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Energy Storage in Niobium(V) Oxide Nanostructures: Fabrication, Conductivity and Degradation

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Jha, Gaurav

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Peer reviewed|Thesis/dissertation

# UNIVERSITY OF CALIFORNIA, IRVINE

Energy Storage in Niobium(V) Oxide Nanostructures : Fabrication, Conductivity and Degradation

DISSERTATION

submitted in partial satisfaction of the requirements for the degree of

### DOCTOR OF PHILOSOPHY

in Chemistry

by

Gaurav Jha

Dissertation Committee: Professor Reginald M. Penner, Chair Professor John C. Hemminger Professor Shane Ardo

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# DEDICATION

To my parents, my sister and all my mentors.

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# CURRICULUM VITAE

## Gaurav Jha

#### **EDUCATION**

**Doctor of Philosophy in Chemistry** University of California Irvine, CA, USA Master of Science in Chemistry 2015National Institute of Science Education and Research Bhubaneswar, Odisha, India

#### **RESEARCH EXPERIENCE**

**Graduate Research Assistant** University of California, Irvine

**Graduate Research Assistant** National Institute of Science Education and Research

#### **TEACHING EXPERIENCE**

**Teaching Assistant** University of California, Irvine

2015 - 2019Irvine, California

2013 - 2015Bhubaneswar, Odisha, India

> 2015 - 2017Irvine, California

2019

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# ABSTRACT OF THE DISSERTATION

Energy Storage in Niobium(V) Oxide Nanostructures : Fabrication, Conductivity and Degradation

By

Gaurav Jha

Doctor of Philosophy in Chemistry University of California, Irvine, 2019 Professor Reginald M. Penner, Chair

Energy storage has been the biggest obstacle in the widespread adoption of renewable energy resources. The work presented in this thesis is aimed at developing and understanding the behavior of Niobium Pentoxide  $(Nb_2O_5)$  based electrochemical energy storage devices.  $Nb_2O_5$  is a Li<sup>+</sup> intercalation metal oxide that is of current interest for lithium ion battery electrodes. In the first part of this thesis, electrophoretic deposition (ED) of  $Nb_2O_5$ thin-films from aqueous,  $NbO_x$  colloidal solutions is described, which exhibit unusually high specific capacities for Li<sup>+</sup> based energy storage as a consequence of 70% porosity. The excellent energy storage metrics are attributed to augmentation of the faradaic capacity by high double-layer capacities enabled by the mesoporous structure of these films. In the second part of this thesis, the effect of  $Li^+$  intercalation on the conductivity of  $Nb_2O_5$  has been explored. The electrical conductivity,  $\sigma$ , of battery and capacitor electrode materials is a factor determining the energy storage performance of these materials but it is difficult to directly measure in-situ particularly for electrodeposited materials. Our approach exploits an array of Nb<sub>2</sub>O<sub>5</sub> nanoribbon, fabricated using lithographically patterned nanoribbon electrodeposition (LPNE).  $\sigma$  of Nb<sub>2</sub>O<sub>5</sub> nanoribbons is measured in-situ in a battery electrolyte as a function of the equilibrium potential and, separately, during repetitive lithiation/delithiation cycling.  $\sigma$  in the non-lithiated Nb<sub>2</sub>O<sub>5</sub> is characteristic of semiconducting metal oxides, but it increases dramatically with lithiation. The last part of the thesis is aimed at uncovering the mechanism of capacity fade upon repetitive cycling for Nb<sub>2</sub>O<sub>5</sub> based energy storage devices. Microscopy, spectroscopy and electrochemical characterization tools have been employed to gain insight into the electronic, structural, compositional and morphological evolution of Nb<sub>2</sub>O<sub>5</sub> thin films as it undergoes thousands of cycles of charge-discharge. Overall, the work in this thesis elucidates a strategy towards fabrication of energy storage devices from materials that are difficult to electrodeposit using conventional redox reactions. Furthermore, it illustrates an approach to combine electrochemical and microscopy based methods, to gain insights into the interactions between  $Li^+$  ions and the active material, during repetitive charge discharge cycling.

# Chapter 1

# Introduction: Nanomaterials for Energy Storage

## 1.1 What makes a good energy storage material?

To replace fossil fuels, we need a sustainable method for both energy generation and storage. While giant strides have been made in the field of solar powered energy generation, the storage of generated energy has been the Achilles heel in the widespread adoption of sustainable energy resources. Nickel metal-hydride (Ni-MH) or Lead Acid batteries do not posses high energy density or power density (explanation in section 1.1.2) to replace fossil fuels as our primary fuel. In 1980, John Goodenough's research group at Oxford developed the first Cobalt oxide based cathode material for Lithium ion (Li<sup>+</sup>) battery.[65] Li-ion batteries are smaller and lighter than other batteries, making them portable. Since their commercialization in 1991 by Sony, Li-ion batteries have been a staple in cell phone and laptops. The era of electric cars has been fueled by the high power density of Li-ion batteries. Prof. Goodenough's work sparked widespread interest in exploration of new materials which are capable of (Li<sup>+</sup>) ion insertion reaction. The types of materials developed so far, as active material for Li-ion batteries can be classified in the following categories.

### 1.1.1 Types of Energy Storage Materials

There are 3 basic mechanisms of Li<sup>+</sup> ion based energy storage:

#### **Conversion** Materials

Materials that fall into category undergo a chemical transformation upon (Li<sup>+</sup>) ion insertion into the material. The flagship material in this class is elemental Silicon in anodes and elemental Sulfur in cathodes.[111, 60, 24, 57] Silicon undergoes the reaction:

$$Si + xLi^+ + xe^- \rightleftharpoons Li_xSi$$
 (1.1)

which results in 400% volume expansion and subsequent contraction that pulverizes the material rapidly. There has been a tremendous amount of work that has been done on incorporating elemental Si into commercial batteries and mitigating the adverse effects of cycling. Conversion material have the advantage of capturing high molar equivalent Li<sup>+</sup> per unit molar mass of the resulting material, which is defined as theoretical capacity (defined in section 1.1.2). However, since Lithiation (process of Li<sup>+</sup> ion insertion into the active material) requires solid state diffusion of Li<sup>+</sup> into the crystal lattice and subsequent chemical transformation, the rate of lithiation in conversion materials is lower than the other mechanisms on this list. The material also tends to break down rapidly due to constant chemical and phase transformation.

#### Intercalation material

For materials in this category, Li<sup>+</sup> ions diffuse through the lattice of host material and are stored in interstitial sites in the matrix. Commercially used cathodes, NMCs (composed of Nickel oxide, Manganese oxide and Cobalt oxide), use this mechanism for Li<sup>+</sup> ion storage as described by the following reactions:

$$TMO_2 + xLi^+ + xe^- \rightleftharpoons Li_x TMO_2 \tag{1.2}$$

where TM refers to the Transition metals (Ni, Mn and Co) and x ranges between 0 and 1. These reactions do not chemically transform the host material, but rather change the oxidation state of metal center to accommodate charge neutrality. The host material may or may not undergo phase transformation, and in majority of the cases it is followed by expansion of the lattice, but not to the same extent as conversion materials. The resulting distortions upon lithiation - delithiation reaction are not significant, which leads to a higher cycle stability than conversion materials. However this comes at the expense of capturing lower molar equivalent of Li<sup>+</sup> per unit mass of active material. Niobium pentoxide, which is the focus of this thesis, falls broadly into this category, however it also shares similarities with the Electric Double Layer Capacitance (EDLC) materials, which is discussed in the next subsection.

#### Electric Double Layer Capacitance (EDLC) materials

When a potential is applied on an electrode, say a negative potential, positive ions (say  $Li^+$  ions) in the electrolyte will be attracted to the surface of electrode. A monolayer of solvent between the ions and the negatively charged species forms in the dielectric layer. Capacitance observed between the layer of charged ions on one side of the dielectric and charges on the electrode on the other side of the dielectric, is termed as the double layer

capacitance. Li<sup>+</sup> ions do not insert into the matrix of the active material in this case, hence the bulk mass of the material has no relevance for this type of energy storage. Merit of materials falling into this category primarily depends on the surface area per unit mass or volume. So materials having high porosity like amorphous carbon, show high EDLC. Since there is no Li<sup>+</sup> intercalation taking place, the material is not affected by repetitive cycling to the same extent as conversion or intercalation materials. However, bulk of the material is not utilized for energy storage, so Li<sup>+</sup> ion stored per unit mass is very low leading to lower capacities for this class of material.

#### **1.1.2** Definitions of Relevant Concepts

To evaluate the energy storage capabilities of an active material, we need to define parameters that quantify the processes occurring during electrochemical cycling.

#### Charge Stored, Q

The amount of Li<sup>+</sup> ions that are captured by the anode while charging and cathode while discharging the active material. For a 3-electrode electrochemical setup (consisting of a Working, Reference and Counter electrode), it is obtained by integrating the anodic current (positive current,  $I_A$ ) or the cathodic current (negative current,  $_C$ ) over the period of charging/discharging time, t:

$$Q = \int I dt \tag{1.3}$$

In cyclic voltammetry (CV), Q is obtained by integrating the area under anodic/cathodic part of the CV and dividing by the scan rate ( $\nu$ ) :

$$Q = (1/\nu) \int I dV \tag{1.4}$$

The unit for charge is Coulombs (C).

#### **Current Density**

Current density is the current per unit area (areal current density, mA/cm<sup>2</sup>) or current per unit mass (gravimetric current density, mA/g). In galvanostatic charge-discharge cycling, working electrode is cycled at a constant gravimetric current density between two limiting potentials (also called Chronopotentiometry, CA).

#### Specific Capacity or Specific Capacitance, $C_{sp}$

Specific capacity is the charge per unit mass that is stored in an energy storage system. SI units of specific capacity are C(coulombs)/g, although the commonly used unit is mAh/g. It is calculated by using gravimetric current density (mA/g) and charging or discharging time (in hours, h):

$$SpecificCapacity(mAh/g) = Currentdensity(mA/g) * Time(hours)$$
 (1.5)

Specific Capacitance  $(C_{sp})$  on the other hand is obtained using charge, Q (in Coulombs, C), active material mass, m (in grams, g) and the magnitude of potential window in which the active material is cycled (in Volts, V):

$$C_{sp} = Q/(m * V) \tag{1.6}$$

 $C_{sp}$  is generally used to describe energy storage in capacitors, not batteries. As a general trend the academic community is moving towards the use of Specific Capacity (mAh/g) for describing all electrochemical energy storage devices. There is a simple conversion between specific capacitance and specific capacity:

$$SpecificCapacity = SpecificCapacitance * V/3.6$$
(1.7)

#### Theoretical Capacitance

The highest faradaic capacity that can be stored by an active material. To evaluate theoretical capacity, for an active material (TMO), with the lithiation - delithiation reaction:

$$TMO + xLi^+ + xe^- \rightleftharpoons Li_x TMO \tag{1.8}$$

the following equation can be used :

$$C_{sp,Theoretical} = x * F/(Molar Mass_{Li_x TMO} * V)$$
(1.9)

where F is faraday constant, which is 96,485.33 C/mol.

$$SpecificCapacity_{Theoretical} = x * F/(Molar Mass_{Li_{x}TMO} * 3.6)$$
(1.10)

#### Cyclic Voltammetry vs Galvanostatic Charge Discharge

In cyclic voltammetry (CV), change of current is observed as potential is ramped up and down at a scan rate ( $\nu$  in mV/s). The shape of the curve can tell us about the charge stored by the active material (by integrating the curve), number of electron transfer events, onset or offset of any electrochemical reaction, resistance in the electrochemical cell, capacitance and much more. However, since the current drawn from the cell is constantly changing, it is not the preferred way of testing a material for battery application. However it is the preferred method of conducting studies into mechanistic details of lithiation-delithiation reaction. Galvanostatic charge discharge is a technique where a constant current is applied and potential is measured between two limiting potentials. It is a simulated condition for a real battery. Also, it helps us find out the length of time the cell takes to charge and discharge. A good energy storage device outputs a constant current for a long period of time over a small range of potential (called the plateau region in a Chronopotentiometry curve). It also shows the difference in potential for charging and discharging as a function of time. However, it is not a good representation of mechanistic details of the electrochemical process in the active material.

#### Specific Energy, Wh/kg

The amount of energy stored per unit mass of an active material. It is calculated using specific capacity (mAh/g) and the potential window (V):

$$SpecificEnergy = SpecificCapacity * V \tag{1.11}$$

. For specific capacitance,

$$SpecificEnergy = (1/2) * SpecificCapacitance * V^{2}$$
(1.12)

Traditionally, batteries are known to have a higher specific energy than capacitors.

#### Specific Power, W/kg

The amount of power stored per unit mass of an active material. This can also be thought of as the rate of transfer of stored energy.

$$SpecificPower = SpecificEnergy/Time$$
 (1.13)

Also, using equation (1.5) and (1.11),

$$SpecificPower = CurrentDensity * V$$
(1.14)

Capacitors have a much higher specific power than batteries. A Ragone plot compares the specific energy and specific power of various materials and can be used to compare the performance of energy storage devices.

#### Pseudocapacitance

Any electrochemical energy storage process which is not limited by solid state diffusion can be termed as pseudocapacitance. As described in section 1.1.1, double layer capacitance depends primarily on the surface area, so the process is fast and does not depend on solid state diffusion. Redox reactions occurring at the material surface are also not limited by solid state diffusion, so this process is also pseudocapacitive. In section 1.3, another process called intercalation pseudocapacitance is discussed. Very few materials have been identified which show this phenomenon, where the rate of intercalation reaction is as high as the rate of surface reactions. Therefore these intercalation reactions can also be termed as pseudocapacitive in nature.[3]

## 1.2 Manganese oxide nanowires for prolonged cycle life

The motivation behind the work presented in rest of the thesis, was to develop a material with high power densities at relatively high energy density. Before moving on to niobium oxide, manganese oxide was the prime candidate for such a modification. Thus, the nanoarchitectures developed in this section have provided a methodology that was followed in the following chapters.

# 1.2.1 Importance of Nanoscopic Architecture in $MnO_2$ Performance

Manganese oxide (Li<sub>x</sub>MnO<sub>2</sub>) is a Li<sup>+</sup> insertion metal oxide with a high theoretical Faradaic charge storage capacity,  $C_{sp}$  of 1110 F/g (assuming a 1.0 V window), powered by Mn centers that can toggle between +2 or +3 oxidation states.[97, 109, 76, 58] This Faradaic C<sub>sp</sub> is higher than many insertion oxides including SnO<sub>2</sub> (640 F/g), RuO<sub>2</sub> (725 F/g), Nb<sub>2</sub>O<sub>5</sub> (726 F/g), and is comparable to Fe<sub>2</sub>O<sub>3</sub> (1249 F/g) and Co<sub>3</sub>O<sub>4</sub> (1206 F/g).  $C_{sp}$  values >1000 F/g are indeed measured experimentally in Li<sub>x</sub>MnO<sub>2</sub> half-cells[105] and equivalent values of  $C_{sp}$ are seen in symmetrical Li<sub>x</sub>MnO<sub>2</sub> capacitors,[107, 87] but only for very slow charge/discharge rates in the 1-2 mV/s range and for very thin MnO<sub>2</sub> layers, with thicknesses <80 nm.[105] At higher rates,  $C_{sp}$  is rapidly reduced by a factor of 10-50 at 100 mV/s, for example.  $C_{sp}$  is also depressed as the mass loading of MnO<sub>2</sub> on a current collector, and the shell thickness, increases. Thus, the tremendous potential of Li<sub>x</sub>MnO<sub>2</sub> for energy storage in either capacitors or batteries is limited by poor rate performance, especially at significant mass loadings. These related phenomena are poorly understood at present.

What is the source of this poor rate performance? Barriers to  $Li^+$  intercalation/de-intercalation at the MnO<sub>2</sub>-electrolyte interface and slow Li diffusion within the MnO<sub>2</sub> are two contribut-

ing factors that have been proposed. [97, 76, 114] The influence of both of these mechanisms is minimized by increasing the level of dispersion of the  $MnO_2$  by, for example, decreasing the  $MnO_2$  particle diameter. Increased dispersion translates into a higher surface area: volume ratio and reduced diffusion path lengths within the  $MnO_2$  for Li. A significant disadvantage of  $Li_xMnO_2$  - again shared by other metal oxides - is its low electronic conductivity which varies from 2-4  $\times$   $10^{-4}$  S/cm (x = 0) increasing to 4-5  $\times$   $10^{-2}$  S/cm (for x = 1.0) as compared with  $\approx 10^5$  S/cm for a metal such as silver.[46] The low conductivity of  $Li_x MnO_2$  necessitates that it be supported at high dispersion on a good conductor such as a metal or carbon, and many examples of this general paradigm have been reported.<sup>e.g.</sup> [56, 49, 32, 104, 100, 83, 29, 51, 23, 110, 53, 22, 33] Our approach [87, 107, 105] has been to embed a gold nanowire within a shell of  $\delta$ -MnO<sub>2</sub> - so-called Au@ $\delta$ -MnO<sub>2</sub> core:shell nanowires - where both the gold nanowires and the  $\delta$ -MnO<sub>2</sub> shell are prepared by electrodeposition. A key point is that the gold nanowire core does not ensure facile electrical communication with the  $MnO_2$  shell when this shell increases in thickness beyond 60 nm or so. In Au@MnO<sub>2</sub> nanowires, the MnO<sub>2</sub> shell must still intercalate  $Li^+$  and communicate electrically with the gold nanowire core, and the strategy outlined here is intended to impact one or both of these processes. In this work, hexamethylenetetraamine (HMTA) has been intercalated into  $MnO_2$  to enhance the conductivity of  $MnO_2$  (Figure 1.1)

## 1.2.2 Fabrication of Au/MnO<sub>2</sub> Core:Shell Nanowires

#### Chemicals and Materials.

Manganese perchlorate hydrate,  $(Mn(ClO_4)_2 \cdot H_2O, 99\%)$ , lithium perchlorate (LiClO<sub>4</sub>, battery grade, 99.99%), hexamethylenetetraamine (HMTA) (99.0%) and iodine (I<sub>2</sub>, 99.8%), poly(methylmethacrylate) (PMMA, MW = 120,000 g/mol, 99.99%) were used as received from Sigma-Aldrich. Dry acetonitrile required for capacitance testing was prepared by pro-



Figure 1.1: Schematic representation of the influence of HMTA on the morphology of Au@ $\delta$ -MnO<sub>2</sub> nanowires prepared by electrodeposition. The properties of these two types of nanowires are compared in this paper.

cessing reagent grade acetonitrile with a Jorg Meyer Phoenix SDS column purification system. Sulfuric acid (ULTREX ultrapure) was purchased from J. T. Baker. Potassium iodide (KI, 99%), acetone, propylene carbonate (PC, 99.7%) and nitric acid were used as received from Fisher (ACS Certified). Positive photoresists, Shipley S-1808 and developer MF-319 were purchased from Microchem Corporation. Nickel and gold pellets (5N purity, Kurt J. Lesker Co.) and chromium powder (3N purity, American Elements) were used for the preparation by thermal evaporation of ultra-thin metal layers.

#### Preparation of Au/MnO<sub>2</sub> Core:Shell Nanowires.

Au@MnO<sub>2</sub> core:shell nanowires were fabricated using a variant of the Lithographically Patterned Nanowire Deposition (LPNE) technique shown schematically in Figure 1.2.[102, 101, 64] A 40 nm thick nickel film was first thermally evaporated on top of precleaned  $1^{"} \times 1^{"}$  squares of soda lime glass (Figure 1.2, step 1). Then a positive photoresist (PR, Shipley, S1808) layer was deposited by spin-coating (step 2), followed by soft-baking at 90°C for 30 min, and a contact mask was used to pattern this PR layer with a 365 nm UV light source combined with a shutter and photolithographic alignment fixture (Newport, 83210iline, 2.3s). The exposed PR region was developed for 20 s (Shipley, MF-319) and then rinsed with Millipore water (Milli-Q,  $\rho > 18 \text{ M}\Omega \cdot \text{cm}$ ). The exposed nickel was removed by etching for 6 min in 0.8 M nitric acid (step 3). The whole device was then dipped into commercial Au plating solution (Clean Earth Solutions) and Au was potentiostatically electrodeposited using a Gamry Series G 300 potentiostat at -0.9 V versus saturated calomel electrode (SCE) using a one-compartment, three-electrode electrochemical cell with a Pt foil counter electrode (step 4). After electrodeposition, the surface was first rinsed with acetone to remove photoresist, and then with Millipore water, revealing patterned Ni pads together with Au nanowires deposited on the edges of these pads (step 5). Nickel was then removed by immersion in nitric acid for 6 min (Step 7). After etching, the device was rinsed with Millipore water and air-dried. On the unetched side of this nanowire array, the Au nanowires still attached to nickel fingers were used as electrical contacts for  $MnO_2$  shell deposition.

 $\delta$ -MnO<sub>2</sub> was electrodeposited onto these nanowires (step 8) using either of two procedures: HMTA-free Au/MnO<sub>2</sub> nanowires were prepared using an aqueous solution of 2 mM Mn(ClO<sub>4</sub>)<sub>2</sub> and 50 mM LiClO<sub>4</sub> by potentiostatic oxidation at +0.60 V vs. MSE, as previously described[105]. Deposition times ranging from 40 s to 500 s produced MnO<sub>2</sub> shells between 400 nm and 2.2  $\mu$ m in thickness. Au/MnO<sub>2</sub> core:shell nanowires containing HMTA were prepared using a two step procedure in which a thin HMTA-free "primer" layer was first electrodeposited as described above, using a  $t_{dep} = 10$  s. Then, HMTA-doped  $\delta$ -MnO<sub>2</sub> was electrodeposited onto MnO<sub>2</sub>-primed gold nanowires from a solution containing 10 mM HMTA in addition to 2 mM Mn(ClO<sub>4</sub>)<sub>2</sub> and 50 mM LiClO<sub>4</sub>.  $t_{dep}$  ranging from 30 s to 490 s resulted in the unique MnO<sub>2</sub> morphology. In both cases, freshly deposited Au@MnO<sub>2</sub> nanowires were removed from plating solutions, rinsed with Millipore water, and dried in the



Figure 1.2: a) Process flow for the preparation using lithographically patterned nanowire electrodeposition (LPNE) of Au@ $\delta$ -MnO<sub>2</sub> nanowire arrays. b) SEM image of five gold nanowires prepared using the process depicted above (steps 1-7). A typical array contained 1800 such nanowires. c) Six Au@ $\delta$ -MnO<sub>2</sub> nanowires prepared by the electrodeposition of  $\delta$ -MnO<sub>2</sub> onto gold nanowires (step 8 above).

oven at 90°C for 30 min prior to electrochemical assessment. All capacitor measurements involved a sandwich of two 1800 nanowire layers.

#### Preparation of the Gel Electrolyte and Sandwich Capacitor Assembly.

Symmetrical,  $Au@\delta-MnO_2$  nanowire "sandwich" capacitors were prepared by fabricating 1800 nanowire arrays on each of two glass substrates, and pressing these two layers together,

using a  $\approx 2 \ \mu m$  thick PMMA gel electrolyte, as previously described.[88] The 1.0 M LiClO<sub>4</sub>, 20 w/w%, PMMA, PC gel electrolyte was prepared by adding 1.6 g (20 w/w%) of PMMA to 5 mL of 1.0 M LiClO<sub>4</sub> in dry propylene carbonate (PC) while stirring at 115°C. The 1.0 M LiClO<sub>4</sub>, 20 w/w%, PMMA, PC gel electrolyte was deposited on the device by spin-coating (2500 rpm, 80 s) resulting in a layer of  $\approx 1 \ \mu m$  thickness. Two of these devices were combined to form a complete sandwich capacitor with a total PMMA gel layer thickness of  $\approx 2 \ \mu m$ . This assembly was accomplished by pressing together these nanowire layers with the electrical contacts oriented on opposite ends of the device. After assembly, sandwich capacitors were hermetically sealed to exclude moisture using hot glue prior to electrochemical characterization.

#### Structural Characterization.

Scanning electron micrographs were acquired using a FEI Magellan 400 XHR system. Energy dispersive spectroscopic (EDS) images were acquired by the same SEM system with EDS detector (Oxford Instruments, 80 mm<sup>2</sup>, with Aztec software). Accelerating voltages of incident electron beams ranged from 1 kV to 25 kV, and probe currents ranged from 13 pA to 0.8 nA. All SEM specimens were mounted on stainless stubs and held by carbon tape.

#### Mass of $\delta$ -MnO<sub>2</sub>.

A value of 0.78  $\mu$ g/mC was used to determine MnO<sub>2</sub> shell masses from the deposition charge as required for the calculation of  $C_{sp}[105]$ .

## 1.2.3 Cycling Performance of Au@ $\delta$ -MnO<sub>2</sub> core@shell nanowires

Electrodeposition of  $\delta$ -MnO<sub>2</sub> From HMTA-Containing and HMTA-Free Plating Solutions.

Linear arrays of 1800 gold nanowires with lateral dimensions of 275 nm (w)  $\times$  40 nm (h) were prepared on glass surfaces using the LPNE process (Figure 1.2a).[102, 101, 64] Gold nanowires were more than 1.0 cm in length, and were prepared with a wire-to-wire pitch of 5  $\mu$ m (Figure 1.2b).

Au@ $\delta$ -MnO<sub>2</sub> core@shell nanowires were obtained by exposing a 0.90 cm length of this array to a MnO<sub>2</sub> plating solution.  $\delta$ -MnO<sub>2</sub> was electrodeposited in a hemicylindrical layer onto each of the gold nanowires in the array (Figure 1.2c). The same potentiostatic oxidation procedure was used for HMTA-containing plating solutions and HMTA-free solutions. This involved the electrochemical oxidation of Mn<sup>2+</sup> at +0.60 V vs. MSE:[87, 46, 107]

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^-$$
(1.15)

The unbuffered plating solution employed for this reaction had a  $pH = 7.2 \pm 0.2$  and the  $pK_a$  of HMTA is 4.9,[18] so it is deprotonated at this pH. The presence of 10 mM HMTA in the plating solution had a subtle influence on the kinetics of MnO<sub>2</sub> deposition, increasing the reaction rate by 2-5% as determined from current *versus* time traces (Figure 1.3a,b), but the gravimetric loading of MnO<sub>2</sub> per nanowire (Figure 1.3c), estimated from coulometry,[105] is the same within the reproducibility of the experiment.



Figure 1.3: Electrodeposition of  $\delta$ -MnO<sub>2</sub> onto a gold nanowire array. a,b) Current versus time traces for the potentiostatic growth of  $\delta$ -MnO<sub>2</sub> at +0.60V vs. MSE in solutions containing no-HMTA (a), and 10 mM HMTA (b), as described in the text. c) Gravimetric loading of MnO<sub>2</sub> per nanowire (0.90 cm length) based upon the measured coulometry obtained from deposition data like that shown in (a) and (b).

#### Characterization of $Au@MnO_2$ core@shell nanowires.

As previously described, [87, 107] the  $\delta$ -MnO<sub>2</sub> shells obtained by electrodeposition from HMTA-free plating solution onto gold nanowires has a morphology that consists of many concentric, wrinkled MnO<sub>2</sub> sheets wrapped one on top of another (Figure 1.4a-d). In TEM images, these sheets appear to have a thickness in the 2 nm range.[107] In the presence of 10 mM HMTA, in contrast, a more open structure is observed for the shell, characterized by MnO<sub>2</sub> "petals" radiating from the gold nanowire core. The apparent thickness of each MnO<sub>2</sub> petal, however, is much thicker in the 10-30 nm range depending upon the deposition duration (Figure 1.4,e-h). The "envelope" of the MnO<sub>2</sub> shell, plotted in Figure 1.4i, is also larger by 20-30% in spite of the fact that the coulombic loading of MnO<sub>2</sub> per nanowire was approximately the same (Figure 1.3c). This suggests that the porosity of the MnO<sub>2</sub> shell obtained in the presence of HMTA is greater than that which is obtained in its absence.

The improved performance of HMTA Au@ $\delta$ -MnO<sub>2</sub> means little if its cycle stability is degraded. Recently,[88, 87] we have demonstrated that no-HMTA Au@ $\delta$ -MnO<sub>2</sub> nanowires cycled in a PMMA gel electrolyte, containing 1.0 M LiClO<sub>4</sub> in propylene carbonate, retain their specific capacity for 100,000 cycles or more.[87, 88] This extraordinary level of cycle



Figure 1.4: Influence of HMTA on morphology and apparent thickness of the  $\delta$ -MnO<sub>2</sub> shell. a-d) SEM images of Au@MnO<sub>2</sub> core@shell nanowires where the MnO<sub>2</sub> shell was prepared in the absence of HMTA. The deposition time,  $t_{dep}$ , is indicated at left. e-h) Au/MnO<sub>2</sub> nanowires prepared in the presence of HMTA. i) Plot of thickness of the MnO<sub>2</sub> shell outer envelope as a function of  $t_{dep}$ , based upon SEM images of these nanowires. The thickness of the shell envelope is one-half of the total width of the Au@ $\delta$ -MnO<sub>2</sub> nanowires in plan-view SEM images like those shown in (a-h).



Figure 1.5: Cycle stability of  $C_{sp}$  for all-nanowire "sandwich" capacitors containing two 4000 Au@ $\delta$ -MnO<sub>2</sub> (HMTA and no-HMTA) nanowire layers. a,b) Schematic diagrams of the "sandwich" capacitor architecture.[88] c,d) Cyclic voltammograms as a function of scan rate for HMTA and no-HMTA capacitors prepared using  $t_{dep} = 300$  s. e)  $C_{sp}$  versus scan rate for both capacitors. f)  $C_{sp}$  (left axis) and coulombic efficiency (right axis), measured at 200 mV/s, as a function of number of scans.
stability represents a new standard for nanowires. "Sandwich" capacitors were fabricated from two planar layers of Au@ $\delta$ -MnO<sub>2</sub> nanowires ( $t_{dep} = 300$  s), each layer containing 1800 nanowires (Figure 9a,b).[88] In these devices, the two nanowire arrays are separated by 5  $\mu$ m of the PMMA gel electrolyte. Capacitors are hermetically sealed and cycled in laboratory air.  $C_{sp}$  retention by Au@ $\delta$ -MnO<sub>2</sub> nanowires was monitored for 50,000 cycles at 200 mV/s.

## 1.3 Niobium Pentoxide based energy storage

Although  $\delta$ -MnO<sub>2</sub> is cost effective and has a high theoretical capacity, low conductivity still leads to a rapid drop in capacity with increase in scan rate. Niobium pentoxide, Nb<sub>2</sub>O<sub>5</sub>, is a Li<sup>+</sup> intercalation material that exhibits intercalation pseudocapacitance as a consequence of the availability of three accessible redox states for Nb centers: Nb<sup>3+</sup>, Nb<sup>4+</sup> and Nb<sup>5+</sup>.[95, 41, 112, 113, 52, 115]. The Li<sup>+</sup> insertion/deinsertion reaction is written as:

$$Nb_2O_5 + xLi^+ + xe^- \rightleftharpoons Li_xNb_2O_5 \tag{1.16}$$

where x in the range from 1.6 - 2.0 has been reported.[68] The intercalation of Li<sup>+</sup> according to reaction (1) causes a color change of the Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> which has been investigated for applications in electrochromic coatings.[26, 82, 78, 34, 19] Nb<sub>2</sub>O<sub>5</sub> is polymorphic and the three most common polymorphs are T-Nb<sub>2</sub>O<sub>5</sub> (orthorhombic), M-Nb<sub>2</sub>O<sub>5</sub> (monoclinic), and H-Nb<sub>2</sub>O<sub>5</sub> (pseudohexagonal). For Li<sup>+</sup>-based energy storage, Dunn and others[41, 3, 113, 43] have demonstrated that orthorhombic niobium pentoxide (T-Nb<sub>2</sub>O<sub>5</sub>) is capable of exhibiting unusually high capacities coupled with rapid charge-discharge rates, as compared with many other transition metal oxides (Table 1). Gray and coworkers[28] have attributed the high rate capability of T-Nb<sub>2</sub>O<sub>5</sub> to low activation barriers, on the order of a few  $k_BT$ , for Li<sup>+</sup> transport in this material, as measured using nuclear magnetic resonance.

### 1.3.1 Significance of Conductivity

The electrical conductivity,  $\sigma$ , of lithium ion intercalating battery electrode materials such as transition metal oxides (TMOs) such as Li<sub>x</sub>MnO<sub>2</sub>[103, 66, 69, 40, 46] and Li<sub>x</sub>CoO<sub>2</sub>[67, 39, 94] can be strongly dependent upon the value of x.  $\sigma$  is also influenced by the formation of defects, dissolution, and irreversible electrochemical processes, all of these promoted by the stress/strain imposed by lithiation/delithiation cycling.[86, 14, 71] *In-situ* measurement of  $\sigma$ as a function of x and during potential cycling is important for understanding mechanisms of degradation and failure for TMOs and other active materials, but there are few methods for measuring the electrical conductivity of battery electrode materials *in-situ*, particularly for electrodeposited battery materials.

The electrical conductivity,  $\sigma$ , of battery and capacitor electrode materials is a factor determining the energy storage performance of these materials but it is difficult to directly measure *in-situ* particularly for electrodeposited materials. A new approach exploits linear arrays of nanoribbon conductors composed of a battery electrode material. These nanoribbon arrays are prepared using lithographically patterned nanoribbon electrodeposition (LPNE). To demonstrate this approach the  $\sigma$  of orthorhombic phase, T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons is measured *in-situ* in a battery electrolyte as a function of the equilibrium potential and, separately, during repetitive lithiation/delithiation cycling.

## **1.4** Scope of this Dissertation

The important parameters used to evaluate electrochemical energy storage devices are outlined in this chapter. This chapter also presented a study on enhancing the cycle stability of Au@ $\delta$ -MnO<sub>2</sub> based core:shell nanowires and explained the relevant electrochemical techniques used to measure the parameters. In the following chapters, methods to fabricate T-Nb<sub>2</sub>O<sub>5</sub> thin films and nanoribbons will be outlined. These films and nanoribbons will be used to evaluate the energy storage capabilities of T-Nb<sub>2</sub>O<sub>5</sub>, effect of Li<sup>+</sup> intercalation on conductivity of Nb<sub>2</sub>O<sub>5</sub>. Finally, the mechanism of Nb<sub>2</sub>O<sub>5</sub> degradation will be discussed in the final chapter. This dissertation is aimed at gaining in-depth understanding of the electrochemical behavior of electrodeposited Nb<sub>2</sub>O<sub>5</sub>, which can reveal the full potential for commercial use of Nb<sub>2</sub>O<sub>5</sub>, as a high power energy storage material.

## Chapter 2

# Electrophoretic Deposition of Mesoporous Niobium (V) Oxide Nanoscopic Films

## 2.1 Introduction

T-Nb<sub>2</sub>O<sub>5</sub> is most often synthesized by hydrothermal methods[95, 41, 3, 113, 43] and highly dispersed T-Nb<sub>2</sub>O<sub>5</sub> on carbon has demonstrated specific capacities of up to 590 F/g.[43] Other methods for preparing Nb<sub>2</sub>O<sub>5</sub> films include electrospinning followed by thermal annealing [47], spray pyrolysis,[77] sol-gel processing methods,[70, 82, 78] electrospinning,[89] and reactive sputtering.[34] Electrodeposition has hardly been attempted, in spite of the fact that it is an attractive method for both electrochromics and battery/capacitor materials because it promotes an electrically intimate contact with an electrode that can also serve as a current collector. The reason is that electrodeposition of Nb<sub>2</sub>O<sub>5</sub> is difficult: The cathodic electrodeposition of niobium oxides (NbO<sub>x</sub>) is complicated by the very negative reduction potential for Nb<sup>3+</sup> (-1.1 V vs. NHE) which makes disruptive H<sub>2</sub> co-evolution unavoidable in aqueous solutions. Crayston and co-workers[48] circumvented this issue by electrodepositing NbO<sub>x</sub> by the precipitation of niobium ions, immobilized in a thin porous film prepared using sol-gel methods, using electrogenerated OH<sup>-</sup>. Zhitomirsky[116] reported an aqueous cathodic electrophoretic deposition technique for the preparation of Nb<sub>2</sub>O<sub>5</sub> films on Pt electrodes. The mechanism they proposed is based upon the peroxo-precursor method used for titania deposition.[117] Both titanium and niobium salts react promptly with water to form precipitates but dissolution of the precursor salt in dilute hydrogen peroxide at low temperature ( $\approx 2^{\circ}$ C) allows for the formation of a stable peroxo-cation, thought to be Nb(OH)<sub>4</sub>(H<sub>2</sub>O<sub>2</sub>)<sup>+</sup> or NbO<sub>2</sub>(H<sub>2</sub>O<sub>2</sub>)<sup>+</sup>.[116] This complex is hydrolyzed by electrogenerated OH<sup>-</sup> at the cathode formed, for example, by H<sub>2</sub> evolution to produce Nb<sub>2</sub>O<sub>5</sub>.[116] The work of Crayston *et al.*[48] and Zhitomirsky provide the only precedents for Nb<sub>2</sub>O<sub>5</sub> electrodeposition, to our knowledge. However Nb<sub>2</sub>O<sub>5</sub> films have also been obtained by the anodization of electrodeposited niobium metal films,[27] which can be prepared by electrodeposition from molten salts[118] and propylene carbonate or acetonitrile using LiNbF<sub>6</sub> as a precursor.[16]

In this work, we describe a robust method for the electrophoretic deposition (ED) of T-Nb<sub>2</sub>O<sub>5</sub> from NbO<sub>x</sub> colloids. NbO<sub>x</sub> colloids were obtained using a modification of the Zhitomirsky method,[116] involving the rapid injection of niobium salt dissolved in methanol into a cold ( $\approx$ 2°C) hydrogen peroxide solution. Phase pure T-Nb<sub>2</sub>O<sub>5</sub> films, with thicknesses varying from 38 nm to 144 nm, are obtained after calcination at 550°C. The gravimetric specific capacity of these films exceeds the theoretical Faradaic capacity (202 mAh/g) and capacitance values (403 F/g, 1.8 V window) expected for Nb<sub>2</sub>O<sub>5</sub>, due to significant contributions from doublelayer capacitance. The wetted surface area of these films is increased by a porosity of 64 - 72% that forms when H<sub>2</sub> bubbles formed during *ED* are adsorbed and trapped on the nascent Nb<sub>2</sub>O<sub>5</sub> surface. The *T*-Nb<sub>2</sub>O<sub>5</sub> films prepared by *ED* retain up to 70% capacity for 5,000 charge-discharge cycles.



Figure 2.1: Electrophoretic deposition (ED) of T-Nb<sub>2</sub>O<sub>5</sub> film. a). Three-step process flow: Starting with a masked FTO coated glass (left) electrode with area, 6 mm × 6 mm area (0.36 cm<sup>2</sup>), in step 1 potentiostatic ED is carried out from a colloidal NbO<sub>x</sub> solution using two electrodes (FTOglass and counter electrode). The deposited Nb<sub>2</sub>O<sub>5</sub> film is amorphous. In step 2, this *a*-Nb<sub>2</sub>O<sub>5</sub> film is calcined at 550°C for 5 hours, producing T-Nb<sub>2</sub>O<sub>5</sub>. In step 3, Li<sup>+</sup> can be reversibly intercalated into this T-Nb<sub>2</sub>O<sub>5</sub> film. b) SEM image of drop-cast NbO<sub>x</sub> colloid particles on FTO glass showing a dispersion of submicron particles. c) Lower magnification SEM images showing several larger, 500-100 nm diameter colloid particles. d). SEM-derived particle diameter histogram of NbO<sub>x</sub> colloid particles showing the smaller mode - at  $\approx 20$  nm - seen in the dynamic light scattering (DLS) fractogram in (e). e). DLS fractogram showing a bimodal distribution of NbO<sub>x</sub> colloid particles. f). Cyclic voltammograms (2 electrode) at 50 mV/s of aqueous 50 mM H<sub>2</sub>O<sub>2</sub> (gray trace) and the colloidal NbO<sub>x</sub> solution described above (red trace). g). Current versus time plots for potentiostatic ED at -2.0 V (two electrode mode). Four plots are overlaid in this plot, corresponding to four coulombic loadings as indicted, demonstrating the remarkable reproducibility of the ED process.

## 2.2 Experimental Methods

#### 2.2.1 Chemicals and Materials.

Niobium pentachloride (NbCl<sub>5</sub>, 99%), hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub> 30% (w/w) in H<sub>2</sub>O), lithium perchlorate (LiClO<sub>4</sub>, battery grade, dry, 99.99% trace metal basis), propylene carbonate (anhydrous, 99.7%) and fluorine doped tin oxide (FTO) coated glass slide (surface resistivity  $\approx 13 \Omega/\text{sq}$ ) were all used as received from Sigma-Aldrich. FTO was cleaned using a commercial cleaning solution Hellmanex 3 obtained from Hellma Analytics. Positive photoresist (Shipley S1808) and developer (Shipley MF-319) were purchased from Microchem Corporation. Acetone and methanol were used as received from Fisher (ACS certified).

#### 2.2.2 Electrophoretic Deposition of $Nb_2O_5$ .

An aqueous colloidal solution of Nb<sub>2</sub>O<sub>5</sub> nanoparticles was prepared as follows: [116] 135 mg NbCl<sub>5</sub> was dissolved in 4 ml methanol and rapidly injected into 96 ml of 0.052 M H<sub>2</sub>O<sub>2</sub> at  $\approx 2^{\circ}$ C, resulting in a clear colloidal solution. The solution was aged at room temperature for 3 hours at RT before *ED*. Colloid solutions were discarded 10 hours after the rapid injection process. After cleaning (Hellmanex 3 solution for 5 min., Millipore water rinse, air dry), 2 × 1 cm FTO glasses were masked with a positive photoresist layer (Shipley S1808). This was spin-coated at 2500 rpm for 80 s onto the FTO, soft baked at 90°C for 30 minutes, and patterned to produce a square 6 mm × 6 mm FTO exposed region (Figure 2.1a). *ED* was carried out in a 100 mL one compartment two-electrode electrochemical cell, using a Gamry Series G 300 potentiostat. The working electrode was the patterned FTO surface, which was immersed into the aqueous colloidal solution of Nb<sub>2</sub>O<sub>5</sub> nanoparticles, leaving the top edge of the FTO outside the solution for contact with the potentiostat. A platinum foil (1 cm × 2 cm) counter electrode was positioned at a 2 cm distance from the center of the exposed FTO

surface. The deposition was conducted at constant potential of -2.0 V, until the required charge was deposited, as shown in Figure 2.1g. After deposition, all photoresist was removed using acetone and the sample was air dried. The sample was annealed at 550°C for 6 hours, with a 4°C/min temperature ramp.

#### 2.2.3 Electrochemical characterization.

All electrochemical measurements were performed by a one-compartment three-electrode cell using a Gamry Series G 300 potentiostat. Cyclic voltammetry and galvanostatic measurements were conducted in 1.0 M LiClO<sub>4</sub> (battery grade, dry, 99.99%) in dry propylene carbonate inside a N<sub>2</sub> glovebox. 1cm x 1cm Pt foil was used as counter electrode with a Ag/Ag<sup>+</sup> non-aqueous reference electrode (10 mM Ag<sup>+</sup>, DMSO) for the electrochemical measurements. All potentials are quoted with respect to the Li/Li<sup>+</sup> couple,  $E_{Li/Li^+} = -3.045$  V versus normal hydrogen electrode[6] by calibrating the Ag/Ag<sup>+</sup> reference electrode against Li/Li<sup>+</sup> using ferrocene/ferrocenium (Fc/Fc<sup>+.</sup>) in 1M LiClO<sub>4</sub>, PC.[45]

#### 2.2.4 Quartz crystal microbalance (QCM) gravimetry.

The mass of the Nb<sub>2</sub>O<sub>5</sub> deposited on by *ED* was directly determined using QCM. The QCM measurements were performed with a Stanford Research Systems (SRS) QCM200 Quartz Crystal Microbalance Digital Controller, in conjunction with a QCM25 5 MHz Crystal Oscillator equipped with an Au-coated 5 MHz quartz crystal (area =  $1.37 \text{ cm}^2$ ). QCM measures the mass deposited onto the quartz/Au electrode by correlating it to the change in frequency,  $\Delta f$ , according to the Sauerbrey equation.[80]

$$\Delta f = C_f \bullet \Delta m \tag{2.1}$$

The sensitivity factor  $(C_f)$  of the immersed quartz/gold electrode was calibrated by galvanostatically electrodepositing silver from aqueous 0.5 M AgNO<sub>3</sub> + 0.5 M HNO<sub>3</sub> solution, following previously reported methods.[25, 106] The  $C_f$  value obtained for silver deposition was 47.7(±0.8) Hz cm<sup>2</sup>µg<sup>-1</sup>. QCM crystals were cleaned by immersion into piranha solution 3:1, conc. H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>(30%) for 5 minutes, rinsing in water, air drying and then 2 hour vacuum drying. The initial frequency of the pristine crystal was recorded in air, immediately after vacuum drying. The electrode holder containing the crystal was then immersed in the colloidal NbO<sub>x</sub> solution for deposition. After deposition, the crystal was removed from holder, rinsed with water, air dried, and vacuum dried for 2 hours. After drying, the crystal was remounted on the QCM controller, to record the change in frequency for the dried sample after deposition. Mean mass *versus* mean charge produced a slope of 6.18 µg/C, which was used to calculate the dry mass of the *ED* thin film (Figure 2.4d).

#### 2.2.5 Structural Characterization.

Scanning electron micrographs (SEMs) were acquired using a FEI Magellan 400 XHR system. Before imaging, samples were sputter-coated with  $\approx 2$  nm of iridium. Accelerating voltages of incident electron beams ranged from 5 kV to 15 kV, and probe currents ranged from 25 pA to 0.4 nA. All SEM specimens were mounted on stainless stubs and held by carbon tape. Grazing-incidence x-ray diffraction (GIXRD) patterns were obtained using a Rigaku SmartLab x-ray diffractometer employing the parallel beam optics. The x-ray generator was operated at 40 kV and 44 mA with Cu K $\alpha$  irradiation. X-ray photoelectron spectroscopy (XPS) was measured using the AXIS Supra by Kratos Analytical Inc. equipped with monochromatic Al/Ag x-ray source.

#### 2.2.6 Transmission Electron Microscopy.

Aberration-corrected scanning transmission electron microscopy (STEM) was performed on a JEOL Grand-ARM transmission electron microscope equipped with two spherical aberration correctors and a 300 kV cold field emission gun. High angle annular dark filed (HAADF)-STEM images were recorded using a convergence semi angle of 22 mrad, and inner- and outer collection angles of 83 and 165 mrad, respectively.

## 2.3 Results and Discussion

#### **2.3.1** Electrophoretic deposition of $Nb_2O_5$ thin films.

In the cathodic electrodeposition described by Zhitomirsky,[116] the aging of the peroxocation solution for 3 days induces cloudiness and sedimentation in the solution; a consequence of the formation of micron sized NbO<sub>x</sub> particles. We found that such solutions yielded inconsistent results. To resolve this, NbO<sub>x</sub> colloid solutions were obtained by rapidly injecting 125 mM NbCl<sub>5</sub> in methanol into 52 mM H<sub>2</sub>O<sub>2</sub> in water at  $\approx 2^{\circ}$ C. This colloidal solution was then aged for 3 hours at RT. The resulting NbO<sub>x</sub> particles can be directly observed and measured by scanning electron microscopy (SEM) after drop-casting the colloid solution onto FTO glass (Figure 2.1b,c). These colloids are concentrated in the diameter range from 20-30 nm (Figure 2.1d), but larger colloids extending to 1.0  $\mu$ m are also seen in these solutions (Figure 2.1b,c). The SEM analysis of these particles is supported by dynamic light scattering (DLS) data (Figure 2.1e) that shows two prominent modes at  $\approx 20$  nm and 1.0  $\mu$ m.

Cyclic voltammograms (2 electrode) of the FTO-glass working electrode in aqueous  $H_2O_2$ (pH = 7.0) shows virtually no Faradaic current, but in the presence of NbO<sub>x</sub> colloid (pH



Figure 2.2: Scanning electron microscopy (SEM). a-c) As-deposited NbO<sub>x</sub> films at three magnifications, d-f) T-Nb<sub>2</sub>O<sub>5</sub> films after calcination at 550°C for 5 hrs.

= 5.0), a reduction is observed that is attributed to migration of the positively charged NbO<sub>x</sub> colloids and H<sub>2</sub> evolution (HER) coupled with ED of the NbO<sub>x</sub> colloid (Figure 2.1f). Potentiostatic ED at -2 V rapidly produces a steady-state current of 2.5 mA/cm<sup>2</sup> (Figure 2.1g) that decreases gradually with time. ED current versus time data traces for four experiments actually overlay one another (Figure 2.1g), demonstrating the reproducibility of this process. Samples were prepared using one of four total charge values,  $Q_{dep}$ : 300, 500, 1000, and 1500 mC. It should be emphasized that  $Q_{dep}$  encompasses both the charge associated with HER and that of ED.

#### 2.3.2 Structural and compositional characterization.

SEM images of as-deposited NbO<sub>x</sub> films (Figure 2.2a,c) show a mud-cracked topography, and some texturing of the film surface on the  $\approx 100$  nm size scale. These cracks can be attributed to dry shrinkage, as previously reported for Nb<sub>2</sub>O<sub>5</sub> films prepared for electrochromic applications,[4] caused by the contraction of metal oxides upon loss of capillary water. After



Figure 2.3: Cross-sectional TEM for AC-STEM characterization of T-Nb<sub>2</sub>O<sub>5</sub> sample. (a) Crosssection view of a T-Nb<sub>2</sub>O<sub>5</sub> on FTO. EDS elemental maps confirm the presence of Nb in the T-Nb<sub>2</sub>O<sub>5</sub> region. Pt and Ir protecting layers were deposited for the TEM sample preparation. (b) Atomic-resolution STEM image of the T-Nb<sub>2</sub>O<sub>5</sub> layer showing characteristic  $d_{(181)}$ -spacings of 2.45 Å. (c) STEM image of the T-Nb<sub>2</sub>O<sub>5</sub> layer showing a grain boundary, confirming its polycrystalline structure.

Compound	Binding Nb 3d <sub>5/2</sub>	Energy Nb 3d <sub>3/2</sub>	(eV) O 1s	Nb:O <sup>a</sup>	Reference
$T-\mathrm{Nb}_2\mathrm{O}_5$ (SG, $d = 120 \text{ nm}$ )	207.3	210.1	530.6	0.40	[70]
$\frac{Nb_2O_5}{(Nb^o \text{ TO})}$	207.7	210.4	530.4	0.46	[26]
$B ext{-Nb}_2 ext{O}_5$	207.1	209.8	530	n.a.	[20]
a-Nb <sub>2</sub> O <sub>5</sub> (MS-ad, $d = 377$ nm)	207.4	210.1	530.5	0.40	[19]
$Nb_2O_5-600^{\circ}C$ (MS-ta, $d = 355$ nm)	207.1	209.9	530.1	0.40	[19]
$egin{array}{llllllllllllllllllllllllllllllllllll$	207.5	210.2	530.5	0.40	this work
$T-\mathbf{Nb}_{2}\mathbf{O}_{5}$ $d = 50 \text{ nm})$	207.2	209.9	530.1	0.43	"

Table 2.1: Comparison of Observed Photoelectron Binding Energies For  $Nb_2O_5$  Films With Literature Values.

<sup>*a*</sup> Nb:O atomic ratio, <sup>*b*</sup>Abbreviations: SG = sol-gel, TO = thermal oxidation in air at 580°C, MS-ad = magnetron sputtering (as-deposited), MS-ta = magnetron sputtering (calcined at  $600^{\circ}$ C).



Figure 2.4: T-Nb<sub>2</sub>O<sub>5</sub> film characterization. a,b) High resolution XPS spectra of 500 mC T-Nb<sub>2</sub>O<sub>5</sub> and a-Nb<sub>2</sub>O<sub>5</sub> films. The observed chemical shifts are compared with literature values in Table 2.1. c) Powder XRD patterns for as-deposited Nb<sub>2</sub>O<sub>5</sub>, a-Nb<sub>2</sub>O<sub>5</sub>, and T-Nb<sub>2</sub>O<sub>5</sub>, as indicated. d) QCM measurements of the deposited Nb<sub>2</sub>O<sub>5</sub> mass as a function of deposition charge, e). AFM amplitude traces for four T-Nb<sub>2</sub>O<sub>5</sub> films, prepared using 300 mC, 500 mC, 1000 mC, and 1500 mC, as indicated. f) AFM-measured film thickness as a function of deposition charge, g). AFM images of film edges for the same four deposition charges shown in (e).

calcination, deep cracks become filled and a smoother topography is seen for the film surface (Figure 2.2d-f).

A cross-sectional STEM image of a T-Nb<sub>2</sub>O<sub>5</sub> film at low magnification shows several of these cracks (Figure 2.3a). Energy dispersive x-ray spectroscopy (EDS) elemental maps (Fig 3a, bottom) confirm the T-Nb<sub>2</sub>O<sub>5</sub> region, labeled in the STEM cross-section. At higher magnification, the crystallinity of the T-Nb<sub>2</sub>O<sub>5</sub> layer is revealed in atomic-resolution STEM images (Figure 2.3b). In this image, (181) and (18-1) planes are observed together with a measured d-spacing of 2.45 Å. Defects are also observed in these layers, as seen for example in Figure 2.3c where a white dashed-line marks a grain boundary confirming the polycrystalline structure of the *ED*-deposited T-Nb<sub>2</sub>O<sub>5</sub> layer.

The surface chemical composition of ED-as-deposited NbO<sub>x</sub> films and T-Nb<sub>2</sub>O<sub>5</sub> films were



Figure 2.5: Cyclic voltammetry (CV) of T-Nb<sub>2</sub>O<sub>5</sub> films. a-c) CVs at scan rates of 5 mV/s (a), 100 mV/s (b), and 500 mV/s (c), for T-Nb<sub>2</sub>O<sub>5</sub> films prepared using four  $Q_{dep}$  values as indicated. d) Specific capacity,  $C_{sp}$ , calculated from the CVs like those of (a-c). Error bars represent the standard deviation for 3 samples. e,f) Plots of Log(Current) versus Log (scan rate) showing two regimes at slow (5 - 50 mV/s) and fast (100- 500 mV/s) scan rates. Calculated b values using Eq. 2 are tabulated in Table 2.4.

	$Q_{dep}{}^{b}$	Slow scan rates $(5 - 50 \text{ mV/s})$	Fast scan rates $(100 - 500 \text{ mV/s})$
Anodic	300  mC	b = 0.94	b = 0.67
	500  mC	0.82	0.6
	1000 mC	0.8	0.42
	1500  mC	0.79	0.36
Cathodic	300 mC	b = 0.96	b = 0.65
	500  mC	0.89	0.59
	1000 mC	0.76	0.44
	$1500~{\rm mC}$	0.74	0.39

Table 2.2: b-Values<sup>*a*</sup> For Nb<sub>2</sub>O<sub>5</sub> Films as a Function of Deposition Charge.

<sup>*ab*</sup>-value, as defined by Eq. (2). <sup>*b*</sup>Nb<sub>2</sub>O<sub>5</sub> ED deposition charge at a 6 × 6 mm FTO electrode with area 0.36 cm<sup>2</sup>.

assessed by XPS (Figure 2.4a,b, Table 2.1). As-prepared films showed binding energies (B.E.) for Nb  $3d_{5/2}$ , Nb  $3d_{3/2}$ , and O 1s at 207.5 eV, 210.3 eV, and 530.5 eV, respectively - all within 0.1 eV of the B.E. reported for amorphous Nb<sub>2</sub>O<sub>5</sub> (Table 2.1).[19] The Nb:O stoichiometry of these films was 0.40, also as previously reported.[19] B.E. values of Nb  $3d_{5/2}$ ,  $3d_{3/2}$  peaks for calcined films slightly decreased to 207.4 and 210.2 eV (Figure 2.4a), respectively while O 1s at 530.4 eV, decreased by 0.2 eV (Figure 2.4b). Similar B.E. decreases for metal oxides have been attributed to a decrease in the bandgap of the oxide caused by the creation of oxygen vacancies during annealing.[19] The O 1s photoelectron envelope can be deconvoluted into a lower B.E. component assigned to niobium oxide ( $\approx 532.2 \text{ eV}$ ), and the higher B.E. component (530.5 eV) assigned to OH<sup>+</sup> and peroxo-complex species which contribute a significant shoulder on the low B.E. side of the O 1s.[19] However these species decompose upon calcination leading to a dramatic reduction in the intensity of this shoulder (Figure 2.4b).

Grazing incidence x-ray diffraction (GIXRD) data was acquired for three films: 1) A spincoated colloidal solution, 2) An as-deposited NbO<sub>x</sub> film, and, 3) A calcined Nb<sub>2</sub>O<sub>5</sub> films (550°C × 5 hrs in air). Samples 1 and 2 showed no crystallinity (line at 38° and 45° are assigned to the gold substrate), but sample 3 produced reflections all of which were assignable to orthorhombic, T-Nb<sub>2</sub>O<sub>5</sub> (JCPDS 30-873). Scherrer analysis[72] of the line widths affords an estimate of the grain size for these films of 19.3 nm, calculated using the (001), (181) and (002) reflections. Quartz crystal microbalance gravimetry (QCM) was used to measure the mass of the dried films which increased in direct proportion to the coulombic loading,  $Q_{dep}$ , yielding a slope of 6.18  $\mu$ g/C (Figure 2.4d). The film thickness, measured by AFM, also increased in proportion to  $Q_{dep}$  (Figure 2.4e,f). The range of  $Q_{dep}$  values explored in this study corresponded to film thickness ranging from 38 nm (300 mC) to 144 nm (1500 mC).

### 2.3.3 Cyclic voltammetry (CV).

The electrochemical properties of T-Nb<sub>2</sub>O<sub>5</sub> film half-cells were investigated in dry, 1.0 M LiClO<sub>4</sub>, propylene carbonate electrolyte using a three-electrode cell with a non-aqueous Ag/Ag<sup>+</sup> reference electrode and Pt counter electrodes. In the following discussion and figures, we convert these potentials to Li/Li<sup>+</sup> (+3.04 V vs. NHE) for convenience. Cyclic voltammograms (CVs) for a 1.8 V window from 1.5 V to 3.3 V versus Li/Li<sup>+</sup> are shown at scan rates of 5 mV/s, 100 mV/s, and 500 mV/s for all four films (Figure 2.5a,b,c).

The theoretical Faradaic capacity of Nb<sub>2</sub>O<sub>5</sub> is 726 C/g assuming x = 2.0 in Eq. (1). [68]. This corresponds to a specific capacitance,  $C_{sp} = 202 \text{ mAh/g}$  or 403 F/g for the 1.8 V window measured in Figure 2.5. All four T-Nb<sub>2</sub>O<sub>5</sub> films produce  $C_{sp}$  values considerably higher than this at 5 mV/s, ranging from 600 F/g to 1250 F/g (Figure 2.5d). As shown in Figure 2.5d,  $C_{sp}$  is rapidly lost with increasing scan rate above 5 mV/s. But the retention of capacity at higher scan rates if very good, with the thinnest of these films ( $Q_{dep} = 300 \text{ mC}$ , d = 38nm) exhibiting the theoretical Faradaic capacity at a scan rate of 500 mV/s (Figure 2.5d). These data require that the Faradaic capacity is augmented by a non-Faradaic, double-layer capacity for these films.

A closer look at the CV data allows the influence of Li<sup>+</sup> transport on  $C_{sp}$  to be better understood. The cyclic voltammetric peak current,  $i_p$ , shows a scan rate,  $\nu$ , dependence given by:[6]

$$i_p = a\nu^b \tag{2.2}$$

where a is a constant and the value of b provides insight into whether diffusional transport limits the measured  $i_p$ . b = 0.5 signifies a diffusion-controlled current whereas b = 1.0 is produced by diffusion-independent processes which could be non-Faradaic (e.g. capacitive charging) or Faradaic (e.g. pseudo-capacitive), provided ion transport is rapid enough.[6] In

Material	Synthesis Method	Film Thickness	Voltage Window	Sp. Energy (Wh/kg)	Sp. Power (kW/kg)	Ref
$Nb_2O_5@CNTs$	HT	$3 \ \mu { m m}$	1.5 V	450-355	1.1-8.5	[95]
$Nb_2O_5@CDC$	HT	$70~\mu{ m m}$	1.8 V	158-130	0.9-3.6	[113]
T-Nb <sub>2</sub> O <sub>5</sub>	HT	$40~\mu{\rm m}$	1.8 V	252-87	0.3-86	[3]
ox. $Nb_2CT_x$	HT	$50 \ \mu { m m}$	1.8 V	133-30	0.13-6	[112]
np $Nb_2O_5$	A&A	$250~\mu{\rm m}$	2.0 V	475-322	0.1-1.6	[75]
$o-Nb_2O_5@C$	HT	$50 \ \mu { m m}$	2.0 V	278-117	2-100	[42]
$Nb_2O_5 nb$ $T-Nb_2O_5$	HT	15  nm	1.8 V	450-150	0.2-180	[96]
$Q_{dep}{=}500~{ m mC}$	$\mathbf{ED}$	60 nm	1.8 V	770-486	9-90	this work
$Q_{dep}{=}1000~{ m mC}$	$\mathbf{ED}$	100 nm	1.8 V	421-84	9-90	this work

Table 2.3: Literature Review of Energy Storage Metrics for  $Nb_2O_5$  Films.<sup>*a*</sup>

<sup>*a*</sup>Abbreviations: ox. = oxidized, np = nanoporous, nb = nanobelts, A&A = anodization and thermal annealing, HT = hydrothermal, ED - electrophoretic deposition, CNT = carbon nanotubes, CDC = carbide-derived carbon, T-Nb<sub>2</sub>O<sub>5</sub> = orthorhombic Nb<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>CT<sub>x</sub> = 2D niobium carbide MXene, *o*-Nb<sub>2</sub>O<sub>5</sub>@carbon = orthorhombic-Nb<sub>2</sub>O<sub>5</sub>@carbon core-shell microspheres. the thinnest T-Nb<sub>2</sub>O<sub>5</sub> films examined here ( $Q_{dep} = 300 \text{ mC}$ , d = 38 nm), b approaches 1.0 at slow scan rates (5 - 50 mV/s, Figure 2.5e,f) suggesting that the diffusion of Li<sup>+</sup> within these films is sufficiently rapid to enable all Nb centers to be charge compensated on the time scale of a single voltammetric scan. For example, at  $\nu = 20 \text{ mV/s}$ ,  $\tau_{CV} \approx RT/F\nu =$ 1.3 s,[6] where R, T, and F are the gas constant, the temperature, and the Faraday constant. Since  $n \approx 1.0$  (Figure 2.5e,f), the film is behaving pseudo-capacitively implying that Li<sup>+</sup> is able to access the entire 38 nm T-Nb<sub>2</sub>O<sub>5</sub> film. This requires that  $D_{Li^+} \geq d^2/2\tau_{CV} = 6 \times$  $10^{-12} \text{ cm}^2/\text{s}$ .[6]. As d increases from 38 nm to 140 nm ( $Q_{dep} = 1500 \text{ mC}$ ), b decreases from ~0.95 to ~0.75 in this slow scan rate regime, suggesting that Li<sup>+</sup> diffusion is no longer able to access all Nb centers and the Faradaic current is increasing diffusion-limited (b = 0.5).

At scan rates of 100 mV/s and above, T-Nb<sub>2</sub>O<sub>5</sub> films of all four thickness show lower *b* values in the 0.36 - 0.67 range (Figure 2.5e,f). Notably, *b* values even lower than 0.5 are observed for the thickest films indicating that uncompensated ohmic resistance and/or rate-limiting electron transfer act to limit the current in addition to Li<sup>+</sup> diffusion.[6] In this fast scan rate regime, thinner films are storing charge both capacitively (n = 1.0) and by accessing Nb centers via Li<sup>+</sup> diffusion (n = 0.5), but the entire film thickness is not accessible to Li<sup>+</sup> on these time scales. For example, if Li<sup>+</sup> transport is diffusion-controlled within the 38 nm film, this requires that  $D_{Li^+} \leq d^2/2\tau_{CV} = 1.4 \times 10^{-10}$  cm<sup>2</sup>/s. Thus, the cyclic voltammetric behavior of the 38 nm sample can be understood if  $D_{Li^+}$  satisfies this inequality:  $6 \times 10^{-12}$ cm<sup>2</sup>/s  $< D_{Li^+} < 1.4 \times 10^{-10}$  cm<sup>2</sup>/s, or approximately  $10^{-11}$  cm<sup>2</sup>/s. This  $D_{Li^+}$  value is in the range of other transition metal oxides used for Li<sup>+</sup> storage.

At  $\nu = 500 \text{ mV/s}$  the cyclic voltammograms for all four films converge (Figure 2.5c). This behavior is expected if  $\tau_{CV}$  limits Li<sup>+</sup> diffusion to distances smaller than the thickness of all four films. In this limit, Li<sup>+</sup> is able to access the same volume, and same number of Nb centers, for all four films. At 500 mV/s,  $\tau_{CV} \approx 50$  ms.

As already noted, the  $C_{sp}$  measured by cyclic voltammetry at slow scan rates is higher than



Figure 2.6: Deconvolution of insertion and non-insertion currents in a cyclic voltammogram using the method of Conway.[55] a). CV at 5 mV/s for a 500 mC T-Nb<sub>2</sub>O<sub>5</sub> film. b). CV for the same film at 100 mV/s, c). Plot of total  $C_{sp}$ , together with the insertion and non-insertion capacities as a function of scan rate,  $\nu$ . The dash blue line marks the theoretical Faradaic capacity, 403 F/g for a 1.8 V window.

the theoretical Faradaic  $C_{sp}$  value of 403 F/g (1.8 V window), and this implies that non-Faradaic energy storage contributes substantially to the measured  $C_{sp}$ , but what experiment evidence supports the existence of this double-layer capacity? A version of Eq. (3) can be used to resolve the total current into insertion and non-insertion components, the latter of which includes double-layer charging as well as the Faradaic capacity of the  $T-Nb_2O_5$ surface.[55, 92, 10] The total current at any potential and scan rate,  $\nu$ , can be written as:[55, 92, 10]

$$i(\nu) = k_1 \nu + k_2 \nu^{1/2} \tag{2.3}$$

where the first term accounts for the non-insertion current (i.e., non-diffusion controlled), the second term is the insertion current (diffusion-controlled), and  $k_1$  and  $k_2$  are scan rate independent constants. A plot of the quotient  $(i(\nu)/\nu^{1/2})$  versus  $\nu^{1/2}$  at each potential point yields the values of  $k_1$  and  $k_2$  as the slope and intercept, respectively. [55, 92, 10] Application of this deconvolution algorithm to a 500 mC *T*-Nb<sub>2</sub>O<sub>5</sub> film (Figure 2.6) allows the insertion and non-insertion currents to be plotted separately, together with the total current (Figure 2.6a,b). At  $\nu = 5$  mV/s, a large non-insertion current is observed that is similar in magnitude to the insertion current (Figure 2.6a) and at 100 mV/s, the noninsertion capacity dominates (Figure 2.6b). The fraction of the total capacity,  $C_{sp}$ , comprised by insertion decreases smoothly with  $\nu$  from 55% at 5 mV/s to 19% at 100 mV/s (Figure 2.6c). This analysis suggest that a large non-insertion capacity that rivals or exceeds the insertion capacity operates in these ED T-Nb<sub>2</sub>O<sub>5</sub> films, providing a mechanism for this material to achieve a total  $C_{sp}$  value that is up to twice the theoretical Faradaic value.

#### 2.3.4 Galvanostatic charge/discharge for cycle stability.

Galvanostatic charge/discharge curves for T-Nb<sub>2</sub>O<sub>5</sub> films, evaluated at 5 - 50 A/g, show appreciable capacity for these films even at 50 A/g (Figure 2.6a-c). For example, 300 mC films (d = 38 nm) produce  $C_{sp}$  approaching ~ 300 mAh/g whereas 1000 mC and 1500 mC films (100, and 140 nm) show  $C_{sp}$  of 40-60 mAh/g at a 50 A/g rate. (Figure 2.6b). For the 500 mC sample (d = 60 nm),  $C_{sp}$  exceeds 400 mAh/g at 10 A/g, which translates to an energy density of >700 Wh/kg, at a power density of 18 kW/kg (Figure 2.6c). As indicated in Figure 2.6c, the two thinnest films exceed the theoretical Faradaic capacity of Nb<sub>2</sub>O<sub>5</sub> of 202 mAh/g even at 50 A/g. As discussed in greater detail below, this requires the participation of non-Faradaic charge storage in the form of double-layer charging.

The cycle stability of charge storage is critically important for all technological applications of energy storage materials. In prior work (Table 2.3), Zhou[96] reported Nb<sub>2</sub>O<sub>5</sub> nanobelts (15 × 60nm in width) produced  $C_{sp}$  values of 50 mAh/g and showed virtually no fade for 50 cycles. Zhang and coworkers[61] demonstrated Nb<sub>2</sub>O<sub>5</sub> nanoparticle/CNT composites that demonstrated 128 mAh/g at a 5 A/g rate for 2000 cycles with 95% retention of this capacity. Extraordinary cycle stability of T-Nb<sub>2</sub>O<sub>5</sub> nanoparticle-decorated carbon fibers was reported by Yun and coworkers[85] who achieved  $C_{sp}$  values in the range from 240 - 356 F/g (0.5 - 10 A/g) and cycle stabilities to 70,000 cycles, unfortunately, at an unspecified rate. Dunn and



Figure 2.7: Galvanostatic charge/discharge and assessments of cycle stability. a,b) Galvanostatic charge-discharge curves for rates of 5A/g (a) and 50 A/g (b). c). Measurements of specific capacity for all four film thicknesses at five galvanostatic rates ranging from 5 A/g to 50 A/g. d) Cycle stability of  $C_{sp}$  for galvanostatic charge/discharge across 500 cycles. e) Cycle stability of  $C_{sp}$  for cyclic voltammetric charge/discharge at 200 mV/s across a 1.8 V window and 5000 cycles.

Charge	Mass	Thickness (nm)	$C_{sp} \text{ at} 5 \text{ mV/s} (\text{F/g})$	$C_{sp}$ at 5 A/g (mAh/g)	$CV cycles^a$ at 200 mV/s	Galvanostatic Cycles <sup>b</sup> at 10 A/g
300 mC	$1.85~\mu{\rm g}$	38	$1255.7 \pm 375.2$	$560.5 \pm 167.5$	1200	200
500  mC	$3.09 \ \mu { m g}$	60	$977.2 \pm 45.7$	$424.6 \pm 19.9$	2800	>500
1000  mC	$6.18~\mu{\rm g}$	102	$892.7 \pm 133.7$	$251.5 \pm 37.7$	2000	300
$1500 \mathrm{mC}$	9.27 $\mu {\rm g}$	144	$679.0 \pm 56.0$	$230.0 \pm 18.9$	1000	>500

Table 2.4: Metrics for T-Nb<sub>2</sub>O<sub>5</sub> Films Synthesized by ED.

 $^a$  Cycles to 20% capacity fade.

<sup>b</sup> Cycles to 20% capacity fade.

coworkers[95] studied the same composite system and reported 500 cycles with 5% fade at 380 C/g (80 mAh/g) cycled at a 20 C rate. These examples, which are representative of the best in terms of demonstrating excellent cycle stability of Nb<sub>2</sub>O<sub>5</sub>, all involve nanostructures or dispersions of Nb<sub>2</sub>O<sub>5</sub> nanoparticles on a conductive support.

T-Nb<sub>2</sub>O<sub>5</sub> films represent a much different type of sample. Since voltage cycling and galvannostatic cycling can produce very different results for the same material, we investigated both. All four films were cycled at 10/g for 500 cycles (Figure 2.6d) and, with different samples, across 1.8V at 200 mV/s for up to 10,000 cycles (5000 shown in Figure 2.6e). These are amongst the highest rates at which stability has been tested for this material, to our knowledge. Galvannostatic cycling under these conditions often resulted in little measurable capacity fade (Figure 2.6d,  $Q_{dep} = 1500$ , 1000, and 500 mC samples), but significant fade (55%) was also seen for some samples (e.g., Figure 2.6d,  $Q_{dep} = 300$  mC). These trends are representative of a larger number of samples examined in this study. T-Nb<sub>2</sub>O<sub>5</sub> films exhibited significantly better stability in CV cycling (Figure 2.6e) where films retained in excess of 60% of their initial  $C_{sp}$  to 5,000 cycles, and more than 40% to 10,000 cycles.



Figure 2.8: T-Nb<sub>2</sub>O<sub>5</sub> film porosity. a,b). Cross-sectional images of a 140 nm T-Nb<sub>2</sub>O<sub>5</sub> film prepared with  $Q_{dep} = 1500$  mC. The porosity of T-Nb<sub>2</sub>O<sub>5</sub> films prepared by ED of 72% - 64% is attributed to voids within the bulk of the T-Nb<sub>2</sub>O<sub>5</sub> film seen in these high angle annular dark field (HAADF)-STEM images. c). Calculated porosity *versus* thickness for T-Nb<sub>2</sub>O<sub>5</sub> films, derived from AFM measurements of thickness and QCM measurements of the mass of each film.

#### **2.3.5** Mesoporosity in ED T-Nb<sub>2</sub>O<sub>5</sub> films.

The nanometer-scale thicknesses of the T-Nb<sub>2</sub>O<sub>5</sub> film studied here precluded the measurement of specific surface areas using the BET method. But porosity data were acquired directly, by measuring the apparent density of the film,  $\rho_{expt}$ , based upon the AFM-measured film thickness, d, and the QCM-measured film dry mass, m. In conjunction with the known density of Nb<sub>2</sub>O<sub>5</sub>,  $\rho_{theor}$ , a porosity is obtained (Figure 2.7c):

$$porosity = 1.0 - \frac{\rho_{expt}}{\rho_{theor}} \tag{2.4}$$

The measured values - ranging from 72% for the 300 mC (d = 38 nm) film to 64% for the 1500 mC (140 nm) film - are surprisingly large.

This porosity can be directly imaged by STEM in cross-sectional thin sections of these films (Figure 2.8a,b). These images show many spherical voids (dark regions in these dark field



Figure 2.9: Ragone plot for comparison of the half-cell performance for T-Nb<sub>2</sub>O<sub>5</sub> films prepared using *ED* with literature results.

images) within the *ED* T-Nb<sub>2</sub>O<sub>5</sub> matrix. These voids range in diameter from 1 - 10 nm where smaller voids (dia. 1-2 nm) are uniformly distributed, but larger voids (8-10 nm) tend to form clusters (one of these is shown in Figure 2.7b). This mesoporosity provides an explanation for the large non-insertion capacities demonstrated in Figure 2.6. Both the double-layer capacity and the surface Faradaic capacities are proportional to the wetted surface area of the film.

How do these voids form? Our hypothesis is that hydrogen nanobubbles that co-evolve during the ED process (macroscopic H<sub>2</sub> bubbles are also seen on the electrode surface during ED), adhere to the nascent NbO<sub>x</sub> film and are covered and encapsulated by NbO<sub>x</sub> colloids during the ED growth process. Confirmation of this mechanism must await further experimentation, however if this mechanism is correct, it could provide a means for controlling the mesoporosity of these films by adjusting the rate of H<sub>2</sub> evolution during the ED process.

## 2.4 Summary

The electrochemical preparation of high quality, crystalline T-Nb<sub>2</sub>O<sub>5</sub> thin films can be achieved using the ED process described here. This method affords control of film thickness from 38 nm to 140 nm. Moreover, these ED T-Nb<sub>2</sub>O<sub>5</sub> films achieve capacities for Li<sup>+</sup> storage of  $\approx$ 1200 F/g at 5 mV/s (1.8 V window) and 610 F/g at 100 mV/s that exceed the theoretical Faradaic capacities for this material (403 F/g), and are unprecedented to our knowledge. These exceptional  $C_{sp}$  values are attributed to a significant porosity of  $\approx$ 70% that enables a large double-layer capacity that is 50% of  $C_{sp}$  at 5 mV/s, and 80% at 100 mV/s. This capacity is sustainable for many charge-discharge cycles, with 500 mC films retaining a  $C_{sp}$ of 350 F/g to 5000 cycles. A similar trend is observed in the galvanostatic charge-discharge, where high energy densities of  $\approx$ 700 Wh/kg are obtained at power densities as high as 18 kW/kg.

## Chapter 3

# In-Situ Electrical Conductivity of Lithium Niobium Pentoxide: Influence of Lithiation State and Repetitive Cycling

## 3.1 Introduction

In-situ measurements of  $\sigma$  for battery electrode materials were first described in the early 1990's. A version of the method employed in the present study was first described by Baudais and Dahn[7] who evaporated WO<sub>3</sub> films onto two aluminum electrodes patterned on glass. The film resistance was then obtained by analyzing the current transients generated by an applied potential step between these two aluminum electrodes. Uchida and coworkers[66] deposited Li<sub>(1-x)</sub>Mn<sub>2</sub>O<sub>4</sub> using an electrostatic spray deposition process onto an interdigitated metal electrode that was then used to measure *in-situ* conduction; a strategy similar to that employed here. More recently, Sauvage *et al.*[81] used a similar approach to investigate the *in-situ* conductivity of LiCoO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> films prepared by pulsed laser deposition (PLD). A different approach described by Wang, Appleby, and Little[90, 91] involved the embedding nickel screen electrodes in solid state batteries in order to directly measure the electrical resistivity of these systems *in-situ*. Prior measurements of  $\sigma$  have focused on films prepared by non-electrochemical means - evaporation, spray deposition, PLD.[7, 66, 81] All of these methods allow the material of interest to be deposited directly onto an insulating surface within the gap between two measurement electrodes as required for the conductivity measurement. This is not possible for electrodeposited materials because an electrode is required to effect the electrodeposition process and this electrode invariably interferes with the conductivity measurement.

The most common tool used for probing the electronic conductivity of battery electrode materials *in-situ* is electrochemical impedance spectroscopy (EIS) in which the resistive and capacitive components of the complex impedance are measured as a function of frequency, often across many orders of magnitude from < 1 Hz to  $10^5$  Hz.[44, 74, 99, 11, 119, 67] EIS is applicable to battery electrode material prepared by any technique including electrodeposition. But an EIS frequency spectrum is not readily translated into a numerical measurement of the electrical conductivity of the battery electrode material for three reasons: 1). Battery active materials are often dispersed on highly conductive current collectors that interfere with quantitative interpretation of the EIS data, 2). The precise dimensions of the battery electrode material through which charge is conducted are often not well defined, and, 3) the resistance (or conductance) of a battery electrode is difficult to deconvolve from the total impedance using an equivalent circuit model that may contain multiple circuit elements including capacitors, ionic resistors, and other contributions. EIS does provide qualitative information on the change in conductance of a battery material as a function of potential, lithiation state, and during cycling.[44, 74, 99, 11, 119, 67].

Recently[46] we adapted the method of Sauvage *et al.*[81] to the *in-situ* measurement of  $\sigma$  for electrodeposited  $\delta$ -Li<sub>x</sub>MnO<sub>2</sub> which demonstrated an increase in  $\sigma$  by up to one order of magnitude upon lithiation to x = 1. This approach is made possible by performing the conductivity measurement on an array of nanoribbons instead of a film.[46] Nanoribbons of  $\delta$ -MnO<sub>2</sub> with controllable dimensions (height  $\times$  width  $\times$  length) were patterned[46] on glass using lithographically patterned nanoribbon electrodeposition (LPNE)[102, 101, 64] (Figure 3.1) which provides for the removal of the electrode in the last step of the process. Here this method is used for the *in-situ* measurement of  $\sigma$  for Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> as a function of x and during extending lithiation/delithiation cycling of these nanoribbon to 3000 cycles. Electrophoretic deposition (EPD) instead of conventional electrodeposition is used to prepare the Nb<sub>2</sub>O<sub>5</sub> nanoribbons.[37] Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> is capable of storing up to 1 electrons per Nb atom (corresponding to x = 2) resulting in specific capacities,  $C_{sp}$ , of 200 mAh/g:[43, 108, 113, 17, 8, 3, 92, 28, 37, 59]

$$Nb_2O_5 + xLi^+ + xe^- \rightleftharpoons Li_xNb_2O_5 \tag{3.1}$$

Relative to other Transition metal oxides (TMOs),  $T-\text{Li}_x\text{Nb}_2\text{O}_5$  exhibits faster lithium ion transport allowing  $C_{sp}$  to be retained at high charge/discharge rates of up to 100 C and for relatively thick films (> 10  $\mu$ m).[43, 108, 113, 17, 8, 3, 92, 28]

### **3.2** Experimental Methods

#### **3.2.1** Chemicals and Materials.

Niobium pentachloride (NbCl<sub>5</sub>, 99%), hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30% (w/w) in H<sub>2</sub>O), lithium perchlorate (LiClO<sub>4</sub>, battery grade, dry, 99.99% trace metal basis), propylene carbonate (anhydrous, 99.7%) and Nochromix powder were all used as received from Sigma-



Figure 3.1: A nanoribbon array platform for the direct, *in-situ* measurement of electrical conductivity. a). An array of nanoribbons are fabricated using lithographically patterned nanoribbon electrodeposition, LPNE (actual arrays contained 200 nanoribbons). Gold electrical contacts isolate a  $\approx 10 \ \mu$ m length of these nanoribbons, and is insulated from the electrolyte by a thick, hard-baked photoresist layer. This system operates in two modes: b). In *equilibration mode*, a three-electrode potentiostat is used in conjunction with a reference electrode and a counter electrode to adjust the equilibrium potential,  $E_{eq}$ , of the nanoribbon array thereby establishing a known and reproducible lithiation state for this system (in the case of Li<sup>+</sup> intercalation). c). In *measurement mode*, the potentiostat is replaced with a source meter (e.g. Kiethley 2400) that measures the resistance of the nanoribbon array using a mV scale DC applied voltage. Alternating equilibration with measurement permits the electrical conductivity of the nanoribbons to be measured as a function of  $E_{eq}$ .



Figure 3.2: LPNE fabrication of a 200 nanoribbon array platform for the *in-situ* measurement of electrical conductivity for  $\text{Li}_x \text{Nb}_2 \text{O}_5$ . a). Process flow: Step 1 - a 60 nm gold film is evaporated on a glass substrate, Step 2 - a photoresist (PR) layer is deposited, Step 3 - the PR layer is photopatterned, Step 4 - Gold is removed by etching; amorphous  $a\text{-Nb}_2\text{O}_5$  is electrophoretically (*ED*) deposited (see (b)), Step 5 - PR and gold are removed, exposing  $a\text{-Nb}_2\text{O}_5$  nanoribbon array, Step 6 - thermal annealing (blah 6 blah hrs), Step 7 - gold film to be used for contacts is again deposited, Steps 8,9 - a PR layer is deposited, and photopatterned, Step 10 - PR and gold are removed by dissolution and etching to expose a  $T\text{-Nb}_2\text{O}_5$  nanoribbon array with gold electrical contacts insulated by PR. b). Schematic illustration of the *EPD* of a Nb}2O\_5 colloid at an LPNE template.

Aldrich. Sodalime glass slides were bought from VWR and cleaned by immersing into Nochromix solution for 24 hours. Positive photoresist (Shipley S1808) and developer (Shipley MF-319) were purchased from Microchem Corporation. Acetone and methanol were used as received from Fisher (ACS certified). Platinum wire (diamaeter 0.5mm) was obtained alfa aesar. Glassy carbon rod (SPI-Glas 22 Glassy Carbon Rod 10mm length and 2mm diameter) were obtained from SPI supplies. Quartz crystal microbalance crystals (1" diameter, 5 MHz frequancy, AT-cut quartz crystal with gold/chrome working area of 1.33 cm<sup>2</sup>) were obtained from Stanford Research Systems.

#### **3.2.2** T-Nb<sub>2</sub>O<sub>5</sub> Nanoribbon Electrophoretic Deposition (ED).

Deposition of T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons was achieved by modification of the LPNE method (Figure 3.1).[64] First, 60 nm layer of gold was thermally evaporated on a clean 1" × 1" glass slide. The slides were then spin coated with positive photoresist (PR, Shipley S1808) and baked at 90°C for 30 min. The PR layer was then photopatterned using a chromium/quartz contact mask (figure A.1) in conjunction with a 365 nm UV light source for 2 s, using a shutter and alignment stage (Newport, 83210i-line). The pattern shown in figure A.1a, consists of 200 exposed rectangles of 1.8 cm length and 4  $\mu$ m width, which leads to the formation of a parallel array of nanoribbons of length 1.8 cm spaced laterally by 4  $\mu$ m. The exposed sample was developed by stirring the sample in MF-319 developer for 20 s (Figure 3.1d). The exposed gold beneath the exposed photoresist was etched for 45 s with aqueous KI/I<sub>2</sub> solution (4 g KI and 2 g I<sub>2</sub> dissolved in 80 ml of H<sub>2</sub>O). The etching process removed the gold, as well as created a trench by overetching the gold beneath the photoresist, as shown in Figure 3.2a, step 4. The 60 nm thick gold surface acts as the nanoelectrode for electrophoretic deposition of NbO<sub>x</sub> nanoparticles.

Details of the EPD procedure can be found in our previously published report.[37] In

short, the colloidal solution used for deposition of NbO<sub>x</sub> nanoparticles was prepared by rapid injection of 135 mg NbCl<sub>5</sub> dissolved in 4 mL methanol, into 95 mL of 0.052 M H<sub>2</sub>O<sub>2</sub> at 2°C. The depositions were conducted at the constant potential of -2.0 V in a two electrode configuration, with the patterned gold electrode as the working electrode and a platinum foil (1 × 2 cm) as the counter electrode. After *EPD*, the photoresist layer is dissolved away using acetone and the gold remaining is etched away using the KI/I<sub>2</sub> solution mentioned above. The remaining nanoribbon on glass substrate (Figure 3.2a, step 6) is annealed at 600°C for 6 hours (with 4°C ramp rate) leading to the formation of T-Nb<sub>2</sub>O<sub>5</sub> nanoribbon. Electrical contacts for electrochemical measurements are then prepared by first evaporating 60 nm of glod on top of the wires (Figure 3.2a, step 7). Then a photoresist layer is coated on the gold and photopatterned using a contact mask as shown in Figure A.1b, creating a gap with a width of 10  $\mu$ m (Figure 3.2a, step 9). The exposed gap is etched to create the final device architecture (Figure 3.2a, step 10) consisting of 200 nanoribbons extending across the 10  $\mu$ m gap between two gold electrode contacts. Finally, acetone is used to remove photoresist from the gold to expose the surface of these contacts.

#### **3.2.3** Electrochemical characterization.

All electrochemical measurements were performed by a one-compartment three-electrode/ two electrode cell using a Gamry Series G 300 potentiostat. Cyclic voltametry and chronoamperometry were conducted in 1.0 M LiClO<sub>4</sub> (battery grade, dry, 99.99%) in dry propylene carbonate (PC) inside a N<sub>2</sub> glovebox. Both the gold contacts were connected to the working electrode for cyclic voltammetry and chronoamperometry experiments (Figure 3.6). Glassy carbon rod (4 mm in diameter and 1 cm in length) was used as counter electrode with a Platinum (Pt) wire pseudoreference electrode for the electrochemical measurements. Pt pseudoreference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple (shown in Figure A.2) after the completion of each experiment, in the same cell used for the rest of the experiment. All potentials are quoted with respect to the Li/Li<sup>+</sup> couple,  $E_{Li/Li^+} = -3.045$  V versus normal hydrogen electrode[6] by converting the potential vs Fc/Fc<sup>+.</sup> to Li/Li<sup>+</sup> (Figure A.2).[45] All conductivity measurements were performed by first, equilibrating the nanoribbon at the required potential for 60s (chronoamperometry) (Figure 8a). Second, working electrode was connected to gold pad on one side of the gap and counter/reference electrode were connected to the gold pad on the other side of the 10  $\mu$ m gap (Figure 3.1c). Subsequently I-V measurements were conducted in a 20 mV potential window at sweeping rate of 0.5 mV/s (Figure 3.8b).

#### 3.2.4 Structural Characterization.

Scanning electron micrographs (SEMs) were acquired using a FEI Magellan 400 XHR system. Before imaging, samples were sputter-coated with  $\approx 3$  nm of Iridium. Accelerating voltages of incident electron beams ranged from 10 kV to 15 kV, and probe currents ranged from 50 pA to 0.4 nA. All SEM specimens were mounted on stainless stubs and held by carbon tape. Grazing-incidence x-ray diffraction (GIXRD) patterns were obtained using a Rigaku SmartLab x-ray diffractometer employing the parallel beam optics. The x-ray generator was operated at 40 kV and 44 mA with Cu K $\alpha$  irradiation. Atomic force microscopy (AFM) images were acquired using an Asylum Research, MFP-3D AFM equipped with Olympus AC160TS tips in ambient laboratory conditions.

# 3.2.5 X-ray photoelectron specta (XPS) of Lithiated and De-Lithiated $T-Nb_2O_5$ nanoribbons.

All XPS spectra were measured using the AXIS Supra by Kratos Analytical Inc., equipped with monochromatic Al/Ag x-ray source. The oxidation state Nb in lithiated T-Nb<sub>2</sub>O<sub>5</sub> was found out to be +4 and de-lithiatede T-Nb<sub>2</sub>O<sub>5</sub> was +5, using XPS of T-Nb<sub>2</sub>O<sub>5</sub> thin films which were equilibrated at the required potentials (Figure A.7). Lithiated T-Nb<sub>2</sub>O<sub>5</sub> (L-Nb<sub>2</sub>O<sub>5</sub>) was obtained by equilibrating the T-Nb<sub>2</sub>O<sub>5</sub> thin film at 1.178 V vs Li/Li<sup>+</sup> for 60 s. De-Lithiated T-Nb<sub>2</sub>O<sub>5</sub> (D-Nb<sub>2</sub>O<sub>5</sub>) was obtained by equilibrating the T-Nb<sub>2</sub>O<sub>5</sub> thin film at 3.478 V vs Li/Li<sup>+</sup> for 60 s. Details on calculation of x in Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> can be found in figure A.6. After equilibration, samples were rinsed with dry PC inside the glovebox. PC was removed by evaporation in a vacuum oven at 100°C for 6 hours. AXIS Supra system is equipped with a gas cluster ion source (GCIS) producing focused energetic Ar ion beam in both monoatomic and cluster mode for sputter cleaning. The samples were cleaned for 500s using 5 KeV Ar<sup>+</sup> 1000 ion clusters to remove surface oxygen species. All the XPS spectra were calibrated using the adventitious carbon peak at 248.8 eV.

## **3.3** Results and Discussion

## 3.3.1 Prior measurements and calculations of $Li_xNb_2O_5$ conductivity.

What is already known about the electrical conductivity of  $\text{Li}_x \text{Nb}_2 \text{O}_5$ ?  $\text{Nb}_2 \text{O}_5$  (x = 0) is a  $d^0$  transition metal oxide with a band gap,  $E_g$ , of 3.7 eV (measured by UPS)[98] or 3.2 - 4.0 eV (measured optically) or 2.0 - 4.0 eV (calculated).[54, 98, 15, 79] Low values of  $E_g$  within this range are attributed to systematic underestimation of band-gaps by density functional theory (DFT) calculations employing functionals of the generalized gradient approximation (GGA) type.[54, 98] Recent DFT calculations using the HSE06 functional[79] produce higher estimates of  $E_g$  (indirect) = 4.05 eV for the orthorhombic polymorph. Based upon these more accurate calculations, Nb<sub>2</sub>O<sub>5</sub> is expected to be an insulator. DFT further predicts[54, 98] that the reduction of Nb centers from +5 to +4 with lithiation causes n-doping as half-filled Nb-4g
states at the conduction band edge are filled and their energy shifts lower. This reduction is predicted by DFT to produce a metallic lithiated state. While DFT calculations do not predict numerical values for the conductivity, these calculations predict that the electrical conductivity will increase dramatically with lithiation as insulating Nb<sub>2</sub>O<sub>5</sub> is converted into metallic Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub>.[54, 98, 15, 79].

In-situ measurements of  $\sigma$  for Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> have not been reported previously to our knowledge. However, some ex-situ data are the following: Direct measurement of  $\sigma$  for bulk Nb<sub>2</sub>O<sub>5</sub> samples yields  $3.3 \times 10^{-5}$  S/cm.[13] Reduction of Nb<sub>2</sub>O<sub>5</sub> to produce oxygen vacancies and a stoichiometry of Nb<sub>2</sub>O<sub>4.96</sub> produces metallic material with a conductivity, "...at least 5 orders of magnitude..." higher than Nb<sub>2</sub>O<sub>5</sub>.[13] These data are not specific to the orthorhombic polymorph. Numerical data for  $\sigma$  have also been reported for the pseudo-hexagonal polymorph, H-Nb<sub>2</sub>O<sub>5</sub> which has  $\sigma = 3 \times 10^{-6}$  S/cm whereas reduction to Nb<sub>2</sub>O<sub>4.978</sub> increases  $\sigma$  to  $3 \times 10^3$  S/cm - or nine orders of magnitude.[1] Several prior experiments also provide evidence that the  $\sigma$  of Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> increases with lithiation without providing numerical measurements of its value. <sup>7</sup>Li NMR data[28] for Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> with x = 0.44 and 1.86 is interpreted in terms of an increase in  $\sigma$  with x. In investigations of the electrochromism of Nb<sub>2</sub>O<sub>5</sub> films[62] associated with the lithiation process, the kinetics and reversibility of the color change has been observed to be enhanced for lithiated films.[62].

#### **3.3.2** EPD-Based Synthesis of T-Nb<sub>2</sub>O<sub>5</sub> Nanoribbons.

With this as background, previously we developed an electrophoretic deposition (EPD) process for the synthesis of phase pure T-Nb<sub>2</sub>O<sub>5</sub> films with thicknesses in the 40-140 nm range.[37] Here a modification of this process was used to prepare lithographically patterned Nb<sub>2</sub>O<sub>5</sub> nanoribbons using the LPNE process[102, 101, 64] (Figure 3.2a). The *EPD* deposition of an amorphous Nb<sub>2</sub>O<sub>5</sub> nanoribbon occurs at a lithographically patterned gold edge

electrode, 70 nm in height, that is recessed into a 700 nm deep photoresist and glass channel (Figure 3.2a, step 4). *EPD* proceeds via the application of a -2.0 V voltage step to this gold electrode *versus* a platinum counter electrode in a solution containing a suspension of NbO<sub>x</sub> colloid nanoparticles. As discussed previously,[37] particles of this NbO<sub>x</sub> colloid are characterized by two prominent diameter modes centered at 30 nm and 1000 nm. Because particles larger than 70 nm can not enter the LPNE trench, just the NbO<sub>x</sub> colloids in smaller of these two modes can be involved in EPD. As  $H_3O^+$  is reduced at the gold electrode, positively changed NbO<sub>x</sub> colloid particles migrate into this horizontal trench forming an aggregated solid (Figure 3.2b).

Two-electrode cyclic voltammograms (CVs) of the  $NbO_x$  colloid suspension at a planar gold working electrode (Figure 3.3a) show an irreversible cathodic peak at -1.2 V superimposed on a sloping cathodic ramp with an onset near -0.60 V. Potentiostatic EPD for this flat electrode at -2.0 V shows current versus time traces characterized by a time-independent current (Figure 3.1c, black trace). At an LPNE-templated gold electrode (Figure 3.3b), the voltammetry is similar to that seen at flat electrodes with one difference: The current peak, assigned to the reduction of  $Nb^{+5}$  in the colloid particles, is also more pronounced at the LPNE templated gold nanoelectrode (Figure 3.3b). As previously demonstrated [37], reduced Nb species re-oxidize to form Nb<sup>+5</sup> upon annealing the film in ambient atmosphere at 600°C at a later stage in the fabrication process. Current versus time traces for four nanoribbon growth experiments (Figure 3.3c) also show time-independent currents that are virtually identical to one another. The width of the nanoribbon is controlled by the EPDduration. At LPNE trenches 70 nm in height, deposition durations of 50 s, 100 s, 200 s and 500 s produce ribbons with mean widths of 110 nm, 225 nm, 329 nm and 593 nm respectively (Figure 3.3d). In the following analysis, we focus attention on the narrowest and widest of these nanoribbons, with widths of  $\approx 600$  nm and  $\approx 100$  nm, respectively.



Figure 3.3: EPD of Nb<sub>2</sub>O<sub>5</sub> films and nanoribbon arrays. a,b) Two-electrode cyclic voltammetry (50 mV/s) of NbO<sub>x</sub> colloidal solutions, at planar gold electrodes for EPD of Nb<sub>2</sub>O<sub>5</sub> films (a), and at LPNE templated gold electrodes 70 nm in height for nanoribbon EPD (b). c). Chronamperometry for four Nb<sub>2</sub>O<sub>5</sub> nanoribbon preparations, corresponding to four EPD times as indicated, and a 500 s Nb<sub>2</sub>O<sub>5</sub> film. Nanoribbon EPD currents for different deposition durations overlap demonstrating the reproducibility of the EPD process at LPNE templated gold electrodes. d) Plot of nanoribbon width versus EPD time for nanoribbons 70 nm in height. Nanoribbon dimensions are measured after thermal annealing to produce orthorhombic, T-Nb<sub>2</sub>O<sub>5</sub>.

#### 3.3.3 Characterization of Nanoribbon Structure and Composition.

After deposition, the nanoribbons are annealed in air at 600°C for 6 hours to convert the amorphous as deposited wires to orthorhombic Nb<sub>2</sub>O<sub>5</sub> (*T*-Nb<sub>2</sub>O<sub>5</sub>). SEM images (Figure 3.4a) shows the morphology and texture of *T*-Nb<sub>2</sub>O<sub>5</sub> nanoribbon surface. This texture, which is more pronounced as compared with MnO<sub>2</sub> nanoribbons[46], is attributed to the EPD process in which individual NbO<sub>x</sub> colloid particles are deposited to form a particle conglomerate which is then coalesced by annealing at 550°C. Nanoribbon height was measured using atomic force microscopy (AFM)(Figure 3.4f). The average height of the wire was determined to be  $72 \pm 5$  nm, slightly higher than the estimated thickness of the gold film evaporated in Step 1 of the LPNE process (Figure 3.2a).

Prior investigations of Nb<sub>2</sub>O<sub>5</sub> by Dunn and coworkers as well as others[43, 108, 113, 17, 8, 3, 92, 28] have concluded that the orthorhombic polymorph of this oxide produce especially rapid lithiation/delithiation kinetics. The annealing protocol applied here of 600°C for 6 hours was optimized to convert amorphous Nb<sub>2</sub>O<sub>5</sub> into crystalline orthorhombic T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons. The orthorhombic crystal structure is confirmed by grazing incidence x-ray diffraction (GIXRD)(Figure 3.5) which were acquired using arrays of 4000 ultra-long (2 cm) Nb<sub>2</sub>O<sub>5</sub> nanoribbons on glass.

X-ray photoelectron spectra (XPS) of Nb<sub>2</sub>O<sub>5</sub> nanoribbons and films are compared in Figure 3.6 and Table 3.1. XPS spectra were acquired for freshly deposited, amorphous a-Nb<sub>2</sub>O<sub>5</sub> films and nanoribbons (Figure 3.6e-h) and for T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons and films (Figure 3.6 a-d). Nb 3d spectra, consisting of  $3d_{3/2}$  and  $3d_{5/2}$  peaks, are similar for nanoribbons and films. These peaks are shifted higher by 0.60 eV for a-Nb<sub>2</sub>O<sub>5</sub> relative to the annealed samples. This reproduces the behavior is seen for thin films of these same materials on FTO substrates.[38] The shift to lower binding energy upon annealing is attributed to formation of oxygen vacancies in the Nb<sub>2</sub>O<sub>5</sub> lattice, leading to lower oxygen stoichiometry (Nb<sub>2</sub>O<sub>5-x</sub>),



Figure 3.4: SEM and AFM data for Nb<sub>2</sub>O<sub>5</sub> nanoribbons. a-d) Representative SEM images of four T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons prepared using *EPD* times of 50 s, 100 s, 200 s, and 500 s. e). Array of T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons patterned at  $\mu$ m pitch on glass. *EPD* time = 500 s, f). AFM height versus distance trace across an array T-Nb<sub>2</sub>O<sub>5</sub> like that shown in (e) showing a mean nanoribbon height of 64 nm. g). Image of T-Nb<sub>2</sub>O<sub>5</sub> nanoribbon array after the deposition of gold contacts. A photoresist layer (not applied in this image) insulates the gold films on both sides of the nanoribbon array to prevent exposure of these gold contacts to the electrolyte. A 10  $\mu$ m length of the nanoribbon array were exposed to electrolyte for *in-situ* conductivity measurements.



Figure 3.5: Grazing incidence x-ray powder diffraction (GIXRD) pattern for an array of T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons prepared using  $\tau_{dep} = 500$  s.

the formation of reduced Nb centers  $(Nb^{4+})$ , and a shift of the Nb 3d peak to lower binding energy. In the case of thin films which afford higher signal-to-noise spectra, this shift can be quantitatively correlated to the stoichiometry of these samples. The O 1s spectrum (Figure 3.6 b,d,f,h) includes contributions from 3 peaks: i) oxygen in the Nb<sub>2</sub>O<sub>5</sub> lattice,  $O_{T-Nb_2O_5}$  and  $O_{a-Nb_2O_5}$ , ii) surface oxygen species consisting of peroxides and hydroxyl groups,  $O_{surf}$ , and, iii) oxygen from the SiO<sub>2</sub> substrate,  $O_{SiO_2}$ .  $O_{Lattice}$  1s of *a*-Nb<sub>2</sub>O<sub>5</sub> thin films is observed at 533.3 eV and shows a similar shift towards lower binding energy to 529.7 eV upon annealing to  $T-Nb_2O_5$  thin films. This behavior is consistent with the shift in Nb 3d peaks. In case of nanoribbons,  $O_{T-Nb_2O_5}$  1s of T-Nb<sub>2</sub>O<sub>5</sub> displays a shoulder at the same peak position as the thin films, but the  $O_{T-Nb_2O_5}$  1s of *a*-Nb<sub>2</sub>O<sub>5</sub> nanoribbons is not distinguishable. The area of the sample covered by nanoribbons is many times smaller than the area of the exposed glass. Therefore, the signal for the  $O_{T-Nb_2O_5}$  1s of a-Nb<sub>2</sub>O<sub>5</sub> nanoribbons might be overshadowed by the much stronger signal from  $O_{Substrate}$  1s at 532.2 eV.  $O_{SiO_2}$  1s peaks are not present in the thin film samples, since the  $Nb_2O_5$  in both the thin film samples, is deposited on a 60 nm layer of gold. The peak at 532.9 eV in the O 1s of  $a-Nb_2O_5$  nanoribbon corresponds to the  $O_{surf}$  species, which carry over from the electrophoretic deposition process. The  $O_{surf}$ 1s is not observed in spectra for  $T-Nb_2O_5$  nanoribbons or thin films because upon annealing



Figure 3.6: XPS analysis of Nb<sub>2</sub>O<sub>5</sub> nanoribbons (NR, a,b,e,f) and films (c,d,g,h). a,c). Nb 3d spectra of T-Nb<sub>2</sub>O<sub>5</sub> NRs and films. e,g) Nb 3d spectra of a-Nb<sub>2</sub>O<sub>5</sub> NRs and films. b,d) O 1s spectra of T-Nb<sub>2</sub>O<sub>5</sub> NRs and films. g,h) O1s spectra of a-Nb<sub>2</sub>O<sub>5</sub> NRs and films.

Compound	Binding Nb $3d_{5/2}$	Energy (eV) Nb $3d_{3/2}$	O 1s	Nb:O <sup>a</sup>	Reference
$T-\mathrm{Nb}_2\mathrm{O}_5$ (SG, $d = 120 \text{ nm}$ )	207.3	210.1	530.6	0.40	[70]
$\frac{Nb_2O_5}{(Nb^o \text{ TO})}$	207.7	210.4	530.4	0.46	[26]
B-Nb <sub>2</sub> O <sub>5</sub>	207.1	209.8	530	n.a.	[20]
a-Nb <sub>2</sub> O <sub>5</sub> (MS-ad, $d = 377$ nm)	207.4	210.1	530.5	0.40	[19]
$Nb_2O_5-600^{\circ}C$ (MS-ta, $d = 355$ nm)	207.1	209.9	530.1	0.40	[19]
$egin{array}{llllllllllllllllllllllllllllllllllll$	207.1	209.9	530.3 (Lattice) 532.8 (Surface)	0.40	this work
$a-Nb_2O_5$ Nanoribbon d = 60nm)	207.1	209.8	530.4 (Lattice) 532.3 (Surface)		"
T-Nb <sub>2</sub> O <sub>5</sub> Thin Film	206.6 (Nb <sup>4+</sup> ) 207.0 (Nb <sup>5+</sup> )	209.4 (Nb <sup>4+</sup> ) 200.6 (Nb <sup>5+</sup> )	$529.7 \ (Lattice)$	0.43	"
a = 70 mm)	207.0 (IND <sup>++</sup> )	$209.0 (IND^{++})$	530.7 (Surface)		
T-Nb <sub>2</sub> O <sub>5</sub> Nanoribbon d = 70 nm)	206.3 $(\mathrm{Nb}^{4+})$ 207.0 $(\mathrm{Nb}^{5+})$	209.1 (Nb <sup>4+</sup> ) 209.8 (Nb <sup>5+</sup> )	529.9 (Lattice)		"
u = 10 mm)	201.0 (110 )		532.0 (Surface)		

Table 3.1: Comparison of Observed Photoelectron Binding Energies For  $Nb_2O_5$  Films With Literature Values.

<sup>*a*</sup> Nb:O atomic ratio, <sup>*b*</sup>Abbreviations: SG = sol-gel, TO = thermal oxidation in air at 580°C, MS-ad = magnetron sputtering (as-deposited), MS-ta = magnetron sputtering (calcined at  $600^{\circ}$ C).

surface oxygen species are either decomposed or converted to lattice oxygen. And again,  $O_{surf}$  1s is not visible in the spectra of a-Nb<sub>2</sub>O<sub>5</sub> nanoribbons because it is buried under the stronger  $O_{SiO_2}$  1s peak. The O 1s XPS region for T-Nb<sub>2</sub>O<sub>5</sub> and a-Nb<sub>2</sub>O<sub>5</sub> nanoribbons are similar. However, the Nb 3d region peaks clearly demonstrate that the composition of T-Nb<sub>2</sub>O<sub>5</sub> versus a-Nb<sub>2</sub>O<sub>5</sub> nanoribbons closely mimic the thin films, and justify the use of these films to evaluate the nanoribbon stoichiometry from the thin films analysis. Hence, T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons have oxygen deficiencies in the crystal lattice, and this deficiency can significantly effect the conductivity of the material, as discussed in detail in the next sections.

#### **3.3.4** Nanoribbon Electrochemistry.

The cyclic voltammetry of T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons (Figure 3.7a) is dominated by a reduction (1.5 V vs. Li/Li<sup>+</sup>, 500s sample or 1.6 V, 50s sample) assigned to  $Nb^{5+} + 1e^- \rightarrow Nb^{4+}$  within the oxide and at its surface. These niobium centers within the oxide are re-oxidized at 2.2 V (500 s sample) or 2.5 V (50 s sample) on the return scan. The shifts in the potential of these voltametric waves across a broad scan rate range from 5 mV/s to 200 mV/s, is small, amounting to < 40 mV, indicating rapid kinetics for this process (Figure 3.7a).

A plot of total capacity ( $C_{total}$ ) versus scan rate ( $\nu$ , Figure 3.7b) shows a maximum value for the 50s sample of 480 mAh/g at 5 mV/s that is reduced to 200 mAh/g at 200 mV/s. The same plot for the 500 s sample is lower at all  $\nu$  by  $\approx$ 100 mAh/g. For both 50 s and 500 s nanoribbons, plots of  $C_{total}$  versus  $\nu^{-1/2}$  are linear with positive, nonzero intercepts (Figure 3.7c). An analysis of these data using the method of Trasatti provides a means for resolving  $C_{total}$  into insertion and noninsertion components:[2, 41]

$$C = C_{noninsertion} + C_{insertion} \tag{3.2}$$

 $C_{insertion}$  is contributed by Nb centers in the bulk of the T-Nb<sub>2</sub>O<sub>5</sub>. Li<sup>+</sup> insertion/deinsertion



Figure 3.7: Cyclic voltammetry of T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons in 1.0 M LiClO<sub>4</sub>, PC. a). Scan rate series for  $\tau_{dep} = 50$  s nanoribbons (top) and 500 s nanoribbons (bottom), b)  $C_{sp}$  versus scan rate, showing higher  $C_{sp}$  values for 50 s nanoribbons, c). Data from (b) replotted as  $C_{sp}$  versus  $\nu^{-1/2}$ .  $\nu^{-1/2} = 0$  intercepts of these plots are: 18 (± 3) mAh/g (500 s) and 128 (± 1) mAh/g (50 s). d) Plot of  $C_{total}$  (filled circles) and  $C_{noninsertion}$  (open circles) versus  $\nu$  for 50 s and 500 s nanoribbons.

coupled with diffusion of  $\text{Li}^+$  within the oxide lattice is required for charge compensation in this case.  $C_{noninsertion}$  is the sum of double-layer charging capacity and the capacity of surface niobium centers that can be charge compensated without the insertion of  $\text{Li}^+$  into the oxide.

The reduction of  $C_{total}$  with increasing  $\nu$  is explained by slow,  $C_{insertion}$ -limiting Li<sup>+</sup> diffusion within the T-Nb<sub>2</sub>O<sub>5</sub> lattice. Since this diffusion limitation does not apply to  $C_{noninsertion}$ , Trasatti was able to deconvolute  $C_{total}$ :[2, 41]

$$C(\nu)_{total} = C_{noninsertion} + const(\nu^{-1/2})$$
(3.3)

where const is a constant containing the diffusion coefficient and other  $\nu$ -independent parameters.[2] The  $\nu$ -dependence of  $C_{total}$  and  $C_{noninsertion}$  (Figure 3.7d) shows a higher noninsertion capacity for the 50 s nanoribbon versus the 500 s nanoribbon (10 mAh/g versus 120 mAh/g). But  $C_{insertion} (= C_{total} - C_{noninsertion})$  is the same for these two nanoribbons to within 5 %. Equation (3) has been applied by Dunn and coworkers to T-Nb<sub>2</sub>O<sub>5</sub> films.[41]. In that work, a limiting capacity of 480 C/g was obtained by extrapolation to  $\nu^{-1/2} = 0$  whereas for the 50 s nanoribbons, the measured  $C_{noninsertion}$  of 128 (± 1) mAh/g corresponds to 460 C/g, closely approximately the earlier result.

#### 3.3.5 Nanoribbon Conductivity.

In-situ conductivity measurements performed using the method shown in Figure 3.1 were performed by first synthesizing the nanoribbon array using either 50 s or 500 s deposition times and then thermally annealing these samples (Figure 3.2a, step 6) prior to the application of gold electrical contacts (Figure 3.2a, steps 7-10). The resulting T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons are unlithiated (x = 0) with an equilibrium potential of  $E_{eq} = 3.48$  V vs. Li/Li<sup>+</sup>. With both sides of the nanoribbon array potentiostatted corresponding to the configuration shown in Figure 3.1b, nanoribbons were equilibrated at eight more negative  $E_{eq}$  values, ranging from 3.18 V to 1.18 V, inducing lithiation. During this process, the current-time transients shown in Figure 3.8a were obtained. Equilibration was taken to be complete in 1.0 min.

After equilibration at each  $E_{eq}$  data point, nanoribbons were reconfigured for measurement of  $\sigma$  as shown in Figure 3.1c. Current *versus* potential (*I-V*) were measured at 20 mV/s across a 20 mV window (Figure 3.8b). The slope of the resulting linear *I-V* traces,  $R^{-1} = I/V$ , were used to calculate R.  $\sigma$  was calculated using the equation:  $\sigma = \ell/(200Rwh)$  where the symbols correspond to mean values of the electrically isolated nanoribbon length ( $\ell$ ), the resistance (R), the height (h), and the width, (w) in an array containing 200 nanoribbons.

The resulting  $\sigma$  data for nanoribbons prepared using  $\tau_{dep} = 50$  s and 500 s are plotted versus  $E_{eq}$  and x (Figure 3.8c,d). For Nb<sub>2</sub>O<sub>5</sub> (x = 0),  $\sigma$  is nearly the same for 50 s and 500 s samples



Figure 3.8: In-situ lithiation (a) and conductivity measurements (b-d). a). Plot of the current transient observed for a potential step from an initial potential of 3.48 V to eight potentials in the range from 3.18 V to 1.18 V for an array of  $\text{Li}_x \text{Nb}_2 \text{O}_5$  nanoribbona prepared using  $\tau = 500$ s. Final potentials for each curve are indicated. Electrolyte: 1.0 LiClO<sub>4</sub>, PC., b) Current versus  $\text{E}_{app}$  for measurement of the conductivity of the nanoribbon array discussed in (a), in the same electrolyte. Note that the total scan range is 20 mV, in order to minimize a perturbation to the nanoribbon lithiation state, c,d). Plot of average conductivity versus  $E_{eq}$  (c) and "x" value (d). Error bars indicate the standard deviation for N = 2 ( $\tau_{dep} = 500$  s) and N = 3 (50 s) nanoribbon array samples.



Figure 3.9: Correlation of  $\sigma$  with  $C_{total}$  as capacity fade occurs with extended cycling. a). Cyclic voltammograms at 200 mV/s for 50 s nanoribbons up to 3000 cycles. b) Plots of  $C_{total}$ ,  $\sigma$ , and coulombic efficiency versus number of cycles.  $\sigma$  was measured for fully lithiated nanoribbons (x = 2), equilibrated at  $E_{eq} = -1.18$  V vs. Li/Li<sup>+</sup> for 60 s.

and equal to 5-6 × 10<sup>-5</sup> S/cm - approximating the previous measurement of Cava *et al.*[13] of 3 × 10<sup>-5</sup> S/cm. The anticipated increase in  $\sigma$  with lithiation (*vide supra*) is also seen for both 50 s and 500 s nanoribbons, however an increase of more than 5 orders of magnitude (estimated by Cava[13]) is not realized. Instead, with increasing x and decreasing  $E_{eq}$ ,  $\sigma$ increases monotonically to 2.6 (± 1) × 10<sup>-3</sup> S/cm (500 s) and 1.8 (± 0.2) × 10<sup>-2</sup> S/cm (50 s). In the plot of  $\sigma$  versus  $E_{eq}$  in particular, an inflection is seen at  $E_{eq} \approx 1.6$  V corresponding to the onset for the reduction wave corresponding to Nb 5+ to 4+ of T-Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> (Figure 3.7a). For  $E_{eq}$  values more negative then 1.6 V, the slope of the  $\sigma$  versus  $E_{eq}$  increases.

#### 3.3.6 Correlating $\sigma$ with Capacity During Extended Cycling.

The data of Figure 3.8 are valuable in establishing the properties of T-Nb<sub>2</sub>O<sub>5</sub> as an energy storage material, but the technique we have described here can also provide *in-situ* conductivity measurements for systems that are undergoing repetitive lithiation/delithiation cycling. In this mode, cycling is interrupted and the protocol already described above is applied to measure conductivity, then cycling is resumed.

The feasibility of this measurement is demonstrated for a 50 s T-Nb<sub>2</sub>O<sub>5</sub> nanoribbon array in Figure 3.9. A loss of capacity is readily apparent in the cyclic voltammograms (200 mV/s) which show a gradual decay in anodic and cathodic peak currents (Figure 3.9a). After 1000 cycles, this loss of capacity become precipitous culminating in a loss of  $C_{total}$  for this array from 72 mAh/g (1 cycle) to 28 mAh/g (3000 cycles). Concurrent measurements of  $\sigma$  (measured for the fully lithiated state, x = 2) show that the negative inflection in the capacity curve at 1000 cycles is matched by an inflection in  $\sigma$  (plotted on a log scale). The result is a collapse of  $\sigma$  by nearly four orders of magnitude, from  $10^{-2}$  S/m to  $10^{-6}$  S/cm. Without additional information, it is difficult to know whether the decay in  $\sigma$  is a cause of the decline in  $C_{total}$ , or a symptom of it. But a complete understanding of the complex process of degradation and failure for energy storage materials will surely require numerical *in-situ*  $\sigma$  data like that of Figure 3.9b.

## 3.4 Summary

An *in-situ* tool for investigating a single Transition metal oxide (TMO) material under conditions that approximate its function in a complete battery, is described here. It is not an *operando* method that is capable to assessing interactions with other components of the battery under operating conditions. LPNE was used to create an array of 200 nanoribbons across 2 contact pads. Nanoribbons can be used as a working electrode to intercalate a desired amount of Li<sup>+</sup>, and then the two contact pads can be used to measure I-V curves for conductivity measurement.  $\sigma$  in the non-lithiated Nb<sub>2</sub>O<sub>5</sub> is characteristic of semiconducting metal oxides, but it increases dramatically with lithiation. For 70 nm (h) × 100 nm (w) Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> nanoribbons, for example, the nonlithiated state (x = 0) has a conductivity of  $\sigma = 5.0(\pm 0.9) \times 10^{-5}$  S/cm that increases by a factor of 360 to  $\sigma = 0.018(\pm 0.002)$  S/cm as x is increases to 2.0. Repetitive lithiation/delithiation of Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub> is associated with a reduction in  $\sigma$  which coincides with a loss of reversible specific capacity,  $C_{sp}$  of these nanoribbon arrays.

# Chapter 4

# Probing Degradation Mechanism of Nb<sub>2</sub>O<sub>5</sub> Thin Film Capacity Loss after Repetitive Cycling

## 4.1 Introduction

Degradation in anode and cathode materials is the primary failure mechanisms for energy storage devices, and has been discussed in detail in several reviews.[9, 93, 30] It is one of the factors that limits the number of times a device can be charged and discharged, and thus creates an economic barrier to widespread use of these devices. Understanding the fundamental changes occurring inside the material during cell operation, can suggest ways to improve the cycle life of energy storage systems and boost the shift towards green energy. Niobium Pentoxide has gained popularity in recent times due to its rapid lithium ion  $(Li^+)$  intercalation kinetics.[95, 41, 3, 113, 43] Theoretical capacity of anodes comprised of  $Li_xNb_2O_5$  with intercalation stoichiometry of 2 as shown in equation 4.1, is 202mAh/g.[68]

$$Nb_2O_5 + xLi^+ + xe^- \rightleftharpoons Li_xNb_2O_5 \tag{4.1}$$

This capacity is decent at best, compared to other widely studied anode materials like silicon, which has theoretical capacity of 3600 mAh/g[57] or transition metal oxide like MoO<sub>3</sub> with theoretical capacity of 1117 mAh/g[12]. But what it loses in capacity, it makes it up in terms of power density. The Li<sup>+</sup> diffusion activation barrier is much lower in Nb<sub>2</sub>O<sub>5</sub>, compared to similar transition metal oxides or conversion materials. This can be attributed to the orthorhombic and monoclinic structures of Nb<sub>2</sub>O<sub>5</sub>, which are comprised of corner sharing octahedra.[3] They create a perfect pathway for rapid lithium intercalation. In-situ X-Ray Diffraction experiments have demonstrated that (180) and (100) are the favored pathway for Li<sup>+</sup> diffusion in orthorhombic Nb<sub>2</sub>O<sub>5</sub> (*T*- Nb<sub>2</sub>O<sub>5</sub>)[17]. It has also been shown that the phase does not change during initial charge discharge cycle. The d-value of (180) plane increases from 3.15 Åto 3.25 Å, upon lithiation, and reversed back on delithiation. The Nb centers shuttle between Nb<sup>+5</sup> and Nb<sup>+4</sup> during lithiation and delithiation.[17]

The 500mC T-Nb<sub>2</sub>O<sub>5</sub> films, deposited directly on FTO, as described in Chapter 2, display a high capacity of more than 450 F/g even at 200mV/s.[38]Usually conductive additives and polymer binders are added to metal oxides for enhancing the conductivity. Degradation study on a material with added binders does not allow the determination of degradation pathways of the active material. Because it would be difficult to deconvolve the capacity loss arising from the additives versus capacity loss due to active material decomposition. These films are ideal candidates for evaluation of the intrinsic degradation mechanism of T-Nb<sub>2</sub>O<sub>5</sub> since there are no complications arising from additive materials. Morphological comparison of fresh samples and samples after 5000 cycles, reveal loss of active material, which indicates pulverization. TEM comparison shows that the orthorhombic crystal structure of the pristine samples become completely amorphous upon long cycling. This is also accompanied by a compositional change in the material from a mixture of  $Nb^{5+}$  and  $Nb^{4+}$  centers present in the pristine material to complete  $Nb^{5+}$ . In-depth characterization of the charging discharging process over thousands of cycles, has the potential to conclusively determine the mechanism of degradation in Niobia. It could also help us predict the path towards mitigation of capacity loss.

## 4.2 Experimental Methods

Chemicals and Materials. Niobium pentachloride (NbCl<sub>5</sub>, 99%), hydrogen peroxide solution (H<sub>2</sub>O<sub>2</sub>, 30% (w/w) in H<sub>2</sub>O), lithium perchlorate (LiClO<sub>4</sub>, battery grade, dry, 99.99% trace metal basis), propylene carbonate (anhydrous, 99.7%) and fluorine doped tin oxide (FTO) coated glass slide (surface resistivity  $\approx 13 \Omega/sq$ ) were all used as received from Sigma-Aldrich. FTO was cleaned using a commercial cleaning solution Hellmanex 3 obtained from Hellma Analytics. Positive photoresist (Shipley S1808) and developer (Shipley MF-319) were purchased from Microchem Corporation. Acetone and methanol were used as received from Fisher (ACS certified).

### 4.2.1 Electrophoretic Deposition of $Nb_2O_5$ .

Electrophoretic deposition of T-Nb<sub>2</sub>O<sub>5</sub> films on FTO was carried out in the same way as the 500mC fabrication described in section 2.2.2.

#### 4.2.2 Electrochemical characterization.

All electrochemical measurements were performed by a one-compartment three-electrode cell using a Gamry Series G 300 potentiostat. Cyclic voltametry and galvanostatic measurements were conducted in 1.0 M LiClO<sub>4</sub> (battery grade, dry, 99.99%) in dry propylene carbonate inside a N<sub>2</sub> glovebox. Glassy carbon rod (2mm diameter) was used as counter electrode with a Platinum foil pseudoreference electrode for the electrochemical measurements. All potentials are quoted with respect to the Li/Li<sup>+</sup> couple,  $E_{Li/Li^+} = -3.045$  V versus normal hydrogen electrode[6] by calibrating the Pt pseudoreference electrode against Li/Li<sup>+</sup> using ferrocene/ferrocenium (Fc/Fc<sup>+.</sup>) in 1M LiClO<sub>4</sub>, PC.[45]

#### 4.2.3 Structural Characterization.

Scanning electron micrographs (SEMs) were acquired using a FEI Magellan 400 XHR system. Before imaging, samples were sputter-coated with  $\approx 2$  nm of iridium. Accelerating voltages of incident electron beams ranged from 5 kV to 15 kV, and probe currents ranged from 25 pA to 0.4 nA. All SEM specimens were mounted on stainless stubs and held by carbon tape. X-ray photoelectron spectroscopy (XPS) was measured using the AXIS Supra by Kratos Analytical Inc. equipped with monochromatic Al/Ag x-ray source.

#### 4.2.4 Transmission Electron Microscopy.

Aberration-corrected scanning transmission electron microscopy (STEM) was performed on a JEOL Grand-ARM transmission electron microscope equipped with two spherical aberration correctors and a 300 kV cold field emission gun. High angle annular dark filed (HAADF)-STEM images were recorded using a convergence semi angle of 22 mrad, and inner- and outer collection angles of 83 and 165 mrad, respectively.

# 4.3 Results and Discussion

#### 4.3.1 Electrochemical Capacity Fade

We cycled T-Nb<sub>2</sub>O<sub>5</sub> at high power densities (200 mV/s in Cyclic voltammetry and 10A/g in Galvanostatic charge-discharge) as shown in Figure 4.1. In cyclic voltammetry, the 300 mC sample starts losing capacity very soon, and in about 2000 cycles, loses 25% of its capacity. The thicker samples take around 5000 cycles to lose 25% capacity. Fig 4.1 shows the decay of the 500 mC sample for 10k cycles, and we observe a change in peak position as well as shrinkage in area under the CV. The change in peak position might be attributed to an overall increase in resistance of the film or a possibly destabilization of interfacial contacts (electrode electrolyte contact). The shrinkage in area under the CV might be due to many reasons. Destabilization of the crystal structure or amorphization of the crystal structure may lead to destruction of Li<sup>+</sup> ion transport pathways, which in turn might lead to capacity fade. Loss of material due to pulverization or dissolution of active material into the electrolyte can also dramatically decrease the capacity. It might also be the combined effect of amorphization and material loss. Probing structural properties of the film during and after many cycles can clarify the mechanism further.

#### 4.3.2 Pulverization Leading to Material Loss

Morphology of T-Nb<sub>2</sub>O<sub>5</sub> film after cycling changes to a rough and seemingly pulverized morphology, as shown in the SEM and Cross-sectional TEM images (fig 4.2 and 4.3). In the SEM image, the surface shows clear signs of chunks of Niobium containing species getting removed after 5,000 cycles. The Energy Dispersive Spectroscopy (EDS) map showing the Nb L $\alpha$ 1 peak shows dark spots where the active material is no longer present. To clarify the reason behind this pulverization, cross-section TEM images were taken, of film before



Figure 4.1: XXChangePotentialwindowXX(Top panel) Representative cyclic voltammetry of T-Nb<sub>2</sub>O<sub>5</sub> at 200mV/s from cycle 1 to 5000, and the resulting decay in capacity, in all 4 films. (Bottom Panel) Galvanostatic charge discharge of T-Nb<sub>2</sub>O<sub>5</sub> from 1 to 500 cycles and resulting capacity decay in all 4 films.



Figure 4.2: SEM images if as prepared film (left) and cycled film (centre), along with EDS map of Niobium in the cycled sample(right). Pulverization of active material, and subsequent material loss leads to capacity fade.

cycling, after 1 cycle and after 1,000 cycle (figure 4.3). The as prepared sample has a uniform contact between  $Nb_2O_5$  layer and FTO current collector. After 1 cycle, we can observe the formation of voids between the film and current collector. After 1,000 cycles, the void has been widened to micrometers in length. The huge gap explains the pulverization seen in figure 4.2. This void can be attributed to repetitive lithiation-delithiation of the film, which continuous leads to expansion and contraction of the film. After thousands of these expansion and contraction cycles, the film de-laminates from the current collector, leading to material loss and simultaneously, capacity fade.

# 4.3.3 Compositional Effects of Cycling: Probed using Ex-Situ XPS

Yu and co-workers in 2016, used ex-situ XPS to monitor the oxidation state of Nb<sub>2</sub>O<sub>5</sub> nanosheet anode, as a function of potential.[50] It is evident from their work that upon lithiation, Nb 3d peaks shift to a lower binding energy due to conversion of most Nb<sup>+5</sup> centers to Nb<sup>+4</sup> centers, and then reverts to higher binding energy upon de-lithiation. The study recorded the first cycle of lithiation and de-lithiation in Nb<sub>2</sub>O<sub>5</sub>, but there is a lack of literature on tracking the compositional changes of metal oxides upon continuous charging



Figure 4.3: Cross-section TEm of as prepared  $FTO@T-Nb_2O_5$  film (left). Film cycled for once (centre) and film cycled for 1,000 cycles (right), showing growing voids between film and the current collector, as a function of cycle number.

and discharging for long term cycling. Figure 4.4 shows the evolution of Nb 3d peaks and O 1s peaks as we cycle T-Nb<sub>2</sub>O<sub>5</sub> for 10,000 cycles and leave the sample in a de-lithiated state after cycling. It is evident from the shifts of Nb 3d peaks towards higher energy, that contribution of Nb<sup>+5</sup> species in the cycled thin film is increasing as cycling progresses. We can also observe the overall broadening of Nb 3d and O 1s peaks. There are 2 possible reasons for this behavior:

- Amorphization of *T*-Nb<sub>2</sub>O<sub>5</sub>: Amorphous state of *T*-Nb<sub>2</sub>O<sub>5</sub> has and oxidation state of Nb<sup>+5</sup>, whereas upon calcination to an orthorhombic structure, oxygen vacancies are observed, rendering the film to be a mixture of Nb<sup>+4</sup>, Nb<sup>+5</sup> species.[19, 13] We hypothesize that continuous cycling creates the stress of lithium insertion and deinsertion, leads to collapse of the orthorhombic structure leaving behind amorphous Nb<sub>2</sub>O<sub>5</sub>.
- Dissolving away reduced Nb species: Material loss from the *T*-Nb<sub>2</sub>O<sub>5</sub> film, is quite evident from the SEM images. Our hypothesis is that Nb<sup>4+</sup> or more lithiated Nb species can be dissolved away into the electrolyte during cycling, leaving behind



Figure 4.4: Evolution in chemical composition of T-Nb<sub>2</sub>O<sub>5</sub> films upon cycling and left in delithiated stage, observed via XPS. Left panel shows the Nb 3d peaks and right panel shows O 1s peaks at regular intervals during electrochemical cycling. Both peaks shift towards a higher binding energy and broaden, as we go on cycling. This points towards amorphization and a shift to composition containing primarily Nb<sup>+5</sup> species.

residual  $Nb^{5+}$  on the thin film.

To corroborate the second hypothesis, XPS of the electrolyte used for electrochemical cycling is presented in Figure 4.5. The Nb 3d peaks are close to the Cl 2p peaks from the perchlorate salt used as electrolyte. However, the Nb 3d5/2 peak and O 1s peak are observed at low binding energies, which are characteristic of Nb<sup>4+</sup> species.



Figure 4.5: XPS analysis of electrolyte obtained after cycling experiments. Left panel shows the Nb 3d peak and the right panel shows the O 1s peak of the electrolyte solution which was composed of 1M LiClO4. Observation of Nb<sup>4+</sup> species in the electrolyte, points towards dissolution of Nb species into the electrolyte, during cycling.

# 4.3.4 Effects on Co-ordination sphere: Probing via Ex-situ Raman Spectroscopy

Amorphous Niobia consists of distorted NbO<sub>6</sub>, NbO<sub>7</sub> and NbO<sub>8</sub> polyhydra, whose stretching modes are depicted by a strong and broad signal around  $650 \text{ cm}^{-1}$ , in the Raman spectrum. [36] There is extensive literature on the changes in Raman spectra of niobium oxides, characteristic of crystal disorders and phase change. [73, 63, 31] Crystalline Niobia shows Nb-O-Nb stretching frequency around 690  $\rm cm^{-1}$ , and it is a much sharper peak than the amorphous phase, since majority of the polyhydra are  $NbO_6$  and only a small fraction of polyhydra have distorted co-ordination. However, there is limited literature on the effect of continuous stress on the stretching frequencies of Niobia. [35] Senna and co-workers showed that upon continuously grinding phase pure monoclinic  $Nb_2O_5$ , they observed a Raman shift towards lower wavenumbers and an increase in the full width half maxima (FWHM) of Nb-O stretching frequency. In our study, we used a similar principle, except for the fact that the stress and strain applied, was due to lithiation and de-lithiation from the  $T-Nb_2O_5$  matrix. Figure 4.6 shows the progress of niobium pentoxide degradation monitored via Raman spectroscopy, at regular intervals from pristine to 10,000 cycles. The 70 nm T-Nb<sub>2</sub>O<sub>5</sub> layer was deposited on a 600 nm fluorine doped tin oxide (FTO) which in-turn was deposited on glass. The glass layer shows a vibration at  $550 \text{ cm}^{-1}$  (shown in red) and the FTO vibration shows up around 590  $\rm cm^{-1}$  and 630  $\rm cm^{-1}$  (shown in green). The uncycled orthorhombic  $Nb_2O_5$  shows a vibration at 697 cm<sup>-1</sup>, and the continuously decreases in wavenumber at all the intervals measured. The decrease in stretching frequencies represent the degrading bond order of T-Nb<sub>2</sub>O<sub>5</sub>. Its clearly co-related to the amorphization predicted from the XPS data. The FWHM tends to increase de-lithiated form of  $T-Nb_2O_5$  (Figure 5, left panel, blue) displaying the inhomogeneity in the polyhydra. However, the trend is much more erratic in the lithiated version. There is clearly a trend towards a higher FWHM than the uncycled sample. Further analysis is underway to decipher more information from the series of Ex-situ



Figure 4.6: Degradation of T-Nb<sub>2</sub>O<sub>5</sub> co-ordination sphere upon cycling to 10k cycles, monitored via raman spectroscopy. Ex-situ Raman spectra of 70 nm T-Nb<sub>2</sub>O<sub>5</sub> film deposited on FTO@glass. Left panel shows the samples at different intervals of cycling left at a delithiating potential and right panel shows the same ones but left at lithiating potentials. Blue curve depicts the streching vibrations for glass substrate, green for FTO and red corresponds to the Nb-O stretching vibrations.

Raman experiments.

## 4.4 Summary

Understanding degradation of battery capacity is crucial to mitigation of battery failure pathways. The mechanisms are often convoluted, and difficult to understand on a microscopic level, because a variety of processes occur simultaneously during battery function, and failure can be caused by any or all of these processes. In this final chapter of the thesis, mechanism of capacity fade in  $T-Nb_2O_5$  was probed using a 3-electrode half cell setup, in order to determine the effect of repetitive interaction between  $T-Nb_2O_5$  and Li<sup>+</sup> ions. Morphologically, the film pulverized and pealed off from the current collector. Cross-section TEM shows the widening of voids between FTO and  $T-Nb_2O_5$  as the number of cycles increased. XPS showed a change in average oxidation state of the cycles film, which tends to shift from a mixture of  $Nb^{+4}$  and  $Nb^{+5}$  to a completely  $Nb^{+5}$  state. Increase in  $Nb^{+5}$  oxidation state has been co-related to decrease in conductivity of the material. This increases the barrier for electrons to reach the Niobium centers and results in capacity loss. There is also a shift in the type of Niobium center co-ordination sphere. Pristine  $T-Nb_2O_5$  is comprised of mainly  $NbO_6$  octahydra. As the film is cycled, an inhomogeneity develops in the co-ordination sphere and we can observe  $NbO_7$  and  $NbO_8$  co-ordinations along with  $NbO_6$ . This leads to destruction of the low energy barrier pathway for Li<sup>+</sup> intercalation, which comprised of the corner shared NbO<sub>6</sub> octahydra. This can lead to a reduction of diffusion coefficient  $Li^+$  and subsequent decrease in capacity.

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## Appendix A

## Chapter 3 Appendix

## Nanowire Quartz Crystal Microbalance

Electrochemical Quartz Crystal Microbalance experiments were performed using a Stanford Research Systems QCM200 system with 5MHz AT-cut quartz crystals acquired from Stanford Research Systems. The QCM crystals were first cleaned by immersion into piranha solution (3:1, Conc.  $H_2SO_4$ : 30%  $H_2O_2$ ) for 10 minutes, at room temperature. After rinsing the crystals with water and air drying, a layer of S1808 photoresist was spin-coated on to the crystals. A 2 mm diameter circle of photoresist was then removed from edge of the QCM



Figure A.1: Contact masks used in Lithographically Patterned Nanowire Electrodeposition (LPNE). a) Mask for creating 100 exposed rectangles on Gold, which leads to 200 trenches for nanowire deposition, lengthwise. b) Mask for exposing a  $10\mu$ m gap, leading to formation of 2 gold pads connected by T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons



Figure A.2: Calibration of platinum pseudo-reference electrode using a Ferrocene/Ferrocenium (Fc/Fc<sup>+</sup>) redox couple. The calibration was carried out in a 3-elecrode cell, with 6 mm x 6 mm gold working electrode, glassy carbon counter electrode, a platinum wire pseudo-reference electrode and 5 mM Ferrocene in 1M LiClO4 in propylene carbonate as electrolyte. The plot shows the  $E_{Anodic}$  peak at -224 mV and  $E_{Cathodic}$  peak at -372 mV, resulting in  $E_{1/2} = -298$  mV. Using reduction potentials of Fc/Fc<sup>+</sup> vs Li/Li<sup>+</sup> (3.240 V) obtained from reported literature,  $E_{Li/Li}^+ - E_{Pt,Pseudo} = 3.538$  V.[45]



Figure A.3: Bloomed T-Nb<sub>2</sub>O<sub>5</sub> nanoribbons. Scanning electron micrographs (SEMs) of nanoribbons deposited for 3600s. After 500s of deposition, the nanoribbons start growing out of the trench (Figure 2). Bright strips in the SEMs (a. 5000 X, b. 30,000 X, c. 100,000 X) represent the overgrowth outside the trench and have thicker deposits of Nb<sub>2</sub>O<sub>5</sub>. The darker nanoribbons are obtained by Nb<sub>2</sub>O<sub>5</sub> depositing within the trench.

face to expose some of the gold contact pad at the front, and then the remaining photoresist was hard baked in an oven ramping up from 90°C - 180°C over a period of half hour and annealing at 180°C for half an hour to avoid cracking of the film. After hard baking, a 4 nm Cr adhesion layer and a 60nm Au layer were evaporated on top of the hard baked photoresist. The earlier removal of the 2 mm circle from the photoresist over the QCM gold contact ensures electrical contact of the gold layer of the QCM crystal, to the evaporated gold layer. After removing from the PVD chamber the QCM crystals are spincoated with another layer of photoresist and then patterned with a 1.8 cm long 4  $\mu$ m pitch 200 nanowire array pattern as shown in figure A.1a. The sensitivity factor of the crystals is determined by performing depositions of Copper metal from a solution of 0.2 M copper sulfate in 1.0 M sulfuric acid onto three crystals from the same batch as those used for the nanowire samples. The average value from these calibrations was 50  $1 \text{ Hz/g}^{*}\text{cm}^{2}$  this value is used as the sensitivity factor for the nanowire sample. The depositions for nanowire samples were performed after developing the photoresist from 1.8 cm long 4  $\mu$ m pitch 200 NW array pattern and etching the exposed Au for 45s in a  $KI/I_2$  Au etching solution followed by a 5 second immersion into a commercial Cr etching solution. a-Nb<sub>2</sub>O<sub>5</sub> nanowires were deposited onto the trench created, in a similar fashion as mentioned in the Nanowire Electrophoretic Deposition section of the experimental section. After depositing the  $NbO_x$  nanowires from the colloidal nanoparticle plating solution the QCM electrodes were gently rinsed with Millipore water and dried under vacuum for one hour. Crystal frequency of the dried crystal was measured in air. Change in crystal frequency was measured at regular intervals of charge deposited, as shown in figure A.4. Using the slope obtained from the Frequency vs Charge plot (1.33 Hz/mC from Figure A.4) and the sensitivity factor of 50  $1 \text{ Hz}/\mu g$ , a relation between mass deposited and charge can be established, which is 26.6  $\mu$ g/C.



Figure A.4: Calibration of Nanowire mass deposited using Quartz Crystal Microbalance (QCM).



Figure A.5: Optical images of a) hard baked PR coated quartz crystal showing the open contact which ensures electrical contact of the gold layer of the QCM crystal to the evaporated gold layer, b) 200 nanoribbon pattern etched out from the evaporated gold, leaving behind trenches which can be used for electrodeposition.



Figure A.6: XPS Survey Spectrum for Amorphous and Crystalline Niobium Oxide Thin Films and Nanowires. Major peaks in the 0-600 eV range can be indexed by known components of thin films and nanowires. Prominent peaks are due to niobium (green dashed lines), oxygen (blue), carbon (red), silicon (purple), gold (gold), and tin (gray). Overlapping peak identities are indicated in parentheses above an existing indexed peak. Tin peaks arise from fluorine doped tin oxide substrate in thin films while gold, sodium, and calcium arise from soda-lime glass substrate and a sacrificial gold film



Figure A.7: Nb oxidation state in lithiated and de-lithiated T-Nb<sub>2</sub>O<sub>5</sub>. X-Ray photoelectron spectroscopy was used to ascertain the oxidation state of Nb in lithiated T-Nb<sub>2</sub>O<sub>5</sub> (Li<sub>2</sub>Nb<sub>2</sub>O<sub>5</sub>) and delithiated T-Nb<sub>2</sub>O<sub>5</sub> (Nb<sub>2</sub>O<sub>5</sub>). The red curve representing Li<sub>2</sub>Nb<sub>2</sub>O<sub>5</sub> shows Nb 3d<sub>3/2</sub> and Nb 3d<sub>5/2</sub> peaks at 207.9 eV and 205.2 eV respectively which correspond to literature reports of Nb<sup>4+</sup> compounds.[84, 21, 5] The blue curve representing Nb<sub>2</sub>O<sub>5</sub> shows Nb 3d<sub>3/2</sub> and Nb 3d<sub>5/2</sub> peaks at 209.4 eV and 206.7 eV respectively which correspond to literature reports of Nb<sup>5+</sup> compounds.[19, 70] Oxidation state of Nb<sup>4+</sup> represents the stoichiometry Li<sub>2</sub>Nb<sub>2</sub>O<sub>5</sub> (i.e. x = 2 in Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub>), whereas Oxidation state of Nb<sup>5+</sup> represents the stoichiometry Nb<sub>2</sub>O<sub>5</sub> (i.e. x = 0 in Li<sub>x</sub>Nb<sub>2</sub>O<sub>5</sub>). All the intermediate values of x at a potential Y vs Li/Li<sup>+</sup> are obtained using linear interpolation based upon the charge deposited in the 60s equilibration according to the following equation:

$$x_{YvsLi/Li^+} = 2 * Q_{YvsLi/Li^+} / (Q_{1.178vsLi/Li^+} - Q_{3.478vsLi/Li^+})$$
(A.1)