

EFFECT OF THERMAL TREATMENT ON STRUCTURE AND PROPERTIES OF
NIOBIUM OXIDE AEROGELS AS ELECTROLYZER CATALYST SUPPORTS

by

Luis A. Albiter, B.S.

A thesis submitted to the Graduate Council of
Texas State University in partial fulfillment
of the requirements for the degree of
Master of Science
with a Major in Chemistry
August 2020

Committee Members:

Christopher Rhodes, Chair

Benjamin Martin

Shane Yost

COPYRIGHT

by

Luis A. Albiter

2020

FAIR USE AND AUTHOR'S PERMISSION STATEMENT

Fair Use

This work is protected by the Copyright Laws of the United States (Public Law 94-553, section 107). Consistent with fair use as defined in the Copyright Laws, brief quotations from this material are allowed with proper acknowledgement. Use of this material for financial gain without the author's express written permission is not allowed.

Duplication Permission

As the copyright holder of this work I, Luis A. Albiter, refuse permission to copy in excess of the "Fair Use" exemption without my written permission.

DEDICATION

This thesis is dedicated to my family, friends and the many people who have been a source of encouragement, support and guidance throughout my education that has inspired me to pursue and complete this research.

ACKNOWLEDGEMENTS

The author would like to thank research group members for their contribution of knowledge throughout this work. The completion of this thesis and study could not have been possible without the expertise of Dr. Christopher Rhodes and Dr. Fernando Godinez-Salomon. The knowledge that Dr. Fernando Godinez-Salomon has passed on has been extremely beneficial throughout this research. The guidance and encouragement that Dr. Christopher Rhodes provided has been of great value. Thanks are due to Dr. Ben Martin and Dr. Shane Yost for their input in this work. Finally, the author would like to thank the Office of Naval Research (Grant: N00014-19-1-2071) and Texas State University for funding this research.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	v
LIST OF TABLES	viii
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xi
ABSTRACT	xii
 CHAPTER	
1. INTRODUCTION	1
1.1. Hydrogen as a Renewable Fuel Source	1
1.2. Background on Electrolyzers	3
1.3. Oxygen Evolution Reaction, Electrocatalysts, and their Limitations	4
1.4. Supported Catalyst	8
1.5. Niobium Oxide as a Support Candidate	10
1.6. Prior Work on Niobium Oxide as a Support for Electrocatalyst	11
1.7. Motivation and Research Objectives	12
2. EXPERIMENTAL METHODS	13
2.1. Chemicals	13
2.2. Synthesis of Niobium Oxide	13
2.3. Preparation of Niobium Oxide Xerogels	13
2.4. Preparation of Substituted Niobium Oxide Xerogels	14
2.5. Preparation of Niobium Oxide Aerogels	14
2.6. Thermal Treatment of Niobium Oxide Xerogel and Aerogel in Air	15
2.7. Thermal Treatment of Niobium Oxide Xerogel and Aerogel in Hydrogen ...	15
2.8. Physical Characterization of Niobium Oxide Xerogels and Aerogels	16
2.9. Electrical Conductivity Measurements	16
3. RESULTS AND DISCUSSION	18
3.1. Overview of synthesis approach	18

3.2. Effects of Drying Methods	20
3.3. Effects of Thermal Treatment in Air	25
3.4. Effects of Metal Substituents	29
3.5. Effects of Thermal Treatment in Hydrogen.....	34
4. CONCLUSIONS AND FUTURE WORK	41
REFERENCES	44

LIST OF TABLES

Table	Page
1. BET surface area analysis of as-prepared NbO _x xerogel and aerogel	23
2. BET surface area and porosity analysis of NbO _x xerogel and aerogel heated to 600 °C in air	28
3. Atomic percent for elemental mapping of substituted NbO _x from energy dispersive spectroscopy.....	32
4. Electronic conductivities of substituted Nb ₂ O ₅	34
5. Calculated conductivity of NbO _x after heating to 875 °C in air and H ₂	35
6. BET surface area and porosity analysis of NbO _x heated at different temperatures under H ₂	37
7. Conductivities of NbO _x heated at different temperatures under H ₂	38

LIST OF FIGURES

Figure	Page
1. U.S. primary energy consumption by energy source, 2019.....	1
2. Capacity additions of renewable energy in the U.S.....	2
3. Electrolyzer diagram.....	3
4. Plot of Gibbs free energy of reactive species and intermediates (horizontal lines) of the oxygen evolution reaction (OER) versus the reaction coordinate.	5
5. Volcano plot of OER activity for various oxide catalysts versus the enthalpy of a lower to higher valent oxide transition.	6
6. Oxygen evolution reaction scan for bulk and nanoparticle catalysis of Ru, Ir, and Pt....	7
7. Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number.....	8
8. Pourbaix diagram for the Nb-H ₂ O system at 25, 75, and 95 °C.	10
9. A schematic illustration of the synthesis reaction for NbO _x	19
10. Schematic illustration of the synthesis process of NbO _x	20
11. (a) NbO _x wet gel during the aging process, (b) NbO _x xerogel, (c) NbO _x aerogel.	21
12. Isotherm of the as-prepared NbO _x xerogel and aerogel.....	22
13. Pore size distribution for the as-prepared NbO _x xerogel and aerogel.....	23
14. Phase diagram of CO ₂	24
15. SEM images of NbO _x xerogel (a, b) and aerogel (c, d) at different magnifications....	25
16. Thermogravimetric analysis of NbO _x xerogel in air.....	26
17. X-ray diffraction pattern of NbO _x aerogel and xerogel as-prepared and heated to 600 °C in air.	27

18. SEM image of the NbO _x aerogel after 600 °C in air.	28
19. Image of in-house conductivity cell and diagram.	29
20. X-ray diffraction pattern of substituted Nb ₂ O ₅	30
21. 2θ values for the (001) plane of the substituted Nb ₂ O ₅ and ionic radii of substituents.	31
22. Energy dispersive spectroscopy elemental mapping of the substituted Nb ₂ O ₅ ; (a) Ti- NbO _x , (b) Ru-NbO _x , (c) W(VI)-NbO _x , and (d) W(V)-NbO _x	32
23. Images of NbO _x before (a) and after heating in air (b) and hydrogen (c).	34
24. X-ray diffraction pattern of NbO _x after heating to 875 °C in air and H ₂	35
25. SEM image of NbO _x after heating to 875 °C in H ₂	36
26. X-ray diffraction pattern for NbO _x heated to 500, 600, and 875 °C.	37
27. SEM images of NbO _x after 600 °C thermal treatment.	38

LIST OF ABBREVIATIONS

Abbreviation	Description
OER	oxygen evolution reaction
PEM	proton exchange membrane
HER	hydrogen evolution reaction
ICP-MS	inductively coupled plasma mass spectrometry
PGM	platinum group metal
DSA	dimensionally stable anodes
MEA	membrane electrode assembly
BET	Brunaur-Emmett-Teller
BJH	Barrett-Joyner-Halenda
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
EDS	energy dispersive spectroscopy

ABSTRACT

Oxygen evolution reaction (OER) catalyst limitations including cost, activity, and stability remain bottlenecks to the wide scale adoption of proton exchange membrane (PEM) water electrolyzers used to split water into hydrogen and oxygen. Distributing the catalyst on a high surface area support can reduce the loading of the active noble-metal OER catalyst (e.g., ruthenium and iridium) and lower the cost of PEM electrolyzers. Carbon, which is typically used as a support material, is highly unstable under the conditions required for OER which makes it unfeasible for long-term use within electrolyzers. Therefore, alternative catalyst supports are needed. Niobium oxide, Nb_2O_5 , is stable under the oxidative potentials and highly corrosive acidic conditions of PEM electrolyzers; however, the low electronic conductivity of Nb_2O_5 significantly limits its use as a catalyst support material. In this work, approaches to obtain high surface area and conductive niobium oxides, NbO_x , for stable supports for OER catalysts were investigated. The effects of synthesis and processing conditions, metal substituents and temperature/atmosphere treatments on the structure, morphology, surface area, and electronic conductivity were evaluated. Niobium oxide was synthesized using a metal alkoxide sol-gel method and dried under either ambient or supercritical drying conditions. To increase the electronic conductivity of NbO_x , different metal (e.g. W^{5+} , W^{6+} , Ti^{4+} and Ru^{4+}) substituents were incorporated during the synthesis process. Thermal treatment under air or hydrogen was investigated to determine the effects of temperature and atmosphere on structure and physical properties. The structure, morphology, composition

and surface area were determined by X-ray diffraction (XRD), scanning electron microscopy, energy dispersive spectroscopy (EDS), thermogravimetric analysis, and nitrogen physisorption measurements. Electronic conductivities were determined using two-point probe measurements. Results show that a high Brunauer-Emmett-Teller (BET) surface area of $454 \text{ m}^2 \text{ g}^{-1}$ and a mesoporous NbO_x structure was obtained by supercritical drying (aerogel) as compared to $389 \text{ m}^2 \text{ g}^{-1}$ and microporous NbO_x structure obtained by ambient evaporative drying (xerogel). The incorporation of W^{5+} and Ti^{4+} within Nb_2O_5 was supported based on XRD and EDS analysis, but no measurable increase in conductivity was observed. The mixed oxide of $\text{RuO}_x\text{-NbO}_x$ heated to 600°C in ambient air had a significantly higher conductivity of $1 \times 10^{-2} \text{ S cm}^{-1}$ which was a substantial improvement from NbO_x which had a conductivity below our detection limit ($\sim 10^{-9} \text{ S cm}^{-1}$). Thermal treatment under hydrogen at various temperatures was investigated, and results showed that the NbO_x aerogel heated in 600°C had an adequate BET surface area of $45 \text{ m}^2 \text{ g}^{-1}$ and an increased conductivity of $1 \times 10^{-5} \text{ S cm}^{-1}$. The development of a high surface area and electrically conductive catalyst support that can withstand the harsh environments of PEM electrolyzers brings the field one step closer to a grid-scale chemical energy storage solution.

1. INTRODUCTION

1.1 Hydrogen as a Renewable Fuel Source

With an ever-growing population, the demand for energy continues to grow to satisfy the needs of modern society. In 2019, 80% of the energy consumed in the US originated from oil, coal, and natural gas, all of which are fossil fuels, and only 11% of energy consumed was from renewable energy sources (Figure 1).¹

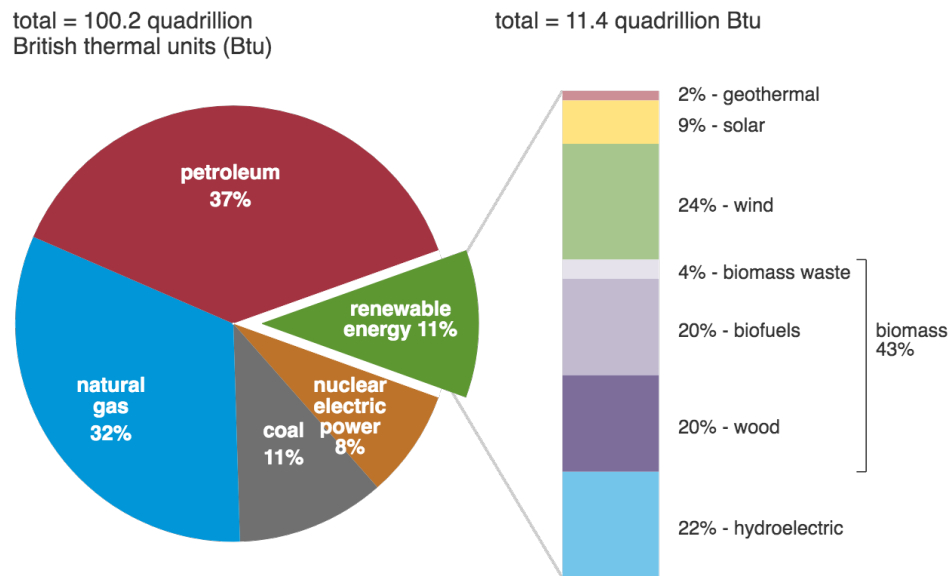


Figure 1. U.S. primary energy consumption by energy source, 2019.¹

Not only are the natural reserves being depleted at an unsustainable rate, the burning of fossil fuels emits a number of air pollutants that are harmful to both the environment and public health. These pollutants include sulfur dioxide (SO₂), nitrogen oxides (NO_x), and carbon dioxide (CO₂). In an effort to eliminate pollutants that arise from energy production, an interest in renewable energy, which includes hydropower, wind and solar has grown. In 2015, renewable energy accounted for 64% of all new electricity generation capacity constructed in the U.S., which of those 64%, 61% accounted for wind and solar (Figure 2).²

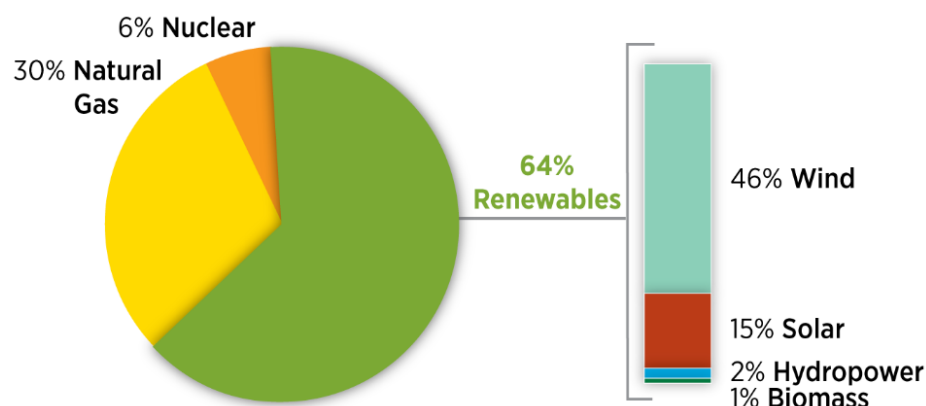


Figure 2. Capacity additions of renewable energy in the U.S.²

Renewable energy sources are intermittent which results in fluctuations in delivery due to changing weather. To be able to provide the required energy during off-peak hours a large scale energy storage solution is needed.

Hydrogen is a good candidate to be used as an energy carrier and as an energy storage solution. Hydrogen is the most plentiful chemical element in the universe. Unlike hydrocarbons, hydrogen is not destroyed by its use since it is in a constant cycle from water to hydrogen. Due to being the lightest element, hydrogen has an energy per mass content of 143 MJ kg^{-1} , three times larger than liquid hydrocarbon based fuels.³ The dominant technology for the production of hydrogen is steam reforming of natural gas or other hydrocarbons. However, steam reforming produces low quality hydrogen and greenhouse gases like CO and CO₂.³

1.2 Background on Electrolyzers

A clean way to produce hydrogen is via water splitting or water electrolysis. High-quality hydrogen can be produced by electrochemical conversion of water to hydrogen and oxygen. Water electrolysis is done on a device known as an electrolyzer. An electrolyzer consists of an anode and a cathode separated by an electrolyte, in this case a solid polymer electrolyte known as a polymer electrolyte membrane (PEM), as shown in Figure 3.

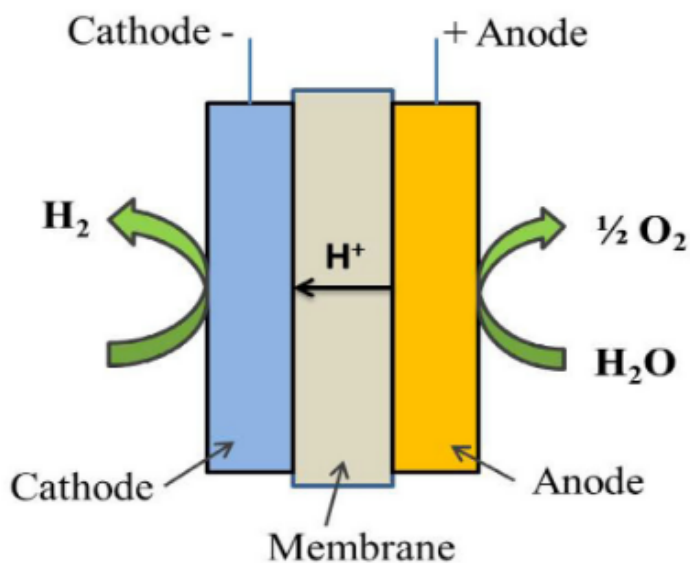
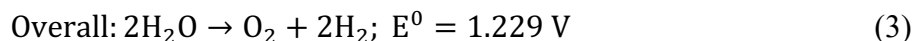
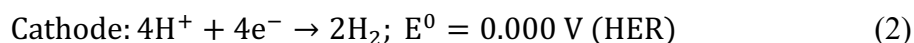
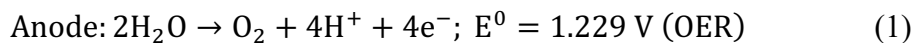


Figure 3. Electrolyzer diagram.⁴

Water is introduced into the electrolyzer cell at the anode via a pump where it is oxidized to form oxygen and positively charged hydrogen ions (protons). The reaction at the anode is known as the oxygen evolution reaction (OER), Equation 1. A renewable energy source, like solar energy, is used to provide the electrons to drive the water electrolysis. Electrons flow in from the external power source, and the hydrogen ions selectively move across the PEM to the cathode. At the cathode, hydrogen ions combine with electrons from the external power source to form hydrogen gas. The reaction at the cathode is

known as the hydrogen evolution reaction (HER), Equation 2. These two reactions occur with the help of electrocatalysts. The half-cell and overall reactions for acidic water electrolysis are shown in Equations 1-3.



Proton exchange membrane electrolyzers exhibit fast kinetics for the cathodic hydrogen evolution reaction; however, in contrast the anodic oxygen evolution reaction exhibits slow sluggish reaction kinetics that result in high overpotentials and significant efficiency losses.⁵ Due to the sluggish kinetics at the anode side, it is of great interest to develop highly-active electrocatalysts that can withstand the oxidative potentials and highly corrosive acidic conditions of PEM electrolyzers. The development of novel PEM OER catalysts with high activity, durability, and lower costs is important to the foundation of the delivery of energy using hydrogen.⁶

1.3 Oxygen Evolution Reaction, Electrocatalysts, and their Limitations

The splitting of water into hydrogen and oxygen is thermodynamically and kinetically unfavorable and requires an applied potential to drive the reaction. The oxygen evolution reaction (OER) has been studied extensively throughout the past several decades. OER is a four electron-proton coupled reaction which requires higher energy to overcome the kinetic barrier when compared to the HER, a two electron-transfer reaction.⁷ To overcome the higher kinetic barriers observed in the OER, an applied potential greater than the equilibrium potential of water, 1.23 V, is required. This extra potential is known as the overpotential, and the deviation from the equilibrium

potential is what determines the electrolysis efficiency. OER involves the transfer of four electrons, and a multistep process with various adsorbed intermediates (OH, O, and OOH) is observed. Various possible mechanisms for the OER have been proposed by different groups.^{8,9} From the Gibbs free energy plot (Figure 4) the formation of the peroxide intermediate (ΔG_4) is the least thermochemically favorable step thus making it the potential-limiting step.¹⁰

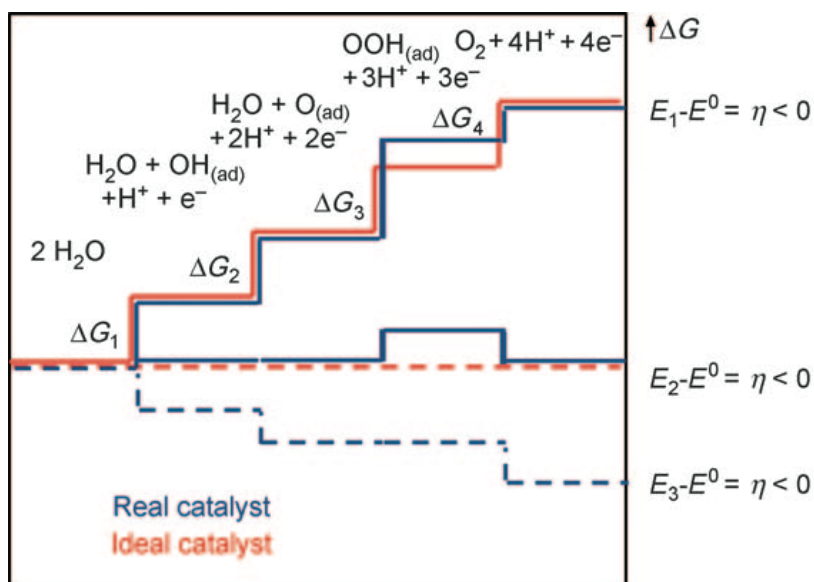


Figure 4. Plot of Gibbs free energy of reactive species and intermediates (horizontal lines) of the oxygen evolution reaction (OER) versus the reaction coordinate.¹⁰

Transition metals have been used as catalysts for the OER. Previous studies have shown that the activity of catalyst is correlated between the overpotential and the standard enthalpy change for the transition from a lower to higher valent state for the oxide.^{11,12} This correlation can be explained by taking the adsorbed intermediates into consideration. As the intermediates interact with the metal (M), the coordination sphere of M will increase and the formation of the surface bound oxygen moieties (MOH, MO, MOOH) is directly related to the heat of formation of the oxide in the next valency state. Therefore, the electrocatalytic activity of transition metals can be determined by the binding strength

of the reaction intermediates to the metal surface. From the volcano plot in Figure 5, RuO₂, IrO₂, and PtO₂ are predicted to have the highest OER activities, which are typical state-of-the-art OER catalysts.

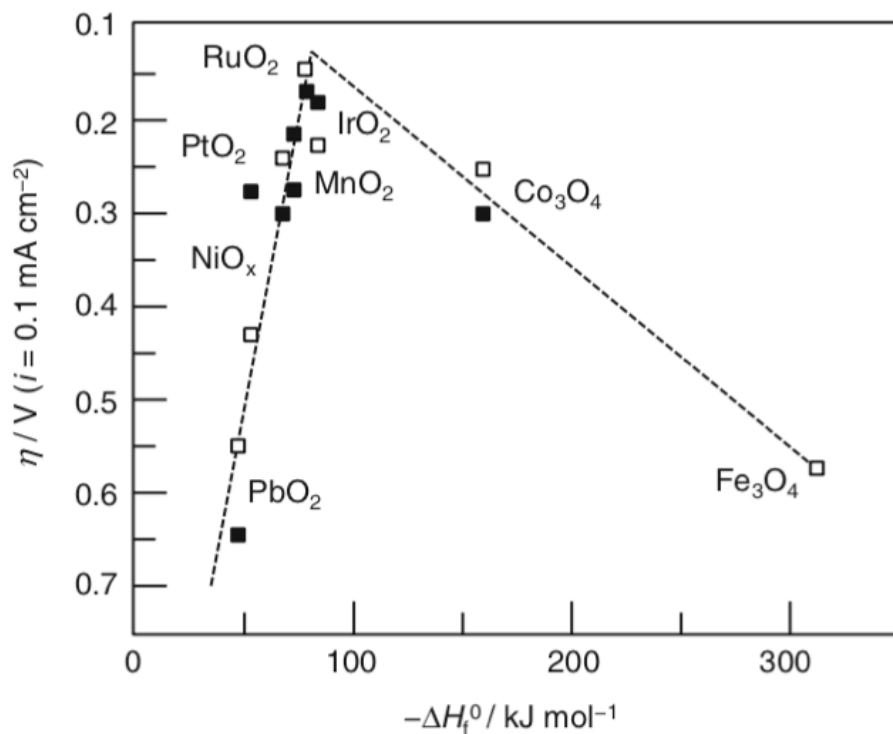


Figure 5. Volcano plot of OER activity for various oxide catalysts versus the enthalpy of a lower to higher valent oxide transition.¹³

Several studies have sought out to demonstrate the intrinsic activity of metal and metal oxides (MO_x) catalysts in a rotating disk electrode.^{14, 15} Reier et al. did a comparative investigation of the activity and durability of carbon supported Ru, Ir, and Pt nanoparticles.¹⁶ The experimentally observed intrinsic OER activities for nanoparticles catalysts decreased in the order of: Ru > Ir > Pt, as shown in Figure 6. Although RuO_x has the highest activity of the three, it was shown that it was the least stable of the three from inductively coupled plasma mass spectrometry (ICP-MS) analysis. IrO_x is the

industry's choice of catalyst which was demonstrated to have a high activity and sufficient stability for OER.¹⁶

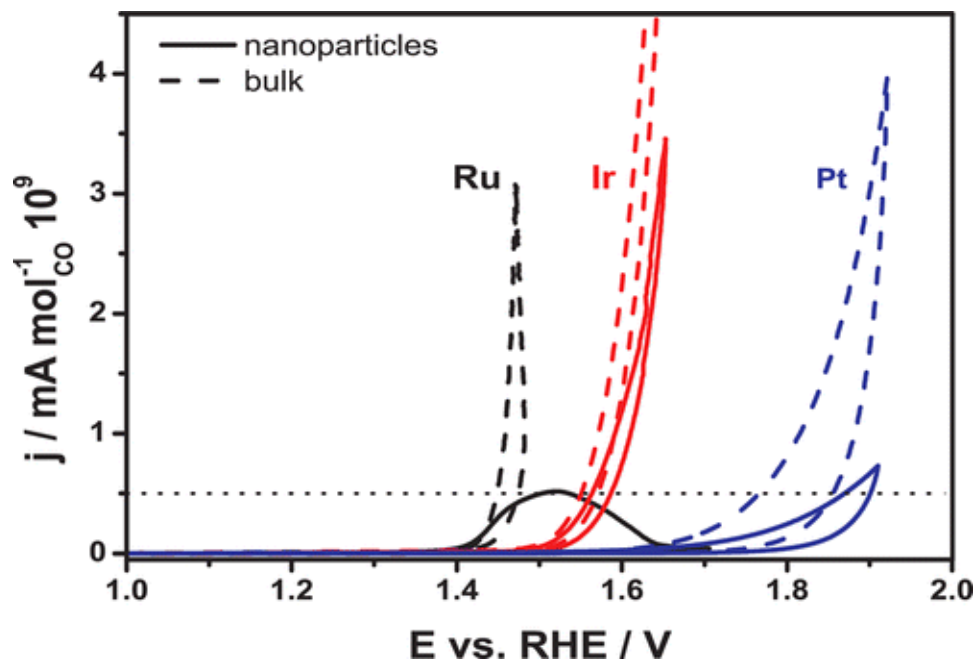


Figure 6. Oxygen evolution reaction scan for bulk and nanoparticle catalysts of Ru, Ir, and Pt.¹⁶

The problem with these platinum group metals (PGM) is their availability. They are extremely rare, and iridium is one of the nine least abundant stable elements in Earth's crust.¹⁷ In Figure 7, it is shown that Ru, Ir, and Pt are among the rarest metals on earth.¹⁸

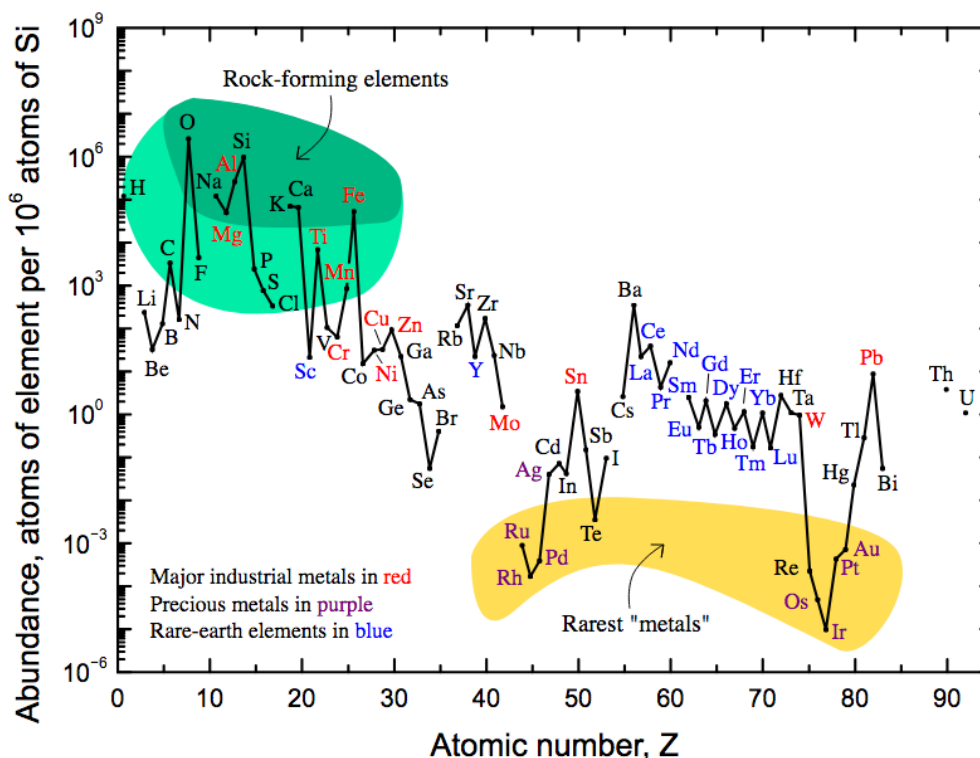


Figure 7. Abundance (atom fraction) of the chemical elements in Earth's upper continental crust as a function of atomic number.¹⁸

In order for the conversion of water to hydrogen using an electrolyzer to be economically viable and sustainable, noble metal oxides as catalyst supports that are plentiful and different approaches to the reduction of the rare metals need to be investigated.

1.4 Supported Catalyst

An approach to reduce the amount of these platinum group metals is using high surface area supports. High surface area supports increase the activity due to the dispersion of small catalyst particles over large areas, which exposes catalytic active sites. In fuel cells, carbonaceous support materials are usually used, which are electrically conductive, around 0.1 S cm^{-1} , and can have high surface area of greater than $100 \text{ m}^2 \text{ g}^{-1}$. However, electrolyzers operate at much higher potentials than fuel cells which makes the use of carbonaceous materials as supports impractical. Carbon is unstable at high

potentials and is oxidized to CO_2 , which leads to aggregation and migration of the PGM.¹⁹ The ideal support material should be electrically conducting, chemically inert, corrosion resistant and have high surface area.²⁰ Support materials must not only sustain the harsh corrosive low pH conditions (pH 0-2), but also the high applied overpotential (~ 2 V) at high current densities. Although there are plenty of inexpensive, chemically inert, and conductive materials, only a few materials are stable in the harsh, corrosive-acidic environment of a PEM electrolyzer.

Metal oxides have been proposed as good electrocatalyst support materials due to their corrosion resistance. Several metal oxides including TiO_2 , Nb_2O_5 , SnO_2 and others have been investigated as alternative supports.²¹⁻²³ These metal oxide supports have also been shown to help stabilize the active material through metal support interactions,^{24, 25} which can provide synergistic effects. The synergistic relationship can be rationalized by different effects explained by Pan et al.²⁶ The three major effects that contribute to the strong metal support interaction are electronic, geometric, and bifunctional effects. The electronic effect results from the charge redistribution at the interfacial contact between a metal and a support. The geometric effect involves the decoration of the metal clusters, either partially covering the metal's surface, or encapsulation that completely covers the metal's surface. This geometric effect can prevent migration of the metal. Lastly, the bifunctional effect creates a "dual site" reaction system. This phenomenon involves the migration of the reactive species from the metal or the support and reactions can occur at the perimeter where the supporting oxide or the metal provides the second reaction site. The main drawback of these stable metal oxides is that they are not good electrical conductors. To increase conductivity of these metal oxides introducing dopants to

increase charge carriers and/or thermal treatment in reducing environment have been investigated.^{27, 28} The metal-support interface can also increase the conductivity of the metal oxide support. The addition of the metal decreases the oxygen vacancy formation energy and results in the stabilization of oxygen vacancy concentrations at the support surface under reducing environments that are not stable for the bare oxide.²⁹

1.5 Niobium Oxide as a Support Candidate

Niobium oxide is a good candidate as a support material, as it is relatively abundant in nature, has low toxicity, and has high corrosion resistance.³⁰ Typically a PEM electrolyzer operates at a temperature of 80 °C and a pH of <1. Asselin et al. studied the corrosion of niobium in concentrated HCl and H₂SO₄ at different temperatures.³¹ At the operating temperate and pH conditions of a PEM electrolyzer, Nb₂O₅ is stable as shown in the Pourbaix diagram in Figure 8.

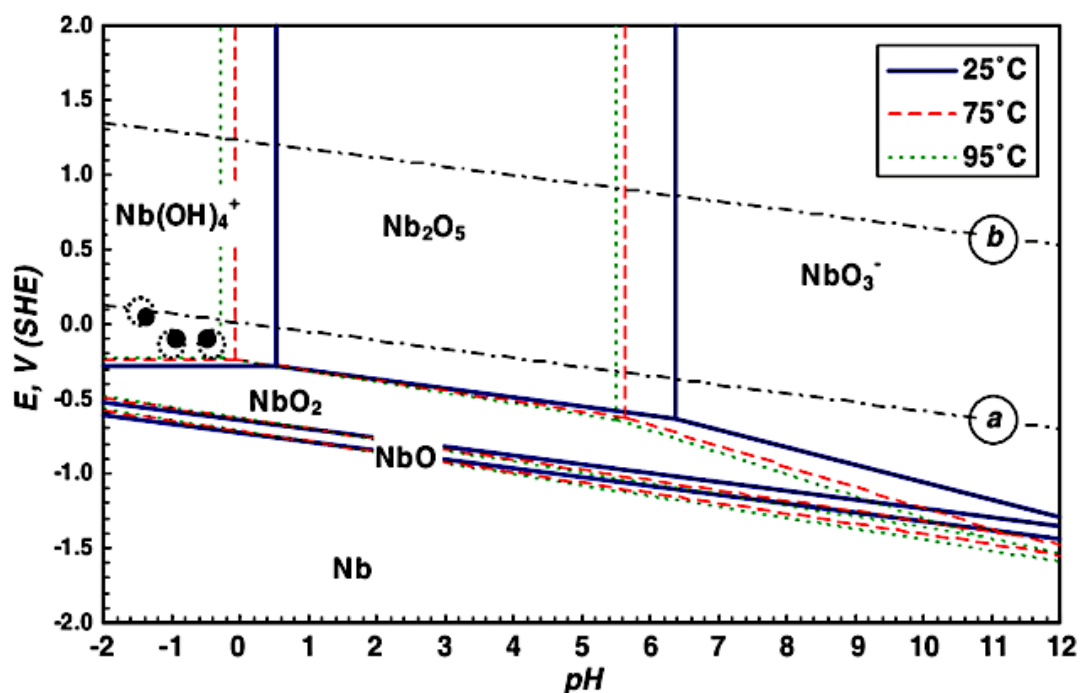


Figure 8. Pourbaix diagram for the Nb-H₂O system at 25, 75 and 95 °C.³¹

Niobium oxide has been synthesized in a relatively quick and easily manner by sol-gel methods. Maurer et al. synthesized Nb_2O_5 via sol-gel method and investigated the effects of different drying methods on the surface area and porosity.³² A Nb_2O_5 aerogel, xerogel, and precipitated form were synthesized and then calcinated to 500 °C. The BET surface area of the Nb_2O_5 aerogel, xerogel and precipitated form, after calcination, was 190 $\text{m}^2 \text{g}^{-1}$, 100 $\text{m}^2 \text{g}^{-1}$, and 85 $\text{m}^2 \text{g}^{-1}$, respectively. This study showed that a high surface area Nb_2O_5 aerogel can be obtainable. It was concluded that the most important factor to increase the surface area and porosity is the drying process of the gels. However, niobium oxide is a wide band gap n-type semiconductor with a conduction band compromised of empty Nb^{5+} 4d orbitals.³³ Further investigation is needed to increase the conductivity of Nb_2O_5 .

1.6 Prior Work on Niobium Oxide as a Support for Electrocatalyst

Niobium oxide thin films have been studied as a support for RuO_2 and IrO_2 in dimensionally stable anodes (DSA),^{34, 35} but thin films results are hard to replicate in a working electrolyzer. In one study, a bimetallic catalyst system consisting of Nb_2O_5 and RuO_2 was synthesized.²² Up to 60% of Nb_2O_5 was added to RuO_2 , and the OER activity and stability were measured in an electrolyzer cell. It was found that the addition of Nb_2O_5 did not increase the OER activity due to the lower electronic conductivity. At 20% Nb_2O_5 addition, the stability was higher than that of RuO_2 after 23 h electrolysis operation using a membrane electrode assembly (MEA) at 1 A/cm^2 current density. In another study, platinum was supported on reduced NbO_2/C support.³⁶ In a rotating disk electrode it was shown that the $\text{Pt}/\text{NbO}_2/\text{C}$ electrocatalyst has three times higher Pt mass activity than a commercial Pt/C electrocatalyst. The stability also increased as the Pt

dissolution decreased. Another study showed similar results which demonstrates that NbO_x has the potential as a catalyst support.³⁷

1.7 Motivation and Research Objectives

Improving the activity and stability while decreasing the loading of PGM is necessary for water electrolysis to be considered a profitable energy carrier. The objectives of this study were to i) synthesize nanostructure NbO_x via sol-gel chemistry, ii) evaluate the effects of evaporative and supercritical drying on the surface area and porosity of NbO_x , iii) evaluate the effects of thermal treatments in air on morphology, and iv) increase the electronic conductivity by substituting different metals within the NbO_x structure and/or thermally treating NbO_x in a reducing (H_2) atmosphere. To the best of the authors knowledge, niobium oxide aerogels have not been investigated as a true support material as an OER catalyst in an electrolyzer. As mentioned above, the prior studies on Nb_2O_5 or NbO_2 differ from this study in that Nb_2O_5 has been used as an additive to either RuO_x or IrO_x . Prior work has explored NbO_2 with carbon added to increase the conductivity³⁶ and have shown promising results; however, the use of carbon will ultimately result in degradation in prolonged use.

Herein, the author investigated the objectives mentioned above to support that i) the supercritically dried NbO_x will result in higher surface area and porosity when compared to the evaporatively dried NbO_x and ii) the NbO_x aerogel thermally treated in H_2 will result in phase transition of Nb_2O_5 to NbO_2 , resulting in higher conductivity. The development of a carbon-free NbO_x support with adequate surface area and conductivity was the goal.

2. EXPERIMENTAL METHODS

2.1 Chemicals

Niobium(V) ethoxide (99.95%), 2-butanol (anhydrous, 99.5%), nitric acid (70%), and titanium(V) isopropoxide ($\geq 97.0\%$) were obtained from Sigma Aldrich.

Ruthenium(III) nitrosyl nitrate, tungsten(V) ethoxide, and tungsten(IV) ethoxide were obtained from Alfa Aesar. Ethyl alcohol (200 proof, 99.5%) was obtained from Acros Organics. Ultrapure water ($\geq 18 \text{ M}\Omega\text{-cm}$) was obtained from ELGA Purelab Classic water purification system.

2.2 Synthesis of Niobium Oxide

In a glovebox with an argon atmosphere ($\leq 1 \text{ ppm H}_2\text{O}$), 0.6274 mL (2.5 mmol) of niobium(V) ethoxide was added into a vial containing 2.5 mL of 2-butanol. The solution was then magnetically stirred for 5 minutes. This solution was then brought out of the glovebox and quickly added to a homogenous solution containing 2.5 mL of 2-butanol, 0.4517 mL of ultrapure water, and 0.1266 mL of nitric acid that was prepared in 12 mL low density polyethylene molds. Gelation occurred within ~ 10 seconds. The gels were then aged for 24 h in their mother solution. Subsequent to the aging step, the gels were transferred into 30 mL glass vials containing 25 mL of ultrapure water and then allowed to soak for 24 hours. After the 24 hours soaking time, 12.5 mL of the water was replaced with clean water, while making sure the gels were always submerged in water to prevent any drying. The water was replaced a total of eight times throughout 24 hours. The gels were then prepared in xerogel and aerogel form as described below.

2.3 Preparation of Niobium Oxide Xerogels

The niobium oxide xerogels were prepared by pouring off excess water and then

dried at 60 °C under atmospheric pressure for 48 hours. The dried, densified monolith obtained was then grounded down into a fine powder using an agate mortar and pestle. The as-prepared synthesized samples were noted as NbO_x-X-AP.

2.4. Preparation of Substituted Niobium Oxide Xerogels

To incorporate tungsten (W), ruthenium (Ru) or titanium (Ti) ions, the metal ion precursor was added at a 20% substitution molar ratio to the NbO_x synthesis, as described above. In the glovebox, 0.5 mmol of either titanium(V) isopropoxide, ruthenium(III) nitrosyl nitrate, tungsten(V) ethoxide, or tungsten(IV) ethoxide were dissolved in a vial containing 2.5 mmol of niobium(V) ethoxide and 2.5 mL of 2-butanol. The solution was magnetically stirred for 20 minutes. The solutions were then brought out of the glovebox and quickly added to 12 mL low density polyethylene molds containing a homogenous solution of 2.5 mL of 2-butanol, 0.4517 mL of ultrapure water, and 0.1266 mL of nitric acid. The gels were aged for 24 hours and were washed the same as previously mentioned for 48 hours. Subsequent to the aging step, excess water was poured off from the molds and then dried at 60 °C at atmospheric pressure for 48 hours. The individual gels were then calcinated in a Thermo Scientific Thermolyne small benchtop muffle furnace to 600 °C for 2 hours in ambient air at a ramp rate of 10 °C min⁻¹. The substituted samples were noted as Ti-NbO_x, Ru-NbO_x, W(VI)-NbO_x, and W(V)-NbO_x, for the corresponding substituents of Ti⁴⁺, Ru⁴⁺, W⁶⁺, and W⁵⁺, respectively.

2.5 Preparation of Niobium Oxide Aerogels

To prepare the aerogels, following the washing procedure an additional solvent exchange step was done to replace water with ethyl alcohol. In the 30 mL glass vials, 12.5 mL of water was replaced with 12.5 mL of ethyl alcohol. The bottom layer of water

was pipetted out and replaced with an additional 12.5 mL of ethyl alcohol. The ethyl alcohol was replaced eight times over 48 hours. Supercritical drying was done in a Leica EM CPD300 critical point dryer. The ethyl alcohol was exchanged with liquid CO₂ for a total of twelve times and dried under supercritical CO₂ conditions (42 °C), the gas CO₂ was removed at a slow setting. The as-prepared aerogels were noted as NbO_x-A-AP.

2.6 Thermal Treatment of Niobium Oxide Xerogel and Aerogel in Air

The niobium oxide xerogel and aerogels were thermally treated in a Thermo Scientific Thermolyne benchtop muffle furnace at 600 °C for 2 hours in ambient air using a ramp rate of 10 °C min⁻¹. After the 2 hour dwell time, the samples were allowed to cool to room temperature before removing them from the furnace. The samples were ground using an agate mortar and pestle after the heat treatment. The thermally treated samples were noted as NbO_x-X-600A and NbO_x-A-600A for the xerogels and aerogels, respectively.

2.7 Thermal Treatment of Niobium Oxide Xerogel and Aerogel in Hydrogen

For the thermal treatment under hydrogen, in a porcelain combustion boat, 100 mg of either niobium oxide xerogel or aerogel sample was heated in a Thermo Scientific Lindberg Blue M Mini-mite tube furnace to either 500, 600, or 875 °C for 2 hours under a 60 mL min⁻¹ flow of 99.999% H₂ using a ramp rate of 10 °C min⁻¹. After treatment, the samples were allowed to cool to room temperature under the flow of H₂ before removing them from the tube furnace. The samples were ground using an agate mortar and pestle, as described above. The thermally treated samples in H₂ were noted as NbO_x-A-500H, NbO_x-A-600H, and NbO_x-A-875H for the NbO_x treated at 500, 600, and 875 °C, respectively.

2.8 Physical Characterization of Niobium Oxide Xerogels and Aerogels

Powder X-ray diffraction (XRD) measurements were conducted using a Bruker AXS D8 Advance powder X-ray diffractometer with a Cu Ka ($\lambda = 1.5406 \text{ \AA}$) radiation source, operating at 40 kV and 25 mA and a high resolution energy dispersive 1D Linxeye XE detector. The scan range of 2θ was $15^\circ < 2\theta < 85^\circ$ with a 0.01° increment. A Si low background holder was used.

Nitrogen physisorption measurements were obtained using a Micromeritics ASAP 2020 surface area and porosimetry analyzer. Before analysis, the samples were degassed under vacuum at 120°C for 16 h. Brunauer–Emmett–Teller (BET) surface areas were obtained from the adsorption-desorption isotherms. Mean pore diameters and cumulative pore volumes were calculated from the adsorption-desorption isotherm using the Barrett-Joyner-Halenda (BJH) method (Micromeritics Microactive software, version 4.02).

Thermogravimetric analysis was performed on a TA Instruments Q500. Starting at room temperature, the samples were heated to 800°C in air at a ramp rate of $10^\circ\text{C min}^{-1}$. The morphology was analyzed by scanning electron microscopy (SEM) using a SEM FEI-Helios Nanolab 400. Samples prepared for SEM were dispersed in isopropanol and casted onto an aluminum sample holder.

2.9 Electrical Conductivity Measurements

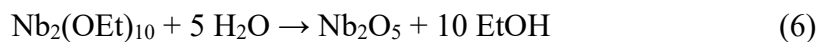
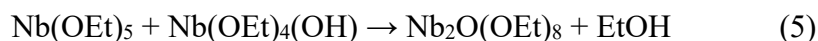
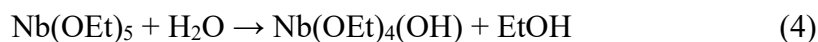
Electrical conductivity measurements were obtained using an in-house two-probe conductivity cell made up of two aluminum plates, a spring, two stainless steel anvils and an insulating plastic cylinder (see Figure 19). The NbO_x samples were loaded between the two stainless steel anvils and sandwiched between the two aluminum plates. An Arbin BT2043 was used to apply a constant voltage of 0.1 V and the steady state current was

measured. The electrical conductivity (σ) was calculated using the formula $\sigma = h/(R \times A)$, where h is the height of the sample, R is the measured resistance, and A is the area of the sample.

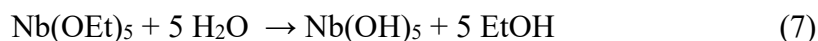
3. RESULTS AND DISCUSSION

3.1. Overview of synthesis approach

Niobium oxide was synthesized by a modified sol-gel technique adapted from a previously reported procedure.³⁸ The main reactions involved in the synthesis are hydrolysis and condensation reactions that yield a macromolecular oxide network. Plausible reactions for hydrolysis (eq. 4), condensation (eq. 5) and the overall reaction (eq. 6) are shown below.³⁹



If a polycondensation between hydroxoalkoxoniobates with elimination of alcohol is predominant, a plausible main reaction would be eq. 4, explained above. However, due to the complexity of sol-gel chemistry, a previous literature showed other possible reaction routes (eq. 7).⁴⁰ Because the high reactivity of niobium alkoxides toward water, gelation may occur from an olation/oxolation process between Nb(OH)_5 molecules with elimination of water, as described by the following equation:



The rate of hydrolysis can be increased with the use of acid catalysts. In eq. 7, all of the ethoxide groups get hydrolyzed with the help of nitric acid. The negative partial charge of the oxygen on the ethoxide groups can be easily protonated by H_3O^+ ions. Under such conditions the prototropic transfer and the departure of the leaving group can no longer be the rate limiting steps, and condensation can occur between these rapidly formed hydrolyzed species.⁴¹

An associative nucleophilic substitution can describe the mechanism (Figure 9). In the first step, the hydrolysis reaction, the positively charged Nb^{5+} atom is susceptible to a nucleophilic addition of water followed by a proton transfer from the entering molecule to the ethoxide group which is subsequently eliminated. In the second step, the condensation reaction forms a Nb-O-Nb network with the elimination of water and an ethoxide group.

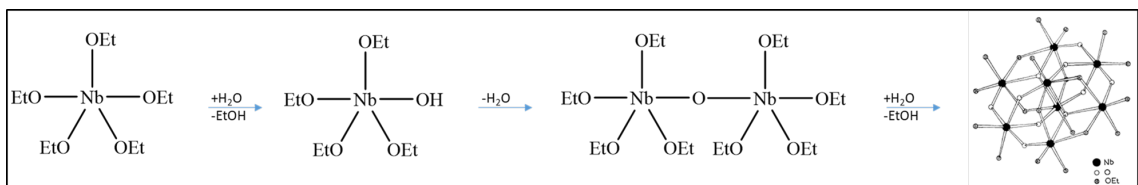


Figure 9. A schematic illustration of the synthesis reaction for NbO_x .⁴²

A direct reaction of the metals with alcohols is possible, and these alcoholysis reactions can be used to modify the reactivity of the metal alkoxides. The facility of the alcoholysis reactions depend on the acidity of the alcohol. Branched aliphatic alcohols, being less acidic, react more slowly than their unbranched counterparts. Therefore, the reactivity sequence is $\text{MeO} > \text{EtO} > \text{Pr}^i\text{O} > \text{Bu}^i\text{O}$ and thus the hydrolysis of an alkoxide strongly depends on the length of the alkyl chain.^{39, 43}

The solvent can also influence the gelation time, as supported by previous work that showed the gelation time of titanium oxide gels was significantly different using methanol, ethanol, propanol, and butanol solvents for the sol-gel reaction.⁴⁴ The solvent and its polarity may play a role in the gelation process by influencing the degree of interaction with the Nb-O-Nb network. Within this work, the use of BuOH solvent within the NbO_x sol-gel reaction resulted in a quick gelation time of 10 seconds. Due to the relatively long chain of BuOH when compared to MeOH or EtOH, BuOH is less polar than MeOH or EtOH. It is possible that BuOH may interact less with the polar bonds of

the Nb-O-Nb network and favor further growth of the Nb-O-Nb network compared with MeOH or EtOH; however, additional experiments are needed to determine the specific role of solvent within the NbO_x sol-gel reaction.

The aging and washing times were adjusted to yield the desired physical properties. The aging step strengthens the gel network by several processes including polycondensation, syneresis, coarsening and phase transformation.⁴⁵ In preliminary work, not shown here, the washing with water to remove any unreacted organic materials seems to have improved the surface area and porosity of the NbO_x powders. The schematic illustration of the overall synthesis process is shown below in Figure 10.

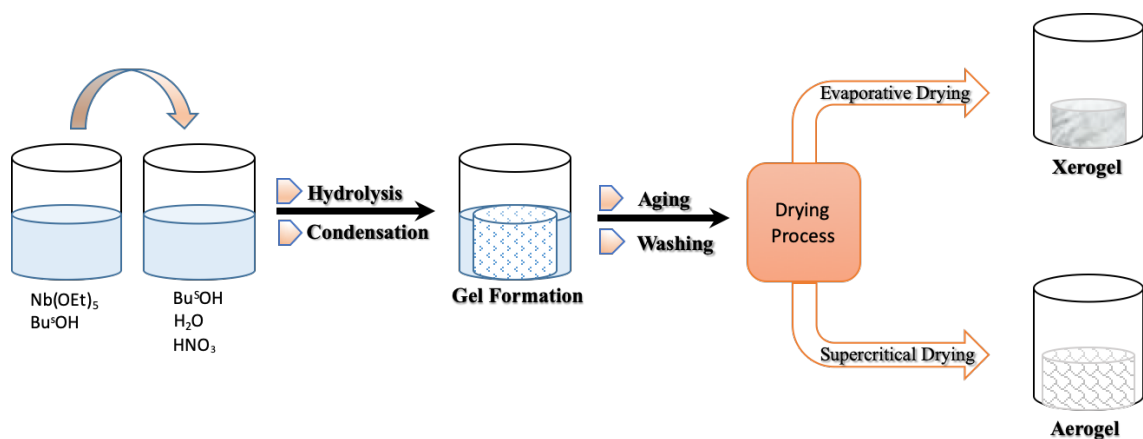


Figure 10. Schematic illustration of the synthesis process of NbO_x.

3.2. Effects of Drying Methods

The two different drying methods, evaporative and supercritical, were performed and evaluated. In evaporative dried NbO_x (xerogel), the overall size of the monolith greatly decreased when compared to the NbO_x wet-gel. The supercritical dried NbO_x (aerogel) monolith retained its size. Pictures of the wet gel, xerogel, and aerogel are shown in Figure 11.

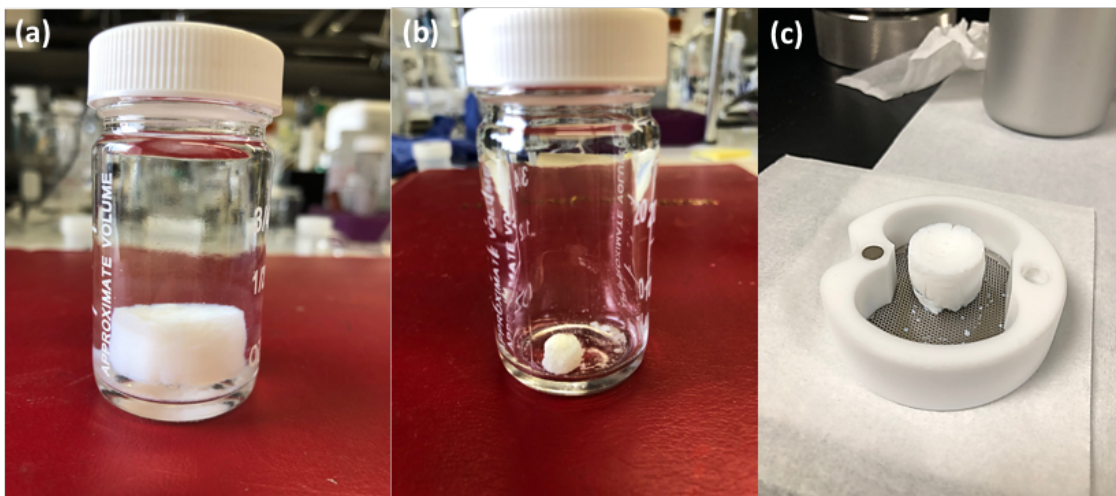


Figure 11. (a) NbO_x wet gel during the aging process, (b) NbO_x xerogel, (c) NbO_x aerogel.

From the isotherm in Figure 12, a type I isotherm was obtained for the xerogel which is typical for a microporous material. For the aerogel, a type V isotherm was obtained, which is characteristics of a mesoporous material.⁴⁶ The BET surface areas, pore volumes and pore size distributions were determined from the adsorption-desorption isotherms.

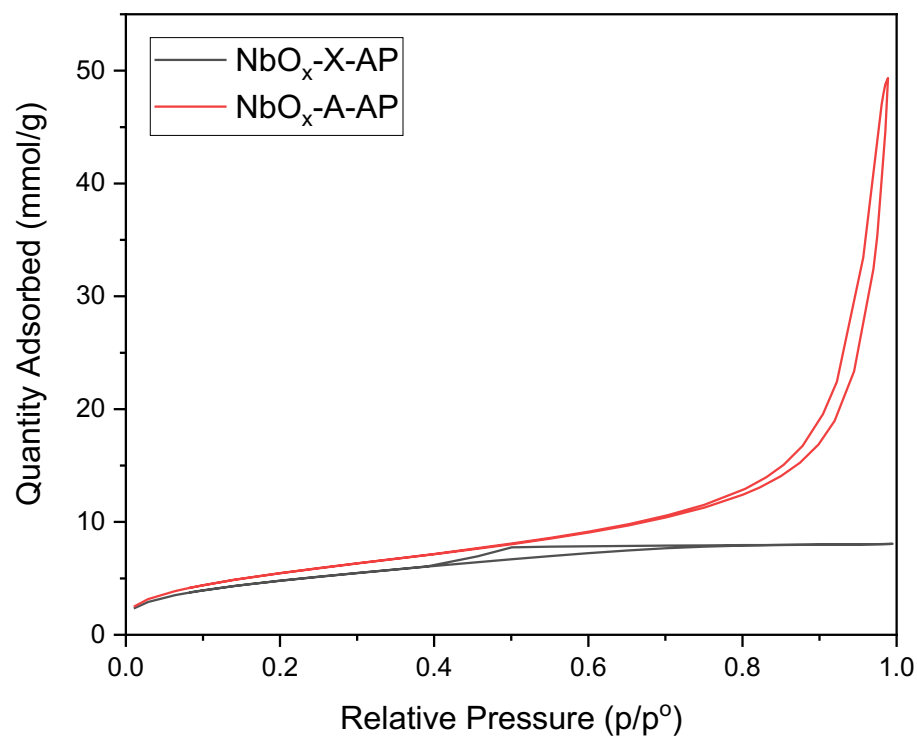


Figure 12. Isotherm of the as-prepared NbO_x xerogel and aerogel.

Results obtained from the pore size distribution plots in Figure 13 agree with the isotherms described above. The xerogel had very low porosity with few pores distributed in the micropore range ($< 2\text{nm}$). The aerogel had a large distribution of mesopores (2-50 nm) and macropores ($> 50\text{nm}$).

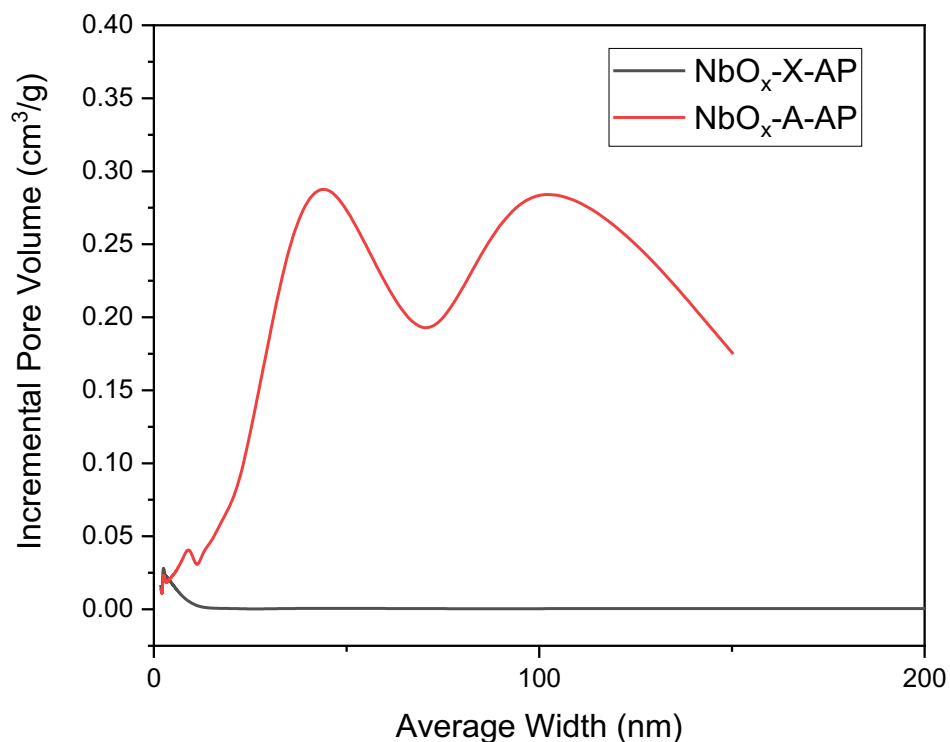


Figure 13. Pore size distribution for the as-prepared NbO_x xerogel and aerogel.

The BET surface area for the as-prepared NbO_x xerogel and aerogel were relatively high at 389 m² g⁻¹ and 454 m² g⁻¹, respectively. The surface area and pore size data are tabulated Table 1 below.

Table 1. BET surface area and porosity analysis of as-prepared NbO_x xerogel and aerogel.

Material ID	BET Surface Area (m ² g ⁻¹)	Cumulative Pore Volume (cm ³ g ⁻¹)	Mean Pore Width (nm)
NbO _x -X-AP	389	0.30	3
NbO _x -A-AP	454	1.8	13

The drying methods had a significant effect on the surface area and a more apparent difference on the porosity of the NbO_x materials. During evaporative drying as the solvent evaporates from the pores of the gel network, a liquid-vapor meniscus forms in the pores of the gels creating a capillary pressure gradient capable of reaching 100-200

MPa (1000-2000 atm).⁴⁷ These high pressures cause the fragile porous structure of the wet gels to collapse and shrink. The collapse and shrinkage of the wet gels can be observed in Figure 11. The NbO_x xerogel is about six times smaller than the NbO_x wet gel, and the collapse of the porous structure is also evident in the pore size distribution plot. During supercritical drying, liquid CO₂ is brought up to the supercritical fluid phase where a distinct liquid-vapor phase does not exist (Figure 14), which allows for the removal of the solvent while avoiding surface tension and preventing the collapse of pores that ultimately preserves the porous structure.

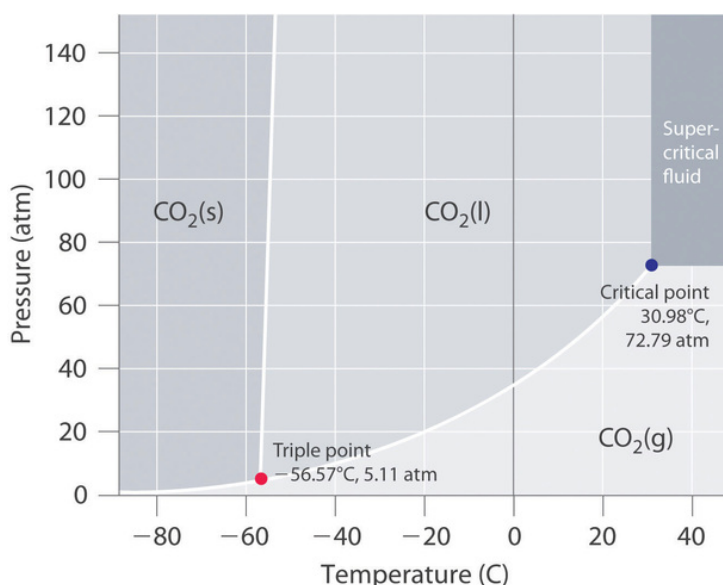


Figure 14. Phase diagram of CO₂.⁴⁸

SEM images of the as-prepared NbO_x xerogel and aerogel are shown in Figure 15. From the SEM images a not very porous structure for the xerogel and a very porous structure for the aerogel are observed. The NbO_x xerogel aggregates were also larger than the NbO_x aerogel. The observations from the SEM images further validate the BET surface area analysis and the porosimetry measurements.

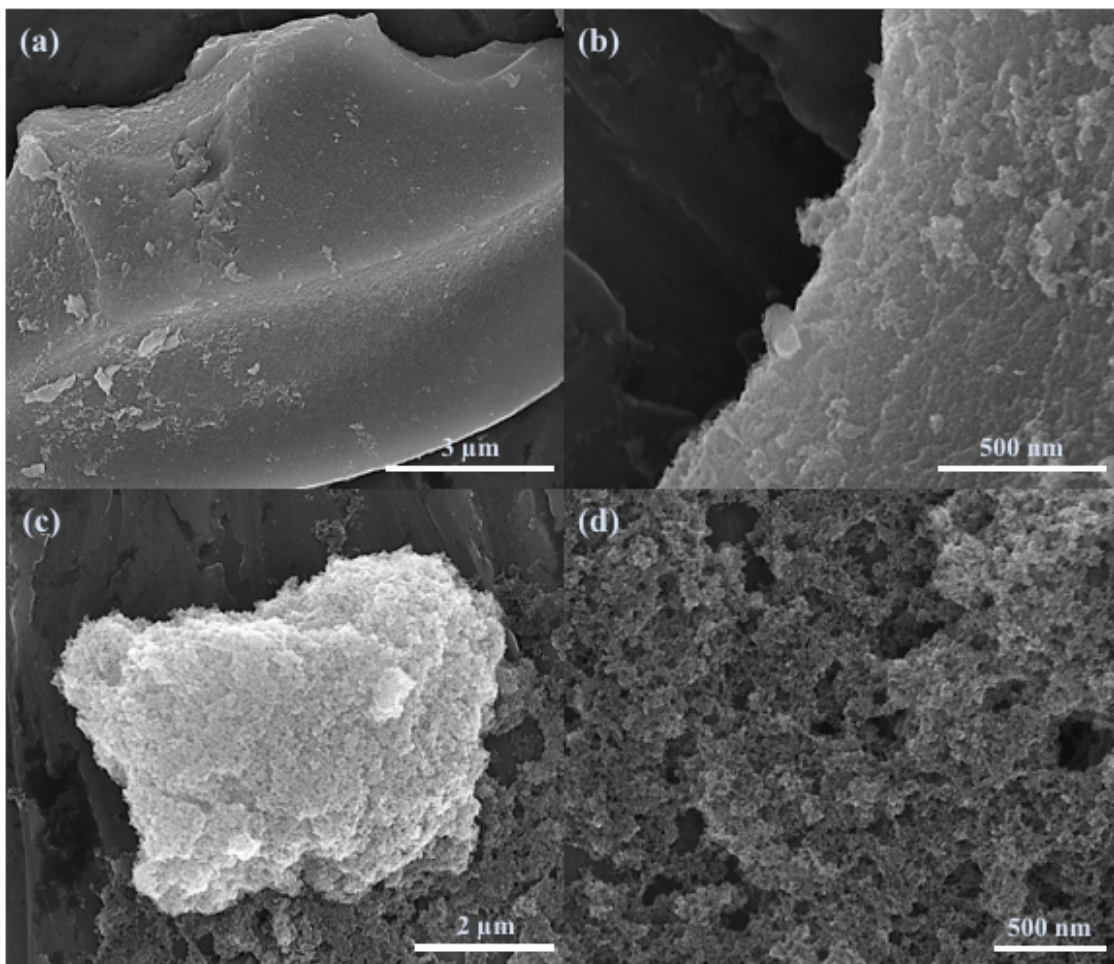


Figure 15. SEM images of NbO_x xerogel (a,b) and aerogel (c,d) at different magnifications.

3.3. Effects of Thermal Treatment in Air

The effects of thermal treatment in air on the as-prepared NbO_x xerogel and aerogel structure were evaluated. The xerogel and aerogel were calcinated to transform them from a network of metal oxides, alkoxides and hydroxides to NbO_x.

Thermogravimetric analysis (TGA) was done to determine the effect of thermal treatment on mass loss and was used to identify a temperature treatment. TGA data for the NbO_x xerogel is shown in Figure 16.

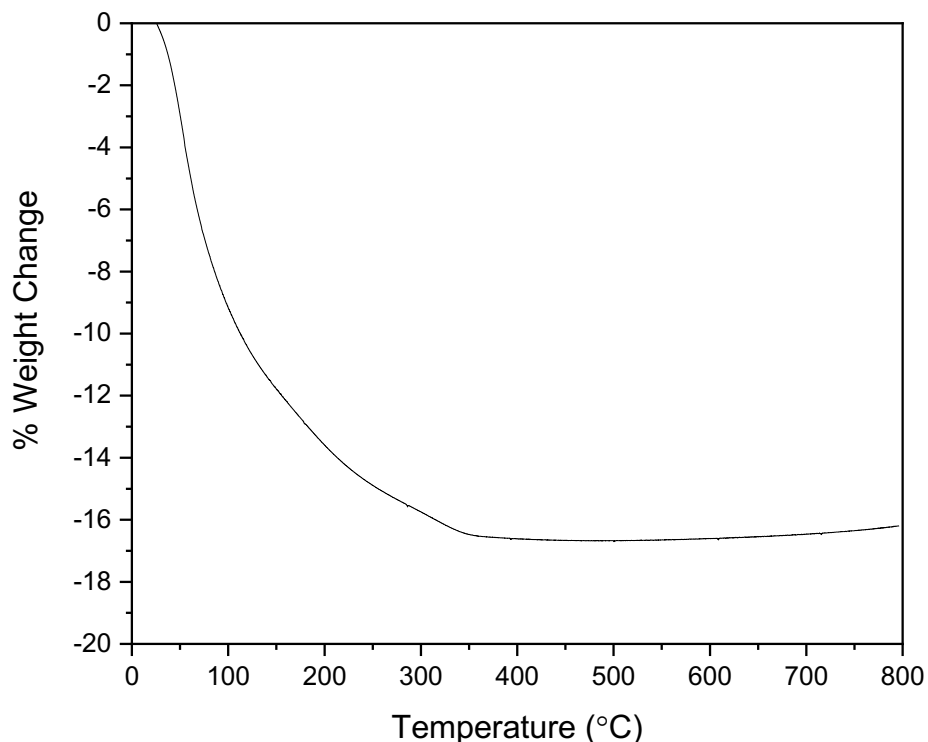


Figure 16. Thermogravimetric analysis of NbO_x xerogel in air.

The TGA showed a steady weight loss up to 350 °C. The 17% weight loss is attributed to residual water loss and removal of unreacted organic materials.⁴⁹ Based on the TGA data obtained and previous work that has shown NbO_x to crystallize at temperatures above 500 °C,⁵⁰ a temperature of 600 °C was chosen.

X-ray diffraction of the as-prepared NbO_x xerogel and aerogel showed significant differences from the thermally treated samples. The as-prepared NbO_x xerogel and aerogel were both amorphous prior the thermal treatment. After the thermal treatment both samples showed peaks consistent with a pseudohexagonal Nb₂O₅ crystal structure, as shown in Figure 17.

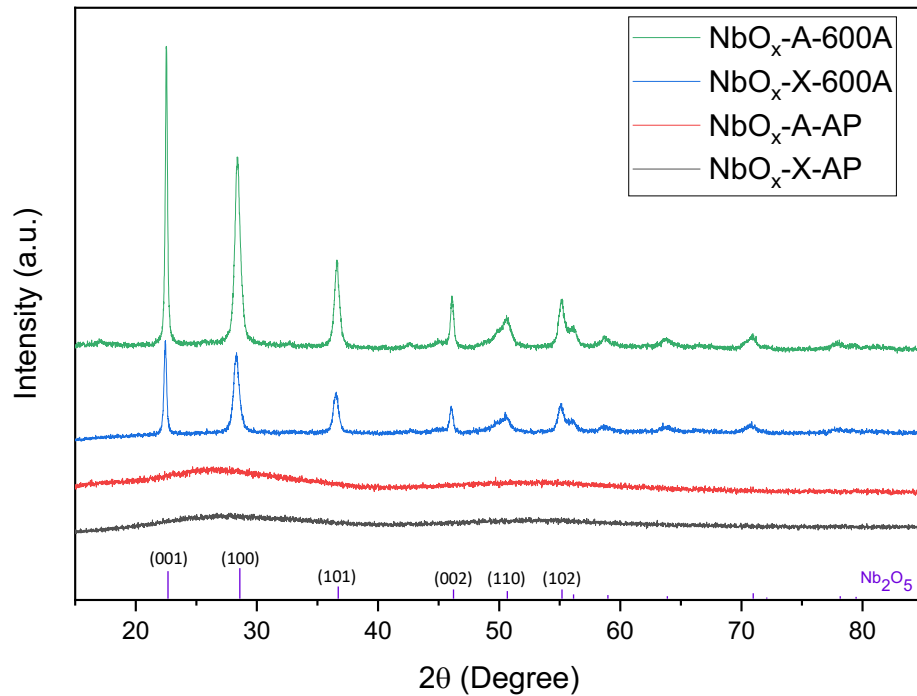


Figure 17. X-ray diffraction pattern of NbO_x aerogel and xerogel as-prepared and heated to 600 °C in air.

After thermal treatment in air at 600 °C, the BET surface area and porosimetry were evaluated. The BET surface area and porosity had a significant change after thermal treatment, and the results are tabulated in Table 2. For the NbO_x xerogel, the surface decreased from 389 m² g⁻¹ to 31 m² g⁻¹ after heating in air at 600 °C. The NbO_x aerogel showed similar decrease in surface area, from 454 m² g⁻¹ to 23 m² g⁻¹. Both, NbO_x-X-600A and NbO_x-A-600H samples had a decreased in porosity after thermal treatment. However, NbO_x-A-600H had a higher mean pore width when compared to the as-prepared NbO_x (NbO_x-X-AP). The decrease in surface area was expected at high temperatures due to particle aggregation and crystal growth.

Table 2. BET surface area and porosity analysis of NbO_x xerogel and aerogel heated to 600 °C in air

Material ID	BET Surface Area (m²g⁻¹)	Cumulative Pore Volume (cm³g⁻¹)	Mean Pore Width (nm)
NbO _x -X-AP	389	0.29	3.0
NbO _x -X-600A	31	0.14	1.9
NbO _x -A-AP	454	1.8	13
NbO _x -A-600A	23	0.18	3.5

An SEM image of NbO_x-A-600A is shown in Figure 18, showing that the porous morphology of the aerogel was retained after the thermal treatment.

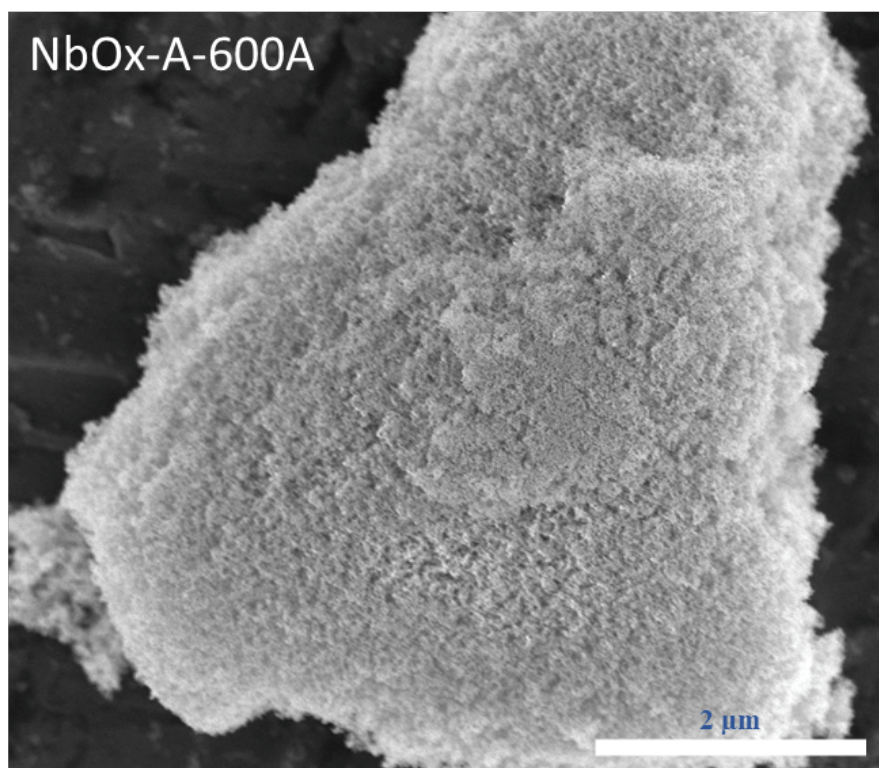


Figure 18. SEM image of the NbO_x aerogel after 600 °C in air.

The conductivities of the NbO_x xerogel and aerogel were measured in an in-house conductivity cell (Figure 19) to determine the effects of thermal treatment in air. The calculated conductivities were below our detection limit of $\sim 1 \times 10^{-9}$ S cm⁻¹ and

subsequently there was no observable increased in conductivity when compared to the as-prepared NbO_x . The conductivity of Nb_2O_5 was expected to be low. Nb_2O_5 is an n-type semiconductor whose electron concentration is determined mainly by the concentration of stoichiometric defects such as oxygen vacancies.⁵¹

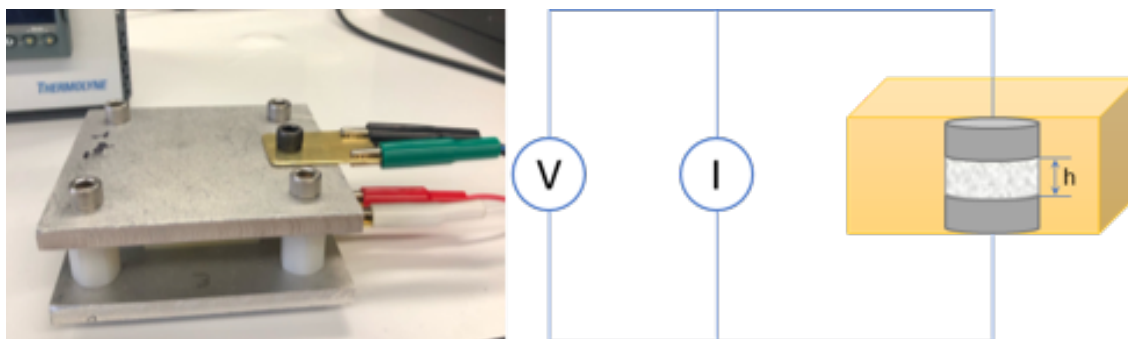


Figure 19. Image of in-house conductivity cell and diagram.

3.4. Effects of Metal Substituents

To increase the electronic conductivity of NbO_x , different metal (e.g. W^{5+} , W^{6+} , Ti^{4+} and Ru^{4+}) substituents were incorporated during the synthesis and then treated to 600 °C in air. The incorporation of W^{5+} , W^{6+} , Ru^{4+} , and Ti^{4+} were evaluated by XRD and energy dispersive spectroscopy (EDS), and the effect on conductivity was measured. From the XRD pattern in Figure 20, when compared to the NbO_x xerogel (NbO_x -600) no new visible peaks were observed for Ti-NbO_x and W(V)-NbO_x . In contrast, Ru-NbO_x showed the appearance of new peaks associated to rutile RuO_2 . The presence of the W^{6+} ions decreased the overall crystallinity of $\text{W}^{6+}\text{-NbO}_x$ when compared to the NbO_x

xerogel. The appearance of new peaks associated to rutile RuO_2 is indicative of phase separation and thus unsuccessful incorporation of ruthenium within the Nb_2O_5 structure.

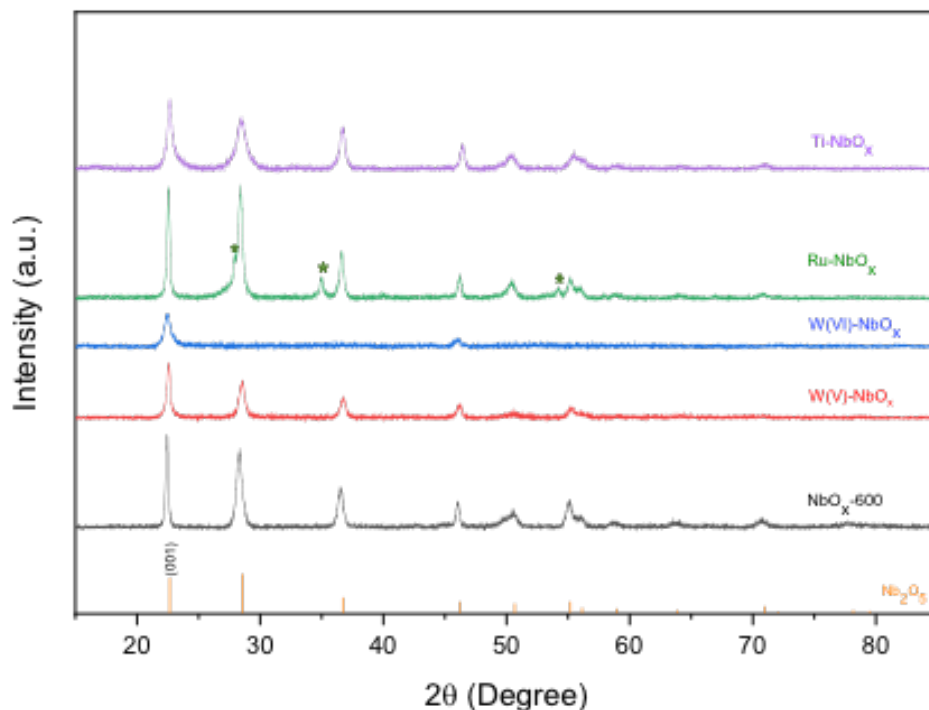


Figure 20. X-ray diffraction pattern of substituted Nb_2O_5 .

A closer look on the (001) of Nb_2O_5 peak was done to determine any shifts in the 2θ values, and the results along with the ionic radii of W^{5+} , W^{6+} , Ti^{4+} and Ru^{4+} are plotted below in Figure 21. The (001) peak shifted to higher 2θ values for Ti-NbO_x , W(VI)-NbO_x , and W(V)-NbO_x . The shift of the (001) peak to a higher degree seen in Figure 1, suggests the successful incorporation of the smaller W^{5+} , W^{6+} , Ti^{4+} ions. The ionic radius of Nb^{5+} is 78 pm, while the ionic radius for W^{5+} , W^{6+} , Ti^{4+} is 76, 74 and 74.5 pm, respectively.

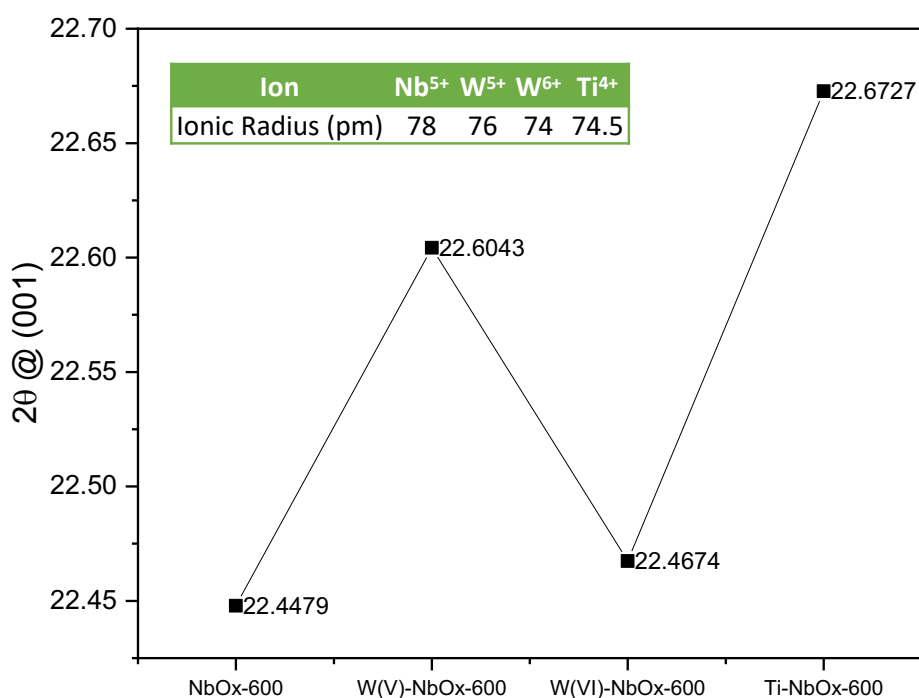


Figure 21. 2θ values for the (001) plane of the substituted Nb₂O₅ and ionic radii of substituents.

EDS analysis was conducted on Ti-NbO_x, W(VI)-NbO_x, Ru-NbO_x and W(V)-NbO_x, and the elemental mapping is shown in Figure 22. The EDS elemental mapping of Ti-NbO_x, W(VI)-NbO_x, and W(V)-NbO_x showed an even distribution of the metal substituents throughout the NbO_x aggregate. The elemental map of Ru-NbO_x shows an uneven distribution of Ru throughout the NbO_x aggregate. The calculated elemental atomic percent based on the EDS analysis of each material is shown in Table 3.

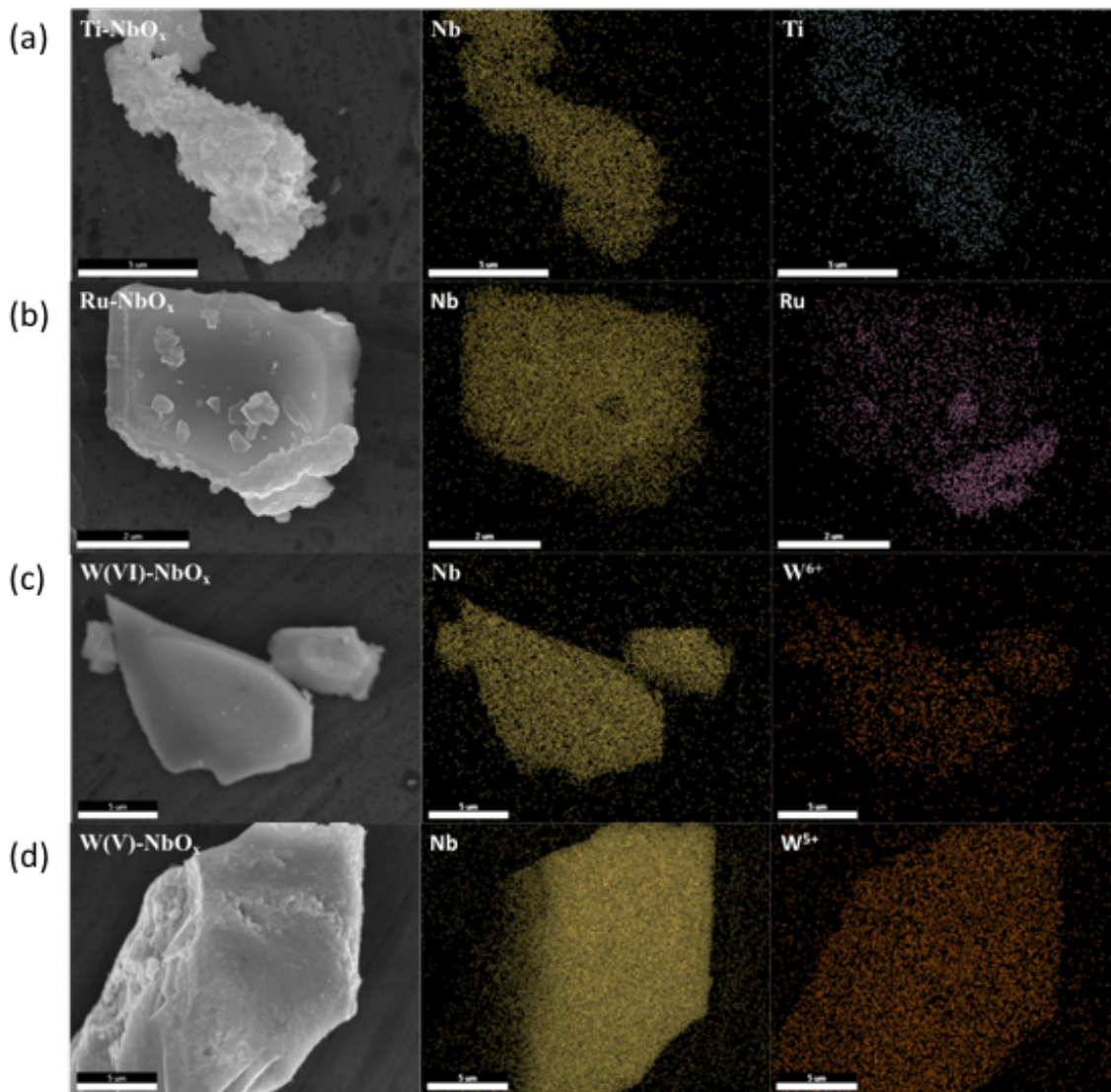


Figure 22. Energy dispersive spectroscopy elemental mapping of the substituted Nb_2O_5 ; (a) Ti-NbO_x , (b) Ru-NbO_x , (c) W(VI)-NbO_x , and (d) W(V)-NbO_x

Table 3. Atomic percent for elemental mapping of substituted NbO_x from energy dispersive spectroscopy.

	Element Atomic %	
	Nb	M
Ti-NbO_x	74	26
Ru-NbO_x	88	12
W(VI)-NbO_x	76	24
W(V)-NbO_x	82	18

The EDS analysis provided further evidence of successful incorporation of the W^{5+} , W^{6+} , Ti^{4+} ions and the unsuccessful incorporation of Ru^{4+} within the NbO_x structure. The elemental mapping of $Ti-NbO_x$, $W(VI)-NbO_x$, and $W(V)-NbO_x$ showed even distribution of the added substituents, while the $Ru-NbO_x$ showed the different phase RuO_x on the NbO_x aggregate. The elemental composition obtained from EDS analysis (Table 3) was in the range of the nominal 20 atomic % of the substituents from the synthesis ratios. The lower atomic percent of Ru was attributed to the Ru precursor not fully dissolving in the niobium(V) ethoxide and 2-butanol solution and the phase segregation.

The electronic conductivities of $Ti-NbO_x$, $W(VI)-NbO_x$, $Ru-NbO_x$ and $W(V)-NbO_x$ were measured, and the results are tabulated in Table 4. Within the estimated detection limit of the measurement ($\sim 10^{-9}$ S/cm), there were no measurable increases in conductivity for the $Ti-NbO_x$, $W(VI)-NbO_x$, and $W(V)-NbO_x$ samples. It is possible that the electronic conductivity of the individual crystallite increased but the interface resistance between crystallites may have been too high, and a measurable effect based on the limit of detection of our conductivity measurement setup was not possible. A significant increase in conductivity for $Ru-NbO_x$ was observed at 1×10^{-2} S cm^{-1} . The increase of conductivity can be explained by the lower band-gap of RuO_2 (1.87 eV).⁵² A previous study has measured the electronic conductivity of a single crystal of RuO_2 to be 2×10^4 S cm^{-1} ,⁵³ which is significantly higher than that of the $Ru-NbO_x$ sample. Because the $Ru-NbO_x$ sample is predominantly composed of low-conductivity Nb_2O_5 and considering grain boundary resistance, the overall conductivity would be significantly lower than that of a single crystal of RuO_2 .

Table 4. Electronic conductivities of substituted Nb₂O₅. *BLD = $\sim 10^{-9}$ S/cm

Sample	Electronic Conductivity (S/cm)
NbO _x -X	BLD*
W(V)-NbO _x	BLD*
W(VI)-NbO _x	BLD*
Ti-NbO _x	BLD*
Ru-NbO _x	1×10^{-2}

3.5. Effects of Thermal Treatment in Hydrogen

The addition of substituents to NbO_x did not yield a desirable conductivity, and a different approach was taken. A similar approach to a study that has shown the reduction of Nb₂O₅ to NbO₂ possible at temperatures higher than 1000 °C was taken.⁵⁴ The as-prepared NbO_x aerogel was heated to 875 °C in a H₂ atmosphere and in air for comparison, as shown in Figure 20. The as-prepared NbO_x powder is white in color, and after the thermal treatment of 875 °C in air the color remained white. A color change from white to a black powder was observed in the 875 °C treatment in H₂.

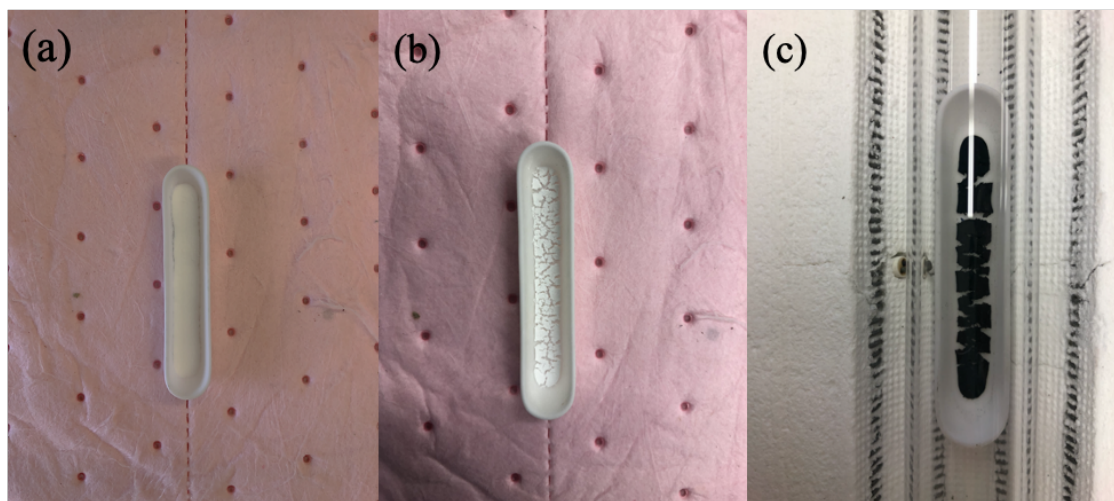


Figure 23. Images of NbO_x aerogel before (a) and after heating in air (b) and hydrogen (c).

X-ray diffraction different patterns for samples heated in air and H₂ were compared in Figure 21. The NbO_x heated in air to 875 °C showed an orthorhombic Nb₂O₅ structure, whereas the NbO_x heated in H₂ showed a tetragonal NbO₂ structure.

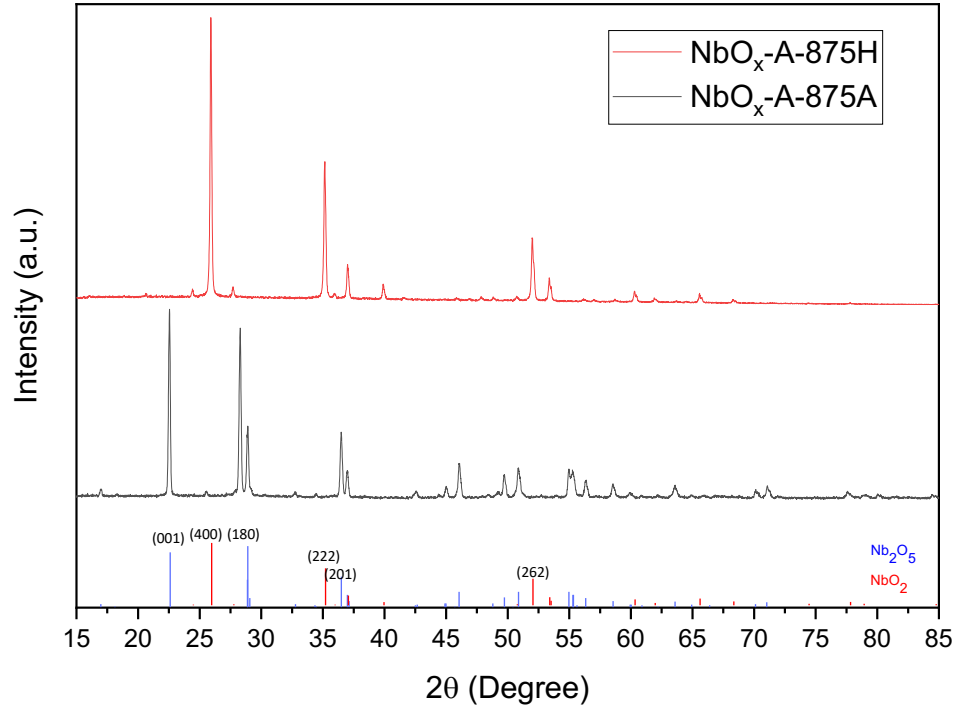


Figure 24. X-ray diffraction pattern of NbO_x after heating to 875 °C in air and H₂.

The conductivity of both samples was calculated and compared in Table 3. There was no observable increase in conductivity of the NbO_x heated to 875 °C in air. The NbO_x sample heated in H₂ atmosphere showed a significant increase in conductivity to $4.85 \times 10^{-5} \text{ S cm}^{-1}$.

Table 5. Calculated conductivity of NbO_x after heating to 875 °C in air and H₂. *BLD = $\sim 10^{-9} \text{ S/cm}$

Sample	Electronic Conductivity (S/cm)
NbO _x -A-875A	BLD*
NbO _x -A-875H	4.85×10^{-5}

The BET surface area of the NbO_x aerogel heated to 875 °C in H₂ was measured to be 7.3 m² g⁻¹, which is significantly lower than the as-prepared NbO_x. The SEM image (Figure 25) showed a coral reef like morphology and a porous morphology.

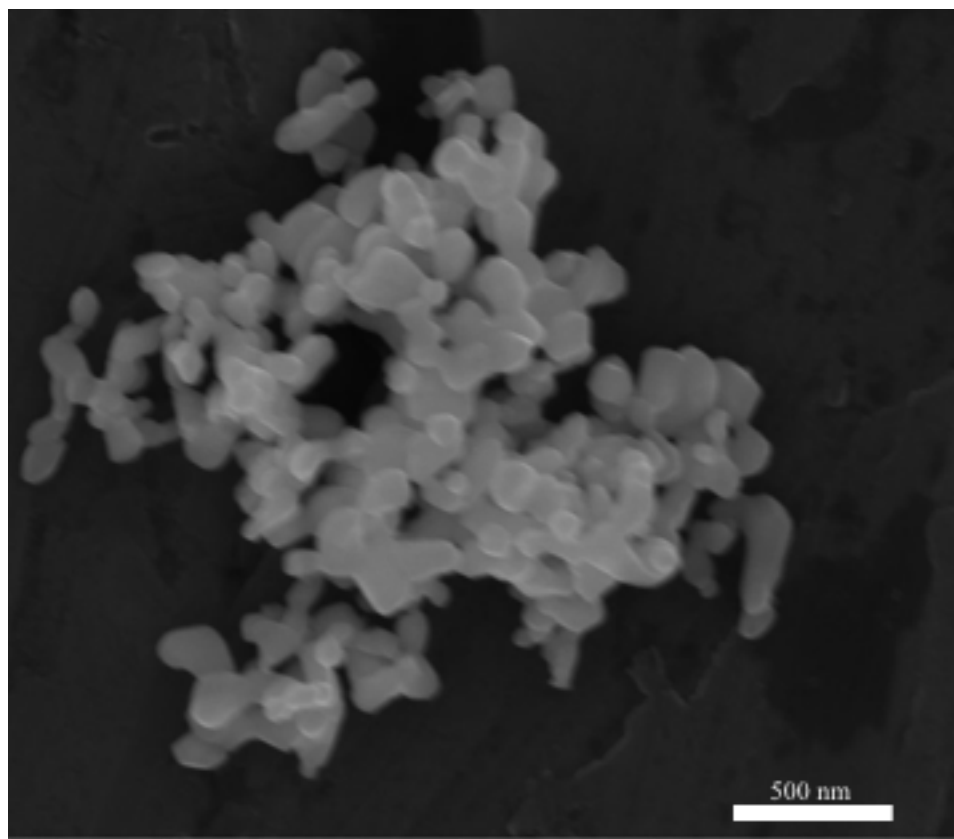


Figure 25. SEM image of NbO_x after heating to 875 °C in H₂.

The very low surface area of 7 m² g⁻¹ obtained at 875 °C in H₂ was too low to function as a practical support material and as a result, lower temperature treatments were evaluated. Thermal treatment of 500 °C and 600 °C in H₂ was performed on the as-prepared NbO_x aerogel. After heating, both 500 and 600 °C treatments resulted in a black NbO_x powder. The XRD pattern of NbO_x aerogels heated to 500, 600, and 875 in H₂ are compared in Figure 26. The sample heated to 500 °C showed Nb₂O₅ and NbO₂ peaks in the XRD pattern, indicating that a full reduction was not obtained at that temperature and time. The XRD pattern of NbO_x treated at 600 °C had no peaks corresponding to Nb₂O₅,

and only NbO₂ peaks were present.

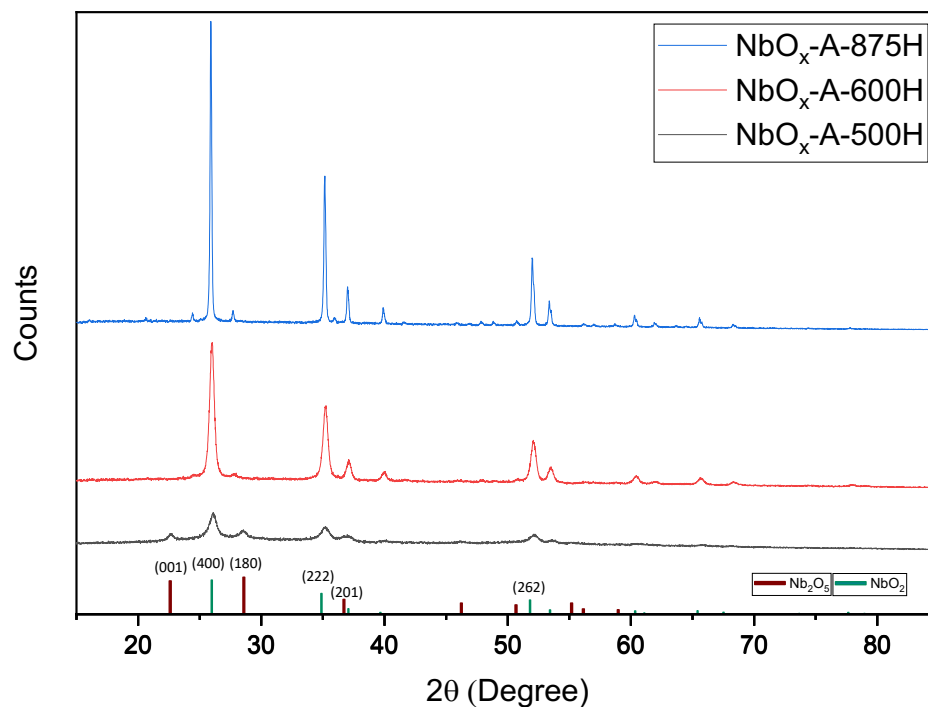


Figure 26. X-ray diffraction pattern for NbO_x heated to 500, 600, and 875 °C.

The BET surface areas of NbO_x treated to 500 and 600, and 875 °C were measured to determine the effects of the temperature variations, and the results are tabulated in Table 4. The sample heated to 600 °C showed a significant increase of surface area of 45 m² g⁻¹, when compared to NbO_x-A-875H. The SEM image of NbO_x-A-600H is presented in Figure 27 and showed a very porous morphology and aggregates about 6 μm wide, as shown in Figure 24.

Table 6. BET surface area and porosity analysis of NbO_x heated at different temperatures under H₂.

Material ID	BET Surface Area (m ² g ⁻¹)	Cumulative Pore Volume (cm ³ g ⁻¹)	Mean Pore Width (nm)
NbO _x -A-AP	454	1.8	13
NbO _x -A-500H	-	-	-
NbO _x -A-600H	45	0.49	42
NbO _x -A-875H	7	0.02	20

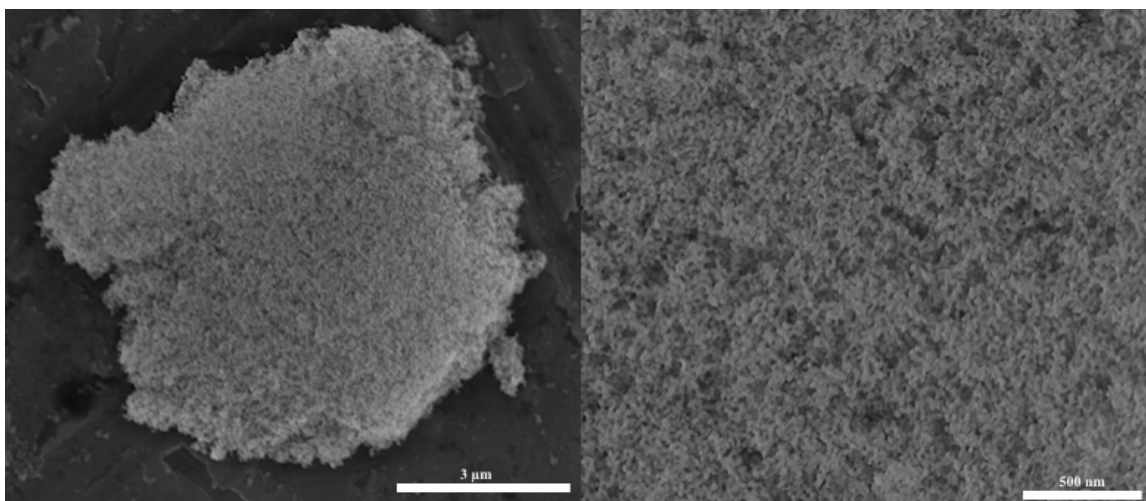


Figure 27. SEM images of NbO_x after 600 °C thermal treatment.

The conductivities of each sample were calculated and are tabulated on Table 6. NbO_x treated to 500 °C had a conductivity of $2 \times 10^{-6} \text{ S cm}^{-1}$, and NbO_x treated to 600 °C had a conductivity of $1 \times 10^{-5} \text{ S cm}^{-1}$ indicating that one order of magnitude difference was observed between both samples. The calculated conductivities were supported by the XRD results, the lower conductivity of NbO_x-A-500H was attributed to the Nb₂O₅ still present in the sample. NbO_x-A-600H had no Nb₂O₅ present, and the conductivity was in same order of magnitude as NbO_x-A-875H.

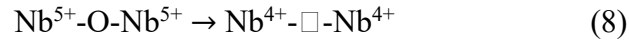
Table 7. Conductivities of NbO_x heated at different temperatures under H₂. *BLD = $\sim 10^{-9} \text{ S/cm}$

Sample	Electronic Conductivity (S/cm)
NbO _x -A-AP	BLD*
NbO _x -A-500	2×10^{-6}
NbO _x -A-600	1×10^{-5}
NbO _x -A-875	4×10^{-5}

The color change of white to black of the as-prepared materials to the thermally treated NbO_x samples can be attributed to the lowering of the band gap band. Materials that appear black absorb wavelengths in the visible light region because electrons can be

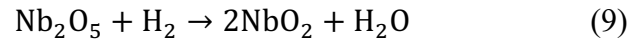
readily excited from the valence band to the conduction band. Wide band gap materials are usually white because the band gap is too large for visible light to be transmitted. One study investigated the band gap of white TiO₂ and black hydrogenated TiO₂. The band gap of the unmodified white TiO₂ and the band gap of the black TiO₂ was 3.3 eV and 1.54 eV, respectively.⁵⁵ The narrowing of the band gap is correlated with the ability to increase electronic conductivity.

The increase in conductivity of NbO_x-A-500H and NbO_xA-600H could be a result of the creation oxygen vacancies and/or a phase transition to a conducting NbO₂ phase. When an oxygen is removed, a vacancy is left behind, and the two electrons left behind are transferred to the empty 3d orbital at the bottom of the conduction band belonging to adjacent metal atoms. This leads to a change in oxidation state of the metal.^{56, 57} An oxygen vacancy of Nb₂O₅ is shown in the following equation:



A previous study has investigated the conductivity of a single crystal of Nb₂O_{5-x} at room temperature and have shown conductivities of 40 S cm⁻¹ for Nb₂O_{4.990} and 3x10³ S cm⁻¹ for Nb₂O_{4.978}.⁵⁸

The typical reduction observed in the thermal treatment of Nb₂O₅ under H₂ is:



The electrical properties of NbO₂ differ from Nb₂O₅, with reported conductivities of 200 S cm⁻¹ at 1000 °C.⁵⁹ The differences of conductivities obtained in this work from other investigations could be due to synthesis routes, temperatures used, and the nanostructured morphology that consists of interconnecting particles that can result in grain boundary resistances with the material. In order to maintain an adequate surface area, lower

treatment temperatures are preferred. A fine balance between temperature treatment to yield high surface area and high conductivity is required.

4. CONCLUSIONS AND FUTURE WORK

Niobium oxide was synthesized using a sol-gel process and was then dried by evaporative or supercritical conditions to yield a niobium oxide xerogel or aerogel, respectively. The as-prepared NbO_x xerogel and aerogel had BET surface areas of 389 m² g⁻¹ and 454 m² g⁻¹, respectively. The NbO_x xerogel showed a microporous morphology while the NbO_x showed a mesoporous and macroporous structure. SEM images showed a predominately nonporous aggregate for the NbO_x xerogel and a very porous aggregate for the NbO_x aerogel. Both the as-prepared NbO_x xerogel and the NbO_x aerogel had low electronic conductivities, below the detection limit which is estimated to be 1x10⁻⁹ S cm⁻¹. To remove any unreacted organic material and obtain a crystalline structure, the NbO_x xerogel and aerogel were subject to a thermal treatment of 600 °C in air. After the thermal treatment, the surface area decreased to 31 m² g⁻¹ and 23 m² g⁻¹ for the NbO_x xerogel and aerogel respectively. The as-prepared NbO_x xerogel and aerogel showed an amorphous XRD pattern, and after the thermal treatment a pseudo-hexagonal Nb₂O₅ XRD pattern was observed. To increase the electronic conductivity of NbO_x, different metal (e.g. W⁵⁺, W⁶⁺, Ti⁴⁺ and Ru⁴⁺) substituents were incorporated during the synthesis and then treated to 600 °C in air. XRD and EDS analysis supported the incorporation of W⁵⁺ and Ti⁴⁺ within Nb₂O₅, but no measurable increase in conductivity was observed. XRD patterns showed phase separation of RuO₂ and Nb₂O₅. The mixed oxide of RuO₂-Nb₂O₅ synthesized in ambient air had a significantly higher conductivity of 1x10⁻² S cm⁻¹, which was a substantial improvement from Nb₂O₅ which had a conductivity below our detection limit (~10⁻⁹ S cm⁻¹). Because the substituents did not yield a solid solution with the desired conductivities, a thermal treatment at three different temperatures of 875, 600,

and 500 °C in H₂ was conducted. XRD analysis of NbO_x-A-875 and NbO_x-A-600 showed from XRD that a NbO₂ tetragonal phase was present, and the NbO_x-A-500 sample showed an XRD pattern that corresponds to a mixture of Nb₂O₅ and NbO₂, indicating an incomplete reduction. The electronic conductivities for NbO_x-A-875, NbO_x-A-600, and NbO_x-A-500 were 4x10⁻⁵, 1x10⁻⁵, and 2x10⁻⁶ S cm⁻¹, respectively. As treatment temperature increased, the BET surface area decreased. The NbO_x-A-875 sample had a surface area of 7 m² g⁻¹ and the NbO_x-A-600 sample had a surface area of 45 m² g⁻¹. SEM images showed that the porous structure was retained after thermal treatments. This work showed that thermal treatment of NbO_x aerogel under hydrogen could effectively increase the electronic conductivity and provide reasonable surface areas and porosities.

Further work is needed to i) increase the electronic conductivity; ii) determine the oxidation state of Nb within the thermally reduced NbO₂ samples; iii) deposit enough active noble metal (e.g., Ru, Ir, Pt) on NbO_x to form a conducting network so as to not rely on the electronic conductivity of the support, and analyze the OER activity and stability. To increase the electronic conductivity, a longer thermal treatment in H₂ at lower temperatures could be explored. In this work, higher temperatures in H₂ have been shown to increase the conductivity of the NbO_x aerogels. However, the increase in temperature had a negative effect on the BET surface area. To negate this reduction of BET surface area, varying the treatment times could be beneficial. We observed partial reduction of Nb₂O₅ treated to 500 °C for 2 hours. Increasing the amount of time to 4 hours could complete the reduction of Nb₂O₅ to NbO₂ while retaining the high surface area that is observed with low temperature treatments. To further understand the reduction process of the thermally reduced NbO_x aerogels, a rough comparative analysis of the oxygen

content in the Nb_2O_5 and NbO_2 using EDS could be done. This would give a better insight of the niobium:oxygen stoichiometry within the material and help explain if the increase in conductivity is primarily due to the NbO_2 phase or if oxygen vacancies significantly contribute. To determine the oxidation state of Nb within the thermally reduced NbO_2 samples, X-ray photoelectron spectroscopy could be explored. Finally, to achieve the required conductivity which may not be possible by a reduction process alone, an approach of depositing enough active material (e.g., Ir or Pt) to form a conducting network above the support material could be explored. This approach would solely rely on the support for the metal-support interaction and on the active metal for the conductivity. Several studies have taken this route and deposited up to 60% of active metal and have obtained enhanced OER activities and stabilities when compared to carbon supports and unsupported catalysts.^{60, 61}

REFERENCES

1. Administration, U. S. E. I. Monthly Energy Review.
2. Energy, U. S. D. o. Renewable Energy Data Book.
3. Mazloomi, K.; Gomes, C., Hydrogen as an energy carrier: Prospects and challenges. *Renewable and Sustainable Energy Reviews* **2012**, *16* (5), 3024-3033.
4. Shiva Kumar, S.; Himabindu, V., Hydrogen production by PEM water electrolysis – A review. *Materials Science for Energy Technologies* **2019**, *2* (3), 442-454.
5. Fabbri, E.; Haberer, A.; Waltar, K.; Kötter, R.; Schmidt, T. J., Developments and perspectives of oxide-based catalysts for the oxygen evolution reaction. *Catalysis Science & Technology* **2014**, *4* (11), 3800-3821.
6. Godínez-Salomón, F.; Albiter, L.; Alia, S. M.; Pivovar, B. S.; Camacho-Forero, L. E.; Balbuena, P. B.; Mendoza-Cruz, R.; Arellano-Jimenez, M. J.; Rhodes, C. P., Self-Supported Hydrous Iridium–Nickel Oxide Two-Dimensional Nanoframes for High Activity Oxygen Evolution Electrocatalysts. *ACS Catalysis* **2018**, 10498-10520.
7. Suen, N.-T.; Hung, S.-F.; Quan, Q.; Zhang, N.; Xu, Y.-J.; Chen, H. M., Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives. *Chemical Society Reviews* **2017**, *46* (2), 337-365.
8. Kobussen, A. G. C.; Broers, G. H. J., The oxygen evolution on La_{0.5}Ba_{0.5}CoO₃: Theoretical impedance behaviour for a multi-step mechanism involving two adsorbates. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1981**, *126* (1), 221-240.
9. Bockris, J. O. M.; Otagawa, T., Mechanism of oxygen evolution on perovskites. *The Journal of Physical Chemistry* **1983**, *87* (15), 2960-2971.
10. Dau, H.; Limberg, C.; Reier, T.; Risch, M.; Roggan, S.; Strasser, P., The Mechanism of Water Oxidation: From Electrolysis via Homogeneous to Biological Catalysis. *ChemCatChem* **2010**, *2* (7), 724-761.

11. Trasatti, S., Electrocatalysis by oxides — Attempt at a unifying approach. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* **1980**, *111* (1), 125-131.
12. Trasatti, S., Electrocatalysis in the anodic evolution of oxygen and chlorine. *Electrochimica Acta* **1984**, *29* (11), 1503-1512.
13. Doyle, R. L.; Lyons, M. E. G., The Oxygen Evolution Reaction: Mechanistic Concepts and Catalyst Design. In *Photoelectrochemical Solar Fuel Production: From Basic Principles to Advanced Devices*, Giménez, S.; Bisquert, J., Eds. Springer International Publishing: Cham, 2016; pp 41-104.
14. McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F., Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *Journal of the American Chemical Society* **2015**, *137* (13), 4347-4357.
15. Danilovic, N.; Subbaraman, R.; Chang, K.-C.; Chang, S. H.; Kang, Y. J.; Snyder, J.; Paulikas, A. P.; Strmcnik, D.; Kim, Y.-T.; Myers, D.; Stamenkovic, V. R.; Markovic, N. M., Activity–Stability Trends for the Oxygen Evolution Reaction on Monometallic Oxides in Acidic Environments. *The Journal of Physical Chemistry Letters* **2014**, *5* (14), 2474-2478.
16. Reier, T.; Oezaslan, M.; Strasser, P., Electrocatalytic Oxygen Evolution Reaction (OER) on Ru, Ir, and Pt Catalysts: A Comparative Study of Nanoparticles and Bulk Materials. *ACS Catalysis* **2012**, *2* (8), 1765-1772.
17. Payne, D., Iridium's impact. *Nature Chemistry* **2016**, *8* (4), 392-392.
18. Haxel, G. B. Rare Earth Elements—Critical Resources for High Technology. <https://pubs.usgs.gov/fs/2002/fs087-02/>.
19. Meier, J. C.; Galeano, C.; Katsounaros, I.; Witte, J.; Bongard, H. J.; Topalov, A. A.; Baldizzone, C.; Mezzavilla, S.; Schüth, F.; Mayrhofer, K. J. J., Design criteria for stable Pt/C fuel cell catalysts. *Beilstein Journal of Nanotechnology* **2014**, *5*, 44-67.
20. Carmo, M.; Fritz, D. L.; Merge, J.; Stolten, D., A comprehensive review on PEM water electrolysis. *Int. J. Hydrog. Energy* **2013**, *38* (12), 4901-4934.

21. Mazúr, P.; Polonský, J.; Paidar, M.; Bouzek, K., Non-conductive TiO₂ as the anode catalyst support for PEM water electrolysis. *Int. J. Hydrog. Energy* **2012**, *37*(17), 12081-12088.
22. Puthiyapura, V. K.; Pasupathi, S.; Basu, S.; Wu, X.; Su, H.; Varagunapandiyan, N.; Pollet, B.; Scott, K., Ru_xNb_{1-x}O₂ catalyst for the oxygen evolution reaction in proton exchange membrane water electrolyzers. *Int. J. Hydrog. Energy* **2013**, *38*(21), 8605-8616.
23. Xu, J.; Liu, G.; Li, J.; Wang, X., The electrocatalytic properties of an IrO₂/SnO₂ catalyst using SnO₂ as a support and an assisting reagent for the oxygen evolution reaction. *Electrochimica Acta* **2012**, *59*, 105-112.
24. Oh, H.-S.; Nong, H. N.; Reier, T.; Gliech, M.; Strasser, P., Oxide-supported Ir nanodendrites with high activity and durability for the oxygen evolution reaction in acid PEM water electrolyzers. *Chemical Science* **2015**, *6*(6), 3321-3328.
25. Tauster, S. J.; Fung, S. C.; Baker, R. T. K.; Horsley, J. A., Strong Interactions in Supported-Metal Catalysts. *Science* **1981**, *211* (4487), 1121.
26. Pan, C.-J.; Tsai, M.-C.; Su, W.-N.; Rick, J.; Akalework, N. G.; Agegnehu, A. K.; Cheng, S.-Y.; Hwang, B.-J., Tuning/exploiting Strong Metal-Support Interaction (SMSI) in Heterogeneous Catalysis. *Journal of the Taiwan Institute of Chemical Engineers* **2017**, *74*, 154-186.
27. Kumar, A.; Ramani, V., Strong Metal-Support Interactions Enhance the Activity and Durability of Platinum Supported on Tantalum-Modified Titanium Dioxide Electrocatalysts. *ACS Catalysis* **2014**, *4* (5), 1516-1525.
28. Lv, H.; Zhang, G.; Hao, C.; Mi, C.; Zhou, W.; Yang, D.; Li, B.; Zhang, C., Activity of IrO₂ supported on tantalum-doped TiO₂ electrocatalyst for solid polymer electrolyte water electrolyzer. *RSC Adv.* **2017**, *7*(64), 40427-40436.
29. Ro, I.; Resasco, J.; Christopher, P., Approaches for Understanding and Controlling Interfacial Effects in Oxide-Supported Metal Catalysts. *ACS Catalysis* **2018**, *8*(8), 7368-7387.
30. Rani, R. A.; Zoolfakar, A. S.; O'Mullane, A. P.; Austin, M. W.; Kalantar-Zadeh, K., Thin films and nanostructures of niobium pentoxide: fundamental properties, synthesis methods and applications. *Journal of Materials Chemistry A* **2014**, *2* (38), 15683-15703.

31. Asselin, E.; Ahmed, T. M.; Alfantazi, A., Corrosion of niobium in sulphuric and hydrochloric acid solutions at 75 and 95°C. *Corrosion Science* **2007**, *49* (2), 694-710.
32. Maurer, S. M.; Ko, E. I., Structural and acidic characterization of niobia aerogels. *Journal of Catalysis* **1992**, *135* (1), 125-134.
33. Sayama, K.; Arakawa, H.; Domen, K., Photocatalytic water splitting on nickel intercalated A₄TaxNb₆-xO₁₇ (A = K, Rb). *Catalysis Today* **1996**, *28* (1), 175-182.
34. Terezo, A. J.; Pereira, E. C., Preparation and characterization of Ti/RuO₂-Nb₂O₅ electrodes obtained by polymeric precursor method. *Electrochimica Acta* **1999**, *44* (25), 4507-4513.
35. Santana, M. H. P.; De Faria, L. A.; Boodts, J. F. C., Investigation of the properties of Ti/[IrO₂-Nb₂O₅] electrodes for simultaneous oxygen evolution and electrochemical ozone production, EOP. *Electrochimica Acta* **2004**, *49* (12), 1925-1935.
36. Sasaki, K.; Zhang, L.; Adzic, R. R., Niobium oxide-supported platinum ultra-low amount electrocatalysts for oxygen reduction. *Physical Chemistry Chemical Physics* **2008**, *10* (1), 159-167.
37. Karimi, F.; Peppley, B. A., Metal Carbide and Oxide Supports for Iridium-Based Oxygen Evolution Reaction Electrocatalysts for Polymer-Electrolyte-Membrane Water Electrolysis. *Electrochimica Acta* **2017**, *246*, 654-670.
38. Ko, E. I.; Maurer, S. M., Synthesis of niobium pentoxide aerogels. *Journal of the Chemical Society, Chemical Communications* **1990**, (15), 1062-1063.
39. Sanchez, C.; Livage, J.; Henry, M.; Babonneau, F., Chemical modification of alkoxide precursors. *Journal of Non-Crystalline Solids* **1988**, *100* (1), 65-76.
40. Alquier, C.; Vandenborre, M. T.; Henry, M., Synthesis of niobium pentoxide gels. *Journal of Non-Crystalline Solids* **1986**, *79* (3), 383-395.
41. Livage, J.; Henry, M.; Sanchez, C., Sol-gel chemistry of transition metal oxides. *Progress in Solid State Chemistry* **1988**, *18* (4), 259-341.

42. Bradley, D. C.; Hursthouse, M. B.; Rodesiler, P. F., The structure of a crystalline niobium oxide ethoxide, Nb₈O₁₀(OEt)₂₀. *Chemical Communications (London)* **1968**, (18), 1112-1113.
43. Schubert, U., 7.10 - Sol-Gel Processing of Metal Compounds. In *Comprehensive Coordination Chemistry II*, McCleverty, J. A.; Meyer, T. J., Eds. Pergamon: Oxford, 2003; pp 629-656.
44. Campbell, L. K.; Na, B. K.; Ko, E. I., Synthesis and characterization of titania aerogels. *Chemistry of Materials* **1992**, 4 (6), 1329-1333.
45. Hench, L. L.; West, J. K., The sol-gel process. *Chemical Reviews* **1990**, 90 (1), 33-72.
46. Lowell, S.; Shields, J. E., Adsorption isotherms. In *Powder Surface Area and Porosity*, Lowell, S.; Shields, J. E., Eds. Springer Netherlands: Dordrecht, 1984; pp 11-13.
47. Scherer, G. W.; Smith, D. M., Cavitation during drying of a gel. *Journal of Non-Crystalline Solids* **1995**, 189 (3), 197-211.
48. LibreTexts Phase Diagrams.
[https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3AGeneral_Chemistry_\(Petrucci_et_al.\)/12%3A_Intermolecular_Forces%3ALiquids_And_Solids/12.4%3A_Phase_Diagrams](https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3AGeneral_Chemistry_(Petrucci_et_al.)/12%3A_Intermolecular_Forces%3ALiquids_And_Solids/12.4%3A_Phase_Diagrams).
49. Aegerter, M. A., Sol-gel niobium pentoxide: A promising material for electrochromic coatings, batteries, nanocrystalline solar cells and catalysis. *Solar Energy Materials and Solar Cells* **2001**, 68 (3), 401-422.
50. Nowak, I.; Ziolek, M., Niobium Compounds: Preparation, Characterization, and Application in Heterogeneous Catalysis. *Chemical Reviews* **1999**, 99 (12), 3603-3624.
51. Wang, Y.-D.; Yang, L.-F.; Zhou, Z.-L.; Li, Y.-F.; Wu, X.-H., Effects of calcining temperature on lattice constants and gas-sensing properties of Nb₂O₅. *Materials Letters* **2001**, 49 (5), 277-281.
52. El-Tantawy, F.; Al-Ghamdi, A. A.; Al-Ghamdi, A. A.; Al-Turki, Y. A.; Alshahrie, A.; Al-Hazmi, F.; Al-Hartomy, O. A., Optical properties of nanostructured ruthenium dioxide thin films via sol-gel approach. *Journal of Materials Science: Materials in Electronics* **2017**, 28 (1), 52-59.

53. Goodenough, J. B., Metallic oxides. *Progress in Solid State Chemistry* **1971**, *5*, 145-399.
54. Janninck, R. F.; Whitmore, D. H., Electrical conductivity and thermoelectric power of niobium dioxide. *Journal of Physics and Chemistry of Solids* **1966**, *27*(6), 1183-1187.
55. Chen, X.; Liu, L.; Yu, P. Y.; Mao, S. S., Increasing Solar Absorption for Photocatalysis with Black Hydrogenated Titanium Dioxide Nanocrystals. *Science* **2011**, *331* (6018), 746.
56. Greener, E. H.; Whitmore, D. H.; Fine, M. E., Electrical Conductivity of Near-Stoichiometric α -Nb₂O₅. *The Journal of Chemical Physics* **1961**, *34* (3), 1017-1023.
57. Pacchioni, G., Oxygen Vacancy: The Invisible Agent on Oxide Surfaces. *ChemPhysChem* **2003**, *4* (10), 1041-1047.
58. Reich, C. M.; Kaiser, A.; Irvine, J. T. S., Niobia Based Rutile Materials as SOFC Anodes. *Fuel Cells* **2001**, *1* (3-4), 249-255.
59. Roberson, J. A.; Rapp, R. A., Electrical properties of NbO and NbO₂. *Journal of Physics and Chemistry of Solids* **1969**, *30* (5), 1119-1124.
60. Huang, S.-Y.; Ganesan, P.; Jung, H.-Y.; Popov, B. N., Development of supported bifunctional oxygen electrocatalysts and corrosion-resistant gas diffusion layer for unitized regenerative fuel cell applications. *Journal of Power Sources* **2012**, *198*, 23-29.
61. Won, J.-E.; Kwak, D.-H.; Han, S.-B.; Park, H.-S.; Park, J.-Y.; Ma, K.-B.; Kim, D.-H.; Park, K.-W., PtIr/Ti₄O₇ as a bifunctional electrocatalyst for improved oxygen reduction and oxygen evolution reactions. *Journal of Catalysis* **2018**, *358*, 287-294.