material usage.^{17, 140, 141} The inherent property of liquid electrolyte is flammability as it uses organic solvent to dissolve Li ion salts. Overcharging or overdischarging of Li-ion batteries lead to severe side reactions that produces highly unsafe byproducts,

specifically Li dendrites on the graphite anode which tends to pierce through the separator and short with the cathode causing thermal runaway.^{142, 143} One proposed way to alleviate the safety aspect of current Li-ion batteries is to utilize solid state electrolytes. Solid state electrolytes remove the flammable solvent from the battery. However, due to the difference in ion conduction mechanisms, solid electrolytes have relatively low ionic conductivity compared to liquid electrolytes.¹⁴⁴

Nanostructuring of bulk electrode materials in liquid electrolytes has significantly improved the electrochemical properties of traditional batteries such as higher energy and power density. This result was due to the shorter ion diffusion distance in the solid electrode. A similar strategy can be applied to solid electrolytes. While the bulk property of the solid state electrolyte has lower ionic conductivity than conventional liquid electrolyte, a thin layer of solid electrolyte can have high ionic conductance. Thus for high power solid state batteries, the electrode and electrolyte have to be thin.¹⁴⁴⁻¹⁴⁶ However, this results in low energy density as only thin layer of battery layers can be made due to the lower material loading per area. Simple increase in electrode thickness will result in poor power density as the ion diffusional distance was increased.¹⁴⁷ In order to achieve both high energy and high power, the thin battery layers can be deposited onto 3D substrates.^{11, 147, 148}

While there are several different types of solid electrolytes available such as garnets, NASICON, and sulfide glass, they are limited in their synthesis method.¹⁴⁹⁻¹⁵¹ Most of these electrolytes are made from powders and are sintered, resulting in thick electrolytes and some with interface problems resulting in high cell resistance.¹⁴⁴

LiPON, on the other hand, is one of the solid electrolyte in which it can be deposited on to the surface of the electrode with chemical vapor deposition, more specifically with atomic layer deposition.¹⁴⁹ Atomic layer deposition technique is self-limiting, conformal deposition technique that is essential for depositing materials into high-aspect ratio nanostructures.

In a previous study performed by Pearse et. al., three micron diameter pores with depth of up to 30 micron were prepared by reactive ion etching of SiO₂ on Si wafer. All of the battery materials were deposited via ALD for conformal coating of this large 3D substrate to fabricate 3D micron-sized solid state battery. With the 70nm thick LiV₂O₅ as the limiting capacity of the full cell, when compared to simple planar structure, the 3D battery had 9.3 times higher capacity at 100 μ A/cm² and about 1000 times higher capacity at 5mA/cm².¹⁴⁷

In order to further improve the energy density, and to understand key features in nanostructured SSB architectures, a different substrate was needed. In this study, an anodized aluminum oxide substrate was fabricated on top of a three inch silicon wafer to demonstrate the ability to fabricate high performance thin film 3D solid state batteries with utilization of standard semiconductor processes such as sputtering, etching, and chemical vapor depositions.

Anodized aluminum oxide (AAO) has been widely used for the fabrication of nanostructured electrodes such as nanowires and nanotubes.^{31, 40, 51, 107, 152-155} Due to the ease of structural customization, the two main geometric parameters of AAO, pore

diameter and interpore distance, can be tailored for specific applications. Liu et. al. were able to demonstrate the conformality of ALD for high-aspect ratio nanobatteries.¹⁰⁷ In their nanobattery, the V_2O_5 cathode and SnO_2 anode, as well as integrated current collectors of Pt, were all deposited into 150nm pore diameter AAO. The cathode and the anode were deposited in opposite sides of the AAO such that they were electronically isolated but ionically connected through the liquid electrolyte filling the pores. The cyclability of this nanobattery was limited by the SnO_2 , a conversion and alloying-type anode. Conversion and alloying electrode materials are thought to degrade in their energy storage properties due to the pulverization of the material through continuous volume expansions and results in loss of electrical contact.^{156, 157} In the literature such degradation mechanism could be minimized through the application of protection layers where the protection layer would physically bind the material together such that the materials are in good electronic contact with each other and nanostructuring to better accommodate such volume changes.^{156, 158-161}

In this study, a high aspect ratio porous scaffold with pore densities up to 2.6×10^{11} pores/cm² were fabricated by the anodization of aluminum. The pore diameters were 400nm with the final pore depth of 50 μ m. The full 3D solid state battery is expected to obtain energy density of 1390 μ Wh/cm² with the pore entirely filled with battery materials in order to maximize the energy density. This, however, may prevent full material utilization of the anode as there would be no room for the volume expansion of the Sn based anode with conversion and alloying mechanism. It may also lead to much higher cell life due to the confinement of the battery materials within the single

pore, leading to little to no pulverization of the anode. The limits of ALD will also be explored as more of the materials that are deposited into the pore, the higher the aspect ratio of the structure becomes, from initial aspect ratio of 125 with bare AAO, and aspect ratio of 313 after the depositions of the cathode current collector, the cathode, and the electrolyte. The preliminary results showed that the 3D substrate resulted in 113 times larger capacity at $10\mu\text{A}/\text{cm}^2$ and 1333 times higher capacity at $0.5\text{mA}/\text{cm}^2$ when compared to the planar substrate.

4.2 Methods

4.2.1 Overall 3D solid state battery fabrication procedure.

The 3D solid state battery fabrication was separated into two major categories, substrate fabrication and battery material deposition. For the 3D substrate fabrication, a two-step anodization method was used to form highly ordered AAO on top of the Si wafer. The first AAO was a sacrificial layer where it was used to leave a patterned surface for the highly ordered second AAO layer. Multiple battery layers were deposited via ALD technique. The active area over the 3D substrate will be then capped by sputtered Al. The excess battery materials around the 3D substrate will be etched away. The 3D solid state battery will be connected to the potentiostat via the Al cap for the anode connection and copper layer beneath the AAO for the cathode connection.

4.2.2 Metal Deposition on Si Wafer

Silicon wafers were purchased from University Wafers in three inch diameter, P type, with $\langle 100 \rangle$ orientation. The Si wafer was oxidized to form $\sim 500\text{nm}$ of SiO_2 as an

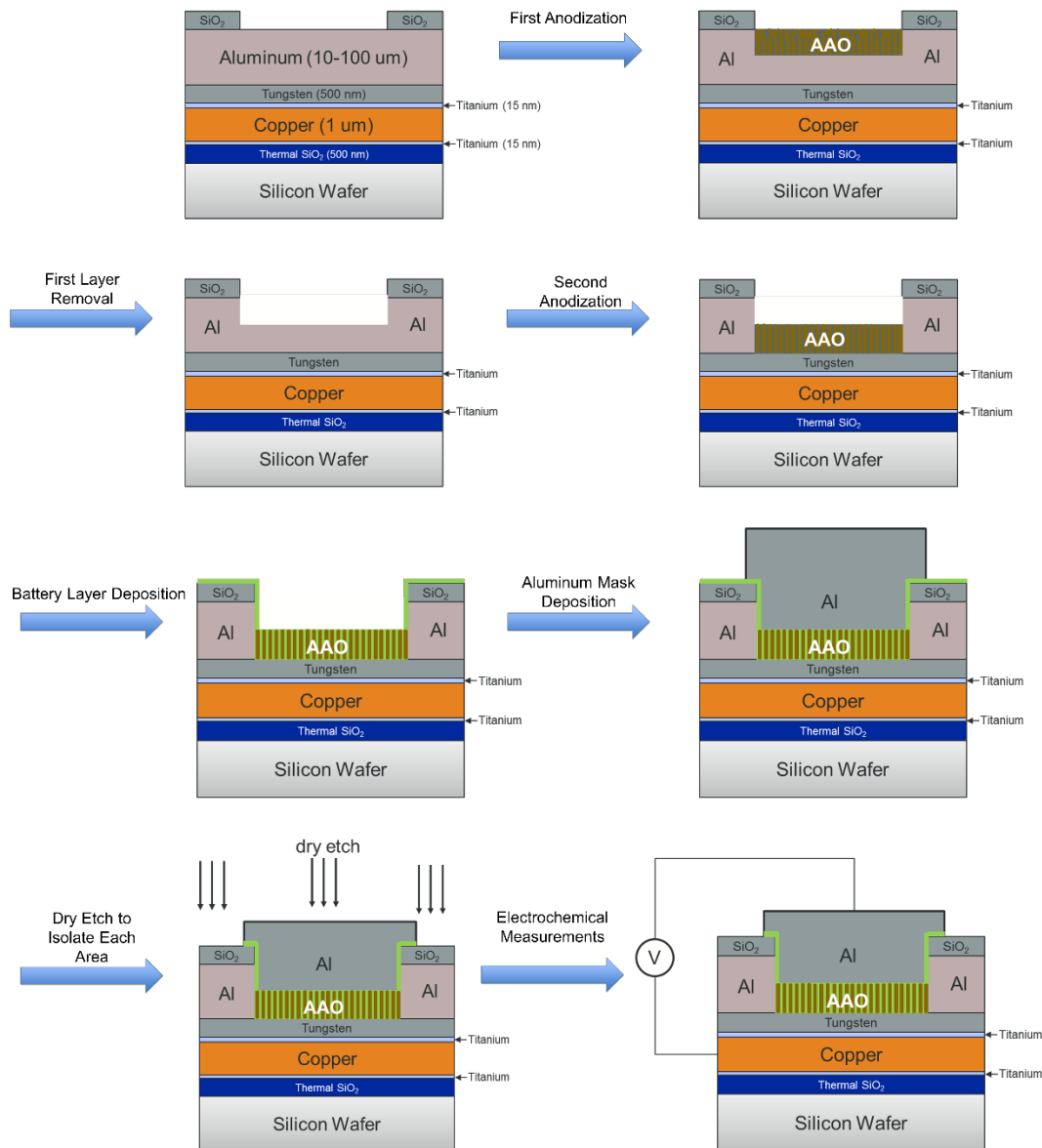


Figure 4.1 – Schematic of the SSB on wafer fabrication procedures.

insulating layer. Metal layers were deposited with AJA ATC Orion 8 Sputtering system. All metals were sputtered at 300W, unless it was specified, with various sputter times. Ti, Cu, and W were in the confocal position of the tool with the stage distance of 10 units while Al was in the center position of the tool with the stage distance of 70 units, unless it was specified. For all metal targets, the initial plasma was ignited at

20sccm of Ar and 20mTorr at 50W of power with the shutter closed. The pressure was changed to 3mTorr, and power was ramped to 300W over one minute. At 300W, the shutter was opened to start the deposition. Cu was unique in that, plasma was ignited while the shutter was opened due to Ar flow issue into that particular confocal gun position. After the plasma was ignited, the shutter was closed and same changes in pressure and power were followed as other targets. Ti was sputtered for 120 seconds, Cu was sputtered for 2637 seconds, and W was sputtered for 3898 seconds. Al sputter time was varied to control the final AAO thickness. First Ar plasma was used to clean the wafer surface. Ti was sputtered first, followed by Cu, Ti, W, and Al.

Some samples were deposited without any substrate heating. These were annealed under Ar atmosphere at 400°C for 4 hour and slowly cooled inside the annealing furnace to about 100°C before they were removed. Other samples were sputtered with substrate heating at 400°C and were not annealed.

4.2.3 Electropolish

The wafers with metal layers were electropolished to minimize surface roughness. 200 proof ethanol was purchased from PharmCo and perchloric acid was purchased from Fisher Scientific and Alfa Aesar. The electropolishing solution contained 180mL of perchloric acid in 800mL of ethanol. First ethanol was cooled in ice/water bath as the mixing was exothermic. Perchloric acid was added to the chilled ethanol under vigorous stirring. Once fully mixed, the solution was placed back in the ice bath until the solution temperature was between 1-2°C.

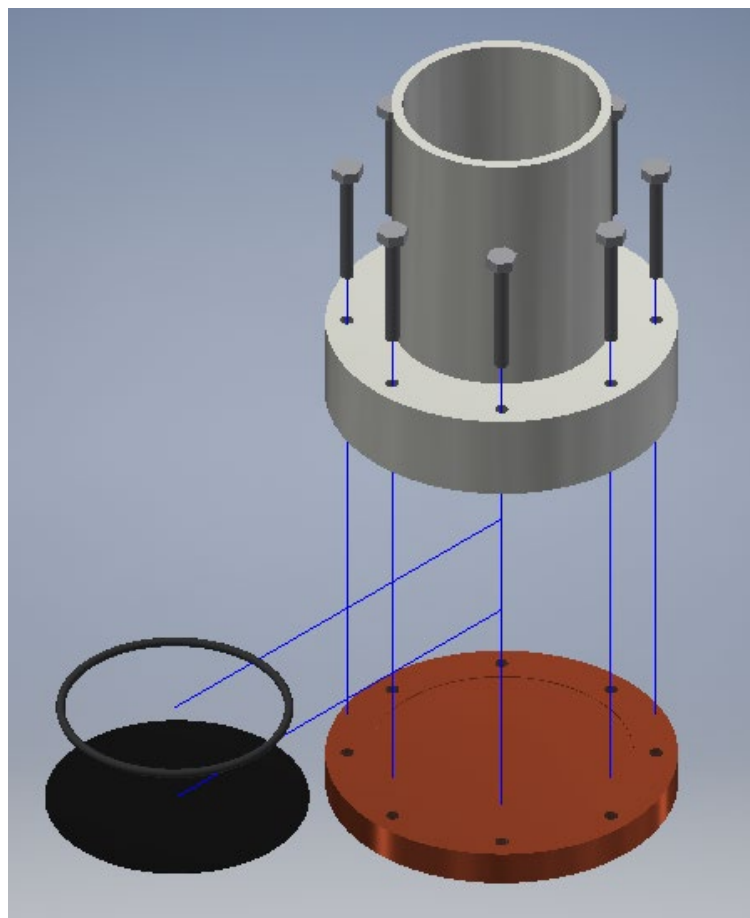


Figure 4.2 - Illustration of the anodization cell specifically designed to hold a three inch Si wafer

The wafer was placed in the anodization cell which is illustrated in Figure 4.2. The peltier stage was set to -2°C in order to keep the electrolyte temperature as low as possible. The peltier stage could not chill the solution on its own and temperature of the electrolyte slowly rose. This was kept consistent between samples to ensure similar electropolishing rates. 15V was applied with the wafer as the anode and stainless steel mesh as the cathode for 40 minutes. Lambda Genesys 600-8.5 was utilized as the power supply.

4.2.4 SiO₂ mask

The electropolished wafers were masked with SiO₂ in order to define the electroactive area. A negative photolithography technique was used. PECVD was used to deposit 500nm of SiO₂ onto the electropolished wafer. HDMS was applied and was allowed to soak onto the wafer for 30 seconds. The excess HDMS was spun off at 4K rpm for 40 seconds. NR9-1500P photoresist was then applied and spun off at 4K rpm for 40 seconds. It was soft-baked at 150°C for 1 minute. It was allowed to cool to room temperature before the wafer was placed under the shadow mask and exposed to 365nm wavelength light for 20 seconds. The wafer was then placed in photoresist developer solution composed of RD6 and water in 3-to-1 ratio for 40 seconds. Undeveloped photoresist was removed by water and was blow dried under nitrogen. It was placed at 120°C for 1 minute to hard bake the developed photoresist. The photo masked wafer was then allowed to cool to room temperature.

An Oxford Plasmalab System 100 was used to remove exposed SiO₂ on the wafer. Five rounds of 30 second etching was used for a total of 2.5 minutes to ensure that the photoresist was not burnt. The photomask then was removed in PG remover solution. The patterned SiO₂ wafer was then blow dried under nitrogen gas and stored until the anodization steps. The photoresist pattern can be seen in Figure 4.3. There were mainly three different sized areas: 0.250cm², 0.141cm², and 0.071cm².

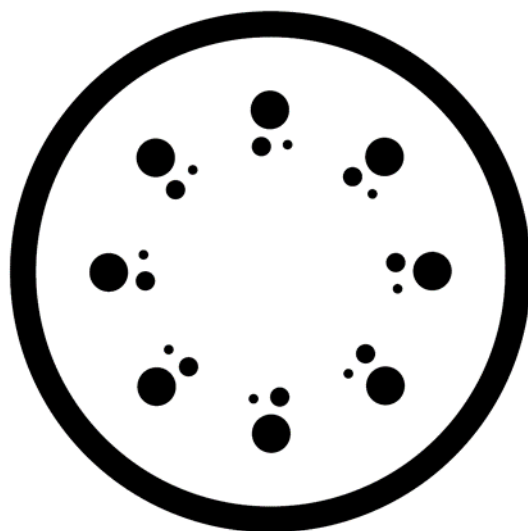


Figure 4.3 – Mask used to define electrochemically active area on the Si wafer. The dark areas are exposed Al. the outer ring is to make sure there was a good place to make electrical contact for anodization/electrochemical testing

4.2.5 Anodization

The first anodization was performed in 0.1M phosphoric acid in 1:4 v/v of ethanol to water solution, unless other specified, at -1.5°C for 6 hours at 195V. The first layer was removed with phosphoric acid: chromic acid etchant for 2 hours at 60°C. Second anodization conditions were the same as the first anodization. The second anodization was performed until the current dropped to the minimum current and was ran for extra one to two hours.

The pore widening step was separated into two steps. This was to maximize pore diameter of the AAO without weakening the AAO/Tungsten interface too much which can lead to delaminating of the AAO from the W substrate. The AAO was first pore widened in 5% phosphoric acid in water at 38°C for 40 minutes. WO₃ was selectively

removed in 0.1M pH 7 phosphate buffer at 38°C for 20 minutes. The final pore widening process was repeated for additional 30 minutes for a total of 70 minutes of pore widening.

4.2.6 ALD procedures

A Fiji 200 reactor was used for all of the battery material deposition. For TiN, tetrakis (dimethylamido) titanium (TDMATi) and ammonia were used as the metal precursor and oxidant respectively. For V_2O_5 , vanadium tri-isopropoxide and ozone were used as the metal precursor and oxidant respectively.

All depositions were performed under the exposure mode where the resident time of each gas vapor was significantly increased to maximize the conformality in high aspect ratio nanostructures such as the AAO scaffold unless specified.

4.2.7 Electrochemical Lithiation of V_2O_5

As deposited V_2O_5 was lithiated prior to the deposition of the LiPON and SnO_2 . The electrolyte used was 1M $LiClO_4$ in PC. Between 2 and 5mA was used to first lithiate the V_2O_5 cathode to 2.6V vs Li and was held until the current reached a steady state. The electrode was then removed and washed several times with PC. It was then vacuum dried for least 8 hours before being placed back into the ALD reactor.

4.3 Results and Discussion

4.3.1 Electropolishing

Electropolishing sputtered Al was significantly different than the conventional Al foil substrate normally used for the anodization. The conventional electropolishing is based on the process of forming aluminum hydroxide by the application of an oxidative potential on the aluminum. The aluminum oxide that is formed on the surface is then removed by the acidic electrolyte. The current density at the surface is highly dependent on the morphology of the surface. Highly rough surface will have higher current density, and therefore a higher oxidation rate of Al and removal leading to faster polishing rate, whereas a smoother surface will have lower current and lower Al removal rate. This difference in electropolishing rate leads to uniform, smooth surface finish on the Al. This process is conventionally performed under vigorous stirring of the electrolyte to aid in the removal of the aluminum oxide. However, for sputtered Al,

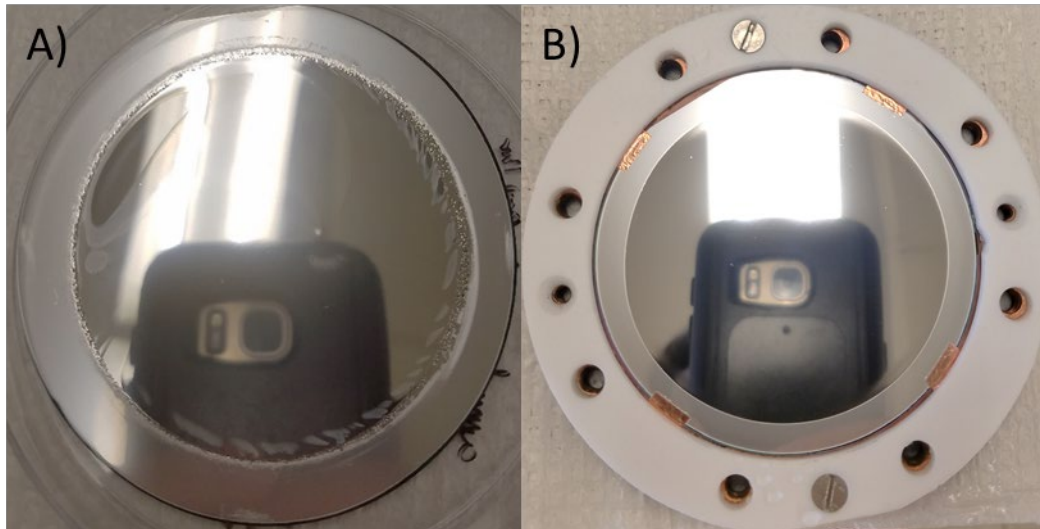


Figure 4.4 - Images of Electropolishing with A) stirring and B) without stirring.

this caused a highly non-uniform surface. As seen in Figure 4.4A, with stirring, a non-uniform electropolishing was seen. It also led to dull finishing near the edge of the electropolished area. The tungsten layer, darker than Al, was also seen on the top left area of the wafer. This uneven electropolished surface led to non-uniform AAO thickness throughout the wafer as some parts had thicker Al than other areas. Clear swirls can be also seen on the electropolished wafer, most likely due to the non-uniform flow of the electrolyte near the surface of the wafer. This would cause concentration gradient to form differently across the surface of the wafer. Areas of the wafer with high level of convection from stirring would have almost no concentration gradient and have fast electropolishing rate whereas areas with low level of convection would have thick diffusion layer and have low electropolishing rate.

In order to achieve more uniform electropolished, the stirring was removed. As can be seen in Figure 4.4B, the electropolished area is highly uniform and highly reflective. With the lack of stirring in the electrolyte in the quiescent electropolishing, the buildup of the diffusion layer was proportional to the current density which was then dependent on the surface morphology. This meant that rougher the surface was, the faster it would build up the diffusion layer and quickly drop the reaction current but at a more flat surface, the diffusion layer would build up slower, leading to slower drop in the reaction current. This self-limiting electropolishing led to highly uniform Al surface for the next anodization step.

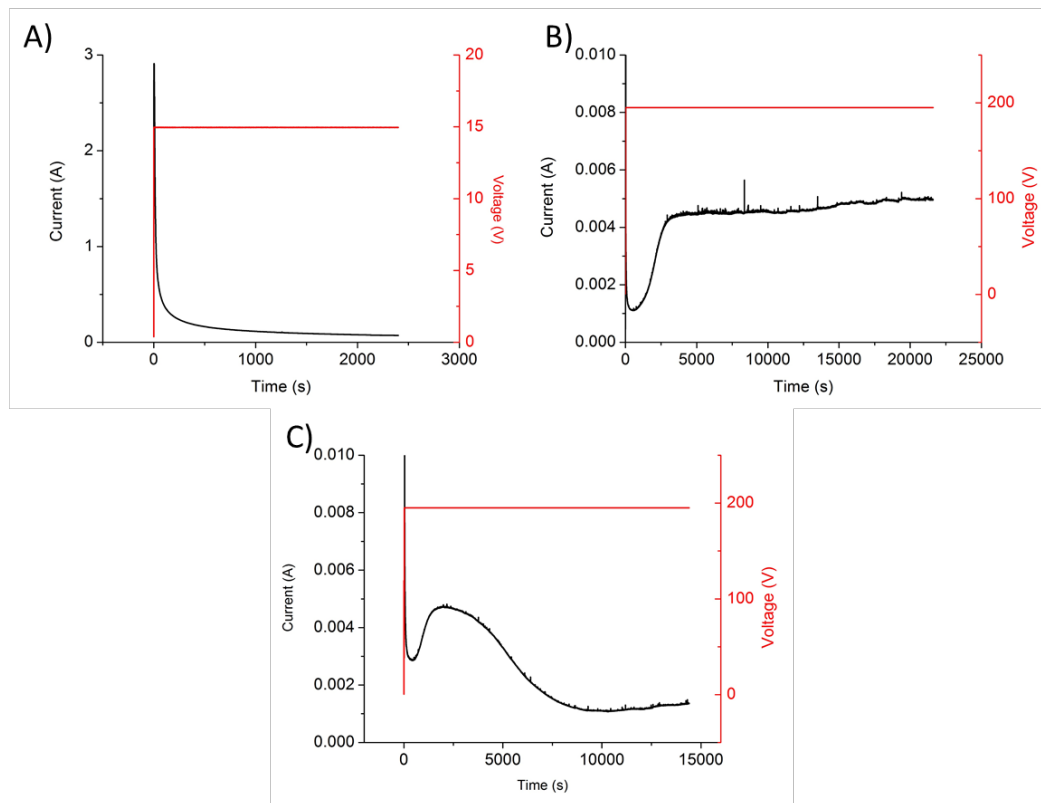


Figure 4.5 - Current-time and Voltage-time profiles for A) electropolishing, B) first anodization, and C) second anodization.

The current-time profile of the electropolishing of Al can be seen in Figure 4.5A. The current decayed exponentially as the surface roughness is decreased and the thickness of the diffusion layer increased.

SEM and AFM measurements were used to not only qualitatively but also quantitatively compare the difference on the surface morphology of as deposited Al and electro polished Al. Figure 4.6 shows the SEM images and AFM measurement of the as deposited Al and electropolished Al. In the SEM, as deposited Al shows large Al particles protruding randomly at the surface. After electropolishing, such protrusion

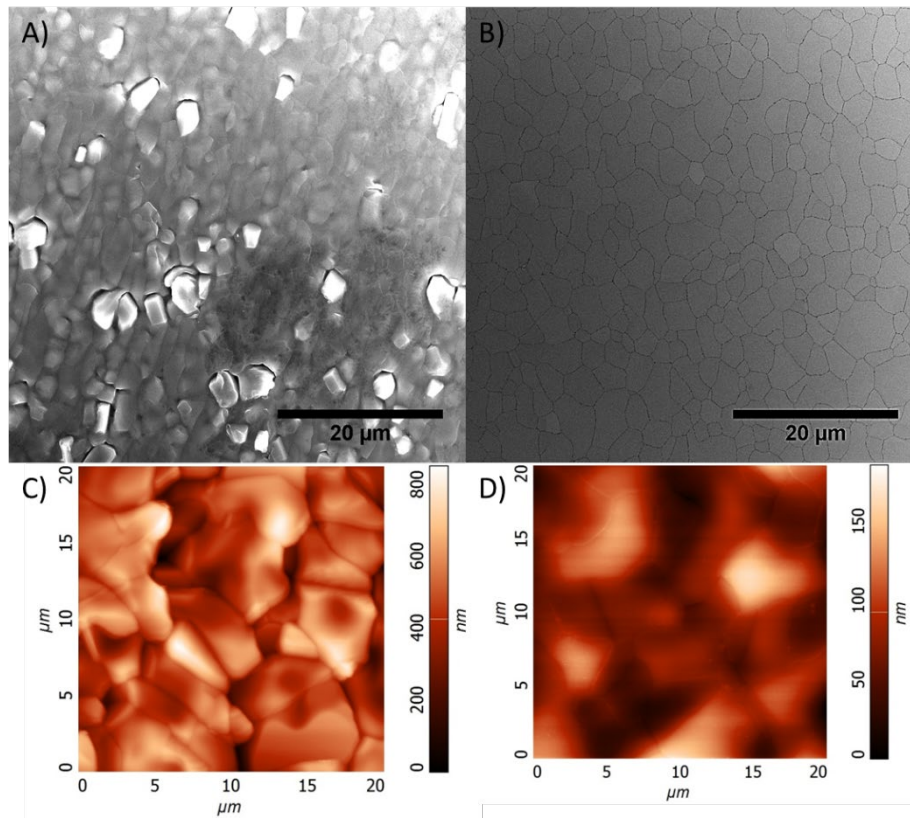


Figure 4.6 - SEM image (A) and AFM measurement (C) of as deposited Al and SEM image (B) and AFM measurement (D) of electropolished Al

is minimized and clear grain boundaries can be seen. With AFM, the surface roughness was measured. The root-mean-squared roughness of the as-deposited Al was 120nm whereas the electropolished Al was 29nm.

4.3.2 Anodization

After the wafer was electropolished, the electrochemically active areas were defined by SiO₂ masking layer fabricated through lithography. Two-step anodization was

performed to achieve highly ordered AAO structures.¹⁶² The two step 195V process in 0.3M phosphoric acid was first reported by Matsuda et al. in 1998.¹⁶³ The initial study required up to 16 hours of first anodization and low temperatures of 0°C to achieve highly ordered AAO with 450nm interpore distance.

In the current setup, achieving such low temperature and keeping it consistent was difficult and led to local burning of the AAO due to the lack of efficient cooling of the Al despite having peltier stage directly underneath and separate electrolyte cooling. A study performed by Li et. al. added ethanol and lowered the phosphoric acid concentration to lower the current density, therefore also lowering the heat generated during the anodization process.¹⁶⁴ They also proposed that the EtOH would evaporate near the surface of the Al, due to the lower boiling point when compared to water and lower the temperatures at the surface of Al. By adding ethanol, a successful first anodization current-time profile was achieved for the sputtered Al and can be seen in Figure 4.5B. The current was initially limited to 9.5mA due to the instrumental limits. The initial high current was from the oxidation of the Al surface with the formation of barrier-type layer. As the layer thickened, the current drops as the electric field drops until initial pores formed. As the porosity of the film increased, the current also increased until a steady-state current was achieved. This steady state current allowed the pore dimensions to equilibrate and the overall pores near the Al/AAO interface to become highly ordered. Due to the initial disordered porous regions, this layer was removed by acid, leaving highly ordered patterns on the Al surface. A second

anodization was performed and the current-time profile can be seen in Figure 4.5C. The details on the second anodization profile is discussed later.

Figure 4.7A shows the SEM images of the top of the AAO after the second anodization. The regions of hexagonally ordered AAO was seen. In order to quantify the ordered nature of the AAO film, Fast Fourier Transform (FFT) was performed on the SEM images and the power density function spectrum was taken from the FFT image as can be seen in Figure 4.7B and C respectively. The ordered nature of the AAO was quantified by the ratio of the peak intensity to the FWHM of the first peak in the power density spectrum.⁶⁹

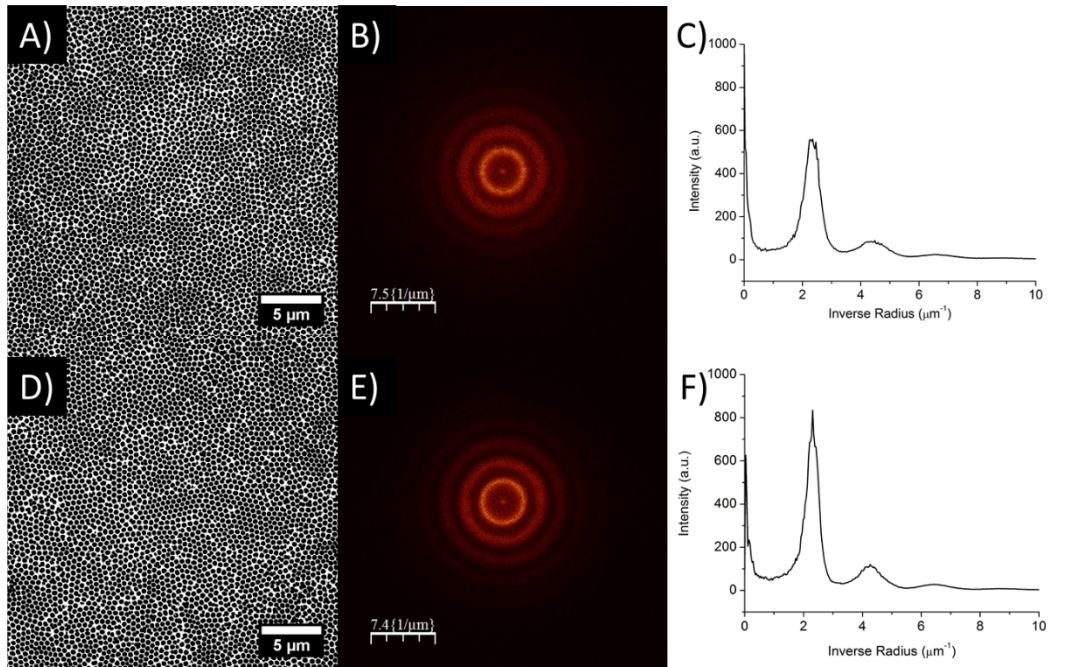


Figure 4.7 – SEM image of the top of the AAO with average current density of 2.7mA (B) and 4.4mA (B). B and E are FFT images of SEM images and C and F are the power density spectrum of the FFT images.

Interestingly, the anodization of the sputtered Al resulted in wide range of average current densities from as low as $1.6\text{mA}/\text{cm}^2$ and as high as $3.7\text{mA}/\text{cm}^2$ with 1:4 EtOH to water ratio. When the ordered nature of the resulting AAO was plotted to the average current density, there was a trend where higher average current density resulted in more ordered AAO film as seen in Figure 4.8. This dependence of the spatial order parameter on the current density is seen more in recent literatures where the anodization voltage is not the only factor in determining the ordered nature of the AAO films but also on the current density.^{164, 165} Li *et. al.* used Al foil and varied the anodization current density by changing the electrolyte concentration.¹⁶⁴ They also saw an increase in the ordered nature of the AAO with increasing acid concentration which resulted in higher current densities. Norek *et. al.* compared electrolytes with and without EtOH. As expected, due to the lower current densities with the added EtOH, AAO films with EtOH resulted in loosely ordered structures whereas without ethanol achieved much higher ordered structures.⁶⁹ However, the ordered structure required hard anodization for the first anodization layer, which again requires thick Al.

In order to minimize the negative effect of EtOH on the current density but still maintain the cooling capability, 1:9 EtOH to water ratio was used. This resulted in much higher range in the current densities, increasing from $3.5\text{mA}/\text{cm}^2$ to $4.4\text{mA}/\text{cm}^2$. The SEM image, FFT, and power density spectrum of the AAO from the $4.4\text{mA}/\text{cm}^2$ is shown in Figure 4.7D, E, and F respectively. There is also another possibility on the higher ordered nature of the AAO with the average current density of $4.4\text{mA}/\text{cm}^2$. All of the first anodizations were performed for 6 hours. With higher current density, a

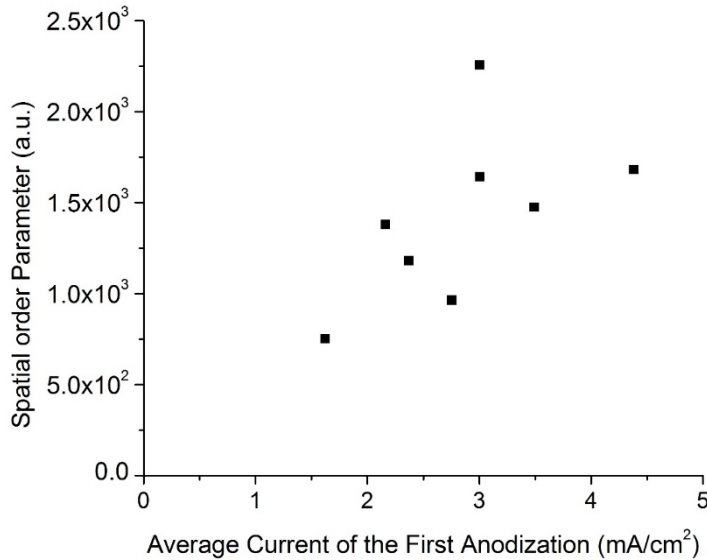


Figure 4.8 – Average current densities during the first anodization process plotted against the resulting spatial order parameter

thicker first anodization layer would form. With a thicker first layer, there was more material in which the ordered pore arrangement could be further established. Masuda et. al. saw that with increasing first anodization time, better ordered structures could be achieved.¹⁶³

The second anodization was performed until the W underneath the Al was anodized. In traditional AAO structure, the bottom of the pore is the barrier layer. The barrier layer is insulating and it must be removed in order to add a good electron pathway for the cathode in the SSB to the edge of the wafer. One method is to add another valve metal underneath the Al that has higher ionic conductivity than Al₂O₃ which can penetrate the barrier layer and then selectively removed. One such metal is W. Oh and Thompson

used W to fully anodize Al layer and then to form WO₃ nanoplugs that would penetrate the AAO barrier layer. The result of WO₃ formation after full utilization of the Al layer was the drop in the anodization current. WO₃ has higher ionic conductivity than Al₂O₃. This allowed formation of WO₃ through the barrier layer, creating a plug. As WO₃ have relatively higher acid stability than Al₂O₃, no dissolution occurs and continuously forms a thick oxide layer and causes a drop in the overall anodization current. Utilizing the difference in the chemical stability of Al₂O₃ and WO₃, WO₃ was selectively etched without damaging the Al₂O₃ of the AAO/W layer underneath the AAO pores.⁸⁶ Oh et al. was then able to use the metallic layers to make direct electronic contact to deposit Ni and Au nanowires.^{86, 166} The effect of WO₃ formation on the anodization current can be clearly seen in Figure 4.5C where the current decays, marking the full anodization of the Al and the beginning of WO₃ formation. Figure 4.9 shows the interface between the AAO and the W layer. Note, these images were taken from the AAO prepared under the 140V hard anodization process which the details on the anodization conditions are in the appendix of this dissertation. In order to maximize the 195V samples, the 140V samples were used first to optimize the WO₃ removal process. Before the WO₃ removal process, small plugs of WO₃ can be seen. It is difficult to see when the secondary electron detector is used. But with more element sensitive backscatter electron detector, the WO₃ plugs can be clearly seen. After the WO₃ removal, WO₃ was no longer seen at the AAO/W interface.

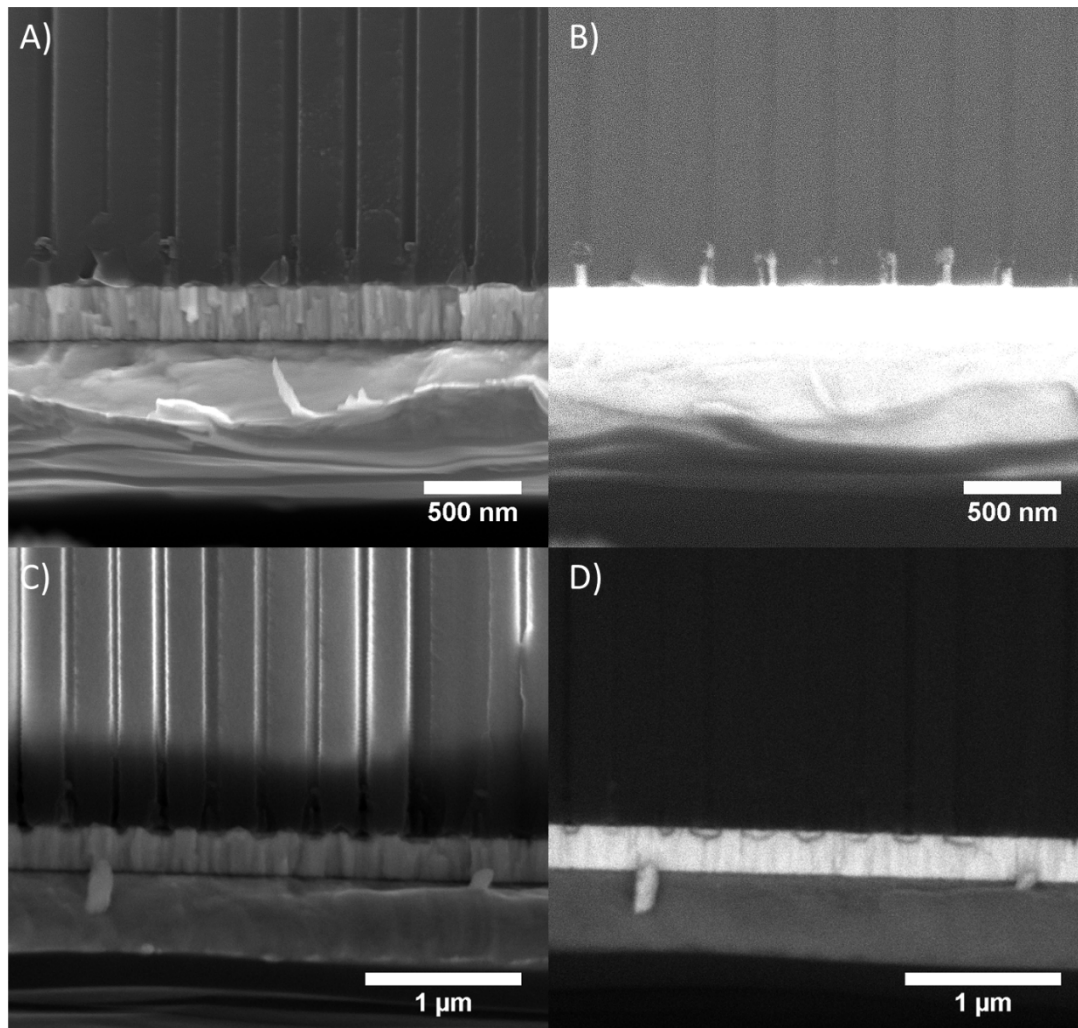


Figure 4.9 - SEM images with SE and BSE detectors of the AAO/W interface before (A with SE and B with BSE detector) and after WO_3 removal process (C with SE and D with BSE detector). The AAO prepared in this figure was prepared using the 140V HA two-step anodization process discussed in the Appendix.

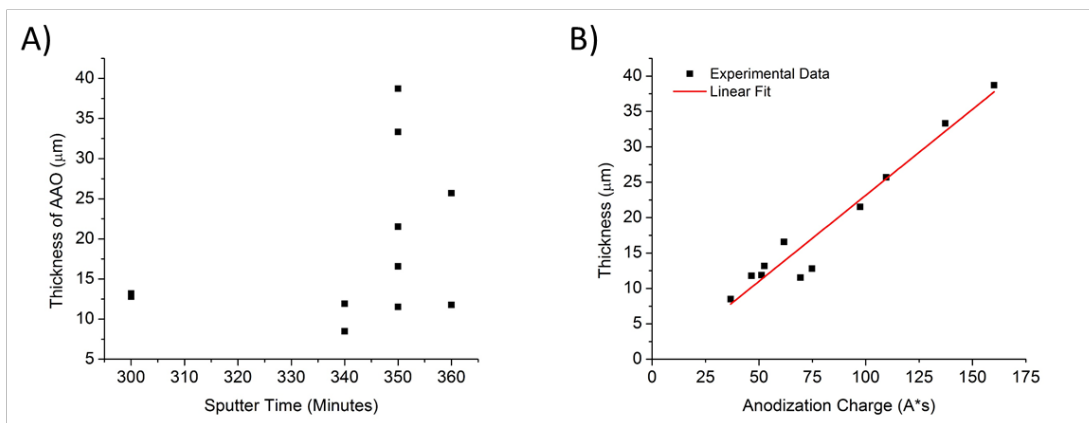


Figure 4.10 (A) – final Thickness of the AAO as a function of total sputter time. (B) Final thickness of the AAO as a function of total charge passed during the second anodization.

In order to fabricate a test-of-concept 3D solid state battery in AAO, a relatively thin AAO thickness was targeted. Initially, the thickness of the final AAO was to be controlled by the thickness of the sputtered Al. However, this was not possible due to the differences not only in the anodization current densities but also on the dependence of the Al sputter rate over the lifetime of the Al target and different current densities during the electropolishing step. This resulted in wide range of second anodization layer thickness values as can be seen in Figure 4.10A. However, the total charge that is passed during the second anodization process can be used to predict the thickness of the AAO. Figure 4.10B plots the accumulated second anodization charge against the measured thickness of the second anodization AAO. The fitted line has the equation shown below where T is the thickness of the AAO in μm and C is the charge that was passed during the second anodization in $\text{A}\cdot\text{s}$.

$$T = 0.243C - 1.143$$

Equation 4.1

The above data includes the samples that were anodized in both 1:4 and 1:9 ratios of EtOH and water which highlights that the AAO thickness is independent of the electrolyte composition. This allows the prediction of the final AAO thickness to tune the ALD recipes for different battery materials without the need to destroy the AAO sample for cross-sectioning characterization. This destructive characterization can be performed after the electrochemical testing to ensure the correct geometries were used for calculations.

4.3.3 Electrochemical characterization of Solid State Battery.

In order to estimate the energy areal density of the 3D solid state films, several assumptions were made based on the experimental data from Pearse et. al. It was assumed that the energy density of the battery was limited by the cathode, V_2O_5 , with a volumetric capacity of $38.6 \mu\text{Ah}/\text{cm}^3$ at a nominal current density of $20 \mu\text{A}/\text{cm}^2$. The anode, SnNx , with a volumetric capacity of $300 \mu\text{Ah}/\text{cm}^3$ at $20 \mu\text{A}/\text{cm}^2$. Due to the larger volumetric density of the SnNx , the volumetric ratio of the cathode to the anode was maintained at 7.7.¹⁴⁷ Some of the estimated energy density of the 3D solid state battery at various configurations are shown in Table 4.1. The area enhancement factor is the amount of total surface area increase from the 3D scaffold to the nominal area of the solid state battery. As AAO is highly a tunable 3D substrate, various geometric

Pore Diameter (nm)	Interpore Distance (nm)	Pore Depth (μm)	V_2O_5 Cathode Thickness (nm)	LiPON Electrolyte Thickness (nm)	Sn_3N_4 Anode Thickness (nm)	Area Enhancement Factor*	Energy Density ($\mu\text{Wh}/\text{cm}^2$)
90	100	10	4.5	20	1.5	327	114
250	300	27	20	25	4	273	403
400	450	11	25	50	5.3	80	153
400	450	27	55	50	16	194	752
400	450	50	55	50	16	360	1390

Table 4.1 – Estimated areal energy density with different 3D geometries of the AAO. *Area enhancement factor is based on the substrate.

parameters area available and can be tailored as needed. With a 400nm diameter, 450nm interpore distance, and optimized thickness of each battery layers, a simple but also highly scalable 3D solid state battery can be achieved at $27.8\mu\text{Wh}$ per nominal cm^2 per μm of the pore depth. With a $50\mu\text{m}$ AAO substrate, the areal energy density is expected to have $1390 \mu\text{Wh}/\text{cm}^2$, significantly higher than the highest reported traditional thin film SSB. Based on the expected cell voltage, this specific 3D solid state battery is expected to have an energy density of $392\text{Wh}/\text{L}$ where a currently available commercial thin film solid state battery EFL700A39 has $17\text{Wh}/\text{L}$. With the thin material thickness, it is also expected to achieve much higher power density as well.

One of the first step towards the 3D SSB was to see how conformal the ALD materials can deposit in such high aspect ratio substrate. The ALD recipe was not optimized for high aspect ratio structures and was expected to have difficulty in depositing within the deeper pores. Figure 4.11 shows the SEM image of the $35\mu\text{m}$ thick AAO substrate before and after non-optimized ALD of 15nm of TiN and 25nm of V_2O_5 . The cross-section shows a gradient in the morphology of surface of the pores. Near the top, where

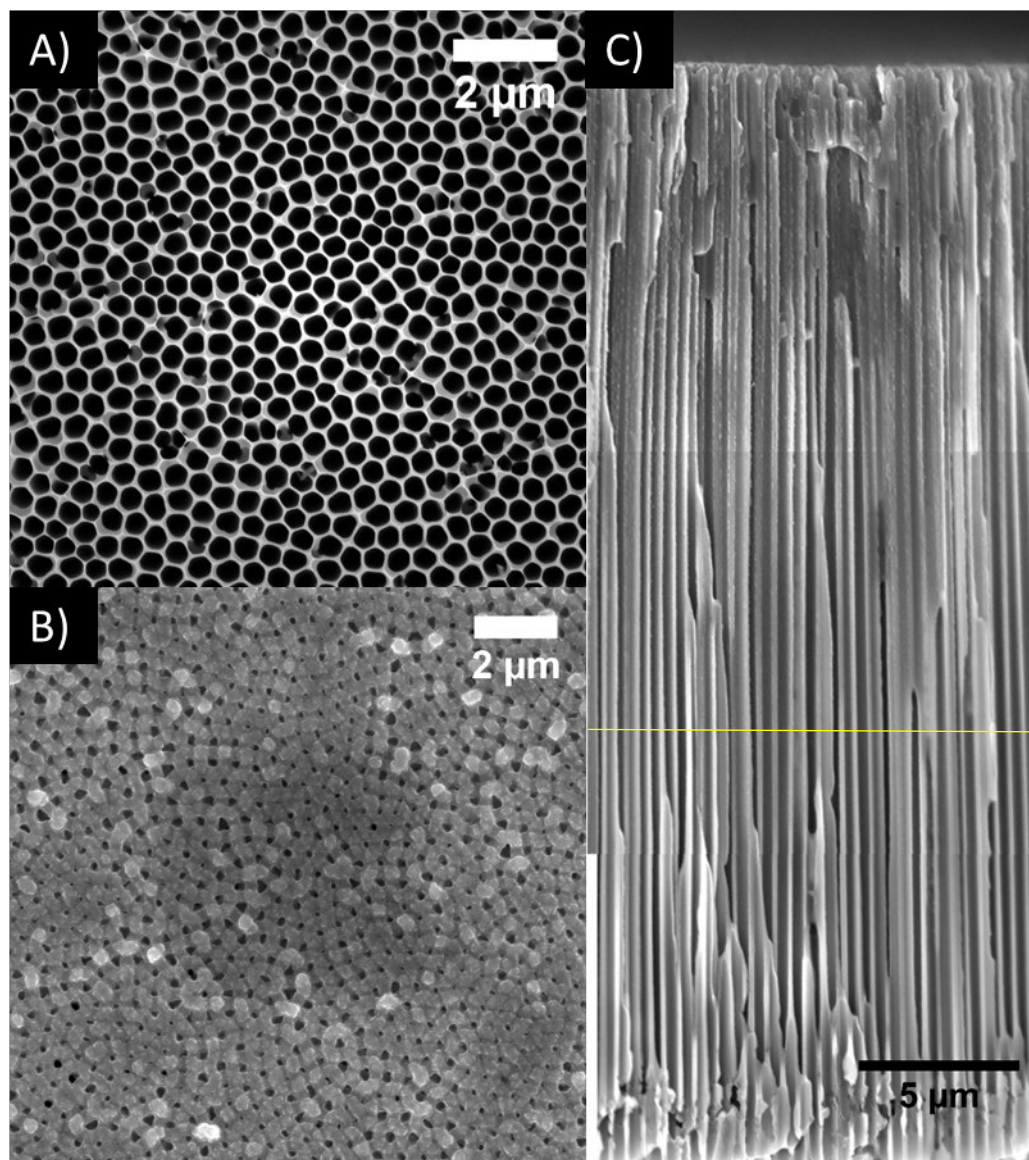


Figure 4.11 – SEM image of top of the AAO (A) before and (B) after 15nm of TiN and 25nm of V₂O₅. C) is the cross section image after the ALD layers of TiN and V₂O₅.

the vapor phase precursors had most resident time, a good film growth can be seen from the increased surface roughness from the V₂O₅. However, in the lower portions of the pores where minimal precursor could access, there was a minimal film growth.

After about 18 μm down, only the smooth surface of the AAO can be seen as marked by the yellow line.

While this was not a perfect sample, it was still used to gauge the effect of the AAO 3D substrate on the electrochemical behavior of the 3D cathode. An image of the electrodes can be seen in Figure 4.12. The image was taken with a ruler to use ImageJ to measure the nominal active area for each sample. For the 3D substrate, the nominal area was 2.00 cm^2 whereas the planar substrate was 1.92 cm^2 . These electrodes were cycled in 1M LiClO_4 in propylene carbonate, a liquid electrolyte, to gauge the impact of 3D substrate.

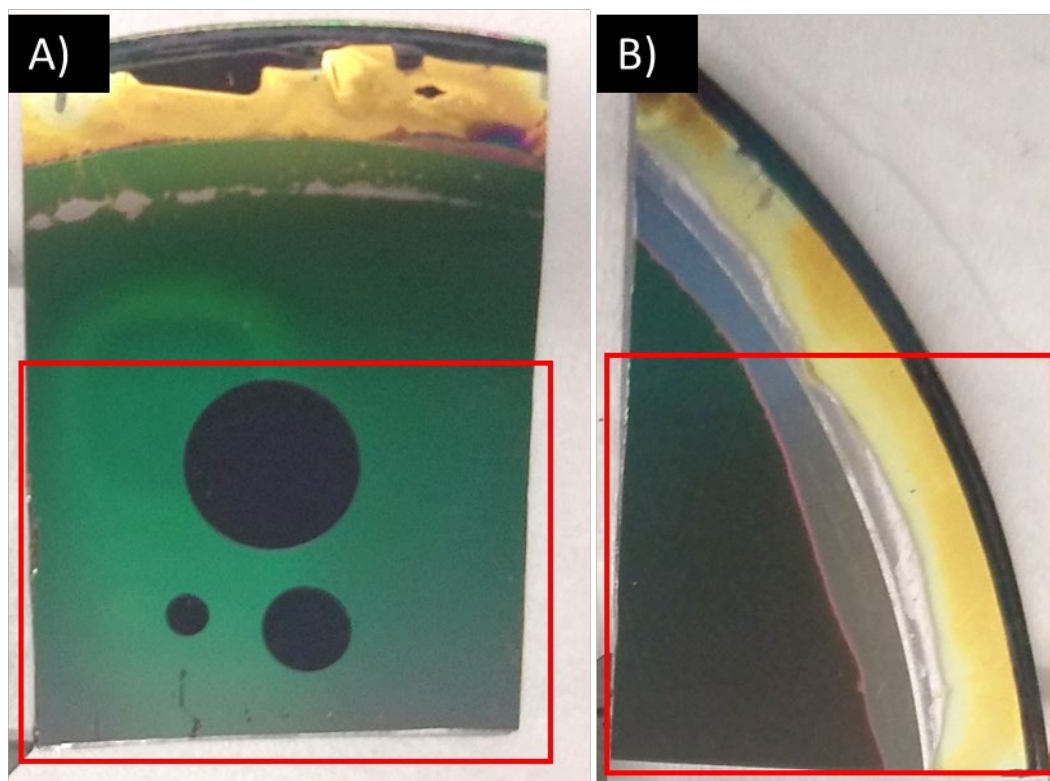


Figure 4.12 – Image of the 3D AAO substrate (A) and planar substrate (B). The area highlighted in red is the electroactive area that was submerged in 1M LiClO_4 in PC.

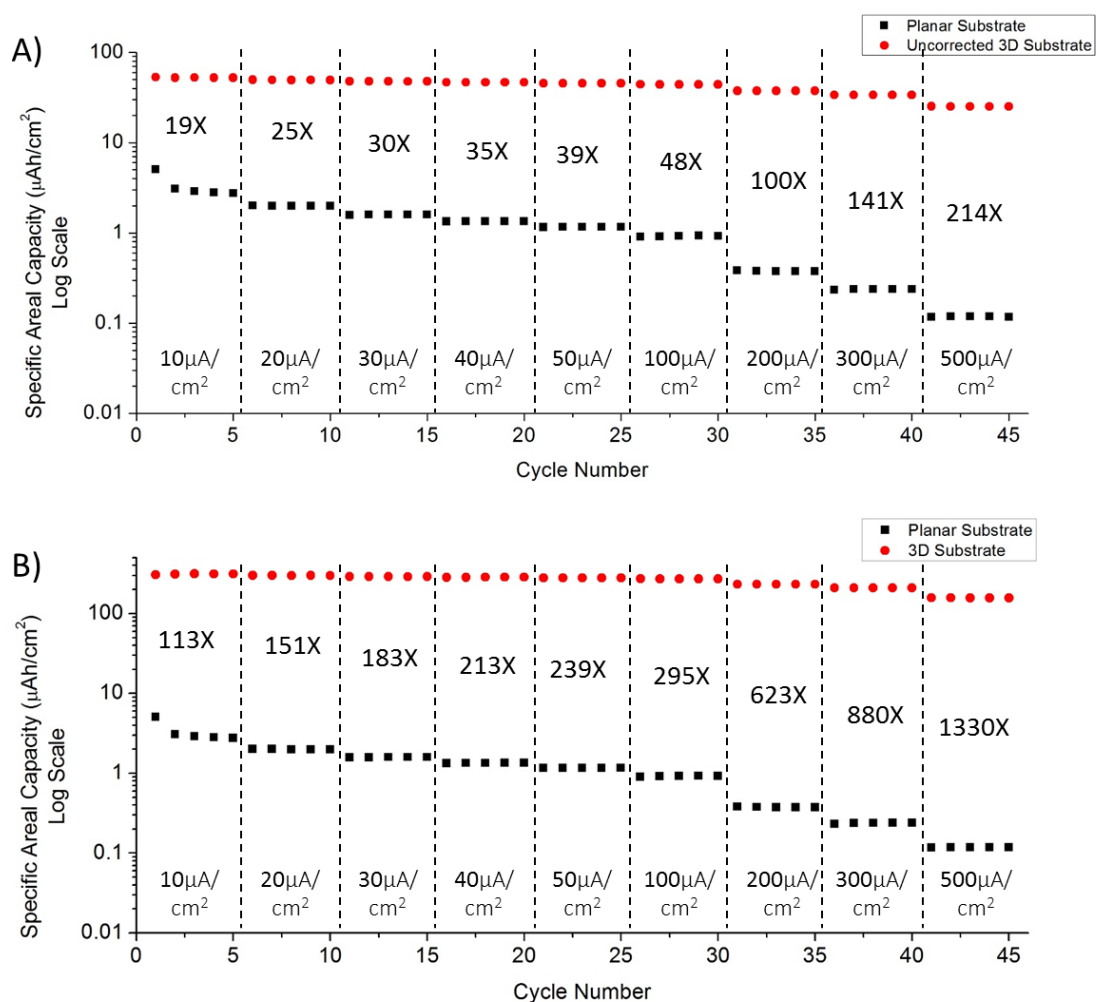


Figure 4.13 – Capacity of planar V_2O_5 and 3D V_2O_5 under various current densities before (A) and after (B) excess V_2O_5 correction on 3D substrate.

Figure 4.13 shows the capacity of the planar and 3D V_2O_5 under various current densities. In Figure 4.13A, the areal capacity of the 3D scaffold V_2O_5 is only 19 times higher than the planar structure. Based on the geometry of the substrate, it should be 207 times higher. This result was due to the difference in the 3D nominal area and planar nominal area on the 3D substrate. As can be seen in Figure 4.12A, the cathode material was coated on all of the surface including both the 3D area and the planar area. This meant that the 2.00 cm² nominal area for the 3D substrate was too large. In the

final version of the 3D SSB, the excess materials were supposed to be etched and removed so only the active materials would be those on the AAO substrate. The dark three circles are where the AAO substrates were grown and their nominal area was 0.32 cm^2 . The rest of the area in red, 1.68 cm^2 , is planar. Since there was a separate planar data, the capacities of the planar portion of the 3D substrate was mathematically removed. This resulted in much higher difference between the capacities of the two substrates where at low current density, the 3D substrate had 113 times more capacity than the planar substrate. This increase in the capacity makes sense as only about half way down the pores were coated, $18 \mu\text{m}$ out of $35 \mu\text{m}$ thick AAO. This difference became even larger as the nominal current density was increased. At $500 \mu\text{A}/\text{cm}^2$, the 3D substrate had 1330 times higher capacity. While the current density applied was the same between the 3D and planar substrate, due the larger surface area of the 3D substrate, the actual current density on the V_2O_5 was much lower and led to higher capacity retention.

4.4 Conclusion

In this study, anodized aluminum oxide was fabricated on a Si wafer as a high-aspect ratio template for a thin nanostructured 3D solid state battery. The ordered nature of the AAO was quantified by FFT and analysis of the power density spectrum. It was found that with higher current density, the higher ordered pores were formed. It is unclear if it is indeed the higher current density or the larger amount of charge passed during the first anodization process that has more influence on the ordered structure of the AAO. A highly linear function was found for the thickness of final AAO and the

amount of charge passed during the second anodization to estimate the thickness of the AAO on wafer without the need to destroy the sample. Preliminary results show that with high aspect ratio nanoscaffold such as the AAO, optimization is required for the ALD processes. Despite the non-ideal deposition of TiN and V₂O₅, they showed promising results in terms of energy density and power density for the final version of full solid state batteries.

5 Summary and Outlook

5.1 Summary

The overall goal of this research was to utilize highly ordered nanostructures to explore the impact of specific structural properties on the electrochemical behavior of well-studied Li-ion electrode materials. The utilization of highly ordered structures with well-known materials allowed accurate analysis of the structural affects.

The three goals of this dissertation include:

- 1) To utilize the highly conformal deposition technique, atomic layer deposition, for deposition of well-known electroactive materials on highly ordered nanostructures.
- 2) To systematically study different nanostructures to increase understanding of structural effects on electrochemistry and to provide guidelines for improved electrochemical behaviors.
- 3) Provide a test bed for exploration of nanostructured 3D solid state batteries.

In the second chapter, the effect of interconnections on the electrochemical behavior of V_2O_5 , a Li ion cathode material, was explored. Two different phenomena were observed depending the degree of lithiation of V_2O_5 . It was determined that when the material's electronic conductivity increased with lithiation, the interconnections led to better material usage and high power densities. On the other hand, when the electronic conductivity decreased with lithiation, then the interconnections led to worse material usage and low power densities. It was also found that these interconnections did not lead to faster degradations of the electrode.

In the third chapter, the effect of nanoconfinement of liquid electrolyte for use in Li-ion battery was explored with TiO_2 as the anode material. With the utilization of microfabrication techniques and ALD, highly ordered and well defined 20nm channels with anatase TiO_2 were fabricated. The results showed that at low ionic concentrations, nanoconfinement led to higher material usage and power densities than the bulk electrolyte. Through the use of finite element simulations, it was determined that at low ion bulk concentrations, the negative surface charge of TiO_2 in the nanochannels caused accumulation of Li ions in the EDL and diffuse layers. This higher local concentration of Li ions caused higher driving voltage at the stern layer, and led to smaller peak separations, better material utilizations, and better power densities. As a follow up to the 20nm channel, two additional sizes were fabricated and tested, a device with 10nm and another device with 3nm channel. These were tested in aqueous electrolyte to first characterize the nanochannels. An interesting phenomenon was observed that was not only channel size dependent but also pH dependent. At a larger

channel size of 10nm, a single conductance state was observed. But at a smaller 3nm channel, multiple conductance states were observed. It was determined that the dissolved CO₂ may be playing a role in the multiple conductance states and that it will require further experimentation to conclude these findings.

In the chapter 4, highly ordered AAO was fabricated on top of a silicon wafer to demonstrate the ability to create high performance 3D solid state batteries with traditional semiconductor processes. It was determined that high current density as well as a thicker first anodization layer led to higher degree of ordering of the AAO. It was also determined that the total charge passed during the second anodization could be used to estimate the thickness of the final AAO without the need to destroy the sample. With non-ideal ALD recipe, a non-conformal V₂O₅ was deposited into these AAO on wafer chips. The results showed that while the expected energy density increase was 207 times, even the non-optimized ALD of V₂O₅ in these high aspect ratio pores resulted in 113 times higher energy density at 10μA/cm². At a higher current density of 0.5mA/cm², the 3D V₂O₅ had 1333 times larger capacity than the planar V₂O₅ and showed highly promising results for 3D solid state batteries.

5.2 Outlook:

In this dissertation, precision nanostructures were utilized to understand how specific structural parameters have an impact on the electrochemistry of Li-ion electrodes. These nanostructure templates can also be used in other ion chemistries such as Na, Mg, and Al. All of these next generation ion chemistries have hurdles such as slow ion transport. Similar strategies should be applied to these next generation battery

chemistries to improve their electrochemical behavior. In this dissertation, ALD has been used for conformal deposition of materials. Unfortunately, there is a limit on the material that can be deposited via ALD. However, there are other self-limiting methods such as electrochemical deposition that can also be utilized to deposit next generation battery electrodes. With the correct deposition technique, the testbeds utilized in this dissertation can be used to further the structural studies and improve beyond Li-Ion battery chemistries.

Appendix

AAO Recipes

40V process

The detailed 40V process has been described in Chapter 2 for fabrication of straight AAO templates. The electropolished Al on wafer was anodized at 40V in 0.3M oxalic acid at 8°C for 6 hours. The first layer was removed with phosphoric acid: chromic acid etchant for 4 hours at 60°C. The second anodization was performed under the same conditions as the first anodization.

140V process.

This process was adapted from Reference 68.⁶⁸. The first anodization was performed in 0.3M oxalic acid at 2°C. Initial anodization voltage was set to 40V and was anodized for 10 minutes. The voltage was then ramped to 140V at 0.7V/s for 15 minutes. The first layer was removed with phosphoric acid: chromic acid etchant for 20 minutes at 60°C. Second anodization was separated into two parts, MA (mild anodization) and HA (hard anodization). MA was done in 4% phosphoric acid (about 0.3M) at 110V at 2°C for 15 minutes. Then HA was done in 0.015M oxalic acid at 140V at 2°C. As the current decayed, 0.3M oxalic acid was added to maintain a current density of 35mA/cm².

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