High Performance Mo_xN Electrode Fabricated by Solution Precursor Plasma Spraying

by

Yakov Gazman

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science Department of Materials Science and Engineering University of Toronto

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Abstract

Changing climate and decreasing availability of fossil fuels stimulate the use of alternative energy sources and energy storage devices such as electrochemical capacitors. The current study investigates the implementation of SPPS (Solution Precursor Plasma Spraying) for the deposition of high surface area electrochemical capacitor electrodes. A high performance Mo_xN electrochemical capacitor electrode was produced by solution precursor plasma spraying for the first time. The best electrode exhibited an initial capacitance of 62.4 mF cm⁻² at a scan rate of 100 mV sec⁻¹. The capacitance decreased by 22% after the first 1000 cycles, but the performance then stabilized, decreasing by only 0.15% over cycles 4000 to 5000 and exhibiting a capacitance of 30mF cm⁻² after 5000 cycles. SPPS is a novel deposition method, thus further understanding and optimization of the process is required to improve the performance and manufacturability, but a clear potential was proven.

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Abbreviations

- SPPS: solution precursor plasma spraying
- EDLC: Electric double layer capacitance
- GD-OES: Glow discharge optical emission spectroscopy
- SD: Standoff distance
- **RD:** Raster distance
- CACT: Center for Advanced Coating Technologies
- TRP: Temperature programmed reaction
- SEM: Scanning electron microscope
- BET: Brunauer Emmett Teller
- CV: Cyclic voltammetry
- TGA: Thermal gravimetric analysis
- DTA: Differential Thermal Analysis
- **RIR:** Relative intensity ration

Chapter 1: Introduction

The constant rise in the world energy consumption forces the scientific community to develop alternative methods of energy production that can be sustainable and with lower environmental foot print. Because the new energy systems rely on the sun, wind and other alternative sources, the production can be limited by the location and process thus increasing the importance of energy storage devices [1-3].

Figure 1-1 presents a common method for the comparison of energy storage devices called a Ragone plot. In this plot the vertical axis, specific power, represents the amount of energy that can be delivered in a given amount of time, and the horizontal axis, specific energy, represents how long the energy can be delivered. Electrostatic capacitors have a large specific power, delivering a large amount of power but discharging very quickly. On the other hand batteries can deliver energy for a very long time but only at relatively low rates.



Figure 1-1: Ragone plot for comparing energy storage devices [4]

One of the leading families in the field of storage devices are the electrochemical capacitors (EC), also known as supercapacitors or ultracapacitors [5], which store electrical charge via surface phenomena and avoid the deterioration of the electrode that occurs in batteries [2].

Electrochemical capacitors occupy the biggest and widest region in the Ragone plot. Along with good efficiency, they offer excellent reversibility (90-95% or higher), long cycle life (> 10^5) [2], and fast charge/discharge which enables them to fill the gap between high energy batteries and high power solid state capacitors [1-4, 6].

	Battery	Electrostatic capacitor	EC
Discharge time	0.3-3 h	10^{-3} to 10^{-6} s	0.3-30 s
Charge time	1-5 h	10 ⁻³ to 10 ⁻⁶ s	0.3-30 s
Energy density (Wh/kg)	10-100	<0.1	1-10
Specific power (W/kg)	50-200	>10,000	≈1000
Charge-discharge efficiency	0.7–0.85	≈1	0.85-0.98
Cycle life	500-2000	>500,000	>100,000

Table 1-1: Energy storage device comparison [2]

Super capacitor electrodes that are based on nano-carbon structures [6-8] store energy via a surface phenomenon called double layer capacitance (EDLC), characterized by a thin polarization layer that separates the charge at the electrode-electrolyte interface [1,2,6,7].

In addition to double layer capacitance, transition metal oxides/nitrides such as V_xN [9], Mo_xN [10,11], TiN [12] and conductive polymers [13] can allow charge transfer between the electrolyte and electrode inducing slow and reversible oxidation-reduction reaction on the electrode surface, called pseudo capacitance, which significantly increases the overall capacitance [1,2,4]. A hybrid electrode combines both surface phenomena using EDLC and pseudo materials on the same electrode; one of these hybrids is a molybdenum carbon electrode [14]. Adding various metals to molybdenum oxide electrodes can also have positive effects on the electrochemical performance of the electrode [15]. As both double layer and pseudo capacitance are surface phenomena, reducing the average grain size and increasing the porosity will create a larger surface area that is most desirable and critical for a high performance supercapacitor electrode [1, 4]. Unlike conductive polymers that have slow diffusion processes that increase the resistance and lower the stability, transition metal oxides have high specific power and low resistance which increases the interest in such electrodes for application in

electrochemical capacitors. The current benchmark transition metal is RuO_2 , but ruthenium is a very expensive metal [9,11,16], thus other low cost alternatives such as MoO_3 and Mo_xN are being developed.



Figure 1-2: Characterization of electrochemical capacitors by their charge storage mechanisms

Although molybdenum nitride has a much larger capacitance then its oxide counterpart, direct deposition is not possible in atmospheric conditions and a temperature programed reaction (TPR) in a nitrogen environment is required to convert the as-deposited oxide coating into nitride.

Many methods for molybdenum oxide deposition exist such as CVD [16, 17], electro deposition [11], and spray pyrolysis [10], but solution precursor plasma spraying (SPPS) offers a robust and controllable process capable of depositing high surface area coatings in atmospheric conditions, and that is compatible with a reel to reel process for mass production. Because traditional thermal spray, specifically DC-arc plasma spraying, involves the injection of powder particles into the high temperature, high velocity plasma plume, the microstructure of the coating is limited by the large size powder [18].

By injecting the feedstock in the form of an atomized solution precursor into the plasma torch, it is possible to create a nano-scale microstructure consisting of hollow and broken spheres and a pore network that is ideal for electrochemical capacitors application [19].

Previous work conducted in our research group has revealed that shorter standoff distances and closer raster patterns increase the total heat to which deposits are exposed, resulting in more complete decomposition of the precursor and a higher capacitance for the molybdenum oxide electrode [19]. But only thick coatings were produced and all electrodes completely disintegrated after only 10 cyclic voltammetry cycles.

SPPS is a novel and not yet fully understood deposition system with various parameters such as substrate material, substrate finish, standoff distance, solution concentration and many more that can affect the final microstructure and electrochemical performance.

1.1 Objective

The objective of this research thesis is to deposit a molybdenum oxide coating with good substrate adhesion by solution precursor plasma spraying, followed by a nitriding heat treatment to transform the coating to molybdenum nitride, and then to perform electrochemical analysis of the electrode capacitance and stability. The electrochemical behaviour will be linked to the process parameters controlling the deposition and nitriding stages by characterizing the microstructure, chemical composition and phase content of the coatings at each stage.

Chapter 2: Literature review

2.1 Electric double layer capacitance (EDLC)

The charge storage mechanism in a double layer capacitor involves an electrostatic adsorption of oppositely charged ions on the surface of the negative electrode. When a potential difference between the electrodes is created, the opposite charges in the electrolyte are drawn to the electrodes, and a charge separation at the electrode/electrolyte accrues forming a 5-10Å interface layer known as a double layer. EDLC electrodes do not undergo redox reactions as part of the electrostatic charge storage; therefore the major difference from batteries is no limitation of the electrochemical kinetics through a polarization resistance and therefore better power performance. The absence of faradic reactions also eliminates the swelling in the active material that batteries show during charge/discharge cycles [1].



Figure 2-1: Schematic illustration of a double layer capacitor [4]

The double layer capacitance is described by (2-1), where ε_r is the dialectic constant of the electrolyte, ε_0 is the dielectric constant of vacuum, d is the effective thickness of the double layer, A is the electrode surface area :

$$\boldsymbol{C} = \frac{\boldsymbol{\varepsilon}_r \boldsymbol{\varepsilon}_0 \boldsymbol{A}}{d} \quad (2-1)$$

At first, it was assumed that the charge accumulation is only due to the charge separation at the electrode/electrolyte interface (Helmholtz layer), however later studies by Gouy-Chapman and Stern Geary proven that a second layer exists (diffuse layer) which is defined by the concentration gradient of the ions from the interface layer to the bulk of the electrolyte, figure 2-2. Presently a joint model is accepted combining both the Helmholtz layer and diffuse layer in the same model (c). Graphitic carbon, such as carbide-derived, carbon fabrics, fibers, nanotubes and many more are suitable for this application [20], due to high conductivity, electrochemical stability and open porosity.



Figure 2-2: (a) Helmholtz layer (b) diffuse layer (c) Helmholtz and diffuse combined [1]

2.2 Pseudocapacitance

Pseudo capacitors utilize both double layer capacitance and pseudo capacitance, and can be composed of either conductive polymers or oxides and nitrides of transition metals such as manganese, vanadium, nickel, cobalt, ruthenium, tantalum, iridium, iron or molybdenum. Due to the multiple oxidation and coordination states of transition metals, the electrostatically adsorbed ions on the electrode can undergo a reversible redox reaction with the electrode thus increasing the overall capacitance [1].

	EDLC	Pseudocapacitance
1. 2.	Non-faradaic 20-50 µF/cm ²	Involves faradaic process(es) 2000 µF/cm ² for single-state process; 200–500 µF/cm ² for multi-state overlapping
3.	C fairly constant with potential, except through the potential of	processes C fairly constant with potential for RuO ₂ ; for single-state process, exhibits marked maximum
4.	zero charge Highly reversible charging/discharging	Can exhibit several maxima for overlapping, multi-state processes, as for H at Pt; Quite reversible but has intrinsic
5.	Has restricted voltage range (contrast non-electrochemical	electrode-kinetic rate limitation determined by R _f Has restricted voltage range
6.	electrostatic capacitor) Exhibits mirror-image voltammograms	Exhibits mirror-image voltammograms

Table 2-1: Comparison between EDLC and Pseudo capacitance [2]

The specific pseudo-capacitance exceeds that of carbon materials using double layer charge storage, justifying the interest in these systems. But because the charge storage mechanism involves redox reactions, like batteries, they often suffer from a lack of stability during cycling. Capacitance of more than 600 F g⁻¹[1] has been reported for ruthenium oxide, which has been the focus of research over the past 30 years. However, Ru-based aqueous electrochemical capacitors are expensive, and the 1V voltage window limits their applications in small electronics. Other transition metal oxides with various oxidation degrees, such as molybdenum oxides, are now being explored as active materials for pseudo-capacitors.

2.3 Surface area and pore network

Initial research on the dependence of capacitance on pore volume and size, showed that the capacitance increase was limited. Even for the most porous samples there was no linear relationship between the capacitance and pore size, suggesting that pores smaller than 0.5 nm were not accessible to hydrated ions.



Figure 2-3: Normalized capacitance as a function of pore size [1]

The peak in capacitance shifted to smaller pores for smaller ions. This behavior cannot be explained by purely electrostatic reasons because all pores were either the same size or smaller than a single ion, thus confirming that ions must be at least partially stripped of solvent molecules in order to occupy the carbon pores in the EDLC structure. A combination of various sizes that can accommodate all ions present in the electrolyte is a key feature in improving the capacitance of ECs.



Figure 2-4: partial stripping and de-solvating of electrolyte ion [21]

Nanomaterials have improved the performance of Li-ion batteries, therefore the effect of nanostructuring EC's is an important research possibility. Because pseudo-capacitors store charge in the first few nanometers from the surface, decreasing the particle size increases active material usage by increasing the specific surface area. The charging mechanism of a thin electrically conducting surface layer of oxide or oxy-nitride includes a combination of an electric double layer and a faradic reaction at the surface of the nanoparticles. The high specific surface area and interfacial exchange improvement of nano-sized particles was shown to improve the specific capacitance and cycling stability for transition metal nitrides or oxides. The perfect candidate for an electrochemical capacitor would be an active pseudo-capacitive electrode with large surface area consisting of small grains/particles, highly porous, with a large pore size distribution and open pore network [22].



Figure 2-5: Schematic of a double layer and importance of porosity [2]

2.4 Transition metal materials

A pseudo-capacitive material could be either a conductive polymer or a transition metal oxide or nitride; conductive polymers have slower diffusive processes and a limited conductivity [13, 23]. Great interest is being shown in transition metal oxides/nitrides which have high conductivity and low resistance, making them some of the best candidates for a pseudo-capacitive material. Transition metal oxides and nitrides can include a variety of material such as V_xN [9], TiN [12] and MnO₂ [24], but the most promising candidate in this family is ruthenium oxide. RuO₂ is a benchmark material in the transition metal family due to its long cycle life, high conductivity, high specific capacitance and excellent reversibility showing capacitance as high as 1340F g⁻¹ for its hydrous from [25,26]. Although RuO₂ is the perfect candidate in terms of electrochemical performance, lack of abundance prevents the implementation of this material in a commercial, mass production way [2]. This encourages research and development on alternative pseudo-capacitive materials. One of this group of developing materials showing great potential is crystalline α -MoO₃ which has a large pseudo-capacitance and double layer capacitance [27].

Molybdenum nitride exhibits an even larger and more stable capacitive behavior which can be processed via topo tactic transformation from the oxide without losing surface area.

2.4.1 Molybdenum oxide and nitride

Molybdenum has a very rich electrochemistry as a result of multiple coordination numbers and oxidation states ranging from –II to +VI, as well as stability in natural and acidic environments as shown in figure 2-6, resulting in the interest in molybdenum oxide and nitride coatings for electrochemical applications such as capacitors and catalysts [28] [29].



Figure 2-6: Molybdenum/water system, potential as a function of pH [30]

A typical cyclic voltammetry diagram of molybdenum oxide (figure 2-7) in acidic electrolyte has shown a partly double overlapping reduction and redox reaction due to molybdenum bronze formation (A_xMoO_3 (0 < x< 2)) which is controlled by the diffusion of electrolyte ions into Mo oxide [31] [32]. Electrochromism of such films is caused by the ion intercalation/deintercalation reaction. Hydrogen ions were inserted into molybdenum oxide films to form hydrogen molybdenum oxide bronzes, which can be formulated as [33, 34]:

$$MoO_3 + xH^+ + xe^- \Leftrightarrow MoO_{3-x}(OH)_x$$
 (2-2)



Figure 2-7: Cycle voltammogram of molybdenum oxide in 5 x 10⁻³ M H₂SO₄, scan rate, 50 mV s⁻¹ [31]

Against Ag/AgCl at -0.5V molybdenum oxide electrodes show capacitive behavior, but the asymmetrical anode and cathode current density and CV profile that has no mirror image causes poor capacitive performance. Mo oxide is not the ideal pseudo capacitive material because at potentials lower then -0.5V hydrogen evolution develops and at potentials higher than 1V the passive layer is broken. In addition to significant separation between the cathodic and anodic peaks, the electrode suffers from low electrical conductivity and poor reversibility [35, 36].

Fable 2-2: Physical and electrochemica	l properties of t	the early transition n	netal nitrides and	carbides [37].
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Material	Surface area (m ² g ⁺¹)	Stability window (V)	Gravimetric capacitance (Fg ⁻¹) ^a	Specific capacitance (µFcm ⁻²) ^b
VN	38	1.1 (KOH)	210	553
VC	6	0.8 (KOH)	2.6	43
B-Mo ₂ C	60	-	-	
Y-MO2N	152	0.8 (H ₂ SO ₄)	346	227
B-W ₂ C	16	0.7 (H ₂ SO ₄)	79	494
B-W2N	42	0.8 (KOH)	25	60

⁴ Gravimetric capacitance estimated using Eq. (1) for scan 25 at scan rate 2 mV s⁻¹.
^b Specific or areal capacitance determined from gravimetric capacitance and physical surface area. Double layer capacitance for most materials is ~25 µF cm⁻² [3].

Transformation of the oxide into nitride forms such as γ -Mo₂N/ δ -MoN/Mo₃N₂ [38] occurs through a reduction mechanism and is strongly dependent on the converting gas and the thermal profile applied during the process.



Figure 2-8: Phase diagrams of Mo-O and Mo-N [39]

Due to the low performance of the oxide form, the nitride form of molybdenum is usually preferred. It has high conductivity, and excellent reversibility and pseudo-capacitive performance [40, 41]. As shown in figure 2-9, the current vs potential curve (CV curve) is very rectangular, symmetrical on the cathodic and anodic sides, with little resistance illustrated by the sharp peaks at the edges of the scanned potential [42]. Experiments conducted on transformation of α -MoO₃ into β phase molybdenum nitride revealed that small differences in impurity content and/or crystallinity of the MoO₃ can strongly influence the morphology and the content of molybdenum nitride in the final product, illustrating the complexity and sensitivity of the process [43, 44].



Figure 2-9: CV profiles of molybdenum nitride film deposited by CVD [16]

2.4.2 Topotactic transformation

A simple transition of α -MoO₃ into γ -Mo₂N/ δ -MoN/Mo₃N₂ under flowing nitriding gas and high temperature will result in grain and particle growth significantly lowering the active surface area. Due to the fact that most deposition methods are not capable of depositing molybdenum nitride coatings directly, a more effective transformation process which preserves the high surface area is required. A very slow heating rate of 0.01K sec⁻¹ between 417°C to 467°C in a N₂-H₂ atmosphere as part of a two stage process was shown by Volpe and Bourdattp to prevent sintering of α -MoO₃ [45].



Figure 2-10: Molybdate unit cells showing the layer-like arrangement of molybdenum (green) and oxygen atoms (red) [46]

Replacing oxygen with hydrogen in the octahedral planes without disruption of the orthorhombic crystal (figure 2-10) structure resulted in formation of an oxygen deficient MoO₂, while a higher heating rate resulted in sintering of the molybdenum oxide particle. The second step was a faster heating rate of 0.05K sec⁻¹ from 467°C to 706°C resulting in transformation of MoO₂ into Mo₂N while avoiding formation of molybdenum metal. This process, also known as TRP (temperature reaction program), was utilized by Jaggers et al. by using NH₃ gas in order to produce high surface area molybdenum nitride powder. The reaction of molybdenum oxide under ammonia has a more reductive activity path then in N₂, involving a molybdenum oxy-nitride intermediate phase shown in figure 2-11 [3, 10, 11].



Figure 2-11: α-MoO₃ transformation path into molybdenum nitride [3]

The DTA plots of α -MoO₃ in figure 2-12 show no activity below a temperature of 375°C, but at 460, 595 and 695°C three endothermic peaks were observed. The first two peaks indicate the formation of MoO₂ and MoO_xN_{1-x}, which are intermediate phases in the transformation process. The third peak corresponds to the transformation into nitride phases. Based on the TGA plot of MoO₂ under flowing NH₃, no weight loss was observed until MoO₂ reached 688°C and at 750°C, the weight loss came to a halt and MoO₂ transformed entirely into Mo₂N with a trace of MoN. In 1993 Choi et al. described a temperature programmed reaction (TPR) for converting α -MoO₃ by heating it under flowing NH₃ gas in which the samples were rapidly heated from room temperature up to 350°C, where the reaction with nitrogen started. Two heating stages followed the preheat; the first from 350 to 450°C and the second from 450 to 700°C. The final step was a 1Hr dwell at 700°C [12].



Figure 2-12: DTA/TGA study of a-MoO₃ under flowing ammonia [3]

Further research conducted by Wise and Markel applied a similar approach, with a gas mixture of 82% H₂ and 18% N₂ and a peak temperature of 660°C. They reported the creation of Mo metal at 500°C and lower oxygen reducing activity thus lower transformation rate into molybdenum nitride phases [13]. Heat treatment under pure N₂ has a low oxygen reduction potential and thus leads to a very limited transformation into intermediate phases of oxy-nitride [3, 13, 14]. In 1997 Roberson, Finello and Davis reported a low oxygen concentration molybdenum nitride electrode prepared using a two stage thermal profile under flowing ammonia. The results in table 2-3 demonstrate that a high conversion rate can be achieved without a dramatic effect on grain coarsening [49].

Table 2-3: The effects of heating rate on the intermediate and final reaction products at a constant NH_3 flow rate of 7 L min⁻¹ [49]

Heating rate, stage 1 (°C h ⁻¹)	MoO _x N _{1-x} /MoO ₂ ratio at 580°C	Heating rate, stage 2 (°C h ⁻¹)	Final reaction products ^a	Average grain size (nm) ^b
20	2/1	80	y-Mo ₂ N, δ-MoN	12
20	2/1	160	y-Mo2N, S-MON	10
40	1.2/1	80	γ -Mo ₂ N, δ -MoN, MoO,	15
40	1.2/1	160	γ-Mo ₂ N, δ-MoN, MoO ₂	15
60	1/1	80	γ-Mo ₂ N, δ-MoN, MoO,	15
60	1/1	160	y-Mo ₂ N, δ -MoN, MoO ₂	15
80	0.9/1	80	γ -Mo ₂ N, δ -MoN, MoO,	15
80	0.9/1	160	γ-Mo ₂ N, δ-MoN, MoO ₂	15

"After completion of the indicated two-stage reaction and annealing in NH₃ for 2 h at 750°C in flowing NH₄.

^b Approximate average grain size calculated using the Debye-Scherrer formula. Differences in grain sizes above 15 nm were difficult to detect.

2.5 Molybdenum deposition techniques

A substantial number of molybdenum oxide deposition methods are available, each with its unique advantages and disadvantages, ranging from technical complications to industrial considerations. For supercapacitor applications that are supposed to compliment or even replace batteries in the field, the cost of the product is critical and often detrimental to the release of the technology itself. Deposition methods such as vacuum evaporation [50], sputtering [51] and chemical vapor deposition [17] require an expensive vacuum system that increases the cost for an electrode, sol-gel deposition [52] requires multiple stages and solutions, complicating the process and making development of a reel to reel process difficult. Electrodeposition [53] has shown great promise in several literature papers due to a relative simple and cost effective deposition process, but relatively low specific surface area is limiting the electrochemical performance. Thermal processing of molybdenum solutions, such as spray pyrolysis [10] and SPPS, have shown the best electrochemical performance due to large surface areas as well as offering simple industrial application. Spray pyrolysis has small number of controllable

parameters thus limiting process control and preventing scale up. On the other hand solution precursor plasma spraying is a simple process using only one solution in an atmospheric environment, is compatible with a reel to reel application set-up, and a number of process parameters offering the capability for process control. It is the method of choice in this thesis work.

2.6 Solution precursor plasma spraying

SPPS is part of a large and well established coating deposition family called thermal spraying which utilizes different thermal sources in order to melt/decompose a feedstock and accelerate it toward a substrate, creating coatings for multiple applications. These include dense coatings for wear and corrosion resistance, moderate porosity coatings such as thermal barrier coatings, and high porosity coatings for applications such batteries and super capacitors. A subgroup of this family is DC-arc plasma spraying in which an electric arc is created between a cathode and anode inside a plasma torch, ionizing the flowing plasma forming gases. The feedstock in either solid or liquid form is injected radially or axially into the plasma plume [54-56].

2.6.1 Plasma plume structure

In order to properly melt the particle feedstock and accelerate it toward the substrate to achieve the desired final microstructure of the coating, many variables need to be sufficiently well controlled. The final coating microstructure is determined by the velocity and temperature of the particles impacting the surface, therefore the particles must spend sufficient time and distance inside the plasma jet prior to the impact with the surface, in order to reach a temperature above the melting temperature. The plasma plume exiting most DC torches is 4-6mm wide, with a plasma velocity range of 600 - 2300m sec⁻¹. The short residence time inside the plasma jet is often not sufficient to melt ceramic particles when using pure argon as the plasma forming gas, and enhanced thermal mixtures are needed. Figure 2-13 shows a schematic DC arc torch illustrating the different torch parts and the plasma plume. An electric arc is created between the

anode and cathode due to a very large electrical potential difference build up, this arc ionizes the plasma forming gases that are forced through the torch opening.



1. Plasma forming gas injection 2. Cold boundary layer at the anode wall 3. The arc column

- 4. connecting arc column 5. Plasma jet exiting the nozzle 6. Large scale eddies
- 7. Surrounding atmosphere bubbles 8. plasma plume

Figure 2-13: Plasma formation and plume structure adapted from [4]

As the plasma expands outside of the torch different temperature zones are created, each zone has an influence depending on the proximity to the core of the plume and the distance from the torch. The effect of the temperature distribution on the coating microstructure of a molybdenum oxide coating deposited by solution precursor spraying with a DC-arc plasma torch is shown in Figure 2-14. As the distance from the torch increases, the lower the plasma temperature becomes, resulting in smaller particles On the other hand if the distance is shorter the higher temperature plasma core has a greater effect resulting in coarsening and particle growth. This relative simple control of the standoff distance (SD) has a dramatic effect on the microstructure, phase composition and eventually the overall electrochemical performance when applied in energy storage devices [57].



Figure 2-14: SEM micrograph illustrating the effect of plasma tail temperature gradient on the formation of different α-MoO₃ morphologies [5]

2.6.2 Plasma forming gases

As well as plasma velocity and in-flight residence time, the thermal properties and composition of the plasma forming gas and feedstock material are substantial factors in creating melted particles or any other desirable form of surface coating. The forming gas is selected according to its ability to transfer thermal energy to an in-flight particle during a short residence time. Depending on the plasma source and the material feedstock, different mixtures of Ar, He, H₂, N₂, O₂, CH₄ and CO₂ are acceptable. A ternary gas mixture of Ar-He-H₂ is one of the most common gas mixtures used in the thermal coating industry. As argon alone has very low enthalpy and heat transfer capabilities an additional gas is needed inside the plasma forming gas mixture [4]. The short in flight time and high velocity of the plasma makes it difficult for particles to melt and impinge on the substrate to form disk shaped lamellae coating structures. Likewise for liquid feedstock the solvent has to evaporate, precipitates form, pyrolize and melt in-flight to have splats. In order to introduce enough thermal energy and enthalpy to transform the feedstock in flight, a high enthalpy and thermal conductivity plasma forming gas mixture is required. The

proposed solution was developed by the coating center at the University of Toronto which uses gases such as CH_4 and CO_2 mixed with Ar, that together with a carbon cathode torch have better thermal properties as shown in figure 2-15 [15, 58].



Figure 2-15: Thermal conductivity and enthalpy [58]

2.6.3 Powder feedstock

Conventional plasma spray techniques use powder material as the feedstock injected into the high temperature zone of the plasma core to allow sufficient heating and subsequent melting of particles prior to the substrate impact. The structure of such coatings is characterized by the final morphology of each molten or semi-molten particle consecutively landing on the substrate surface. These conventional micro-structured coatings are made up of many single splats formed through a successive course of impacting, flattening, rapid cooling and solidification of an individual molten or semi-molten particle [4, 59].



Figure 2-16: Creation of coating by stacking molten splats [4]

In order to create a sub-micron coating with high surface area and high porosity the powder size has to be reduced. Although commercial nano-size powders are available, injecting them into the core of the plasma jet by entraining them in a carrying gas as is done for larger particle size powder requires a large carrying gas flow rate, which cools and disrupts the plasma plume. As illustrated in figure 2-17 as the size of the powder is decreases the force needed for adequate injection increases, requiring higher carrying gas velocity. For nano-size powder the velocity required is in the same order of magnitude as the plasma jet itself, resulting in physical disruption of the plasma jet and limitation of this process to a minimum of 5µm particles in laboratory experiments [4, 60].



Figure 2-17: In-flight velocity of Al_2O_3 particles of diameters 18, 23, 39 and 46µm suspended in the Ar – H₂ plasma forming gas with the velocity of 600m sec⁻¹ [59]

2.6.4 Liquid feedstock and nano-structured coatings

SPPS uses precursor solutions as the feedstock injected into DC-arc plasma instead of the powder used in conventional thermal spray processes to deposit nanocrystalline oxide coatings.

The deposits typically exhibit fine grain sizes, high porosity levels, and high surface area, which are ideal for application as electrochemical electrodes in devices such as solid oxide fuel cells, Li-ion batteries, super-capacitors, and sensors [61]. Studies have revealed fractured hollow spheres to be the signature structure of these porous, high surface area coatings. The liquid atomization while entering the plasma, such as primary breakup caused by the Rayleigh instability and secondary break-up caused by the plasma velocity, has a significant effect of the coating structure. Additional parameters of the solution and plasma process itself must be taken into account. The gas Weber number represents the competitive effects of inertia and surface tension forces, thus illustrating the likelihood of a droplet to undergo further breakup, is expressed by equation 2-3:

We =
$$\frac{\rho_g \times u_r^2 \times d_1}{\sigma_1}$$
 (2-3)

Where ρ_g is the gas mass density, u_r is the relative velocity between gas and liquid, d_1 is the droplet or liquidjet diameter, σ_1 is the surface tension of the liquid.

Plasma properties such as temperature and velocity affect the Weber number. In addition the method of liquid injection into the core of the plasma jet has a major effect on the break up mechanism and droplet size [62, 63].

2.6.4.1 Gas atomization

Gas atomization is a method in which the injected liquid stream is broken up by a high velocity gas stream. The breakup mechanism depends on liquid and gas velocity as described by the Weber number. The mechanisms are classified as bag break-up (12<We<100) where the droplets is stretched and swept in flow direction, stripping break-up (100<We>350) where thin sheets are drawn from the deforming droplets, and catastrophic break-up (We>350) where a multi stage effect is happening. The biggest disadvantage of the gas atomization method is the addition of a complexity factor in the form of controlling the atomization gas that requires additional valves and gas controlling features.

2.6.4.2 Mechanical atomization

Mechanical atomization has two systems associated with it. In the first a pressurized reservoir feed liquid to a nozzle where a magnetostrictive rod superimposes pressure pulses at frequencies up to a few tens of kHz. In pulse mechanical break-up the droplet diameter is a function of liquid flow velocity therefore the droplet size and velocity cannot be controlled separately. In a second system, which was utilized in this thesis work, the liquid from a pressurized tank is forced though a nozzle with a given diameter d_i and produces a liquied jet with velocity v_1 and a diameter of about $1.5 - 1.8d_i$. The liquid exits the nozzle and breaks up at a distance of $100 - 150d_i$ from the nozzle due to Rayleigh–Taylor instabilities. Because of the natural physical break-up of the liquid it has less disruption effect on the plasma jet and is the preferred injection method in many cases.



Figure 2-18: suspension stream penetration and break-up under different injection pressures (a) 0.4MPa (b) 0.7MPa [6]

In low concentration precursor solutions the evaporation of the solvent results in the solubility limit being reached at the surface of the droplet, causing precipitation at the surface and thus forming hollow spheres [64]. In contrast, high concentration solution result in a more uniform composition and precipitation occurs throughout the bulk and surface of the droplets resulting in solid particles and dense coatings, figure 2-19. Understanding and controlling the evolution of the precursor solution droplets in the plasma jet is crucial in producing α -MoO₃ deposits of fine grain sizes, high porosity levels and high surface area.


Figure 2-19: Decomposition process of solution droplet inside a plasma jet [5,7]

The full system illustrated in figure 2-20 shows the different elements described above in a complete system configuration. The plasma forming gases which are controlled by the torch control console are being forced with high velocity into the torch chamber where a powerful arc between the cathode and anode is ionizing the flowing gas creating a high temperature and enthalpy plasma. Air is being used in order to pressurize a solution that is injected into the plasma creating in flight material that is deposited on a substrate at different standoff distances.



Figure 2-20: Schematic representation of the SPPS setup [19]

2.6.5 Effect of liquid injection and standoff distance

In DC plasma torches used for spraying (power level of generally <50 kW), typical temperatures are between 8000 and 14 000 K, depending on the plasma forming gases. The room temperature liquid that is injected into the plasma has a cooling effect on the plasma jet; this cool down can be as much as 3000K depending on the amount of liquid injected and the downstream location where the temperature is measured (standoff distance). As illustrated in figure 2-21, without injection of water the spectroscopy measurement shows a temperature drop of about 2000K as the standoff distance increased from 5mm to 15mm. With water injection at a rate of 20 mL min⁻¹ the temperature was roughly 2000K lower at both distances [65].



Figure 2-21: Cooling effect of standoff distance and water injection on DC-arc plasma [8]

2.7 Previous results

This thesis work is based on research that was conducted in the CACT in 2012 by Mehdi Golozar. This research work has proved the concept of molybdenum oxide electrode deposited by SPPS. As shown in figure 2-22 the result achieved by this research where an capacitive behavior of molybdenum oxide electrode on stainless steel substrates and a connection to the thermal history of the coating, but the relative capacitance to other deposition methods and other transition metal electrodes is very low and the stability of the electrode was shown to be very problematic as the electrode disintegrated after only 10 cycle voltammetry cycles. A better understanding of the thermal history of the coating, higher electrochemical performance and better stability were the major objective of this research thesis [66].



Figure 2-22: Normalized capacitance as a function of standoff distance shown in Mehdi Golozar research [5]

Chapter 3: Experimental Procedure

3.1 Substrate preparation

Substrate preparation and modification was shown to increase coating adhesion thus increasing the electrochemical performance of the electrode because this characteristic is strongly affected by the structural integrity of the coating and electrode. One of the theories on coating adhesion of thermal spraying process has shown that if the surface roughness is in the order of the splats that are formed by the spaying process a maximum coating substrate adhesion can be achieved. The solution droplets created during the primary and secondary breakdown are on the order of 20-30µm, therefore in order to achieve maximum adhesion of the coating the roughness should of the same order. Three types of surface modification were implemented in this thesis work aimed to increase surface adhesion and control the created oxide phases. The first is polishing with 320 grit particle size of SiC which was implemented on all 75×12.5mm, 1mm thick stainless steel (304) and titanium (Grade 2) samples, creating surface roughness in the order of the droplets [67]. The two additional modifications were implemented on Ti substrates only as results of a literature reference to increases coating adhesion and control of oxide phase after nitridation process [10]. Following this guideline two sets of experiment were performed, the first consisted of only cleaning the surface with Alcohol (Commercial Alcohols), Acetone ((CH₃)₂CO, CALEDON) following by immersion in 0.1M Hydrochloric acid (HCl, J.T.Baker) at 90°C for 10 minutes in order to remove organics and surface oxides in order to increase surface adhesion The third set was cleaned in the same way that the previous, but then also nitrided inside a tube furnace at 700°C for 1Hr in ammonia gas (4.5 Grade, Praxair) flowing at 0.115 mL sec⁻¹.

3.2 Solution preparation

Solution properties have an effect on the coating porosity and process limitation due to precipitation of molybdenum salt that clogs the injection nozzle during spraying. As a result only one solution precursor variation was prepared by mixing 0.1 Kg of ammonium molybdate (para) tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, Alfa Aesar) with 900 mL of DI water and stirred with a magnetic stirrer for 10 minutes to dissolve all the salt in the water.

3.3 Molybdenum oxide electrode fabrication

Fabrication of electrodes was performed in a monitored spray booth which houses an x,y,z axis robot to which the torch was attached, with gas lines and water line for cooling. The prepared substrates were placed in front of the torch on sample holders. The solution injection nozzle, which was connected to a pressurized tank containing the 10% solution at 0.48MPa, was attached under the plasma torch at the plume exit oriented to allow radial injection into the plume (figure 3-1). Thermocouples connect to the back of the sample substrate, with temperatures recorded through a Omega TC-08 data acquisition module in order to measure the temperature developed on the substrate during spraying.



Figure 3-1: Torch and sample setup (a) torch with connecting gas, water and solution lines (b) sample and sample holders

The torch parameters include current, voltage and power during spraying, as well as the gas flow rates of the plasma forming gases. The process parameters consisted of substrate material, preparation method, standoff distance, raster distance, number of layers, injection nozzle size and nitridation gas. Table 3-1 presents all torch and process parameters that were considered during deposition.

Unchanged	Solution	Solute: 10% wt NH ₄ Mo ₇ O ₂₄
Parameters		Solvent: 90% wt DI water
	Torch	Current: 300A
		Voltage: 110V
		Power: 35kW
		CO ₂ : 5.5LPM
		CH ₄ : 3SLPM
		Ar: 30LPM
Studied Parameters	Substrate	Material: Stainless steel, Titanium
		Preparation: Polish, polish+clean, polish+clean+nitride
	Process	SD: 55, 65, 75mm
		RD: 5.3, 8.4mm
		Layers: 3,4,5
		Nozzle: 100, 150, 200, 250, 330µm
	Nitridation	Gas: NH ₃ , N ₂

Table 3-1: Unchanged and studied parameters during the thesis research

As shown in the table 3-1 some parameters, such as those related to the torch and solution, are not changing. Due to the lack of literature sources on SPPS research, especially on electrochemical coating for capacitor applications, it's extremely hard to compare and evaluate the data from the experiments. This is way the basic research was conducted on process parameters that can be controlled rather than changing the torch parameters and introducing another level of variability.

3.4 Oxide to nitride transformation

Nitridation after deposition was preform by passing ammonia gas (4.5 grade, Praxair) at 0.115 mL sec⁻¹ flow rate through a tube furnace running a four stage temperature programmed reaction (TPR) specified in table 3-2. To conduct the transformation in inert environment nitrogen was passed through the tube for 30 min at a flow rate of 0.115 mL sec⁻¹, the same was applied after the thermal profile to passivate the coating The same profile was used when the nitridation gas was nitrogen, instead of switching into ammonia the profile continued with nitrogen after displacing the air.

T _{initial}	T _{final}	Heating Rate	Dwell Time
[°C]	[°C]	[°C min ⁻¹]	[Hr]
25	350	7.5	
350	450	0.66	
450	700	3.3	1

Table 3-2: Temperature program reaction used in nitridation process

Chapter 4: Characterization Techniques

4.1 X-ray diffraction (XRD)

X-Ray diffraction analysis occurs when an incident monochromatic x-ray radiation interact with target material by scattering x-rays from the atoms in the material. The diffraction from the atomic planes is detected by a solid state detector and the planar spacing determined through a relationship between the wavelength, atomic layer spacing and the diffraction angle called the Bragg law: $n \cdot \lambda$ =2dsin θ . XRD was used in this thesis work in order to characterize the phase composition and crystal structure of the as deposited and nitrided coatings. A Rigaku MiniFlex 600 x-ray diffractometer with monochromatic radiation of Cu K_a (λ =1.54Å) was used, the diffraction angle range was 5°-100° with 0.02° step size. The diffraction peaks were compared with standard patterns from the International Center for Diffraction Data (ICDD) in order to identify molybdenum oxide/nitride as well the not fully decomposed solution precursor phases. Quantitative phase analysis was performed based on relative intensity ratios by the XRD machine software package. The strongest peak of each phase is compared to the reference corundum peak, resulting in a relative intensity ratio ($\frac{l}{l_c}$) that can be used to calculate the quantitative phase ratios.

4.2 Scanning electron microscope (SEM)

A scanning electron microscope produced images by scanning an electron beam which interacts with the sample material inducing various signals such as secondary and back scattered electrons. These signals are analyzed and a topographic image can be produced. The morphology of the samples was examined by detecting secondary electrons in the microscope. The sample was sufficiently conductive that coating the samples was not required. For low resolution images a Hitachi TM3000 SEM was used in order to verify coating existence, porosity and morphology, in addition a Hitachi SU 3500 VPSEM SEM was used for higher resolution imaging in order to detect the grain size.

4.3 Energy dispersive x-ray spectroscopy (EDS)

Interaction of the electron beam with the sample surface produces not only secondary and back scattered electron signals, but characteristic x-rays which can be detected by a silicon detector. Because the energy emitted by this process is specific to the material which provoked the signal, the chemical composition and element distribution can be detected (0.5% tolerance). In this thesis work the low resolution SEM Hitachi TM3000 was used as the electron beam source, but by changing the detector in the system to a SwiftED3000 with a Bruker Quantax 70 analytical software package, EDS analysis of the coatings was conducted.

4.4 Glow discharge optical emission spectroscopy (GD-OES)

Glow discharge optical emission spectroscopy is a widely used technique for rapid depth profile analysis of surface, thin films and coatings. For many years the method was used mostly in the automotive industry where it was extremely effective for the analysis of surface treatments such as carbonization, nitriding, passivation and oxidation, but in recent years the technique has spread into the microelectronics industry in silicon analysis applications. In GD-OES the target sample/coating is uniformly sputtered by a stream of argons ions under low pressure. The cathodic sputtering removes material layer by layer without change to the coating chemistry, which is then excited away from the surface by a low pressure plasma discharge. The light emitted from the excited material is then analyzed by an optical emission spectrometer and the weight percentage (1% tolerance) of each detected element is then plotted against the sputtering depth enabling understanding of coating composition, concentration and thickness (figure 4-1) [68,69]. In this thesis a HORIBA Scientific GD-Profiler HR model of GD-OES was used with a sputtering rate of 30nm sec⁻¹.



Figure 4-1: GD-OES analysis chart example

4.5 Cyclic Voltammetry (CV)

Cyclic voltammetry is a common way to identify and measure the electrochemical properties of supercapacitors. Any electrode immersed in an electrolyte solution will form a specific interfacial region called the double layer. The electrical properties of such a layer are important, since they significantly affect the electrochemical measurements. A simple electrical circuit used to represent the electrochemical cell used to measure the current that flows at a particular working electrode, the double layer can be viewed as a capacitor. The capacitance C_d corresponds to double layer and is described by: $C = \frac{\partial Q}{\partial E}$.



Figure 4-2: Cyclic voltammetry represented as a simple electronic circuit

The double-layer structure and its capacity depend on several parameters such as electrode material, material porosity, the presence of other layers, type of solvent, type of supporting electrolyte, specific adsorption of ions, and temperature. Cyclic voltammetry is one of a variety of methods that are used in electrochemistry to measure the double layer effect and capacitive current. By recording the cell current vs. potential the electrochemical behavior of species diffusing to an electrode surface, interfacial phenomena at an electrode surface, and bulk properties of materials can be studied. A typical three-electrode cell usually includes a reference electrode, a counter electrode, and a working electrode (figure 4-3). In order to perform a cyclic voltammetry measurement a potentiostat is connect to the three electrodes, the potential between the working and the reference electrode is measured while the counter electrode compensates for the cell resistance by acting as a sink for electrons. The scan potential is linear and switches direction according to pre-set values of the scan range and scan rate. The scan rate can be chosen over a wide range, typically from 0.001 to 200 or more V s⁻¹. The output of cyclic voltammetry is a plot of the current flowing in the electrochemical cell versus the potential.



Figure 4-3: Three electrode CV schematic for film testing [9]

Consider a solution containing electro-active specie "O" in a cell with low resistance and minimal electrical migration, containing a metal working electrode. Reversible and rapid reduction of "O" occurs following the reaction

$$0 + ne^- \rightarrow R(1)$$

where n is the number of electrons transferred from the electrode to "O". Reaction (1) is controlled by the rate of diffusion of "O" to the electrode surface. In some cases, when the rate of the electrode reaction is slow with respect to the rate of the potential scan it is governed by kinetic control. Cyclic voltammetry can be used to decide if an electrode reaction is reversible by observing the shape of the voltammogram. If the peak shape is unsymmetrical but of equal height on the anodic and cathodic sides, as shown in figure 4-4, the reaction is reversible. In the case of a thin film as the working electrode under very low scan rates thin-layer conditions can be achieved, characterized by a symmetric cyclic voltammetry peak shape indicating that all of the "O" in the film has been reduced during the scan. The same model applies to adsorbed monolayers on electrodes.



Figure 4-4: Ideal shapes of cyclic voltammograms for a reversible, diffusion-controlled reaction (left) and thin-layer conditions for a reversible reaction in a thin film (right). [9]

Fully symmetric CV voltammograms for films are rarely obtained, because of influence on cathodic and anodic peaks by the interactions between electro-active species in the films. At relatively high scan rates the material in the film will be only partially electrolyzed and a depleted "O" region at the diffusion layer will be generated. If the diffusion layer in the film is much smaller than the film thickness the peak shape changes to that in Figure 4-4 (a). At low scan rates the film is under the thin film condition, in which the peak current is proportional to v(scan rate). Increasing the scan rate will create depletion in the diffusion layer and changes in the peak current depend on $v^{0.5}$. The charge transport diffusion coefficients in the film can be estimated by conducting experiments with a different scan rates while observing the shape of the peaks and the dependence. In principle the same behaviours can be transferred to oxidation reactions. Slow electron transfer will expand the potential between the cathodic and anodic peaks and broaden the peaks. It is also possible for "O" and "R" to be involved in a variety of chemical reactions, which can be detected by the shape of the peaks and voltammogram [7, 8]. In this thesis stainless steel and titanium were used as substrates to deposit molybdenum precursor salt via the SPPS technique. CV testing with $0.5M H_2SO_4$ (sulfuric acid) electrolyte was preformed using an Ivium CompactStat to measure the capacitance properties of the coating, reversibility of the electrolysis process, and stability of the electrode.

Chapter 5: Results and Discussion

5.1 Study of coating thermal history

As was shown in past work, the thermal history of the coating is a major factor in the coating structure, particle size and electrochemical performance. The uniqueness of SPPS in the way that the energy and material are being utilized separates the thermal history into three categories according the stage of influence and coating structure. This concept of division into categories is employed throughout the discussion in terms of the three factors of thermal history.

<u>The first factor</u> in the thermal history of the coating is the solution evaporation, precipitate formation, and decomposition in-flight in the plasma jet, which depends on the torch parameters such as power, plasma forming gas flow rate and composition, and standoff distance. In addition, solution concentration and solvent composition influence the extent of decomposition and structure of the material arriving at the substrate.

<u>The second factor</u> in the thermal history of the coating is the temperature of the substrate (or previously deposited material) on which the deposit forms. The heat flux to the substrate and the effectiveness of substrate cooling processes determine the substrate temperature, which depends on the plasma temperature, the standoff distance (SD), gun translation speed, and raster step distance (RD).

<u>The third factor</u> is the coating history during spraying. In order to cover a 2D area the robot holding the torch is moving in a raster pattern to cover the sample. Each pass over the sample heat treats the already deposited coating with the plasma.

In order to investigate the thermal history of the coating it is critical to know the substrate temperature resulting as a function of spraying and torch parameters. Thermocouples were attached to the back of the substrate and recorded the temperature during deposition in two cases: changing standoff distance and changing nozzle diameter.

5.1.1 Standoff distance effect

Samples were deposited at 55, 65 and 75mm SD with a 150µm diameter solution injection nozzle and a 5.3mm RD on polished stainless steel. Each coating consisted of 5 layers. Figure 5-1 shows the substrate temperature as a function of deposition time. The five large peaks shown in the figure correspond to the layers, while the short, sharp peaks superimposed on the large peaks correlate with individual passes of the torch, each offset by the raster distance, as the torch follows the 2D pattern. The gradual increase in the average substrate temperature due to heat accumulation in the substrate from the heat flux of the plasma on the substrate illustrates the second factor of the thermal history. The area under the curve from the time coating is being deposited on the substrate to the end of the run describes the heat treatment of the coating after deposition, the third factor in the thermal history of the coating. The temperature difference among the samples is clearly visible. The sample deposited at 55mm SD has about 100°C higher temperature across the 5 deposition layers.



Figure 5-1: Substrate temperature as a function of deposition time

XRD patterns of samples deposited at 55 and 75mm SD are shown in figure 5-2. The α -MoO₃ peaks (PDF #00-005-0508) are stronger for the sample deposited at 55mm, while peaks associated with the undecomposed ammonium molybdenum oxide phase (PDF #00-018-0117) are larger for the sample deposited at 75mm. The calculated fraction of crystalline α -MoO₃ is 97% for the sample deposited at 55mm SD and 80% for the sample deposited at 75mm. In both patterns the average crystallite size was found to be approximately 10nm according to the peak broadening calculation with the Scherer formula.



Figure 5-2: XRD patterns of samples deposited at 55mm and 75mm standoff distances

The color of the as deposited samples changed with standoff distance, becoming darker green/grey at shorter SD and lighter green/grey at 75mm SD as shown in figure 5-3. This agrees with observations from DTA analyses performed on the precipitate formed by drying the solution, which showed that samples with a high fraction of α -MoO₃ were dark green/grey in color.



Figure 5-3:As deposited samples at (a) 55mm (b) 65mm (c) 75mm standoff distance

The sample deposited at 55mm SD had a shorter inflight time, which would result in less decomposition inside the plasma jet (first factor) than the sample deposited at 75mm SD. Interpretation of these results according to the three thermal history factors therefore suggests that the higher fraction of α -MoO₃ at 55mm SD is not due to inflight processes but rather to the higher substrate temperature at deposition and increased post-deposition heat treatment (factors 2 and 3), resulting from the higher heat flux from the plasma jet at the 55mm SD. A higher fraction of α -MoO₃ would be expected for higher post deposition heat treatment temperature.

5.1.2 Solution flow rate effect

As shown in the literature review, higher solution injection flow rates cool down the plasma jet. This cooling effect would be expected to result in less decomposition inside the plasma jet, a lower substrate temperature and a smaller heat treating effect from the torch during deposition. In order to understand the effect of solution flow rate on the sample temperature, samples were deposited at a standoff distance of 65mm with 5 different nozzles resulting in different solution flow rates. Figure 5-3 presents substrate temperature as a function of deposition time during a 4 layer deposition. A smaller diameter nozzle results in a lower flow rate, less cooling of the plasma jet, and a lower substrate temperature. The Mo oxide fraction calculated from XRD patterns is 97% for the 100µm nozzle, 80% for the 200µm and 29% for the 330µm. As was seen for the standoff distance, a higher substrate temperature results in a higher fraction of

molybdenum oxide in the coatings. It is important to notice that according to figure 5-5, which shows the dependence of the peak substrate temperature on nozzle size, none of the samples reached the temperature needed for complete decomposition into α -MoO₃.



Figure 5-4: Substrate temperature as a function of deposition time for five different nozzles



Figure 5-5: Peak temperature as a function of nozzle diameter

The higher temperature plasma jet impinging on the substrate results in a higher temperature for the substrate and previously deposited material, thus transforming more material into the fully decomposed oxide phase. The transformation of solution into a crystalline α -MoO₃ structure with high porosity is visible by looking at SEM micrographs taken of samples deposited using three different of nozzles (figure 5-6). Samples deposited with a 100µm diameter nozzle (a) exhibit the presence of small, roughly spherical particles than samples deposited with larger diameter nozzles, due to more extensive decomposition inside the plasma because of the higher plasma temperature. As nozzle size increases (b,c) the plasma is cooler and less decomposition is happening inflight. In addition, cooler substrate temperatures reduce the extent of decomposition after deposition, reducing the amount of porosity formed by shrinkage and the evolution gaseous decomposition products.



20 um

D4.0 x5.0k

035 NaCl



20 um



N D5.1 x4.0k 20 um

Figure 5-6: SEM micrographs of samples deposited with changing nozzle diameter (a) 100μm, (b) 200μm, (c) 330μm

5.1.3 GD-OES analysis

Glow discharge optical emission spectroscopy was used to identify elemental concentrations and coating thickness. Elemental weight percentage versus sample depth for a 4 layer sample deposited using a 150 μ m diameter nozzle on a titanium substrate at a standoff distances of 55mm and 75mm are presented in figures 5-7 and 5-8. The stoichiometric O/Mo mass ratio for MoO₃ is 0.50 and for ammonium molybdate oxide, (NH₄)₄ Mo₈O₂₆, is 0.54. The O/Mo mass ratio would be even higher if water or hydroxides remained trapped in the coating due to incomplete vaporization. Therefore the O/Mo ratio as a function of depth in the coating may help to understand the thermal history effect on the phase composition of the coating.



Figure 5-7: GD-OES analysis of as deposited samples at 55mm SD



Figure 5-8: GD-OES analysis of as deposited coating at 75mm SD

The composition at any particular sputtering distance represents the average composition within the 5mm diameter area analyzed. Although the depth resolution of the technique is on the order of a few nanometers, the practical resolution is limited by the surface roughness of the coating and substrate. The surface of the Ti substrates was ground using 320 grit SiC paper to produce a surface which provides good adhesion of the coating. This type of surface finish produces a surface with a roughness of typically a few micrometers. Therefore the gradual change in composition over a range of approximately 2.5 μ m through the coating-substrate interface seen in the depth profiles is predominantly due to the interfacial roughness. Estimating the position of the interface to be at the point where the Ti content reaches $\frac{1}{2}$ of the bulk value, the coating thickness is in the range 1-1.5 μ m or 250-230nm per layer. Nitrogen is seen at a level of 10-20% in figure 5-7 and at 4-10% in figure 5-8, throughout the spattering process. This indicates a slow leakage of air into the sample analysis chamber, due to the porosity of the coating, and is not reflective of the concentration of nitrogen in the coating.

The oxygen weight fraction is lower in the sample deposited at the 55mm standoff distance, consistent with more complete decomposition of the precursor and crystalline oxide formation at the higher temperatures found at the shorter standoff distance.

In both samples, especially for the sample deposited as 75mm standoff distance, the O/Mo ratio was higher near the surface of the coating, then decreasing as sputtering continued. This behavior may be explained by considering that the first layers deposited were exposed to the high temperature during the subsequent torch passes, whereas the last layer deposited was not exposed to additional heating from the torch.

5.2 Molybdenum oxide/nitride on stainless steel

5.2.1 Molybdenum oxide

The first attempts to fabricate a functional supercapacitor electrode employed stainless steel substrates as in previous research conducted in CACT. Some capacitive behavior was observed but very bad adhesion prevented reliable characterization of the electrode because the electrode disintegrated into the solution after only 10 CV cycles. In order to understand the effect of thermal history on the electrochemical performance, multiple samples were deposited using a 200µm diameter solution nozzle on polished stainless steel substrates. Five layers were deposited at 55, 60, and 65mm standoff distances with 5.3 and 8.3mm raster distances. Figure 5-9 displays results of cyclic voltammetry at 100mV sec⁻¹ scan rate of samples deposited at different SD's with a constant RD, allowing comparison of the effect of substrate temperature on the capacitance of the electrodes. Recall that features of good electrochemical performance for a super capacitor would include a rectangular shaped CV curve and a large area of hysteresis. The samples presented in figure 5-9 lack these features, although comparison with the curve showing the bare substrate performance reveals that the electrodes are electrochemically active. There is some charge accumulation indicated by the curves; the calculated capacitance is 129.77mF cm⁻² for 55mm, 76.63mF cm⁻² for 60mm and 66.55mF cm⁻² for 65mm SD. However the "cigar" shape indicates that a large resistance is present in the samples and the charge accumulation is probably not due to reversible surface phenomena such as EDLC and pseudo-capacitance but rather to irreversible reactions with the electrode material. The electrochemical activity of the electrodes increases as the standoff distance decreases, corresponding to a higher fraction of fully decomposed molybdenum oxide phase.



Figure 5-9: Cycle voltammetry plots of as deposited samples at 55, 60, 65mm SD and 5.3mm RD

The thermal history of the coating is not determined only by the distance between the torch and substrate, but rather can be affected by several types of process controls. Increasing the raster distance from 5.3mm to 8.3mm means that covering the 12.5mm long sample takes fewer passes than with a smaller RD, dramatically changing the thermal history. The lower exposure time leads to lower temperature and less decomposition of the solution, resulting in lower fraction of capacitive phases and lower capacity as shown in figure 5-10.



Figure 5-10: Cyclic voltammetry of as deposited samples on stainless steel at different RD

The suggestion that the electrochemical activity observed for the samples was likely due to irreversible reactions was confirmed by the results of extended cycling. After only 10 cycles the coatings have almost completely disintegrated into the solution leaving dark blue flakes of coating on the electrode, as shown in figure 5-11. The severe reactions with deposited coating generated charge transfer but also destroyed the electrode.



Figure 5-11: As deposited coating on stainless steel substrate post CV

5.2.2 Molybdenum nitride

Establishing the thermal history concept and realizing the major effect it has on the deposited electrode aided in understanding the behavior shown in the CV plots, but the fact that molybdenum nitride is known to have a better electrochemical stability encouraged conducting experiments on nitrided coatings deposited on stainless steel. Nitridation was performed on samples deposited on polished stainless steel substrates at 55, 65 and 75mm SD and a 5.3mm RD. Five layers were deposited using a 150 μ m solution nozzle Ammonia gas was used in the thermal process (TRP) described in the procedure section. The cyclic voltammetry tests were conducted in 0.5M solution of H₂SO₄, over a voltage range of -0.15 to 0.45V, at a scan rate of 100mV sec⁻¹ with a Ag/AgCl counter electrode. From the plots shown in figure 5-12 it can be seen that all the coatings showed the same non-capacitive behavior, as all plots are not rectangular and the current does not go below zero indicating dissolution of the electrode, leading to large resistance in the coating. The resistance is so high that the charge can only flow in one direction.



Figure 5-12: Cyclic voltammetry testing on nitride samples deposited on stainless steel

Due to poor adhesion of the coating to the substrate surface and the stress induced by the nitridation process, exposed substrate was generated. Cracks in the coating which reach the bare

substrate can be seen in the SEM micrograph shown in Figure 5-13. Evidence that the substrate is involved in the creation of resistance and damaging the capacitive performance of the electrode is found in figure 5-14. This image shows samples deposited on stainless steel substrates, nitrided, and electrochemically tested by cyclic voltammetry. Instead of blue flakes of coating that were shown after CV testing of non-nitrided coatings, a rust residue was found on nitrided coatings, pointing to a reaction between the Fe-based substrate and the electrolyte solution.



Figure 5-13: SEM micrograph of post nitridation coating on stainless steel, showing exposed substrate



Figure 5-14: Post CV samples of nitrited coatings deposited on stainless steel at 55, 65 and 75mm SD

5.3 Molybdenum oxide/nitride on titanium

Because samples deposited on stainless steel substrates have produce very little capacitance with poor stability, and nitrided coatings on the same substrate have showen no capacitance at all, focus was directed to titanium substrates. These substrates have shown superior adhesion properties with molybdenum oxide coatings in various literature sources, and other groups in the Department of Materials Science and Engineering have reported much improved results using Ti substrates.

5.3.1 Molybdenum oxide

A grade 2 titanium sheet 1mm in thickness was cut into the same 75×12.5mm samples as the stainless steel and the same 320 grit polishing method was applied as an initial preparation stage. In addition all torch and spraying parameters were kept the same in order the compare the different substrate properties without introducing additional influencing parameters. In figure 5-15 SEM micrographs of 2 samples deposited at 55mm and 75mm standoff distances are presented. As in the as deposited samples on stainless steel, the Ti substrate samples show the same dependence on the thermal history concept, with higher porosity visible on the sample deposited at 75mm SD.



Figure 5-15: SEM micrographs of as deposited samples on Ti substrate

In order to understand if the substrate change has made a difference on the stability and performance of the electrode, CV testing was performed on the as-deposited samples (figure 5-16). The shape of the plots is not an ideal rectangular, indicating some cathodic and anodic resistance is still present, however the shape is better than for the samples deposited on stainless steel substrates suggesting that the stability is higher. The area for the sample deposited at 55mm is the largest, followed by the samples deposited at 65mm and 75mm SD. The calculated capacitance was of 104 mF cm⁻², 80mF cm⁻² and 71mF cm⁻², respectively. Based on the XRD results of coatings deposited on stainless steel substrates under these conditions, molybdenum oxide in the form of α -MoO₃ is present in a higher fraction in coatings deposited at shorter SD. The larger area inside the CV plot indicating larger charge accumulation therefore correlates with the amount of the desirable electrochemically active phase.

In order to understand the short term stability of the coatings, the samples were cycled for 100 cycles at $1V \text{ sec}^{-1}$, then 5 additional cycles at $100\text{mV} \text{ sec}^{-1}$, after which the capacitance measurement was performed again. The results are shown in figure 5-17 for a sample deposited at 75mm SD. The reduction in capacitance was 26% after 100 cycles illustrating that the samples still unstable; some reaction is creating resistance and reducing the capacitance. The CV results for samples deposited at 55 and 65mm SD are similar, with reductions in capacitance of 25% and 22% respectively, after 100 cycles.



Figure 5-16: Cyclic voltammetry testing for as-deposited samples on Ti substrate



Figure 5-17: CV plot of as deposited sample at 75mm SD after 4 and 104 cycles

Higher magnification SEM examination of the samples reveals that the grain size is very small, (figure 5-18) agreeing with the peak broadening calculation presented in previous sections, and is probably responsible for the large capacitance of the as-deposited samples on Ti substrates. The small grain size illustrates one of the biggest advantages of the SPPS method when compared with a simple heat treatment of molybdenum salt precursor at 700°C for 1hr (figure 5-19), where very large grains of 50 μ m are achieved with very sharp α -MoO₃ peaks in the XRD pattern.



Figure 5-18

Figure 5-18: High magnification SEM micrograph of as deposited sample of Ti substrate



Figure 5-19: Molybdenum oxide solution after 1hr at 700c heat treatment

5.3.2 Molybdenum nitride

In order to make the electrode more stable, the samples were nitrided using ammonia gas under the programed thermal profile presented in the experimental procedure section. Figure 5-20 shows SEM micrographs of samples deposited at 55 and 75mm SD. The images illustrate the island microstructure that was created after the thermal treatment.



Figure 5-20: SEM micrographs of nitrided samples deposited at 55mm and 75mm SD



Figure 5-21: High magnification SEM micrographs of post nitridation sample deposited at 55mm SD

To investigate if the area between the large islands was exposed substrate, as observed for nitride coatings on stainless steel substrates, EDS was performed on islands and on the area between islands. According to the results presented in figure 5-22, the area between the islands has a Mo/N ratio consistent with Mo₂N₃, which is a phase usually created in thin films of molybdenum nitride [42]. No peaks associated with the Ti substrate were observed, indicating this area was fully covered by the molybdenum nitride. The Mo/N ratio for the island was high, indicating the presence of other nitride phases such as γ -Mo₂N_{0.92}, γ -Mo₂N, and/or δ -MoN.



Figure 5-22: EDS analysis of sample deposited at 55mm SD (a) on island (b) between islands

As seen in figure 5-20, the different thermal histories of the coatings deposited at 55mm and 75mm SD prior to nitridation has resulted in differences in the coating microstructure after nitridation. The XRD patterns presented in figure 5-23 (Mo₂N-PDF #00-025-1366, Ti-PDF #00-001-1197) show that the most intense peaks of molybdenum nitride phases such as γ -Mo₂N_{0.92}, γ -Mo₂N, δ -MoN are larger relative to the major peak for MoO₃ for the coating deposited at 75mm SD than for the coating deposited at 55mm SD. The calculated phase fractions indicate that nitride phases make up 91% on the coating deposited at 75mm SD and 46% of coating deposited at a standoff distance of 55mm resulted in more completed decomposition of the precursor and a higher fraction of α -MoO₃ in the coating than for coatings deposited at longer standoff distances. It appears that transformation of the molybdenum oxides into the nitride phases is more difficult in coatings where the crystallization of α -MoO₃ has been extensive.



Figure 5-23: XRD patterns of nitrided samples deposited on Ti substrate

The results of cyclic voltammetry testing of the nitride electrodes are presented in figure 5-24. Three samples deposited at 55, 65 and 75mm were cycled at 100mV sec⁻¹ in 0.5M H₂SO₄ against a Ag/AgCl reference electrode. The nearly rectangular shape of the curve indicates that the samples are stable and reversible in terms of electrochemical cycling, with a low resistance. The capacitance of the nitrided samples deposited at the three standoff distances was inverted compared to the capacitance of the as-deposited samples. Samples deposited at 75mm SD have a calculated capacitance of 62.4 mF cm⁻², but at the shorter SD distances the capacitance is 42 and 25.2mF cm⁻² for 65 and 55mm SD respectively. The increase in capacitance with increased standoff distance correlates with the increase in the fraction of nitride phases at longer standoff distances.

In order to investigate the stability of the nitrided electrodes, samples that were deposited at the three different SD have been cycled 100 times with a 1V sec⁻¹ scan rate, and then again for 5 cycles at 100mV ^{sec-1} as was done for the as-deposited coatings. The reduction in capacitance was 14%, 11%, 9% for the 55, 65 and 75mm standoff distances, respectively. This reduction is more than 10% lower than the reduction observed for as-deposited samples on Ti after 100 cycles.

Although the shape of the CV curves for the nitrided samples is closer to the ideal rectangular shape than the curves for the as-deposited samples, the capacitance of the as-deposited (oxide)

coatings are higher than the nitrided coatings deposited at the same standoff distance. The largest difference is found for coatings deposited at 55mm SD, where the capacitance of the nitrided coating is approximately 40mF cm⁻² lower than the as-deposited counterpart. Two reasons can be offered as a possible explanations for this difference. The first is a coarsening of the grain size and reduction in porosity during the nitridation process which would decrease the specific surface area, an extremely important factor for high performance electrochemical capacitors. The second is the instability observed in the behavior of the as-deposited coating. Irreversible processes may be contributing significantly to the apparent capacitance of as-deposited coatings, as indicated by the reduction of approximately 25% in the capacitance after 100 cycles. The behavior of the nitride coatings appears to be more stable.



Figure 5-24: Cyclic voltammetry of nitride electrode deposited on Ti substrate at 55, 65 and 75mm SD

5.3.3 High cycle testing

As established by testing nitride coatings deposited on Ti substrates, the capacitive performance was promising, suggesting stability and low resistance for current cycling in the electrode. The stability over 100 cycles increased the interested in the high cycle behavior of the electrodes to
understand the potential of high surface area molybdenum nitride electrodes deposited SPPS. The midrange electrode deposited at 65mm SD on Ti substrate and nitride in ammonia was cycled over 5000 cycles at a voltage sweep rate of 1V sec⁻¹. Every 1000 cycles the electrode was subjected to a slower scant rate of 100mV sec⁻¹ for 10 cycles. Figure 5-25 shows CV plots of the samples at the beginning, after 1000 cycles and after 5000 cycles. The stable, almost rectangular shape is remains indicating that the behaviour is reversible with low resistance, but a reduction in area inside the plot is also indicates a loss in capacitance.



Figure 5-25: High cycle CV plot of nitrided sample deposited on Ti substrate

Although the overall capacitance reduction is 28%, the reduction between the first cycles and 1000 cycles is 22%, emphasizing that most of the reduction accrued in the in the first 1000 cycles. If the capacitance in plotted versus the number cycles a flatting trend is apparent. The reduction flattens in an almost exponential rate to the point where the reduction between 4000 and 5000 cycles is 0.15% as shown in figure 5-26.

The reasons for the initial reduction in capacitance are not fully understood. Possibilities include the elimination of reactive phases in the coating or impurities that may have accumulated during the various stages of the process: deposition, transformation, or preparation of samples for CV testing.



Figure 5-26: Capacitance as a function of cycle number for sample deposited at 65mm SD

5.4 Titanium electrode modification

In order to understand better how different process parameters influence the electrochemical performance of the Mo oxide and nitride coatings, a series of process modifications were investigated. Since no other group has reported the use of SPPS for deposition of these types of coatings, ideas have been borrowed from work involving other deposition methods and applied to our SPPS process. The following section describes how process modifications such as substrate surface treatment, variation in coating thickness, and use of different gases in the oxide to nitride conversion treatment influenced the electrochemical performance of electrodes deposited by SPPS.

5.4.1 Substrate surface modification

There are reports in the literature [54] that in spray pyrolysis deposition, cleaning and nitridation treatment of the Ti surface prior to deposition has reduced the remnant molybdenum oxide fraction after nitridation and increased the capacitance. In order to see if surface modification has an effect on samples deposited by SPPS, three sets of samples were prepared. The first are Ti

substrates polished as described previously, the second are Ti substrates polished and then cleaned by Alcohol (Commercial Alcohols), Acetone ($(CH_3)_2CO$, CALEDON) following by immersion in 0.1M Hydrochloric acid (HCl, J.T.Baker) at 90°C for 10 Minutes in order to remove organics and surface oxides in order to increase surface adhesion. The third set was cleaned in the same way described above , but then also nitrided inside a tube furnace at 700°C for 1Hr in ammonia gas (4.5 Grade, Praxair) flowing at 0.115 mL sec⁻¹. Samples were deposited at 55, 65 and 75mm SD with a 5.3mm RD, using a 150µm diameter liquid injection nozzle.



Figure 5-27: Cyclic voltammetry of (a) Cleaned Ti substrate (b) Cleaned and nitrided Ti substrate

In figure 5-27 CV plots of nitride coatings deposited on the modified Ti substrate surfaces are presented. The rectangular shape of the CV curve is still present, but unlike coatings deposited on polished Ti substrates which showed an approximately linear increase in capacitance with increasing SD, coatings deposited at 55mm SD on polished and cleaned substrates exhibited a lower capacitance then those deposited at 65 and 75mm SD. For coatings deposited on polished, cleaned and nitrided substrates, the capacitance for the coating deposited at 75mm SD is much higher than for coatings deposited at 55mm or 65mm SD. This behavior, shown in figure 5-28, is not well understood. Additional experiments would be required to confirm the behaviour. In general, no significant change in capacitance has been proven, and coatings deposited on polished Ti substrates perform as well or better than coatings deposited on the modified surfaces.



Figure 5-28: Capacitance as a function of standoff distance for different surface modifications

5.4.2 Coating thickness modification

In order to understand the effect that coating thickness has on the electrochemical performance of the electrode, a thinner, 3 layer, set of electrodes was deposited at 55, 65 and 75mm SD with a 150µm liquid injection nozzle on polished Ti substrates and then converted by heat treatment in ammonia gas. According to the thermal history concept developed in previous sections, fewer passes of the torch over the sample would result in a lower substrate temperature and a shorter time of exposure to elevated temperatures. The expectation under such conditions would be that the sample would have a higher fraction of incompletely decomposed phases of the molybdenum precursor and a lower fraction of α -MoO₃ in the coating than in the 5 layer coatings, creating a situation leading to a higher fraction of nitride phases after the ammonia heat treatment. The fraction of nitrided phases was found to be 95%, 97%, and 92% for coatings deposited at 55, 65 and 75mm SD, respectively. The difference in the fraction of nitride phases in coatings deposited at 55mm and 65mm SD is likely not significant, however the fraction of nitride phases in the coating deposited at 75mm SD slightly lower. This is not consistent with the trends seen in the 5 layer coatings, but may be within the range of experimental variability. The electrochemical behaviour of theses coatings shown in the CV curves plotted in figure 5-29 are similar. The coating deposited at the 65mm SD has the largest hysteresis area, indicating the largest capacitance. The calculated capacitance values are 8.5, 13.3, and 8mF cm⁻² for the coatings deposited at standoff distances of 55, 65 and 75mm, which correlates with the nitride fraction in the coatings, although the differences are small. Overall the capacitance values are lower than found for the 5 layer samples. This could be due to a lower total surface area in the 3 layer coatings simply due to less material being present on the substrate.



Figure 5-29: Cyclic voltammetry of 3 layer deposition

5.4.3 Converting gas modification

The gas used in the oxide to nitride conversion process was changed from NH_3 to N_2 in response to results reported by another group in the Materials Science and Engineering Department [64]. An additional set of samples was deposited with the same 5 layer coating conditions that were employed before. The same thermal profile was used as previously for the oxide to nitride transformation process, however NH_3 was replaced by N_2 . The low resolution SEM image in figure 5-30 reveals a completely different microstructure to the one obtained using NH_3 in the process. The microstructure consisted of small, angular particles scattered over the surface of the substrate. Higher magnification images of this structure reveal faceted, roughly equiaxed particles 1-3µm across.



Figure 5-30: Low resolution SEM image of sample deposited at 75mm SD and heat treated in N_2



Figure 5-31: high resolution SEM micrographs of samples heat treated by N₂

The results of the XRD analysis, figure 5-32, of the coating heat treated in N_2 were also quite different than obtained when NH_3 was used. Due to the less reducing nature of N_2 gas, 75% of the coating deposited at 55mm SD consists of MoO_2 and only 21% of nitride phases. EDS analysis of the coating supported the finding from the XRD, with significantly higher O content than found for coatings heat treated in NH_3 , figure 5-33.



Figure 5-32: XRD pattern of sample deposited at 55mm SD and heat treated by N₂

In figure 3-34 the CV curves for samples deposited at 55 and 75mm SD are shown. The shape of the curves is not as rectangular as was found for samples heat treated in ammonia. The calculated capacitance for these samples is 4.4 and 3.7 mF cm⁻² for coatings deposited at 55 and 75mm SD, respectively. The shape of the curves is likely due to the high fraction of oxide phases present in the coating. The lower capacitance relative to coatings heat treated in NH₃ may be attributed to the larger particle size and lower surface area of these coatings.



Figure 5-33: EDS analysis of sample transformed in N₂



Figure 5-34: Cyclic voltammetry plot of samples transformed by N₂

Chapter 6: Conclusions and Future Work

The objective of this thesis was to explore and demonstrate the concept of high surface area molybdenum oxide/nitride electrodes for electrochemical capacitor application deposited by SPPS. Several critical deposition parameters, substrate material and oxide to nitride transformation cycles were investigated in order to determine the overall process performance and compatibility for industrial application.

- 1. Molybdenum oxide was successfully deposited by SPPS on stainless steel substrates revealing a high surface area, sub-micron grain size and a variety of α -MoO₃ fractions depending on the substrate to torch distance (SD).
- Standoff distance, raster distance and solution injection rate have a great effect on substrate temperature which affects the decomposition of the precipitates and intermediate products, creating changes in the microstructure and phase composition of the coating.
- 3. The variation in the phase composition and microstructure directly affect the electrochemical performance, closely linking the process control of the deposition to the electrode performance.
- Oxide coatings on stainless steel were found to have some apparent capacitive behaviour generated from unstable electrochemical activity on the electrode surface. The coatings completely disintegrated after only 10 CV cycles.
- 5. Transformation of the oxide coating on stainless steel into nitride by a multiple stage heat treatment with flowing ammonia gas resulted in the formation of cracks in the coating and exposed the substrate, resulting in very high electrode resistance and no charge accumulation.
- 6. Changing the substrate material to titanium for molybdenum oxide electrodes increased the coating adhesion substantially, stabilised the electrode and resulted in high capacitance, but due to the electrochemical nature of Mo oxide the CV plot is not rectangular and some resistance is still present in the coating.

- Nitriding the molybdenum oxide coating on titanium created a very stable, low resistance, rectangular shaped CV curve, extremely desirable for electrochemical applications.
- 8. Unlike oxide coatings for which shorter standoff distances and higher substrate temperatures have resulted in better electrochemical performance due to a larger fraction of α -MoO₃, nitride coating have shown higher capacitance for longer standoff distances due to more extensive transformation from oxide phases into nitride phases.
- 9. A schematic illustration of the electrode dependence on thermal history and deposition parameters is shown in figure 6-1, were the thermal history concept is presented for the oxide and nitride coatings.
- 10. High cycle testing of electrodes deposited on titanium by SPPS at a standoff distance of showed good performance during the 5000 cycles, with a total of 28% reduction in capacitance and a final capacitance of 30mF cm⁻² over the 5000 cycles. The behaviour stabilized with increased cycles: the capacitance decreased by 22% after the first 1000 cycles, but by only 0.15% for cycles 4000 to 5000.
- 11. Process modifications such as changes in substrate preparation, changes in deposition thickness and gas used for conversion into nitride did not improve the performance of the electrode, but rather decreased the capacitive performance.
- 12. SPPS was shown to be an effective, simple, process for the deposition of molybdenum nitride electrodes. The potential for scale up to industrial applications is favored by deposition under atmospheric conditions and the ability to deposit on sheet substrates in a reel to reel configuration.



Figure 6-1: Schematic flow chart for better capacitance performance for oxide and nitride coatings

6.1 Future work

- The injection system was a very simplistic design and was the weak link in deposition process, clogging and reducing the level of control over sample deposition, as many commercially available injection systems are offering high level of control and automated stirring and temperature control of the solution.
- 2. The injection process and torch configuration allowed only radial injection intensifies the over and under spray phenomena reducing the control over the process, but torch manufacturer have introduced axial injected torches that are available in the CACT.
- 3. GD-OES analysis of electrodes deposited on stainless steel in order to oxygen and nitrogen distribution in the coating, understanding better the thermal history concept and the affect and the adhesion between the coating and substrate.
- SEM, EDS and XPS of coating cross sections to investigate the bonding and phase formation at the coating-substrate interface and better understanding the adhesion properties.

- 5. Better calculation of capacitance as a function of surface area based on BET analyses for comparison with literature results.
- 6. Additional experimentation is needed in order to fine tune the process parameters and electrochemical performance.
- High cycling was conducted for mid-range molybdenum nitride electrode, other high cycling experiments are needed in order to determine what the optimum process is for deposition, in addition, higher cycling such as 10K and 50K is required to determine long term stability.

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