OXIDE COMPOSITE MATERIALS

FOR SUPERCAPACITORS

COLLOIDAL FABRICATION OF ADVANCED OXIDE COMPOSITE MATERIALS

FOR SUPERCAPACITORS

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A Thesis Submitted to the School of Graduate Studies in Partial Fulfilment of the Requirements for the Degree Master of Applied Science

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LAY ABSTRACT

The modern world has an insatiable appetite for energy and must have access to it for stationary and mobile applications. To meet this demand, it is of paramount importance to develop new, high performance energy storage technologies. The energy requirements for different applications, however, necessitate storage devices that have suitable properties. The energy stored in a large pool of hot water is not in a suitable form to power a cellphone. The key goal of this work was to further develop one particular energy storage technology, called electrochemical supercapacitors. Novel processing techniques were developed and new materials investigated with the aim of producing supercapacitor electrodes that would exceed the performance of what is already available today. The materials that were produced exhibited very high performance and offered new insight and direction for further research in this exciting field.

ABSTRACT

With a unique blend of power and energy densities, as well as long cycling lives, electrochemical supercapacitors are finding greater application in energy storage solutions. Among candidate materials for supercapacitors, MnO₂ has garnered a great deal of attention. However, its low intrinsic electrical conductivity has proven to be a serious hindrance on performance when used in supercapacitor electrodes. Efficient use of conductive additives is a demonstrated, effective method to combat this problem, however there is still a great need for improvement. Two new colloidal processing techniques have been developed to mix chemically synthesized MnO₂ and conductive multi-walled carbon nanotubes (MWCNT). The first strategy involved the linking of MnO₂ and MWCNT through the formation of a Schiff base. 3,4dihydroxybenzaldehyde (DB) was used to modify MnO₂, while MWCNT were dispersed with the dye New Fuchsin (NF). These compounds were selected due to the presence of molecular features previously identified as conducive to strong adsorption and good colloidal dispersion, as well as the necessary functional groups required to form a Schiff base. The second involved the use of liquid-liquid extraction, primarily in an attempt to prevent post synthesis MnO₂ particle agglomeration. Lauryl gallate (LG) was used as an extracting and dispersing agent for MnO₂ synthesized via the reaction between aqueous potassium permanganate (KMnO₄) and 1-butanol. LG facilitated the co-dispersion and mixing of both MnO₂ and MWCNT in the 1-butanol phase. V_2O_3 was also investigated as a replacement for MnO₂, as its high intrinsic electrical conductivity gives it a potential advantage over MnO₂. In each of these three projects, electrodes were produced with exceptionally high areal normalized capacitances at high active mass loadings. The MnO₂-MWCNT composites were used to fabricate full asymmetric supercapacitor devices that were able to deliver a useable amount of energy.

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TABLE OF CONTENTS

LAY A	BSTRACT	iii
ABSTR	RACT	iv
ACKN	OWLEDGEMENTS	v
TABLE	E OF FIGURES	ix
TABLE	E OF TABLES	xvi
TABLE	E OF ABBREVIATIONS AND SYMBOLS	- xvii
DECLA	ARATION OF ACADEMIC ACHIEVEMENT	xxi
Chapter	r 1: Introduction	1
Chapter	r 2: Literature Review	6
2.1	Capacitor Fundamentals	6
2.2	Electrical Double Layer Capacitors (EDLC) and the structure of the double layer	8
2.3	Pseudocapacitance	13
2.4	Materials that exhibit pseudocapacitance – Focus on MnO ₂	20
2.5	MnO ₂ – Historical vs New application in supercapacitors	21
2.6	MnO ₂ – Charging mechanism, structure and morphology effects	21
2.7	MnO ₂ – Performance and use in composite electrode materials	28
2.8	Carbon nanotubes – Conductive additive of choice for MnO ₂ supercapacitors	31
2.9	MnO ₂ supercapacitors – The problem of mass loading	31
2.10	Adsorption and dispersion of carbon nanotubes and MnO ₂	33
2.11	Supercapacitor electrolytes	38
2.12	Aqueous asymmetric supercapacitors	41
Chapter	r 3: Problem Statements and Objectives	44
Chapter	r 4: Experimental Procedure	45
4.1	Table of chemicals and materials	45
4.2	Synthesis of MnO ₂ for post drying mixing procedures	47
4.3	Fabrication of MnO ₂ -MWCNT composites using a Schiff base reaction	48
4.4	Fabrication of MnO ₂ -MWCNT composite using a Liquid-Liquid Extraction proced 48	lure.
4.5	V ₂ O ₃ -MWCNT composite synthesis and activation	49
4.6	Activated carbon- carbon black	50
4.7	Materials characterization	51
4.7	Crystallinity	51
4.7	V.2 Morphology	51

4.7	7.2 Composition	52
4.8	Electrode fabrication and characterization	52
4.8	8.1 Cyclic voltammetry	54
4.8	8.2 Electrochemical impedance spectroscopy	
4.8	3.3 Galvanostatic Cycling	60
Chapte	r 5: Colloidal route for MnO ₂ -MWCNT composite through the formation of a S	Schiff base
		62
5.1	Background and details of approach	62
5.2	Characterization of Schiff Base MnO ₂ -MWCNT composite	66
5.3	Electrochemical performance of Schiff base MnO2-MWCNT composite	69
5.4	Conclusion	75
Chapte	r 6: Use of liquid-liquid extraction for the colloidal assembly of MnO ₂ -MWCN	T
compos	sites	77
6.1	Background and details of approach	77
6.2	Characterization of Liquid-Liquid Extraction MnO ₂ -MWCNT composite	81
6.3	Liquid-Liquid Extraction MnO ₂ -MWCNT electrode characterization	85
6.4	Conclusion	92
Chapte	r 7: Use of V_2O_3 as the electrochemically active material for supercapacitor ele	ctrodes -94
7.1	Background and details of approach	94
7.2	Electrochemical activation and operational conditions of V ₂ O ₃ -MWCNT electrochemical	ctrodes96
7.3	Proposed explanation for the observed electrochemical activation	101
7.4 MW	Evidence of the proposed explanation for the electrochemical activation of V CNT electrodes	₂ O ₃ 103
7.6	Results of electrochemical testing	110
7.7	Conclusion	116
Chapte	r 8: Final Conclusions and Future Work	118
Append	dix A	119
Elect	trode Error Analysis	119
Append	dix B	124
AC-0	CB performance	124
Referen	- nces	125

TABLE OF FIGURES

Figure 1.1: Ragone plot showing the variation of power and energy densities of various energy
storage media. Source: [10]. 12
Figure 2.1-1: Schematic of simple parallel plate capacitor charged by an external source. 2 6
Figure 2.2-1: Schematic of potential across a double layer capacitor in open circuit condition and
during discharge. Source: [23]. 39
Figure 2.2-2: Schematic showing the Helmholtz, Gouy-Chapman and Stern models of the
electrical double layer. Source: [23]. 410
Figure 2.2-3: Equivalent circuit for electrical double layer. 510
Figure 2.2-4: Grahame model of the electrical double layer considering the differing distance of
closest approach for anions and cations. Source: [23]. 611
Figure 2.3-1: Schematic showing the pseudocapacitance curves resulting from adsorption
isotherms with and without interaction effects. Source [13]. 717
Figure 2.3-2: Plot of pseudocapacitance (y-axis) vs potential (x-axis) for various scan rates
normalized to the rate constant s/k. Source: [30]. 819
Figure 2.6-1: Schematic cyclic voltammogram for MnO ₂ showing the spread of redox reactions
responsible for the pseudocapacitive behaviour. Source: [41]. 923
Figure 2.6-2: MnO ₂ crystal structures: Each structure is assembled from MnO ₆ octahedra. a –
pyrolusite β -MnO ₂ , b - birnessite δ -MnO ₂ , c - hollandite α -MnO ₂ , d - ramsdellite γ -MnO ₂ .
Source: [45]. 1025
Figure 2.6-3: Schematic showing the charging/discharging mechanism for birnessite MnO ₂ .
Source: [48]. 1127

Figure 2.7-1: Schematic of proton/electron hopping in MnO ₂ in contact with a KOH electrolyte.	
Source: [49]. 1229	9
Figure 2.10-1: Schematic showing the proposed interaction mechanisms for catechol compounds	\$
(left), salicylic compounds (right, top) and chromotropic acid compounds (right, bottom) with a	
particle surface. Source: [81]. 1335	5
Figure 2.10-2: Chemical structure for A – trans-cinnamic acid, B – p-coumaric acid, C – 2,4-	
dihydroxycinnamic acid, D – caffeic acid. 1436	б
Figure 2.11-1: Illustration of the complimentary voltage windows in an asymmetric device,	
allowing for a larger overall device voltage. Source: [15]. 1542	2
Figure 2.11-2: Linear sweep voltammograms of an acidic, neutral and basic electrolyte on a	
platinum electrode showing the electrochemical stability window of each. Source: [96]. 1643	3
Figure 4.8-1: Photograph of a typical completed electrode. Tick-scale adjacent to electrode is in	
millimeters. 1753	3
Figure 4.8.1-1: Schematic cyclic voltammograms of a supercapacitor electrode. 1855	5
Figure 4.8.2-1: Schematic Nyquist plot showing general features typically displayed by a	
pseudocapacitive electrode. 1957	7
Figure 4.8.3-1: Schematic of galvanostatic curves for a capacitor. 2060	0
Figure 5.1-1: General structure of an imine. R ₂ is restricted from being a hydrogen atom in a	
Schiff base. 2162	2
Figure 5.1-2: Chemical structure of aromatic dispersing agents for MWCNT. A-pyrocatechol	
violet, B-crystal violet, C-New Fuchsin. 2263	3

Figure 5.1-3: Qualitative sedimentation test of carbon nanotubes dispersed with New Fuchsin
after 48 hours. A – 0.1 g L ⁻¹ New Fuchsin in water, B – 1 g L ⁻¹ MWCNT in 0.1 g L ⁻¹ New
Fuchsin in water and C – 1 g L^{-1} MWCNT in water. 2364
Figure 5.1-4: Schiff base MnO ₂ -MWCNT colloidal processing schematic. 2465
Figure 5.2-1: A, C – Mechanically mixed MnO ₂ and MWCNT, B, D – Schiff base MnO ₂ -
MWCNT. MnO ₂ :MWCNT mass ratio is 4:1 for both composites. 2566
Figure 5.2-2: FTIR spectra of: a-MnO ₂ mixed with 3, 4-dihydroxybenzaldehyde and b-Schiff
base MnO ₂ -MWCNT. Source: [115]. 2668
Figure 5.3-1: A - Cyclic voltammograms of Schiff base MnO ₂ -MWCNT composite: a – 5 mV s ⁻
¹ , b – 10 mV s ⁻¹ , c – 20 mV s ⁻¹ , B – Gravimetric and C- Areal normalized capacitance vs scan
rate. 2769
Figure 5.3-2: Impedance data for Schiff base MnO ₂ -MWCNT composite. 2870
Figure 5.3-3: A – capacitance retention versus cycle number and B – 1^{st} , 2500 th and 5000 th cyclic
voltammogram for the Schiff base MnO2-MWCNT composite. Arrow indicates increasing cycle
number 2971
Figure 5.3-4: Performance composite for Schiff base MnO ₂ -MWCNT/AC-CB asymmetric
device, A- cyclic voltammograms: $a - 5 \text{ mV s}^{-1}$, $b - 10 \text{ mV s}^{-1}$, $c - 20 \text{ mV s}^{-1}$, $B - capacitance$
calculated from CVs vs scan rate, C – galvanostatic curves: a – 30 mA, b – 10 mA, c – 5 mA, D
- capacitance calculated from galvanostatic curves vs applied current. E - Energy calculated
from galvanostatic curves vs applied current. 3073
Figure 5.3-5: Second performance composite for Schiff base MnO ₂ -MWCNT/AC-CB
asymmetric device, A – device Nyquist plot, B – cycling stability. 3174
Figure 6.1-1: Schematic of primary particle agglomeration due to drying. 3278

Figure 6.1-2: Schematic of the liquid-liquid extraction and colloidal processing of MnO ₂ -
MWCNT composites. 3378
Figure 6.1-3: Images showing the extraction of MnO ₂ particles from the water rich to the 1-
butanol phase. Photographs from Source: [126]. 3480
Figure 6.2-1: A-SEM image of MnO ₂ , B-TEM image of MnO ₂ , inset is the selected area electron
diffraction pattern, C-High resolution TEM image of 1-butanol MnO ₂ . Circled areas were used to
estimate the size of the MnO ₂ nanocrystals, D-XRD of MnO ₂ , chevrons correspond to JCPDS
87-1497. All images from Source: [126]. 3582
Figure 6.2-2: FTIR spectra of: a-pure lauryl gallate and b-MnO ₂ extracted using lauryl gallate. 36
83
Figure 6.2-3: A, B – SEM images of L-L extraction MnO ₂ -MWCNT. Image credit: Patrick
Wojtal. C, D – TEM images of L-L extraction MnO ₂ -MWCNT, Source: [127]. 3784
Figure 6.3-1: Performance composite of liquid-liquid extraction MnO ₂ -MWCNT composite
using KMnO ₄ as the manganese source. A – selected cyclic voltammograms: $a - 5 \text{ mV s}^{-1}$, $b - 10$
mV s ⁻¹ , $c - 20$ mV s ⁻¹ , $B - cycling$ stability, $C - a - 1^{st}$ and $b - 1000^{th}$ cyclic voltammogram of
cycling stability test. 3886
Figure 6.3-2: A - Gravimetric capacitance comparison for different mass loadings on regular
nickel foam current collectors (a - 48.4 mg cm ⁻² , b - 28.0 mg cm ⁻²), B - Areal capacitance
comparison for different mass loadings on regular nickel foam current collectors (a - 28.0 mg
cm ⁻² , b - 48.4 mg cm ⁻²) C, D – Gravimetric: C, and areal: D, capacitance comparison on different
current collectors at the similar mass loadings (a – regular nickel foam, 28.0 mg cm ⁻² , b –
graphene coated nickel foam, 31.6 mg cm ⁻²). 3987

Figure 7.2-3: A – Cyclic voltammogram at a scan rate of 20 mV s⁻¹ after repeated cycling, B – Cyclic voltammograms of V₂O₅ electrode produced by Chen et al. Source: [137]. 45 ------98 Figure 7.2-4: Vanadium-water Pourbaix diagram. y-axis potential is vs the standard hydrogen electrode Source: [138]. 46 ------99 Figure 7.2-5: Cyclic voltammograms showing the activation procedure. A – Scan rate: 50 mV s⁻¹, B – Scan rate: 100 mV s⁻¹, C – Scan rate 5 mV s⁻¹, D – Scan rate: 2 mV s⁻¹. Arrows indicate increasing cycle number. 47 ------ 101

Figure 7.2-6: Burke-O'Sullivan model for oxide formed by potential cycling of a metal electrode
in an aqueous environment. Source: [140]. 48 102
Figure 7.2-7: Schematic showing the formation of an amorphous hydrous oxide layer on the
surface of a V ₂ O ₃ particle due to potential cycling. 49 103
Figure 7.2-: Photograph showing the precipitate formed after the attempted activation of a V_2O_3
electrode in 1 M NaCl at pH=3.6. 50 105
Figure 7.2-8: XPS results for: A-pure V ₂ O ₃ , B-V ₂ O ₃ -MWCNT before activation and C- V ₂ O ₃ -
MWCNT after activation. 51 106
Figure 7.2-9: SEM images for: A, B-pure V ₂ O ₃ , C, D-V ₂ O ₃ -MWCNT before activation and E, F-
V ₂ O ₃ -MWCNT after activation. Arrow indicates a particle with noticeable surface texture. 52108
Figure 7.2-10: XRD results for: A-pure V ₂ O ₃ , B-V ₂ O ₃ -MWCNT before activation and C- V ₂ O ₃ -
MWCNT after activation. 53 109
Figure 7.6-1: Performance composite for V ₂ O ₃ -MWCNT in 0.5 M Na ₂ SO ₄ electrolyte at pH=3.6.
A – selected cyclic voltammograms: $a - 5 \text{ mV s}^{-1}$, $b - 10 \text{ mV s}^{-1}$, $c - 20 \text{ mV s}^{-1}$, B – cycling
stability, C – gravimetric and D – areal capacitance vs scan rate. Mass loading: 29.1 mg cm ⁻² . 54
111
Figure 7.6-2: EIS performance composite for V ₂ O ₃ -MWCNT in 0.5 M Na ₂ SO ₄ electrolyte at
pH=3.6. A – Nyquist plot with low real resistance inset, B – Real capacitance vs frequency, C –
Imaginary capacitance vs frequency. 55 112
Figure 7.6-3: Performance composite for V ₂ O ₃ -MWCNT in 1 M NaNO ₃ electrolyte at pH=3.6. A
- selected cyclic voltammograms: a - 5 mV s ⁻¹ , b - 10 mV s ⁻¹ , c - 20 mV s ⁻¹ , B - cycling
stability, C – gravimetric and D – areal capacitance vs scan rate. Mass loading: 33.6 mg cm ⁻² . 56
114

Figure 7.6-4: Figure 7.6-2: EIS performance composite for V ₂ O ₃ -MWCNT in 1 M NaNO ₃
electrolyte at pH=3.6. A – Nyquist plot with low real resistance inset, B – Real capacitance vs
frequency, C – Imaginary capacitance vs frequency. 57 115
Figure A-1: Schematic showing the effect the current measurement error has on the integrated
area of a hypothetical cyclic voltammogram. 58 121
Figure B-1: Performance of AC-CB negative electrode material. A – selected cyclic
voltammograms, arrow indicates increasing scan rate, B – gravimetric capacitance vs scan rate.
59 124

TABLE OF TABLES

Table 4.1-1: List of chemicals used over the course of the projects described in the results
section, their uses and suppliers. 146
Table 4.5-1: Activation procedure used for all V_2O_3 -MWCNT for which capacitance data was
acquired. 250
Table A-1: Various cases accounting for the error in the areal and gravimetric capacitance due to
electrode area measurement and overcoating with epoxy. 3 119
Table A-2: Adjusted areal and gravimetric capacitance due to error in electrode area
measurement and overcoating with epoxy. 4 120
Table A-3: Final minimum and maximum areal and gravimetric capacitances used to determine
the error bars of electrodes measured in a three-electrode configuration. 5 122
Table A-4: Tabulated error in capacitance calculation due to linear fitting of discharge curve for
the Schiff base MnO ₂ -MWCNT/AC-CB device presented in Chapter 5. 6 123
Table A-5: Tabulated error in capacitance calculation due to linear fitting of discharge curve for
the liquid-liquid extraction MnO ₂ -MWCNT/AC-CB device presented in Chapter 6. 7 123

TABLE OF ABBREVIATIONS AND SYMBOLS

[ox]	Concentration of oxidized species
[red]	Concentration of reduced species
mA, A (unit)	Milliamp, Amp
mL (unit)	milliliter
mV, V (unit)	Millivolt, Volt
μF, F (unit)	Microfarad, Farad
μg, mg, g (unit)	Microgram, milligram, gram
nm, µm, cm, m (unit)	nanometer, micrometer, centimeter, meter
C (unit)	Coulomb
J (unit)	Joule
K (unit)	Kelvin
s (unit)	Second
Ω (unit)	ohm
A	Electrode area
AC	Activated carbon
BET	Brunauer-Emmett-Teller
C	Capacitance
С'	Real component of capacitance calculated
	from EIS data
C"	Imaginary component of capacitance
	calculated from EIS data
C+ve/-ve	Positive/negative electrode capacitance for
	asymmetric device
C+ve/-ve,grav	Gravimetric capacitance of active material for
	positive/negative electrode of asymmetric
	device
CA	Caffeic acid
CB	Carbon black

C _{Diffuse}	Capacitance associated with diffuse section of
	electrical double layer
C _{double}	Capacitance associated with total electrical
	double layer
C _{Helmholtz}	Capacitance associated with compact
	Helmholtz plane of electrical double layer
C _{Pb2+}	Concentration of Pb ²⁺
C _{pseudo}	Capacitance associated with pseudocapacitive
	faradaic charge transfer
CV	Cyclic voltammetry or cyclic voltammogram
d	Separation distance
DB	3,4-dihydroxybenzaldehyde
DCA	2,4-dihydroxycinnamic acid
DI	Deionized
E	Electrode potential
e	Electron
E°	Standard electrode potential
E _{cap}	Energy stored in capacitor
EDLC	Electrical double layer capacitor
EIS	Electrochemical Impedance Spectroscopy
F	Faradays constant
FTIR	Fourier transform infrared spectroscopy
g	Constant characterizing the lateral interaction
	between adjacent lead atoms during the
	underpotential deposition of lead on gold
ī, ī	Current associated with forward and reverse
	reaction of a general redox reaction
Ι	Current
I _{max power}	Current at capacitor maximum power
IR drop	Voltage drop due to internal resistance of
	capacitor

Κ	Proportionality constant
k1 , k-1	Constants associated with forward and reverse
	reaction of a general redox reaction
LG	Lauryl gallate
L-L extraction	Liquid-Liquid extraction
m+ve/-ve	Mass of active material for positive/negative
	electrode of asymmetric device
MWCNT	Multi-wall carbon nanotube
NF	New Fuchsin
Ox	Oxidized chemical species
PCA	<i>p</i> -coumaric acid
PEDOT	Poly(3,4-ethylenedixoythiophene)
PEDOT-PSS	Poly(3,4-ethylenedixoythiophene-polystyrene
	sulfonate)
P _{max}	Maximum power of capacitor
PVB	Poly(vinyl butyral-co-vinyl alcohol-co-vinyl
	acetate), Average $M_w = 50000-80000$
PVDF	Poly(vinylidene fluoride)
Q	Charge
QCM	Quartz Crystal Microbalance
R	Ideal gas constant
Re	Reduced chemical species
R _{internal}	Internal resistance of capacitor
SCE	Standard calomel electrode
SEM	Scanning electron microscopy
Т	Temperature
TCA	Trans-cinnamic acid
TEM	Transmission electron microscopy
V	Voltage
V _{max}	Maximum capacitor voltage
V _{max power}	Voltage at capacitor maximum power

t	time
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction
Z	Charge associated with general redox reaction
Ζ'	Real component of impedance measured
	using EIS
Z"	Imaginary component of impedance measured
	using EIS
β	Bronsted factor
ΔΕ	Change in electrode potential
ΔG	Change in Gibbs free energy
ε ₀	Permittivity of free space
ε _r	Dielectric permittivity
θ_{Pb2+}	Fractional surface coverage of lead during
	underpotential deposition of lead on gold
λ	General property related to redox conversion
	of an electroactive species
φ	Phase shift of measured sinusoidal signal
	during EIS
ω	Frequency of sinusoidal signal used in EIS

DECLARATION OF ACADEMIC ACHIEVEMENT

This dissertation was used to fulfill the requirements of the degree: Master's of Applied Science. The major research project ran from May 2015 to August 2017. The content of this dissertation was covered in three papers, published in peer-reviewed journals, with a fourth still to be published:

- C. Wallar, D. Luo, R. Poon, and I. Zhitomirsky, "Manganese dioxide carbon nanotube composite electrodes with high active mass loading for electrochemical supercapacitors," *J. Mater. Sci.*, vol. 52, no. 7, pp. 3687–3696, 2017.
- C. Wallar, T. Zhang, K. Shi, and I. Zhitomirsky, "Synthesis of metal and metal oxide nanoparticles, liquid – liquid extraction and application in supercapacitors," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 500, pp. 195–202, 2016.
- D. Luo^γ, C. J. Wallar^γ, K. Shi, and I. Zhitomirsky, (γ: The authors contributed equally to this work.) "Enhanced capacitive performance of MnO2- multiwalled carbon nanotube electrodes, prepared using lauryl gallate dispersant," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 509, pp. 504–511, 2016.
- C. J. Wallar, R. Poon, I. Zhitomirsky, "High areal capacitance of V₂O₃-carbon nanotube electrodes." *Unpublished*.

I also contributed to an additional five papers, published in peer-reviewed journals, that are not covered in this dissertation.

 C. J. Wallar, T. Zhang, D. Luo, and I. Zhitomirsky, "Electrophoretic deposition of functional organic molecules and composite films," *Mater. Manuf. Process.*, vol. 32, no. 4, pp. 389–393, 2017.

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- A. M. Abdalla, R. P. Sahu, C. J. Wallar, R. Chen, I. Zhitomirsky, and I. K. Puri, "Nickel oxide nanotube synthesis using multiwalled carbon nanotubes as sacrificial templates for supercapacitor application," *Nanotechnology*, vol. 28, no. 7, p. 75603, 2017.
- J. Li, P. Wojtal, C. J. Wallar and I. Zhitomirsky "Electrochemical deposition of polypyrrole-carbon nanotube films using steroid dispersants," *Materials and Manufacturing Processes*, (just-accepted), 2017

Chapter 1: Introduction

As Earth's population continues to grow and develop there is an imminent need for low impact, renewable sources of energy and efficient means with which to store it. However, the plethora of applications demanding stored electrical energy necessitates a range of storage devices with use specific properties. From the smallest capacitors in integrated circuitry, to the lightweight, high energy density power packs in common consumer electronics and electric vehicles, to proposed grid scale distribution installations, energy storage media can be found at all length scales in the modern world.

Electrochemical supercapacitors are one such class of energy storage media. These devices exhibit the electrical response characteristics of traditional capacitors, however, with significantly greater electrode footprint normalized energy densities. They form a bridge in the power and energy densities achievable in classical solid-state capacitor and battery systems, as shown in the so-called Ragone plot, Figure 1.1, on the next page. This balance of power and energy characteristics, in combination with large cycling lives, make supercapacitors particularly useful for several applications where neither capacitor or battery systems are well suited. These include synergistic application *with* batteries in hybrid electric vehicles [1], specifically during the high-power acceleration stage and in capturing energy generated by regenerative braking, to reduce the intermittency of some renewable energy sources such as wind [2] and solar [3], [4], energy grid power management [5], [6] and even as the power supply for cordless power tools [7]. There are even proposals to integrate supercapacitors into clothing as wearable energy storage [8], [9].



Figure 1.1: Ragone plot showing the variation of power and energy densities of various energy storage media. Source: [10]. 1

The general physical construction of a supercapacitor is as follows: two current collectors in contact with active material, the positive and negative electrodes, are immersed in an electrolyte and separated by an electrically insulating, electrolyte permeable separator. This separator serves to prevent a short circuit between the two electrodes, while still allowing ion migration. This single cell can then be encased in some form of external packaging and stacked in series or parallel with other cells to create supercapacitor modules of varying energy density and operational voltage, depending on the application.

Supercapacitors have been commercially available since the 1970s, but the groundwork for these devices was laid by as early as the 1950s. Conway cites a 1957 General Electric patent as being the beginning of supercapacitor research [11]. Today, many commercially available supercapacitors are of the "electrical double-layer" (EDLC) class, utilizing high surface area M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering materials with organic electrolytes. For instance, Maxwell Technologies supercapacitor products use an acetonitrile electrolyte [12].

As will be discussed in the next section, because of the *electrostatic* nature of the charge storage in EDLCs the total amount of energy that can be accumulated is significantly lower than in a conventional battery which primarily rely on faradaic chemical reactions for this purpose. A second class of supercapacitor, appropriately called "pseudocapacitors" also store charge through faradaic chemical reactions as in a conventional battery. However, the electrical response of a true pseudocapacitor is the same as an *electrostatic* capacitor, but with greater energy densities afforded by the faradaic reactions. The fundamentals of pseudocapacitance will be presented in the literature review. As a brief introduction, pseudocapacitance arises when, for special thermodynamic and kinetic reasons, faradaic reactions at or near the surface governed by the adsorption/desorption and intercalation/deintercalation of electrolyte ions results in the electrode displaying the characteristic electrical response of a capacitor[13]. Many oxide materials, such as RuO₂, V₂O₅ and MnO₂ have been shown to exhibit pseudocapacitance at anodic potentials [14]. RuO₂ in particular has been called the "gold standard" [15] for pseudocapacitance due to its exceptional performance in acidic electrolytes, with capacitances reported to be in excess of 700 F g^{-1} in voltage windows up to 1 V vs the standard calomel electrode (SCE) [16]. Pseudocapacitive materials that operate at more cathodic potentials have been developed, albeit to a lesser extent [17]. VN in particular was initially reported to exhibit pseudocapacitance in an alkaline KOH electrolyte in the voltage window -1.2-0 V vs the HgO/Hg reference electrode [18].

Despite this "gold standard" rating in terms of performance, supercapacitors based on RuO₂ never saw general consumer application. The insurmountable drawback of this material is

3

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering the cost, as ruthenium is a platinum group metal. In addition, a highly acidic electrolyte is required for maximum performance, albeit this would likely not have been as great a hindrance if the cost were more reasonable.

MnO₂ is a possible alternative, as it is an abundant, cheap material, displays large faradaic pseudocapacitance in a relatively wide voltage window and operates in neutral aqueous electrolytes. Unfortunately, there is one serious drawback for this system and that is the low electrical conductivity of the bulk material. As a result, the full potential of MnO₂ can only be realized in very thin films [19], [20] as the low conductivity is partially responsible for limiting the electrochemically active area to a very narrow surface region. The achievable capacitance thus quickly falls off as the material mass loading is increased [21], with the bulk of the added material serving as nothing more than dead weight. It also limits the high-power performance of any electrode using this material, which is unacceptable for virtually all applications that would require supercapacitors. To combat this problem, MnO₂ must be efficiently mixed with conductive additives. If done correctly, this will create a composite material whose performance will scale reasonably to the mass loading levels that will result in useable energy densities. If done incorrectly, the conductive additive will simply be more dead weight. It was pointed out that loading levels of 10 mg cm⁻² are common in commercial supercapacitor electrodes [22] and is thus a reasonable target for electrodes using MnO₂.

The primary goal of this work was to find novel strategies for mixing chemically synthesized MnO₂ with conductive additives, specifically carbon nanotubes, in order to create electrodes with excellent power characteristics at practically useful energy densities. A secondary goal of this work was to investigate new materials that exhibit pseudocapacitance that may offer benefits over MnO₂, specifically higher conductivity. Two new colloidal processing

4

techniques for MnO_2 and carbon nanotubes were developed. These strategies resulted in electrodes with excellent capacitance, rate performance and cycling lives at high active mass loadings. A new material, vanadium sesquioxide (V₂O₃) was investigated as an alternative electrochemically active component to replace MnO₂. High capacitance and unusually long cycling life for a vanadium based material was achieved, again at high active mass loading.

Chapter 2: Literature Review

2.1 Capacitor Fundamentals

A minor review of the fundamentals of conventional capacitors is prudent before beginning a discussion of supercapacitors, as many of the operating equations and general concepts are applicable. A schematic of a planar, dielectric capacitor is shown in Figure 2.1-1 below. This simple device consists of two conductive plates or contacts separated by a dielectric.



Figure 2.1-1: Schematic of simple parallel plate capacitor charged by an external source. 2

A voltage is applied between the plates causing a flow of charge from the positive to the negative plate. Charge continues to flow until the potential difference between the two plates of the capacitor is the same as that of the source used to charge it. The amount of charge stored in this condition is then: M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering

$$Q = C \cdot V \text{ where } C = \varepsilon_r \varepsilon_o \frac{A}{d}$$
(Eq. 2.1-1)

with Q being the charge, V the voltage between the plates and C the capacitance in units of Farads. The capacitance depends on the dielectric permittivity or the medium separating the plates, ε_r , the plate area, A and the separation distance between the plates, d. The state of charge in the capacitor is thus a linear function of voltage, assuming that the capacitance does not depend on the state of charge. The total energy stored in a capacitor can be calculated as:

$$E_{Cap} = \int_{0}^{V_{max}} V dQ \text{ with } Q = C \cdot V, \therefore E_{Cap} = C \int_{0}^{V_{max}} V dV = \frac{1}{2} C V_{max}^{2}$$
(Eq. 2.1-2)

From the above equation, there are clearly two ways to increase the energy stored in the capacitor: increasing the capacitance C or increasing the voltage V. The maximum power of the capacitor is obtained by considering the voltage drop across the capacitors own internal resistance:

$$V = V_{max} - IR_{internal}$$
, $P = I \cdot V = IV_{max} - I^2R_{internal}$

$$P_{max} at \left. \frac{dP}{dI} \right|_{I_{max\,power}} = 0 = V_{max} - 2I_{max\,power}R_{internal}, I_{max\,power} = \frac{V_{max}}{2R_{internal}}$$

$$V_{\max power} = V_{max} - I_{\max power} R_{internal} = V_{max} - \frac{V_{max}}{2} = \frac{V_{max}}{2}$$

$$P_{max} = I_{\max power} V_{\max power} = \frac{V_{max}^2}{4R_{internal}}$$
(Eq. 2.1-3)

This equation indicates that the maximum power deliverable by the capacitor can be increased by increasing the operating voltage, as with the energy density, and by minimizing the internal resistance of the capacitor.

2.2 Electrical Double Layer Capacitors (EDLC) and the structure of the double layer

In this section, EDLCs will be described in terms of aqueous solutions as the conceptual framework is simpler to describe in this context, even though commercial EDLCs almost universally use non-aqueous electrolytes. Figure 2.2-1 below is adapted from Figure 6.1 in the seminal textbook by Conway [23]. This diagram is a "zoomed-out" view of an EDLC. In the simplest terms, these devices consist of a positive and negative electrode as in a conventional capacitor, however the charge at both electrodes is balanced by ions of opposite charge from the electrolyte existing in the so-called electrical double layer. It is important to note that in the full device there exist two of these double layers at the positive and negative electrodes balanced by ions of opposite charge [23].

The positive and negative electrodes are partitioned by an electrically insulating separator that is permeable to the electrolyte. This separator serves to prevent an internal short between the two electrodes while still allowing ions in solution to flow in response to an applied voltage, as was mentioned in the introduction. The total potential of the charged device is dropped over both the positive and negative electrode double layers as well as through IR losses as shown in Figure 2.2-1 [23]. It should also be pointed out that in the system described all charge stored is purely *electrostatic*, there is no faradaic current transfer across the double layer. It is important to make this distinction since this is not the case for supercapacitors based on *pseudocapacitance* which will be described in Section 2.3.



Figure 2.2-1: Schematic of potential across a double layer capacitor in open circuit condition and during discharge. Source: [23]. 3

The treatment of the electrical double layer of a charged electrode immersed in an electrolyte is incredibly complex and has undergone several iterations, a schematic of which is shown in Figure 2.2-2 below, adapted from Figure 6.3 of Conway [23]. The left most schematic of Figure 2.2-2 shows the so-called Helmholtz model, which attempts to describe the electrical double layer as a compact sheet of electrolyte ions at the charged electrode surface. The middle schematic shows the Gouy-Chapman model, which treats the electrolyte ions as point charges subject to not only the influence of the electric field of the charged electrode, but also thermal fluctuations according to Boltzmann statistics [23]. The right schematic, and the most accurate of the three, is the Stern model, which can be thought of as a combination of the prior two models. In this treatment, Stern described the compact layer in terms of the finite sizes of hydrated ions in the electrolyte obeying a Langmuir adsorption isotherm and the diffuse region beyond the compact layer according to the Gouy-Chapman model [23].

9

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering



Figure 2.2-2: Schematic showing the Helmholtz, Gouy-Chapman and Stern models of the electrical double layer. Source: [23]. 4

The total capacitance of the double layer could then be thought of as a series combination of the capacitance of the compact and diffuse layers as shown in Figure 2.2-3 below.



Figure 2.2-3: Equivalent circuit for electrical double layer. 5

Grahame further refined the Stern model by considering the distance of closest approach for anions and cations. Because cations tend to have a stronger affinity for their solvation shells, they do not get as physically close to the electrode interface compared to anions [23]. This differing distance of closest approach separates the inner and outer Helmholtz layer in Grahame's model as shown in Figure 2.2-4 below, adapted from Figure 6.6 of Conway [23]. The practical



Figure 2.2-4: Grahame model of the electrical double layer considering the differing distance of closest approach for anions and cations. Source: [23]. 6

consequence of this is that the double layer capacitance tends to be greater under positive polarization due to the smaller distance separating the anion charge from the electrode interface compared to cations under negative polarization [23] (recall from Eq. 2.1-1 that the capacitance scales inversely with the separation distance of the charge). The situation becomes even more complex when consideration is made for the structure and polarization of the solvent molecules as well as the penetration, into the electrolyte, of the wavefunction of the electrons accumulated at the electrode surface [23].

Because capacitors in series add in reciprocal [i.e. for the circuit in Figure 2.2-3: $1/C_{double}$ $_{layer} = (1/C_{Helmholtz}) + (1/C_{Diffuse})$] the total double layer capacitance is governed by the smaller of the two capacitances [23]. The capacitance of the diffuse double layer only governs the overall double layer capacitance in dilute electrolytes and in a very limited window around the point of M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering zero charge for the electrode [23]. In commercial EDLCs, very high electrolyte concentrations are used to minimize internal resistance and large voltages are used to maximize energy and power density [23] as per Eq. 2.1-2, 3. As such, it is the Helmholtz layer which governs the double layer capacitance from a practical device standpoint and interfacial capacitances on the order of 15-50 μ F cm⁻² are easily achievable in aqueous electrolytes [11]. Commercial double layer capacitors typically use high surface area carbon materials that can display specific surface areas up to 1000-2000 m² g⁻¹. Using the figure of 20 μ F cm⁻², this would imply a gravimetric capacitance on the order of 200-400 F g⁻¹ which is only a small overestimation when compared to literature values for these materials [24], [25]. If a current collector contained 10 mg cm⁻² of such a material (which as will be seen later in the results section is easy to obtain using nickel foam current collectors) then a footprint normalized capacitance of 2-4 F cm⁻² should be achievable. This is an astounding improvement compared to the nano to micro farad capacitances of conventional solid-state and electrolytic capacitors of the same electrode footprint size.

For completeness, it should be noted that the above simple calculation and models ignore several other factors and makes some implicit assumptions when extended to real device systems, not the least of which is that the calculated gravimetric capacitance would scale with the mass loading on a current collector. In addition, it is assumed that these double layer models, which were developed for a planar surface, extend to the restricted pore of a high surface area carbon material. As it turns out, the spatial extent of the diffuse region of the double layer scales inversely with electrolyte concentration [23]. Because high electrolyte concentrations are required to minimize cell resistance there is little to no overlap of the double layer even within a confined pore on the order of 10s of nanometers in diameter [23]. Thus, the effects of an overlapping double layer from opposite sides of a confined pore are not a practical device issue.

12

2.3 Pseudocapacitance

In conventional solid-state capacitors and ideal EDLCs the charge is stored purely electrostatically as was mentioned above. In classical battery systems such as zinc-carbon, alkaline or even the familiar lead-acid battery, energy is extracted by the bulk conversion of distinct phases through a set of corresponding redox reactions. It is reasonable and often possible to determine a Gibbs free energy change for such reactions and thus a unique cell voltage corresponding to:

$$\Delta G = -Q\Delta E \tag{Eq. 2.3-1}$$

with ΔG being the change in Gibbs free energy, Q the charge transferred and ΔE the potential for some reaction:

$$Ox + e^{-} = Re$$
 (Eq. 2.3-2)

Pseudocapacitance arises when electrode potential obeys a logarithmic relation to the extent of redox conversion of an electroactive component in the system [13]. This conversion is governed via a series of faradaic reactions typically restricted to a narrow near surface region [13]. In contrast, the electrode potential of a battery system is set by the Gibbs free energy change associated with the redox conversion between a series of distinct bulk phases, as was mentioned previously. Thus in battery systems, any dependence of the electrode potential on the extent of conversion of the electroactive material is not thermodynamically intrinsic and arises for secondary reasons such as changing inter-particle resistance between the oxidized and reduced species during discharge [13]. It is important to note that, in the case of pseudocapacitance, the redox reactions do not result in a phase change of the active material whereas for a classical battery this is almost always the case. For some property λ , related to the redox conversion of an
M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering electroactive species, one can write the aforementioned logarithmic dependence, expressed in exponential form, as:

$$\frac{\lambda}{1-\lambda} = Kexp(\frac{VF}{RT})$$
(Eq. 2.3-3)

with K being a constant, V the electrode potential, F is Faradays constant, R the ideal gas constant and T is the temperature in Kelvin. Taking the derivative of this equation with respect to electrode potential:

$$\frac{d\lambda}{dV} = \frac{F}{RT} \frac{Kexp(VF/RT)}{\left(1 + Kexp(VF/RT)\right)^2} [=] \frac{C/mol}{(J/mol * K)K} [=] \frac{C}{J}$$
(Eq. 2.3-4)

Noting the units of this expression, Coulomb/Joule, a capacitance can be defined by multiplying by the charge Q associated with the redox conversion governed by the quantity λ :

$$C_{pseudo} = Q \frac{d\lambda}{dV} [=] C \frac{C}{J} [=] \frac{C^2}{J} [=] F$$
 (Eq. 2.3-5)

It is thus seen that such a logarithmic dependence on redox conversion gives rise to a capacitance. Conway described the underpotential deposition of Pb onto a Au surface from a Pb salt solution using this formalism [13]. In this case, the quantity λ is the fractional surface coverage of the Au surface by Pb and the equation is an electrochemical Langmuir adsorption isotherm which assumes no interactions between the adsorbed species [13]. The reaction equation and the equation describing the fractional surface coverage are given in Eq. 2.3-6, 7:

$$xPb^{2+} + 2xe^{-} + Au = Au \cdot xPb$$
 (Eq. 2.3-6)

And

$$\frac{\theta_{Pb2+}}{1 - \theta_{Pb2+}} = KC_{Pb2+} \exp\left(\frac{VF}{RT}\right)$$
(Eq. 2.3-7)

where θ_{Pb2+} is the fractional surface coverage of the Au surface by Pb, K is a constant and C_{Pb2+} is the concentration of Pb²⁺ in solution. Although illustrative, this system has no practical use for energy storage, but the same reasoning can be extended to materials that do exhibit useful charge storage [13]. Despite not necessarily being readily apparent, the familiar Nernst equation has the appropriate form to define a pseudocapacitance [13]. Using the simple redox reaction Eq. 2.3-2 the Nernst equation can be written:

$$E = E^{\circ} + \frac{RT}{F} \ln\left(\frac{[ox]}{[red]}\right), \ln\left(\frac{[ox]}{[red]}\right) = \frac{\Delta EF}{RT}$$
(Eq. 2.3-8)

Where [ox] and [red] are the concentration/proportion of oxidized and reduced species.

$$let R = \frac{[ox]}{[ox] + [red]} then \frac{[ox]}{[red]} = \frac{R}{1-R} = \exp(\frac{\Delta EF}{RT})$$
(Eq. 2.3-9)

This equation has the same form as was presented at the beginning with the quantity R, representing the extent of oxidation of the electroactive species, replacing λ . The more familiar application of the Nernst equation is to a solution system; however, it applies in general to any system where the degree of oxidation/reduction can be continuously varied with potential [13]. Indeed, through careful XPS measurements of thin films of hydrous MnO₂, Toupin et al. [19] observed a change in the oxidation state of Mn from Mn³⁺ to Mn⁴⁺ when cycled in the potential window 0-0.9 V vs Ag/AgCl in aqueous Na₂SO₄.

For completeness, it should be noted that the above equations and the corresponding expressions for pseudocapacitance imply a very limited operating voltage window (See Figure 2.3-1 below). Conway [23] used the example solution redox couple of ferri-ferrocyanide to illustrate this:

$$[Fe(CN)_6]^{3-} + e^- = [Fe(CN)_6]^{4-}$$
(Eq. 2.3-10)

It follows that in the expression for R on the previous page, [ox] would be the concentration of $Fe(CN)_6^{3-}$ and [red] would be the concentration of $Fe(CN)_6^{4-}$ in solution. The function defining the pseudocapacitance for this redox couple would then have a maximum at the standard redox potential and would decay to 0 at roughly ±0.100 V about the standard redox potential [23]. This voltage window is hardly large enough to store a useful amount of energy and the stark potential dependence of the pseudocapacitance would make the operation of a device based on such a redox couple tricky.

There is an implicit assumption in trying to describe the pseudocapacitance of a solid system such as hydrous RuO₂ and MnO₂ using the Nernst equation and that is the absence of any interaction between the redox centres in the solid structure during charge and discharge. The logarithmic form of the Nernst equation is the same form as the Langmuir adsorption isotherm used to describe the underpotential deposition of Pb onto Au. The Langmuir model has, as one of its key assumptions, that there is no interaction between adsorbed species. When this assumption is discarded, something closer to what is observed experimentally in these systems can be derived [13]. Conway illustrated this concept through modification of the adsorption isotherm describing the underpotential deposition of Pb on Au by incorporating an extra energy term to account for lateral interactions between the adsorbed Pb atoms [13]. Sarangapani, Tilak and Chen made similar arguments [26]. The modified model is as follows:

$$\frac{\theta_{Pb2+}}{1 - \theta_{Pb2+}} = Kexp(-g\theta_{Pb2+}) C_{Pb2+} \exp\left(\frac{VF}{RT}\right)$$
(Eq. 2.3-11)

Where the term $exp(-g\theta_{Pb2+})$ attempts to quantify the lateral interaction between the adsorbed Pb atoms. A positive value for g indicates repulsive interactions. The capacitance is then:

$$C_{pseudo} = \frac{QF}{RT} \frac{\theta_{Pb2+}(1 - \theta_{Pb2+})}{1 + g\theta_{Pb2+}(1 - \theta_{Pb2+})}$$
(Eq. 2.3-12)

The effect of a positive value of g is shown in Figure 2.3-1 below, taken from [13]. It can be seen that the effect of this extra term is to spread out the pseudocapacitance over a much wider potential window compared to the case which ignores these interactions.



Figure 2.3-1: Schematic showing the pseudocapacitance curves resulting from adsorption isotherms with and without interaction effects. Source [13]. 7

As will be seen in the results section of this thesis, as well as extensively in the literature on MnO₂ supercapacitors [27], [28], [14], the electrical feature of electrodes using this material is that of a capacitor with a capacitance that is seemingly potential *independent*. These experimental results correspond more closely to the model which incorporates some form of lateral interaction. The physical interpretation is, however, different than the case of adsorption isotherms for underpotential deposition. Conway and co-workers postualted, at least in the case of hydrous RuO₂, that as the material was oxidized the excess positive charge would cause a shift in the redox potential for further oxidation leading to a spreading of the pseudocapacitance over

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering a larger voltage window [13], [29]. In the context of the interaction parameter introduced, this can be thought of as a repulsive interaction between an oxidized redox site and an adjacent redox centre yet to be oxidized, except spread globally over a complex, porous 3-D structure [13].

A discussion of pseudocapacitance would not be complete without commenting on the kinetic aspects of the processes involved. Yet another implicit assumption in attempting to explain pseudocapacitance using thermodynamic relations (i.e. the Nernst equation or the Langmuir adsorption isotherms) is that the system is in equilibrium. Returning to the example of underpotential deposition of Pb onto Au, the following kinetic equations for the forward and reverse reactions, corresponding to Pb deposition and dissolution can be written [13]:

$$\vec{i} = zFk_1(1 - \theta_{Pb2+})C_{Pb2+}\exp\left(\frac{-\beta VF}{RT}\right)$$
 (Eq. 2.3-13)

$$\bar{\iota} = zFk_{-1}\theta_{Pb2+}\exp(\frac{(1-\beta)VF}{RT})$$
(Eq. 2.3-14)

If the system is in equilibrium then the forward and reverse reactions are equal and the resulting equation is the same as that of the Langmuir isotherm presented earlier [13]. If cyclic voltammetry is performed on such a system, then it can be imagined that at some value of voltage sweep rate this equality and thus the kinetic reversibility of the reaction would break down [13]. This would manifest as an *asymmetry* in the cyclic voltammograms as was plotted by Angerstein-Kozlowska, Klinger and Conway [30] shown in Figure 2.3-2 below.

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering



Figure 2.3-2: Plot of pseudocapacitance (y-axis) vs potential (x-axis) for various scan rates normalized to the rate constant s/k. Source: [30]. 8

It is this analysis that leads to the common jargon in supercapacitor literature of observing *mirror-image* cyclic voltammograms. The kinetic equations and Figure 2.3-2 above were generated for the case of underpotential deposition however, although illustrative, the discussion should again be brought back to the case of materials that are practically useful for supercapacitors such as MnO₂. The question becomes: are reaction kinetics a limiting factor for supercapacitors based on pseudocapacitive materials? The answer is, to some degree. The reversibility/rate of the redox reactions giving rise to the pseudocapacitance in materials such as MnO₂ are an upper limiter on device power capability [13]. However, for current electrode configurations there are other factors that limit performance. Guillemet et al. [31] created a volummetric model to describe the pseudocapacitance of MnO₂-carbon composite electrodes. After fitting to experimental cyclic voltammetry data at low scan rates their model very accurately predicted the behaviour at high scan rates. They found that of the three limiting factors considered (solid state diffusion of electrolyte cations into the MnO₂ matrix, kinetics for

the $Mn^{3+} \leftrightarrow Mn^{4+}$ redox reaction and the potential diffusion into the electrolyte filled pores of the composite), the reaction kinetics had the fastest time constant while the potential diffusion into the porous structure had an order of magnitude larger time constant. The aurthors make very clear that all three factors, including reaction kinetics, contribute to capacitance loss at high scan rates [31]. However, the other two factors can be improved through material and device design and thus there is significant room for improvement before the theoretical limitation set by reaction kinetics is reached.

2.4 Materials that exhibit pseudocapacitance – Focus on MnO₂

The several decades of active research into pseudocapacitance has resulted in an extensive array of materials with a wide range of forms and properties. The underlying driving force for continued research is the 1-2 order of magnitude increase in interfacial capacitance achievable with pseudocapacitance over standard double layer capacitance [32]. Single transition metal oxides [14] such as RuO₂, MnO₂ [27] and V₂O₅ [33], various complex transition metal oxides [34], transition metal nitrides including VN, TiN, Fe₂N and Mo_xN [35], [36], [37], and polymer materials such as polypyrrole [38] and polyaniline [39], with diverse synthesis procedures and mixed with a variety of additives such as conductive carbon allotropes (e.g. carbon nanotubes, graphene) are a few excerpts from the thousands of studies conducted in the broader field to date. Indeed, the simple search "MnO₂ supercapacitor" returns >10000 results in Google Scholar as of the writing of this thesis.

2.5 MnO₂ – Historical vs New application in supercapacitors

 MnO_2 is by no means a new material. It has been used for decades as the cathode component of the common alkaline battery [28]. However, a fundamental difference in its use in an alkaline battery versus a supercapacitor is the pH of the electrolyte used. The highly basic concentrated KOH electrolyte used in the alkaline battery configuration leads to irreversible conversion of the oxidized Mn^{4+} to Mn^{3+} , whereas neutral or near-neutral electrolytes allow for reversible conversion between these oxidation states, as will be shown. Lee, Manivannan, and Goodenough took detailed measurements of the charge passed during the anodic and cathodic sweeps during cyclic voltammetry of MnO_2 prepared through thermal decomposition of KMnO_4 [40]. They used a KCl electrolyte with the pH adjusted between 1 < pH < 13. They observed that outside the range 5 < pH < 11 the charge passed during the anodic and cathodic sweeps were unequal, indicative of an irreversible electrochemical process. In unmodified 2 M KCl at a pH of 6.7 however, MnO₂ prepared from a simple reaction between KMnO₄ and Mn(C₂H₃O₂)₂ had a perfectly symmetric cyclic voltammogram [27].

2.6 MnO₂ – Charging mechanism, structure and morphology effects

There is still some disagreement on the exact mechanism involved in the charging and discharging of MnO_2 supercapacitors, however a number of conclusions have still been made over the almost two decades of investigaiton. Toupin et al. [19] took careful XPS measurements of thin (~5 µm) and thick (~100 µm) films of MnO_2 , precipitated from a reaction of KMnO₄ and MnSO₄, after polarizing the electrodes at 0V and 0.9 V vs the Ag/AgCl (3M NaCl) reference electrode in 0.1M Na₂SO₄. In the thin film samples they observed the manganese to be in a 3+ oxidation state after polarization at 0V and a 4+ oxidation state after polarization at 0.9 V vs Ag/AgCl (3 M NaCl), compared to the initial mixed state of 3.6-3.7. However, the thick film

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering sample showed no detectable change in oxidation state after polarization compared to the initial value. In addition, particularly for the thin film electrodes, the change in the amount of Na detected between the two polarizations could not account for the complete change of the Mn oxidation state. The authors thus came to three very significant conclusions:

- 1) The pseudocapacitive response of MnO_2 was indeed the result of a redox transition between the Mn^{3+} and Mn^{4+} oxidation states.
- Only a very thin surface layer was electrochemically active, as evidenced by the complete switch between Mn³⁺↔Mn⁴⁺ in the thin film, versus no detectable oxidation state change in the thick film.
- Charge compensation in the thin film could not be solely from the Na⁺ of the electrolyte, necessitating the involvent of protons despite the neutral pH of the electrolyte.

These conclusions lead to the following generalized charging mechanism, illustrated in Figure 2.6-1 below for a series of overlapping/spread of redox processes [41], as was discussed in the section on pseudocapacitance above:

$$Mn(IV)O_{2} + xNa^{+} + yH^{+} + (x + y)e^{-} \longleftrightarrow Mn(III)_{(x+y)}Mn(IV)_{1-(x+y)}OONa_{x}H_{y}$$
(Eq. 2.6-1)

Kuo and Wu expanded on the work by Toupin et al. and came to very similar conclusions [42]. They, like Toupin et al., performed XPS analysis on chemically prepared and electrodeposited MnO₂ electrodes, however they also performed *in situ* XRD and quartz crystal microbalance (QCM) analysis along with the measurement of the open circuit potential as a function of pH.



Figure 2.6-1: Schematic cyclic voltammogram for MnO₂ showing the spread of redox reactions responsible for the pseudocapacitive behaviour. Source: [41]. 9

In addition, they used multiple electrolytes, Li, Na, K, Cs and Ca chloride in order to try and discern the contribution of the electrolyte cation in the charge storage process. In the QCM experiments, by comparing the mass loss/gain during the passage of a known amount of charge to the equivalent weight of the electrolyte cation, the authors concluded that in none of the electrolytes did the associated cation dominate the charge storage process. Particularly for the NaCl electrolyte, the measured mass change more closely fit that of the hydronium ion H₃O⁺. They observed a reversible lattice expansion in all electrolytes during cycling through the *in situ* XRD analysis, indicating that the charge storage process involved at least some degree of cation intercalation instead of being restricted purely to the surface [42]. Chen et al. [43] expanded upon this by using Raman spectroscopy to investigate the change in interlayer spacing of MnO₂ cycled in Li, Na and K nitrate. They concluded that at the edge of the anodic sweep the interlayer

gaps become filled with water molecules while at the edge of the cathodic sweep there is significant cation incorporation. Back to the investigation by Kuo and Wu [42], measurement of the open circuit potential in a NaCl electrolyte from 7 < pH < 11 in increments of 0.5 lead to a linear trendline with slope of -65 mV pH⁻¹ compared to the theoretical slope of -59.2 mV pH⁻¹ for the reaction:

$$Mn(IV)O_2 + xe^- + xH_3O^+ = [Mn(III)_x Mn(IV)_{1-x}]O_2(H_3O)_x$$
 (Eq. 2.6-2)

The authors cited the similarity in these slopes as further evidence that the charge storage was dominated by the hydronium ion, at least in the NaCl electrolyte.

Wen et al. [44] took a different approach in trying to determine the contribution of the electrolyte cation versus protons by cycling a MnO₂ electrode in aqueous and aprotic acetonitrile electrolytes containing the same concentrations of Li and Na perchlorate. They also measured the capacitance as a function of salt concentration in an aqueous KCl electrolyte. They observed a significant drop in capacitance in the aprotic acetonitrile compared to the aqueous electrolyte of the same salt concentration. They also observed an increase in capacitance with increasing KCl concentration up to a concentration of ~0.1 mol L⁻¹ followed by roughly static capacitance with further concentration increase. This lead the authors to conclude that both electrolyte cations and protons were involved in the charge storage process [44].

Zhai et al. attempted to quantify the contribution to the total capacitance of the surface vs intercalation mechanisms by synthesizing hollandite α -MnO₂ with or without Ba²⁺ or K⁺ ions present within the tunnel structure [45]. A schematic of four of the common structures of MnO₂ including the hollandite form is shown in Figure 2.6-2 below.



Figure 2.6-2: MnO_2 crystal structures: Each structure is assembled from MnO_6 octahedra. a – pyrolusite β -MnO₂, b - birnessite δ -MnO₂, c - hollandite α -MnO₂, d - ramsdellite γ -MnO₂. Source: [45]. 10

The authors discovered that when the hollandite tunnels were occupied by either Ba or K ions the charge storage was significantly reduced. They attributed this to a blocking effect by these ions to ions from the electrolyte, essentially restricting the charge storage to surface reactions. When the hollandite tunnels were left unoccupied the authors estimated the intercalation mechanism accounted for between ~80-90%, the surface mechanism ~8-17% and double layer charging ~1-4% of the total charge stored [45].

The conclusions of Zhai et al. fit well with the observations of Ghodbane, Pascal and Favier [46] who attempted to correlate the structure of MnO₂ with the measured specific capacitance. The authors observed that the only clear trend in specific capacitance was a

correlation with bulk ionic conductivity. No relation between specific capacitance and the measured Brunauer-Emmett-Teller (BET) surface area was seen. The authors pointed out that a strong correlation with BET surface area would be expected if the charge storage was dominated by surface reactions [46]. However, if some form of bulk insertion/intercalation dominated the charge storage a correlation with ionic conductivity would be expected, as they observed. Indeed, several years prior Brousse et al. [47] had come to the conclusion that there must be a mix of surface and bulk insertion charge storage when they were unable to find a clear trend between BET surface area and the compiled literature data for MnO₂ capacitance available to them at the time. Ghodbane, Pascal and Favier also observed that there was no correlation between specific capacitance and electrical conductivity. They assumed electrical conductivity would have an impact on performance, however because all the forms of MnO₂ investigated had varying degrees of incredibly large resistivity they concluded it would not be a limiting factor, thus the lack of a clear trend [46].

Kanoh et al. [48] provided perhaps the most detailed explanation for the charging mechanism of MnO_2 in neutral electrolytes. Through careful measurement of crystalline birnessite MnO_2 in aqueous KCl, as well as in other alkali metal chloride electrolytes, the authors concluded that the electrolyte cation was not in fact electrochemically active, but still participated in the overall charge compensation during the charging/discharging process. The electrochemically active component in their experiments was solely electrolyte protons. They arrived at this conclusion primarily through the measurement of the open circuit potential of two birnessite MnO_2 electrodes, one of which had intercalated K⁺ and the other electrochemically deintercalated of K⁺. They found that for both electrodes the open circuit potential, which essentially indirectly measures the oxidation state of the Mn in the electrode material in this case,

was invariant with the concentration of KCl in the electrolyte. In contrast, the open circuit potential of the intercalated material varied linearly with electrolyte pH, with a slope of -58.3 $mV pH^{-1}$ compared to the theoretical value of -59 mV pH⁻¹ [48]. This is a very similar result to that of Kuo and Wu presented previously, who made the same measurements in a NaCl electrolyte for their MnO₂ electrode [42]. They however stopped short of measuring the open circuit potential as a function of NaCl concentration. The conclusion of Kanoh et al. [48] was further reinforced through the observation that there was a discrepancy between the amount of intercalated alkali metal cation from the various electrolytes they tested versus the area of the intercalation peaks on the corresponding cyclic voltammograms. If the alkali metal cation was in fact electrochemically active then these two measurements would show the same trend [48]. This led the authors to propose the following mechanism:

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering



Figure 2.6-3: Schematic showing the charging/discharging mechanism for birnessite MnO₂. Source: [48]. 11

The charging mechanism essentially involves the oxidation of a Mn^{3+} via reaction with an intercalated water molecule and a concomitant release of a proton. A neighbouring Mn^{4+} site with an oxygen ligand carrying an excess negative charge is balanced by a K⁺ ion present in the birnessite tunnel. The K⁺ is deintercalated in response to the anodic scan and the charge on the neighbouring site is balanced by the proton released previously. On the cathodic scan, the oxidized Mn^{4+} site is reduced back to Mn^{3+} releasing the bound OH group as a hydroxide ion. The neighbouring Mn^{4+} - O⁻ site then undergoes an ion exchange with a K⁺ intercalated from the electrolyte and subsequent rejection of the proton to the electrolyte. This model effectively incorporates all previous observations discussed for the behaviour of MnO_2 in neutral electrolytes, lending credence to its accuracy.

2.7 MnO₂ – Performance and use in composite electrode materials

An implication of the charging model presented by Kanoh et al. is that the supply of electrons flowing to and from the electrochemically active Mn site considered must pass through the bulk MnO₂ material. Indeed, this was shown schematically by Conway several years prior for the case of MnO₂ used in an alkaline battery configuration [49], shown in Figure 2.7-1 below. Conway's schematic closely resembles the charging model proposed by Kanoh et al. As was pointed out by Ghodbane, Pascal and Favier, mentioned in a previous paragraph, the bulk electrical conductivity of MnO₂ is extremely low and is thus a limiter on the charging-discharging rate performance. A wide variety of strategies have thus been explored to try and tackle this limitation.



Figure 2.7-1: Schematic of proton/electron hopping in MnO₂ in contact with a KOH electrolyte. Source: [49]. 12

It was discovered early on in the research on MnO₂ supercapacitors when Toupin, Brousse and Bélanger [50] investigated MnO₂ composite electrodes that, in the absence of a conductive additive, bulk MnO₂ electrodes did not display capacitive behaviour, i.e. symmetrical box-shaped cyclic voltammograms (see Section 4.8-1 below). It was only when upwards of 15 wt% of the composite was composed of a conductive additive that the electrodes had appreciable capacitive performance. Lee, Kim and Lee observed similar behaviour [51]. The use of conductive additives in this way is by far the most common approach to handling the low conductivity of MnO₂. Toupin, Brousse and Bélanger [50] used a mixture of acetylene black and graphite particles where these components and MnO₂ were simply mechanically mixed with a pestle and mortar. Lee, Kim and Lee [51] incorporated conductive carbon during the synthesis of the MnO₂ in order to try and improve the mixing of the two components. Various groups have used carbon nanotubes as the conductive additive for MnO₂ composites either by attempting to deposit the MnO₂ directly onto the carbon nanotubes through electrochemical [52] or hydrothermal means [53], through direct reaction of the Mn precursor with carbon nanotubes M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering [54], or through post synthesis mixing of the components [55]. Similar procedures were used with graphene as the conductive additive of choice, either *in situ* [56] or again through post synthesis mixing [57].

Various attempts have been made to incorporate conductive polymers with MnO₂. For example, Lee, Shin and Jang began by electrodepositing MnO₂ onto carbon cloth followed by coating with polypyrrole using a vapour deposition-polymerization procedure [58], while Liu and Lee elected to electrochemically co-deposit MnO₂ and poly(3,4-ethylenedioxythiophene) (PEDOT) [59]. Expanding on these binary composites further are ternary composites incorporating MnO₂, a conductive additive such as carbon nanotubes and typically a conductive polymer such as PEDOT-PSS or polypyrrole [60], [20]. The idea with these systems is to essentially use the conductive additive as a matrix while the polymer acts as a kind of conductive wrapping to quickly transfer charges generated at the surface of the MnO₂.

Another strategy was the use of dopants during the synthesis of MnO₂ [61], [62] to intrinsically modify its properties. In particular the use of Al as a dopant [61] seemed to offer some improvement in the rate performance and cycle life of the MnO₂ electrodes. The authors ascribed this boost in performance to an increase in the conductivity of the MnO₂ through doping, however no conductivity measurement was provided. However, a separate study did show that Al doping could indeed reduce the resistivity of MnO₂ [63].

2.8 Carbon nanotubes – Conductive additive of choice for MnO₂ supercapacitors

Carbon nanotubes are particularly suitable as the necessary matrix conductive additive for MnO₂ based supercapacitors due to the low percolation threshold afforded by their high aspect ratio. This low percolation threshold was demonstrated almost two decades ago by Sandler et al. who investigated the use of carbon nanotubes in insulating epoxy matrices as a conductive additive to reduce electrostatic charging [64]. The authors found that carbon nanotubes were significantly more efficient in terms of weight and volume percent at achieving the desired bulk conductivity compared to carbon black, which they attributed to the high aspect ratio of the carbon nanotubes. Sandler et al. [65] further showed that by improving the dispersion of the carbon nanotubes they became even more efficient in terms of the percolation threshold for insulating epoxy matrices. Thus, it can be inferred that the dispersion and mixing of carbon nanotubes in a supercapacitor electrode based on insulating MnO₂ would also be an important consideration.

2.9 MnO₂ supercapacitors – The problem of mass loading

Despite all of the strategies for composite MnO_2 electrodes presented, the limitations of ionic and electrical conductivity still prohibit MnO_2 from achieving maximum performance in any configuration other than incredibly thin films. The theoretical specific capacitance for MnO_2 is determined by considering the single electron transfer for $Mn^{3+} \leftrightarrow Mn^{4+}$ over a particular potential window. Typically, MnO_2 is cycled over a potential window of 0.9V. This corresponds to a theoretical capacitance of:

$$\frac{1.602 * 10^{-19}C}{e^{-}} * \frac{6.022 * 10^{23}e^{-}}{1 \text{ mol } e^{-}} * \frac{1 \text{ mol } e^{-}}{1 \text{ mol } MnO_2} * \frac{1 \text{ mol } MnO_2}{86.9368g} * \frac{1}{0.9V} = 1233 \frac{C}{V * g} [=] \frac{F}{g}$$

Indeed, in the study by Toupin et al. [19] cited earlier, it was found that by increasing the film mass loading merely from 5 μ g to 25 μ g the capacitance dropped from 1380 F g⁻¹ to 930 F g⁻¹ corresponding to the minimal real electrode capacitances of 0.0069 F and 0.023 F respectively. The authors interpreted this to be the result of only a thin surface region, essentially a monolayer in their estimation, to be electrochemically active. In composite films of appreciable thickness, on the order of 10µm instead of hundreds of nanometers, the charge stored per gram of material had dropped by an order of magnitude. Devaraj and Munichandraiah [21] observed the same phenomenon, with the capacitance decreasing from 1330 F g⁻¹ at a mass loading of 0.03 mg cm⁻² to $<300 \text{ Fg}^{-1}$ by a mass loading of 0.9 mg cm⁻², corresponding to small areal capacitances of 0.04 and 0.27 F cm⁻² respectively. Li and Zhitomirsky [66] observed a linear decrease in capacitance with increasing mass loading for electrophoretically deposited films of MnO₂ and carbon nanotubes from 190 F g^{-1} at 50 µg cm⁻² to 120 F g^{-1} at 300 µg cm⁻² at a scan rate of 20 mV s⁻¹. Unfortunately, the loss of capacitance is not the only performance degradation that occurs with increasing mass loading. As the mass loading is increased, the ability for an electrode using MnO_2 as the active material to deliver energy at a quick rate also diminishes. Zhai et al. [67] prepared supercapacitor electrodes by depositing MnO₂ onto a graphene hydrogel nickel foam current collector with mass loadings from 0.31 mg cm⁻² to 13.6 mg cm⁻². For the 0.31 mg cm⁻² electrode the areal normalized capacitance dropped from ~ 0.25 F cm⁻² to 0.15 F cm^{-2} (60% of initial) while for a 6.11 mg cm⁻² electrode the areal normalized capacitance dropped from ~1.5 F cm⁻² to 0.45 F cm⁻² (30% of initial) at scan rates of 10 mV s⁻¹ and 100 mV s^{-1} respectively. For their 13.6 mg cm⁻² electrode the areal normalized capacitance dropped from ~2.25 F cm⁻² to ~1 F cm⁻² between the scan rates of 10 mV s⁻¹ and 40 mV s⁻¹. The trend for their

data is clear in that as the mass loading increases the gravimetric capacitance decreases markedly, the areal capacitance at low scan rates increases modestly, while the ability for the electrodes to deliver charge at elevated scan rates decreases dramatically. This trend, particularly for electrodes with mass loadings around 5-10 mg cm⁻² is the norm. Ramirez-Castro et al. [68] tabulated the rate performance between 2 mV s⁻¹ and 100 mV s⁻¹for a number of MnO₂ electrodes with what Zhai et al. considered "high" mass loading (>1 mg cm⁻²) in the range 1-10 mg cm⁻². They found the capacitance retention to be within 12-62% between 2 mV s⁻¹ and 100 mV s⁻¹, with there own electrodes boasting the upper 62% retention at a mass loading of 10 mg cm⁻². However, it should be noted that the composite material that Ramirez-Castro et al. used was composed of less than 50 wt% of MnO₂, the rest being mostly conductive carbon.

2.10 Adsorption and dispersion of carbon nanotubes and MnO₂

Effective dispersion and mixing of conductive carbon nanotubes with insulating MnO_2 will be required to produce high performance composite materials. To this end, a review of past successful dispersion strategies will inform the selection of new dispersing agents, with the aim of further improvement in electrode performance.

Because of their high aspect ratio, surface area and flexibility, carbon nanotubes tend to form large entangled agglomerates [69]. The nanotubes must be disentangled and dispersed into a stable suspension to use them effectively. Strategies to disperse carbon nanotubes can be broadly divided into two categories: covalent functionalization and non-covalent functionalization [70]. Covalent functionalization relies on the introduction of various functional groups, such as carboxylic and hydroxyl, to the carbon nanotubes through the disruption of the graphitic sp² hybridized structure and the formation of new chemical bonds. It is believed that carboxylic groups in particular diminish the van der Waals interactions between the nanotubes,

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering allowing for their dispersion [70]. However, the advantageous conductive properties of carbon nanotubes depends on a continuous network of π -bonds; thus such functionalization can significantly reduce the conductivity of the nanotubes [71]. Common techniques to achieve such functionalization typically revolve around harsh chemical treatments with strong acids and oxidants [72], [73]. In extreme examples, such treatments can actually result in the complete destruction of the nanotube structure [73].

A preferable strategy is non-covalent functionalization. This essentially involves the use of a dispersing agent which will modify the surface structure of the carbon nanotube through an adsorption or wrapping mechanism without disruption of the graphitic network [70]. Long chain ionic surfactants such as sodium dodecylsulfate and centrimonium bromide contain a hydrophilic, charged group and a hydrophobic carbon chain. These surfactants will form a micelle structure around the carbon nanotube with the hydrophobic chain adsorbing to the nanotube surface and the charged hydrophilic end facing outward towards the solvent. The nanotubes are then dispersed through the electrostatic repulsion of the adsorbed micelles. For non-ionic surfactants, the extension of long hydrophilic polymer chains into the solvent away from the adsorbed surface allows for dispersion of the nanotubes [74].

It has been known for decades that aromatic compounds show strong adsorption on graphitic surfaces [75], [76]. This has been explained by the energetically favourable π - π stacking of benzene rings on the graphitic surface, which also applies to carbon nanotubes [70], [77], [78]. Indeed, Islam et al. [77] observed that sodium dodecylbenzene sulfonate was more efficient at dispersing carbon nanotubes compared to sodium dodecyl sulfate, which the authors attributed to the stronger adsorption afforded by the benzene ring of sodium dodecylbenzene sulfonate. Thus, it seems reasonable to conclude that the next generation of dispersing agents for

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering carbon nanotubes will contain some form of aromatic structure. Indeed, organic dyes with such aromatic structures such as pyrocatechol violet [79] and crystal violet [80] were found to be excellent dispersing agents for carbon nanotubes.

Modification and dispersion of MnO₂, or any other electrochemically active component is a separate challenge from the dispersion of carbon nanotubes. It has been shown that molecules derived from catechol, salicylic acid, gallic acid and chromotropic acid show strong adsorption on the surfaces of oxide particles [81]. This is attributed to the interaction between adjacent hydroxyl or hydroxy-carboxylic groups with the particle surface as shown in the bonding schematics below. Interestingly, these kinds of interactions are thought to be partially responsible for the ability of sea mussels to bind to various wet surfaces, due to the presence of proteins containing 3,4- dihydroxyphenyl-L-alanine in their adhesion plaques [82].



Figure 2.10-1: Schematic showing the proposed interaction mechanisms for catechol compounds (left), salicylic compounds (right, top) and chromotropic acid compounds (right, bottom) with a particle surface. Source: [81]. 13

The binding of both oxygen atoms with a single metal site is referred to as bidentate chelating bonding. When the two oxygen atoms bind to two different metal sites this is referred to as inner sphere bidentate bridging bonding. It is important to note that in both these cases if the metal previously contained surface oxygen, the oxygen atoms of the catechol ligand replaces it [83], [84]. Outer sphere bidentate bridging bonding does not involve such replacement; the adsorption is the result of an electrostatic or hydrogen bonding mechanism [85]. The importance of adjacent bonding sites on the complexing molecule was determined through a systematic variation of the molecular structure in an investigation by Liu and Zhitomirsky [55]. They attempted to anodically deposit MnO₂ particles with electrophoretic deposition using a series of related compounds: *trans*-cinnamic acid (TCA), *p*-coumaric acid (PCA), 2,4-dihydroxycinnamic acid (DCA) and caffeic acid (CA). The structures for these molecules are shown in Figure 2.10-2 below.



Figure 2.10-2: Chemical structure for A – *trans*-cinnamic acid, B – *p*-coumaric acid, C – 2,4dihydroxycinnamic acid, D – caffeic acid. 14

The only difference between the molecules is the number and positioning of the aromatic hydroxyl groups. CA has adjacent hydroxyl groups on the benzene ring, like the schematics shown in Figure 2.10-1. TCA has no hydroxyl group, PCA has a single hydroxyl group and DCA has two hydroxyl groups that are not adjacent. Of the four compounds, CA was the only one that resulted in the successful deposition of MnO₂ in water. The authors attributed this to the preferential adsorption of H⁺ from deprotonated TCA, PCA and DCA resulting in a reduction of the natural surface charge of MnO₂ while deprotonated CA showed preferential adsorption leading to deposition in its case [55]. This demonstrates that the catechol functionality was critical for adsorption onto MnO₂. As a result, the presence of catechol or the similar groups listed above is an important parameter when selecting dispersing agents for MnO₂.

2.11 Supercapacitor electrolytes

The choice of electrolyte in a supercapacitor has a direct impact on the final powerenergy characteristics, having a large influence on the operating voltage window as well as the internal resistance of the device. The excellent review paper by Zhong et al. [86] summarizes many of the electrolytes tested for supercapacitors to date as well as their properties, advantages and disadvantages. Two of the major classes of supercapacitor electrolytes considered by Zhong et al. were liquid, which can be subdivided intro aqueous and non-aqueous and solid state/quasi solid state.

Aqueous electrolytes can be acidic, basic or neutral depending on the salt used. They, in general, have the highest ionic conductivities of all possible electrolytes leading to very low cell resistances. Acidic and basic aqueous electrolytes have the highest conductivities due to the advantageous proton hoping mechanism between water molecules [23]. Among all electrolytes, they are by far the easiest to process and require no special equipment or tight purity control during cell production [86]. In addition, they are inherently non-flammable and many of the suitable neutral salts such as NaCl and Na₂SO₄ are environmentally benign. However, they also have the lowest theoretical operating voltages due to the thermodynamic breakdown potential of water being only 1.23 V. Because both maximum energy and power density scale with the square of voltage this can be a serious drawback. However, there is a more nuanced balancing act when considering power density since often times aqueous electrolytes will result in an almost order of magnitude smaller internal cell resistance [86], [87].

Non-aqueous electrolytes can be broadly divided into two classes: 1) organic solvents with a dissolved salt and 2) ionic liquids. The general argument for using non-aqueous electrolytes over aqueous is the much larger operating voltage windows leading to higher energy

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering densities. However, non-aqueous electrolytes tend to exhibit lower capacitances and much higher cell resistances compared to aqueous electrolytes, making their outright superiority debatable. In addition they tend to be very sensitive to contamination, especially from moisture, and require careful processing and purification to achieve adequate performance [86]. Some organic electrolytes, such as acetonitrile, are also flammable making them somewhat of a safety risk in handling, storage and operation.

Organic electrolytes can operate at potentials up to 2.5 V-2.8 V and currently are the most widely used in commercially available supercapacitors [86]. Examples of organic electrolyte systems for carbon based supercapacitors are 1M tetraethylammonium tetrafluoroborate in acetonitrile [88] and 1M lithium hexafluorophosphate in a mixed ethylene carbonate/diethyl carbonate [89], however many more have been tested [86]. Organic electrolytes have also been used for systems that exhibit pseudocapacitance. An interesting example of a material where pseudocapacitance can only be achieved in an organic electrolyte is Nb₂O₅. Augustyn et al. [90] observed Li⁺ intercalation pseudocapacitance in Nb₂O₅ using a 1M lithium perchlorate/propylene carbonate electrolyte at very cathodic potentials. However, in an aqueous environment, reduction of the Nb oxidation state does not occur before hydrogen evolution begins [91], making pseudocapacitance inaccessible. As mentioned previously, double layer supercapacitors such as those based on carbon materials will, in general, have lower capacitance values in organic versus aqueous electrolytes due the smaller dielectric constants of organic solvents as well as larger solvated ion sizes [86]. The lower ionic conductivity in organic electrolytes can also increase internal cell resistance resulting in a loss of power density.

Ionic liquid electrolytes are relatively new to the supercapacitor field. They are special ionic salts, typically containing a large organic cation and an organic or inorganic anion, with the

defining feature being that they are liquid at or very near room temperature. Depending on the specific salt, ionic liquids boast very high stability, both thermally and electrochemically leading to large operating voltage windows, with low volatility and non-flammability [92]. Example cations include imidazolium, pyrrolidinium, sulfonium and some example anions are tetrafluoroborate, hexafluorophosphate and bis(fluorosulfonyl)imide [86]. The performance of a supercapacitor using an ionic liquid electrolyte is obviously highly dependent on the choice of cation and anion. For example, ionic liquids with a imidazolium cation tend to have higher ionic conductivities, which has been repeatedly related to internal cell resistance and power density, while ionic liquids with a pyrrolidinium cation tend to have larger voltage windows [86]. In general, ionic liquids will have larger operating voltage windows compared to organic and definitely aqueous electrolytes. However, they also have, in comparison, much lower ionic conductivities and very high viscosities leading to very high cell resistance and thus poor power performance [86]. In addition, the high cost of most ionic liquids could be a serious barrier to commercial application.

Solid state electrolytes used in supercapacitors are generally in the form of a polymer that is mixed with a liquid electrolyte to form a solid gel [86]. The polymer acts as a matrix while the liquid phase is responsible for all ionic conduction. One of the greatest benefits of this kind of electrolyte is that the gel acts as a separator, eliminating the need for it as a separate component. In addition, the gel electrolyte eliminates the risk of leakage and allows for flexible device geometries not achievable with liquid electrolytes [93]. However, one of the greatest drawbacks for this kind of electrolyte is poor utilization of active material, particularly in nano-structured materials, leading to lower capacitance and higher cell resistance [86]. In addition, the operating voltage window will still be limited by the liquid component and can be relatively small in the

case of a polymer-aqueous electrolyte. As an example, Yuan et al. [94] utilized an aqueous gel polymer electrolyte consisting of a polyvinyl alcohol polymer matrix and aqueous phosphoric acid for electrodes fabricated from the electrodeposition of MnO_2 on carbon fabric. Their device could be bent in half as well as cycled up to 10000 times in the unbent position without significant loss in capacitance. Lu et al. [95] used a polyvinyl alcohol-lithium chloride solid state electrolyte in a device with a VO_x cathode and VN anode. They found that the solid-state electrolyte significantly improved the cycling stability of the VN anode over aqueous lithium chloride. The authors suggested this was due to a suppression of the oxidation of the VN and subsequent dissolution of soluble VO_x species that would otherwise occur in an aqueous electrolyte [95].

2.12 Aqueous asymmetric supercapacitors

In order to try and combat the small voltage window afforded by aqueous electrolytes, an asymmetric electrode configuration can be utilized. This configuration uses different materials for the positive and negative electrodes with complimentary operating voltage windows as shown in Figure 2.11-1 below. Ideally the positive electrode material will have a large overpotential to oxygen evolution while the negative electrode material will have a large hydrogen evolution overpotential, maximizing the operating voltage. With such materials in this configuration, the overall operating voltage for the device can be extended well beyond the thermodynamic breakdown voltage of water, with some devices reported operating up to 2 V [28]. In this case, the asymmetric device begins to approach the operating voltages of symmetric devices using organic electrolytes, eliminating their principle advantage. In such a configuration, it is imperative that the total capacitance of both the positive and negative electrodes be balanced. Without proper balancing, one of the two electrodes can become overcharged,



Figure 2.11-1: Illustration of the complimentary voltage windows in an asymmetric device, allowing for a larger overall device voltage. Source: [15]. 15

inevitably leading to deterioration and loss of cycle life. This can be achieved by independently measuring the gravimetric capacitance of the positive and negative electrode material and carefully controlling the mass loading of both electrodes such that:

$$C_{+ve} = C_{+ve,grav} * m_{+ve} = C_{-ve} = C_{-ve,grav} * m_{-ve}$$
(Eq. 2.12-1)

Where $C_{+ve/-ve}$ represents capacitance while $m_{+ve/-ve}$ represents mass.

Although cost, ease of handling and environmental benignity were mentioned as the main advantages, neutral salt aqueous electrolytes actually have another distinct advantage in an asymmetric configuration. These electrolytes have the largest intrinsic electrochemical stability window compared to acidic and basic aqueous electrolytes as shown for the example of HCl, KCl and KOH in Figure 2.11-2 below, from [96]. Because of the lack of availability of H⁺ and OH⁻ ions in a neutral electrolyte, gas evolution can only occur through the breakdown of water molecules, which doesn't occur until either ~1.1 V or -0.9 V vs the Ag/AgCl reference electrode. In contrast, H⁺ reduction to H₂ gas occurs at -0.2 V vs Ag/AgCl in 1M HCl, while OH⁻ oxidation to O₂ gas occurs at 0.7 V vs Ag/AgCl in 1M KOH. Thus, neutral electrolytes offer the potential for the greatest voltage windows and thus energy densities.



Figure 2.11-2: Linear sweep voltammograms of an acidic, neutral and basic electrolyte on a platinum electrode showing the electrochemical stability window of each. Source: [96]. 16

Porous carbon based materials are particularly well suited as the negative electrode material in an asymmetric device, using neutral aqueous electrolytes, due to large hydrogen evolution overpotentials [15]. This is believed to be caused by a pH shift in the vicinity of the carbon surface/electrolyte interface, locally changing the hydrogen evolution potential from that of the bulk electrolyte pH [97]. The porous nature of the carbon material exasperates this phenomenon due to low diffusion/electro-migration of species within the pores [97]. The charge storage mechanism for these materials is predominantly due to double layer capacitance [97], however faradaic pseudocapacitive contributions to the overall capacitance are possible [15]. MnO₂ on the other hand is well suited as the positive electrode in such a device. As described earlier, this material has a large capacitance and operates in the anodic potential window of 0-0.9 V vs SCE [98] in neutral electrolytes.

Chapter 3: Problem Statements and Objectives

As was outlined in the literature review above a wide range of strategies have been investigated with the goal of fabricating high performance MnO₂ supercapacitors. However, the full potential of MnO₂ can only be realized in very thin films and attempts to scale composite materials to practically useful mass loadings results in significant performance degradation. The primary goal of this investigation is, as a result, a simple one: To produce MnO₂ composite electrodes with high capacitance and good capacitance retention at fast scan rates with practically useful mass loadings.

The post synthesis mixing of MnO_2 and carbon nanotubes via advanced colloidal processing strategies has already proven effective in obtaining composite materials with good performance at high active mass loading [55], [99]. Capacitances greater than 100 F g⁻¹ at low scan rates and mass loadings exceeding 20 mg cm⁻² are readily achievable using colloidal processing and high porosity nickel foam current collectors. However, this still falls short of the ~1000 F g⁻¹ capacitances of thin films and the rate performance at high scan rates is still relatively low. Developing new colloidal processing strategies to improve the mixing of MnO_2 and carbon nanotubes appears to be a promising methodology to achieve the primary objective.

A secondary goal of this investigation is to investigate potential alternatives to MnO_2 that may address some of its intrinsic disadvantages, particularly the low electrical conductivity. To this end, vanadium sesquioxide (V₂O₃) is explored as a replacement active material for supercapacitor electrodes.

Chapter 4: Experimental Procedure

4.1 Table of chemicals and materials

The following is a table of all chemicals and materials used in the fabrication of various supercapacitor composite materials:

Chemical Use	Chemical Name	Supplier/Source
Active material/active material synthesis	Potassium Permanganate (KMnO ₄)	Sigma-Aldrich (Canada)
	2-propanol	Caledon Laboratory Chemicals (Canada)
	1-butanol	Fischer Chemical (Canada)
	Vanadium sesquioxide (V ₂ O ₃)	Sigma-Aldrich (Canada)
	Activated carbon (AC): Picacatif Supercap BP10	Pica USA, Inc. (USA)
Washing	Ethanol	Commercial Alcohols (Canada)
	Methanol	Caledon Laboratory Chemicals (Canada)
Dispersing agent/material modifier	Lauryl gallate (LG)	Sigma-Aldrich (Canada)
	New Fuchsine (NF)	Sigma-Aldrich (Canada)
	3,4-dihydroxybenzaldehyde (DB)	Sigma-Aldrich (Canada)
Conductive additive	Multi-walled carbon nanotubes (MWCNT) (ID: 4nm, OD: 13nm, Length: 1-2µm)	Bayer Inc. (Germany)
	Carbon black (CB): Vulcan XC72R	Cabot Corporation (USA)
Electrolyte/electrolyte pH adjustment	Sodium Sulfate (Na ₂ SO ₄)	Caledon Laboratory Chemicals (Canada)

	Sodium Nitrate (NaNO ₃)	Caledon Laboratory Chemicals (Canada)
	Sodium Chloride (NaCl)	Caledon Laboratory Chemicals (Canada)
	Sulfuric acid (H ₂ SO ₄)	Caledon Laboratory Chemicals (Canada)
	Nitric acid (HNO ₃)	Caledon Laboratory Chemicals (Canada)
	Hydrochloric acid (HCl)	Caledon Laboratory Chemicals (Canada)
Current Collector	Nickel foam	Vale (Canada)
	Graphene coated nickel foam	CVD Equipment Corporation's Application Laboratory (USA)
Slurry preparation Binder	Ethanol	Commercial Alcohols (Canada)
	1-Methyl-2-pyrrolidinone	Sigma-Aldrich (Canada)
	Poly(vinyl butyral- co -vinyl alcohol- co -vinyl acetate, Average M _w = 50000- 80000	Sigma-Aldrich (Canada)
	(PVB)	
	Poly(vinylidene fluoride)	Alfa Aesar (USA)
	(PVDF)	
Reference electrode solution	Potassium Chloride (KCl)	Fisher Chemical (Canada)

 Table 4.1-1: List of chemicals used over the course of the projects described in the results

section, their uses and suppliers. 1

4.2 Synthesis of MnO₂ for post drying mixing procedures.

Large batches of MnO₂ were synthesized via reduction of aqueous KMnO₄ with 2propanol for use in post drying mixing strategies. In a typical batch synthesis, 3 g of KMnO₄ is dissolved in 100 mL of deionized water in a 250 mL beaker under stirring for approximately 10 min at 300 rpm. Next 50 mL of 2-propanol is added to the aqueous KMnO₄, and the mixture allowed to continue stirring at the same rate for at least 4 hours with the beaker covered with a piece of laboratory paraffin wax. Typically, within 15 minutes the characteristic purple colouration of the KMnO₄ solution completely disappears and a light brown gelatinous precipitate forms. The precipitate is extracted via vacuum filtration using a Whatman 1 μ m pore size cellulose filter membrane and washed with copious amounts of deionized water and ethanol/methanol (typically at least 1000 mL deionized water and 250 mL of ethanol/methanol). The washed gel-like powder is then dried in air at ~70°C, usually for 12 hours.

The reduction of primary and secondary alcohols by KMnO₄ is common in organic chemistry. In the case of 2-propanol, it is oxidized to propanone with the concomitant reduction of KMnO₄ to MnO₂ and the liberation of hydrogen ions via the following reaction:

$$(H_3C) - (CHOH) - (CH_3) + KMnO_4 \rightarrow (H_3C) - (CO) - (CH_3) + 2H^+ + MnO_2$$

(Eq. 4.2-1)

The molar ratio of 2-propanol to KMnO₄ is approximately 34:1. This ratio was used for ease of measurement of the precursors and based on the observations of Wu, Ma and Lu [100] who determined that the peak capacitance of MnO₂ formed through the reduction of aqueous KMnO₄ by ethanol occurred in the molar ratio range ethanol:KMnO₄ = 4:1 to 40:1.

4.3 Fabrication of MnO₂-MWCNT composites using a Schiff base reaction

Dried MnO₂ powder synthesized by the reduction of KMnO₄ by 2-propanol was used in the fabrication of the composite material. In a typical procedure, a 0.5 g L⁻¹ 3,4dihydroxybenzaledhyde (DB) solution is first made by dissolving 10 mg of DB in 20 mL of DI water in a 100 mL beaker. Next, 80 mg of MnO₂ is added such that the MnO₂ concentration is 4 g L⁻¹. In a separate 50 mL beaker containing 20 mL of DI water 10mg of New Fuchsine (NF) is dissolved such that the concentration is 0.5 g L⁻¹. Next 20 mg of MWCNT are added to this solution such that the MWCNT concentration is 1 g L⁻¹. Both beakers are sealed with a piece of laboratory paraffin wax and transferred to a bath ultrasonicator. The mixtures are ultrasonicated simultaneously for 15 minutes. After this 15 minute period, the NF-MWCNT suspension is transferred to the DB-MnO₂ suspension and ultrasonicated for another 15 minutes. The mass ratio of MnO₂:MWCNT is 4:1. After this second ultrasonication step the suspension is vacuum filtrated through a Whatman 1 µm pore size cellulose filter membrane and washed with copious amounts of water and ethanol (typically at least 1000 mL deionized water and 250 mL of ethanol). The filtered product is dried in ambient air prior to electrode fabrication.

4.4 Fabrication of MnO₂-MWCNT composite using a Liquid-Liquid Extraction procedure.

In a typical procedure 1 g of KMnO₄ is dissolved in 100 mL of DI water in a 400 mL beaker by stirring at 300 rpm for 10 minutes. To this solution 50 mL of 1-butanol is added with continued stirring for 1.5-2 hours until the characteristic purple colouration of aqueous KMnO₄ disappears, replaced by a dark brown gelatinous precipitate. In a separate 50 mL beaker 0.1 g of

lauryl gallate (LG) is dissolved in 25 mL of 1-butanol. The lauryl gallate solution is then added to precipitate solution and stirred for another 5 minutes. In a separate 100 mL beaker 0.139 g of MWCNT are added to 50 mL 1-butanol with or without 0.140 g of dissolved lauryl gallate. Both beakers are transferred to a bath ultrasonicator, sealed with laboratory paraffin wax and ultrasonicated for 30 minutes. After this first ultrasonication period, the MWCNT suspension is added to the MnO₂ suspension followed by further ultrasonication for another 30 minutes. The mixed MnO₂-MWCNT composite is allowed to settle to the 1-butanol-water interface for 1 day. The excess 1-butanol is decanted, while the bottom aqueous phase is partially removed with a pipette. The remaining gelatinous composite in 1-butanol is then solvent exchanged into methanol/ethanol via repeated ultrasonication with excess ethanol/methanol and vacuum filtration, typically at least two washing/filtration cycles.

4.5 V_2O_3 -MWCNT composite synthesis and activation.

V₂O₃-MWCNT composites were prepared using commercially available V₂O₃ powder from Sigma Aldrich. In a typical procedure 0.080 g of V₂O₃ is dispersed for 10 minutes via ultrasonication in 40 mL 50:50 ethanol:water containing 0.040 g of lauryl gallate. Simultaneously 0.020 g of MWCNT are dispersed for 10 minutes via ultrasonication in 20 mL of 50:50 ethanol: water containing 0.020 g of lauryl gallate. These two solutions are mixed and ultrasonicated for a further 5 minutes before vacuum filtration using a Whatman1µm cellulose membrane and washing with ethanol/methanol and water, typically 500 mL total. The composite material is then dried at ~70°C for 2 hours.

After electrode fabrication (see section 4.8), the electrode is subjected to an activation procedure before testing the capacitance performance. This activation procedure is outlined in
Table 4.5-1 below. A 15 s cell equilibration time preceded each step in the activation procedure. The steps were performed sequentially.

Step	Potential Window (V vs SCE)	Scan rate (mV s ⁻¹)	Number of cycles
	0.07	50	100
1	0-0.7	50	100
2	0-0.7	100	50
_		100	
3	0-0.7	5	8
4	0-0.7	2	8

Table 4.5-1: Activation procedure used for all V_2O_3 -MWCNT for which capacitance data was acquired. 2

4.6 Activated carbon- carbon black

An activated carbon-carbon-black (AC-CB) composite was used as the negative electrode material in fabricating asymmetric devices. The composite was prepared by dispersing activated carbon and carbon black in ethanol followed by filtration. In a typical synthesis, 0.425 g of activated carbon is dispersed via ultrasonication in 200 mL of ethanol for 15 minutes. Simultaneously 0.075 g of carbon black is dispersed in 75 mL of ethanol, again via ultrasonication for 15 minutes. The two suspensions are mixed, ultrasonicated for a further 15 minutes and vacuum filtrated using a Whatman 1 µm pore size cellulose membrane.

4.7 Materials characterization

4.7.1 Crystallinity

X-Ray diffraction (XRD) testing was performed using a Nicolet I2 diffractometer with monochromatized Cu K α radiation. 2 θ values from 5-95° were typically acquired at a scan rate of 5° min⁻¹. Each collected pattern was subjected to median image smoothing using the GADDS software package. The smoothed patterns were then passed to the EVA software package where they were integrated to obtain the final plot of signal intensity vs 2 θ .

4.7.2 Morphology

Composite microstructures were primarily investigated using scanning electron microscopy (SEM) at the Canadian Centre for Electron Microscopy. The instrument employed was a JEOL JSM-7000F. The accelerating voltage and working distance are displayed on each presented SEM image. The beam current was typically set to the auto-low or auto-medium setting for the instrument. Samples for SEM were prepared by applying a small amount of powder to the centre of a piece of double sided copper tape adhered to a stainless-steel sample stub. Nickel paste was applied along the edges of the copper tape to improve sample conductivity. Unless otherwise specified, samples were platinized to a thickness of 5nm to further improve sample conductivity.

The structure of the MnO₂-MWCNT composite prepared via liquid-liquid extraction was further investigated using transmission electron microscopy (TEM). The instrument employed was a FEI Tecnai Osiris microscope. A dilute suspension of the composite powder was prepared in ethanol, dropped via a micro-pipette onto a TEM grid and subsequently dried.

4.7.2 Composition

Fourier transform infrared spectroscopy (FTIR) was used to study the adsorption and chemical state of dispersing agents used to produce MnO_2 -MWCNT composites. The instrument used was a Bio-Rad FTS-40. Scanning photoelectron spectroscopy (XPS) was performed at the McMaster Biointerfaces Institute to study the oxidation state of vanadium in pure V₂O₃ and V₂O₃-MWCNT composites. The instrument used was a Physical Electronics Quantera II.

4.8 Electrode fabrication and characterization

Supercapacitor electrodes were fabricated using a slurry impregnation method. A piece of 95% porosity nickel foam, cut typically to a length of 17 mm and width of 10 mm, is cleaned via ultrasonication in ethanol and acetone for 10 minutes each then dried using a hair dryer. The nickel foam is then weighed using a Toledo AX105 scale prior to impregnation. The composite materials MnO₂-MWCNT and V₂O₃-MWCNT are ground in an agate mortar with between 1-2 mL of ethanol and 2-3 wt% of PVB binder (see Table 4.1-1) for 5 minutes to form a viscous slurry. The slurry is manually applied to the clean nickel foam using a laboratory micro-spatula. The process is controlled such that an area of $\sim 10 \text{ X} 10 \text{ mm}$ is impregnated with between 15-50 mg of active material. The nickel foam is then rolled to between 20-30% of its initial thickness, approximately 0.38-0.57 mm. Once rolled, the mass of the electrode is measured again using a Toledo AX105 scale. The difference in mass between the initial, clean and impregnated nickel foam is taken to be the active mass loading of the electrode. A piece of copper wire is soldered to the nickel foam on an unimpregnated area. The copper wire is inserted into a soda glass tube and the base of the electrode set against the opening of the tube. The electrode is then attached to the soda glass tube using a quick setting epoxy such that the tube opening, solder joint and any

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering exposed nickel foam are sealed by the epoxy. A photograph of a completed electrode is shown in Figure 4.8-1 below.



Figure 4.8-1: Photograph of a typical completed electrode. Tick-scale adjacent to electrode is in millimeters. 17

Activated carbon-carbon black (AC-CB) negative electrodes were fabricated using a very similar method. However, the slurry was prepared using 1-methyl-2-pyrrolidinone instead of ethanol and 5 wt% polyvinylidene fluoride as the binder. Typical mass loadings for the negative electrodes was in the range 15-25 mg cm⁻².

Asymmetric devices were fabricated using MnO_2 -MWCNT composites as the positive electrode material and AC-CB as the negative electrode material. Both electrodes were fabricated using nickel foam current collectors. Every attempt was made to balance the mass loadings of the two electrodes according to Eq. 2.12-1. The three-electrode performance of the AC-CB material used in the asymmetric devices is shown in Appendix B. The electrodes were separated using a piece of insulating, micro-fibrous cloth and sealed in a plastic container with aqueous Na₂SO₄ as the electrolyte. Electrochemical characterization of single fabricated electrodes was carried out in a three-electrode configuration. Each electrode had an exposed surface area of ~1 cm². Cyclic voltammetry and impedance spectroscopy experiments were conducted using a ParaSTAT-2273 potentiostat using a Standard Calomel Electrode, saturated KCl (SCE) as the reference electrode and platinum gauze as the counter electrode. Cyclic stability was conducted using a VersaSTAT-3 potentiostat with the same reference and counter electrode in a three-electrode configuration.

Galvanostatic charge-discharge of fabricated asymmetric devices was conducted using a MTI 8-Channel Battery Analyzer, either 5 V/10 mA or 5 V/3 A depending on the current tested. Cyclic voltammetry and impedance spectroscopy of asymmetric devices was conducted using the ParaSTAT-2273 potentiostat in a two-electrode configuration.

Unless otherwise specified the electrolyte used was $0.5M Na_2SO_4$, degassed with N_2 prior to measurement.

4.8.1 Cyclic voltammetry

In a cyclic voltammetry experiment, the potential is varied at a constant linear rate, i.e. dV/dt = constant, v, and the current response is measured.

$$q = CV \rightarrow \frac{dq}{dt} = \frac{d}{dt}(CV)$$
(Eq. 4.8.1-1)

If capacitance does not depend on time it can be pulled out of the above derivative. This implies, since voltage is varying linearly with time, that the capacitance is potential *independent*, i.e. does not depend on the state of charge. Realizing as well that dq/dt is the current:

$$\frac{dq}{dt} = I = C \frac{dV}{dt} = Cv = constant$$
(Eq. 4.8.1-2)

Thus, potential independent capacitive behaviour will result in a constant current response during a cyclic voltammetry experiment. Combining the anodic and cathodic sweeps, the cyclic voltammogram will be in the shape of a box ($\pm v$ leads to constant $\pm I$). This is the origin of the common jargon in supercapacitor literature describing cyclic voltammograms of measured electrodes as having an "ideal box-shape". An schematic is shown in the Figure 4.8.1-1 below.



Figure 4.8.1-1: Schematic cyclic voltammograms of a supercapacitor electrode. 18

The red curve is characteristic of a low scan rate voltammogram while the black curve is the common shape observed at high scan rates. The rounding of the voltammogram corners is the result of the electrode materials resistance and becomes more pronounced at elevated scan rates [101].

Capacitance is calculated from a cyclic voltammogram by dividing half the integrated area of the voltammogram by the product of the applied voltage window and scan rate used according to Eq. 4.8.1-3 below.

$$C = \frac{1}{2(V_{max} - V_{min})\nu} \int_{V_{min}}^{V_{max}} I(V) dV [=] \frac{A * V}{V * \left(\frac{V}{S}\right)} [=] \frac{A * S}{V} [=]F \qquad (Eq. \, 4.8.1-3)$$

 MnO_2 -MWCNT composites were tested in the voltage window 0-0.9 V vs SCE at scan rates of 2 mV s⁻¹, 5 mV s⁻¹, 10 mV s⁻¹, 20 mV s⁻¹, 50 mV s⁻¹, 100 mV s⁻¹. These scan rates were tested

sequentially with a 15 second equilibration period between tests at different scan rates. 2 cycles were performed at 2 mV s⁻¹, 3 cycles at 5 mV s⁻¹, 5 cycles at 10 mV s⁻¹, 10 cycles at 20 mV s⁻¹, 10 cycles at 50 mV s⁻¹, and 10 cycles at 100 mV s⁻¹. The same protocol was used in testing V_2O_3 -MWCNT electrodes except in the potential window 0-0.7 V vs SCE.

The value of the definite integral in Eq. 4.8.1-3 used for presented capacitance values was determined using the numerical integration function of Origin v8.1.

4.8.2 Electrochemical impedance spectroscopy

In an impedance spectroscopy experiment, a sinusoidal voltage signal of a particular amplitude is superimposed onto a bias voltage and the resulting current response is measured. Multiple voltage signals are applied in succession, each with a different frequency. The amplitude and the phase shift of the current response with respect to the applied voltage signal yields information on the real and imaginary components of the impedance of the electrode being investigated.

$$E(t) = E_{bias} + E_o \cos(\omega t)$$
 (Eq. 4.8.2-1)

$$I(t) = A\cos(\omega t - \varphi)$$
 (Eq. 4.8.2-2)

If the electrode exhibited purely resistive behaviour then the lag in the current response with respect to the voltage signal (quantified by the term φ) would be 0. In all other cases, including capacitive or in complex capacitive circuits, the quantity $\varphi \neq 0$. Pure capacitive behaviour will result in $\varphi=90^{\circ}$. Taking $E_{bias}=0$ for simplicity:

$$E(t) = E_o \cos(\omega t) = E_o \exp(j\omega t)$$
(Eq. 4.8.2-3)

$$I(t) = A\cos(\omega t - \varphi) = Aexp(j(\omega t - \varphi))$$
(Eq. 4.8.2-4)

$$Z = \frac{V}{I} = \frac{E_o}{A} \exp(j\varphi) = Z' + jZ''$$
(Eq. 4.8.2-5)

The plot of the imaginary vs real component of the measured impedance shown below in Figure 4.8.2-1 is called a Nyquist plot. Each point on the graph corresponds to a different frequency ω for the applied voltage signal and the corresponding measured current signal. The highest frequency points are clustered in the semi-circular feature on the left of the graph while the lowest frequency points are part of the near vertical line of the right of the graph.



Figure 4.8.2-1: Schematic Nyquist plot showing general features typically displayed by a pseudocapacitive electrode. 19

Some general comments on the features of the plot are possible without equivalent circuit modeling. The first feature of note is that at the highest frequencies on the left side of the plot the imaginary portion of the impedance goes to zero at a non-zero real impedance. This corresponds to the combined real resistance of the electrode system such as the ionic resistance of the electrolyte, the resistance of the active material and the contact resistance between the active material and the current collector [56]. The semi-circular feature at high frequencies is the result of the resistance to the faradaic reactions governing the pseudocapacitance which can be thought of as existing in parallel with the double layer capacitance. This feature is observed in a wide

range of materials that display pseudocapacitance such as RuO₂ [102], MnO₂ [103], and Co₃O₄ [104]. The medium frequency section of the plot is a transition region. It is a common feature observed in porous materials and arises principally because of the distribution of resistances the porous structure creates [105]. The near-vertical section of the Nyquist plot in the low frequency region corresponds to pure capacitive behaviour. The frequency at which pure capacitive behaviour is observed is of particular interest because it is informative of the electrodes power capability. Electrodes that have a higher transition frequency will maintain capacitive behaviour as well as charge storage capability at higher charge/discharge rates compared to those with a smaller transition frequency. This transition frequency can be readily observed by treating the electrode as a pure capacitance. This simplification makes no attempt to model the physical processes involved or separate the contributions of the pseudocapacitance vs double layer. The only objective is to obtain a figure of merit for the electrodes global performance, as was its original intention when devised by Miller [106]. The capacitance can be broken down into its real and imaginary components with the peak in the imaginary capacitance curve corresponding to the transition frequency [107].

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering

$$Z(\omega) = \frac{1}{j\omega C(\omega)} \text{ and } Z(\omega) = Z'(\omega) + jZ''(\omega)$$
 (Eq. 4.8.2-6)

$$C(\omega) = \frac{1}{j\omega(Z'(\omega) + jZ''(\omega))} * \frac{-Z''(\omega) - jZ'(\omega)}{-Z''(\omega) - jZ'(\omega)} = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} + \frac{-jZ'(\omega)}{\omega|Z(\omega)|^2}$$
(Eq. 4.8.2-7)

The real and imaginary components of the capacitance are then calculated by:

$$C(\omega) = C'(\omega) - jC''(\omega) \to C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2}, C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2}$$
(Eq. 4.8.2-8)
(Eq. 4.8.2-9)

All EIS measurements were conducted in the frequency range $0.01 \text{ Hz}-100 \times 10^3 \text{ Hz}$ with an AC voltage amplitude of 5 mV. The real and imaginary components of the capacitance were calculated according to Eq. 4.8.2-8 and Eq. 4.8.2-9 respectively.

4.8.3 Galvanostatic Cycling

In galvanostatic cycling the electrode is charged and discharged under constant current conditions. Beginning from Eq. 4.8.1-2:

$$I = C \frac{dV}{dt} \rightarrow \frac{dV}{dt} = \frac{I}{C}$$
(Eq. 4.8.3-1)

The current is held constant by the nature of the experiment. Assuming the capacitance is also constant i.e. as with cyclic voltammetry assuming the capacitance does not depend on the state of charge/voltage, then during charging:

$$\int_{0}^{V} dV = \frac{I}{C} \int_{0}^{t} dt \, \therefore \, V(t) = \frac{I}{C} t + integration \, constant \qquad (Eq. \, 4.8.3-2)$$

It is seen that under constant current conditions and with a capacitance that does not vary with the state of charge, the charge curve generated from a galvanostatic experiment should be linear. This will hold true for the discharge curve; the slope will simply be negative. This leads to the common jargon in supercapacitor literature of seeing a "pyramid" or "triangular" shape galvanostatic charge-discharge curve.



Figure 4.8.3-1: Schematic of galvanostatic curves for a capacitor. 20

The figure above shows an example of an electrode exhibiting such behaviour. The three curves represent three different current densities, with the blue curve having the lowest current and thus longest charge/discharge time. The vertical drop seen on the blue curve labelled "I-R Drop" is a common feature observed during galvanostatic cycling and is the voltage lost to the internal resistance of the electrode on discharge. The capacitance is calculated rather simply by rearranging the first equation and examining only the discharge curve. This prevents overestimation of the capacitance by accounting for the IR drop on discharge. dV/dt is just the slope of the curve.

$$C = \frac{I}{(dV/dt)_{discharge}}$$
(Eq. 4.8.3-3)

Galvanostatic cycling was performed at currents ranging from 3-50 mA. The current density depended on the specific device tested as they typically had electrodes of varied area. The maximum potential in a galvanostatic cycling protocol was visually determined as the potential where the charging curve deviated significantly from linearity. The slope of the discharge curve was determined by fitting a linear curve using Origin 8.1.

Chapter 5: Colloidal route for MnO₂-MWCNT composite through the formation of a Schiff base

5.1 Background and details of approach

For a colloidal processing technique of MnO₂ and MWCNT to be effective, a relatively uniform distribution of both components in the final composite needs to be obtained. This means that self aggregation of the components must be avoided. The components must somehow be dispersed and linked to avoid this self aggregation, otherwise the composite materials performance will be very poor. The specific methodology for dispersing and linking the MnO₂ particles and MWCNT however, is open for imaginative design. The strategy suggested here involves individual adsorption of dispersing agents onto MnO₂ and MWCNT. The dispersing agents are selected such that they contain particular functional groups that, when combined, will form a link called a Schiff base.

A Schiff base is defined as "Imines bearing a hydrocarbyl group on the nitrogen atom R2C=NR' ($R' \neq H$)" [108]. They are a subdivision of imines where only the group R₂, shown in Figure 5.1-1 below, is restricted from being a hydrogen atom.



Figure 5.1-1: General structure of an imine. R₂ is restricted from being a hydrogen atom in a Schiff base. 21

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering The carbon-nitrogen double bond is the defining feature of the Schiff base and imines in general. They can be formed via the reaction of an amine and aldehyde according to the following general reaction:

$$R - NH_2 + R' - COH \rightarrow R - N = CHR' + H_2O$$
 (Eq. 5.1-1)

Thus, if dispersing agents are selected for MnO₂ and MWCNT that contain such functional groups it is suggested that a Schiff base linkage could be formed between both components. This could potentially lead to a composite with reduced agglomeration and better mixing of the components; if they are bound together then they can't re-agglomerate. This kind of reaction was used recently in the fabrication of aerogels by chemically crosslinking hydrazide and aldehyde modified cellulose nanocrystals. [109], [110], and may have promise for transition metal based catalysts [111], [112].

As was mentioned in Section 2.10, organic dyes containing aromatic structure such as pyrocatechol violet and crystal violet were found to be excellent dispersing agents for carbon nanotubes. Expanding on this trend, the compound New Fuchsin was selected as a potential



Figure 5.1-2: Chemical structure of aromatic dispersing agents for MWCNT. A-pyrocatechol violet, B-crystal violet, C-New Fuchsin. 22

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering dispersing agent for carbon nanotubes in the Schiff base strategy. The chemical structure is shown along with pyrocatechol violet and crystal violet in Figure 5.1.2 above. It can be seen in Figure 5.1-2 that New Fuchsin contains the same aromatic backbone as pyrocatechol violet and crystal violet, but also contains the necessary -NH₂ groups for Schiff base formation.

Figure 5.1-3 shows a qualitative sedimentation test for 0.1 g L⁻¹ New Fuchsin in water. Without New Fuchsin present the MWCNT suspension in water is unstable and readily precipitates. In contrast, the MWCNT suspension containing 0.1 g L⁻¹ New Fuchsin still appeared stable after 48 hours. It is suggested that as with crystal violet [80], and benzyldimethylhexadecylammonium chloride [55], the adsorbed New Fuchsin imparts a positive charge to the MWCNT allowing for their dispersion.



Figure 5.1-3: Qualitative sedimentation test of carbon nanotubes dispersed with New Fuchsin after 48 hours. A - 0.1 g L⁻¹ New Fuchsin in water, B - 1 g L⁻¹ MWCNT in 0.1 g L⁻¹ New Fuchsin in water and C - 1 g L⁻¹ MWCNT in water. 23

With the dispersing agent for MWCNT containing $-NH_2$ groups the compound used to modify MnO_2 had to contain an aldehyde group to successfully form a Schiff base. As was discussed extensively in the literature review section above, chemicals containing a catechol structure can show strong adsorption on the surface of oxide particles, including MnO₂. Thus, one of the simplest molecules that satisfies the requirements of catechol structure with an aldehyde group was selected to modify MnO₂: 3,4-dihydroxybenzaldehyde, for which the structure can be seen in the overall process schematic, Figure 5.1-4 below. It should be noted that this compound likely only imparts minor steric stability to the MnO₂ suspension and was chosen instead for the presence of an aldehyde group and the possibility of strong adsorption on the MnO₂ particle surfaces.

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering



Figure 5.1-4: Schiff base MnO₂-MWCNT colloidal processing schematic. 24

5.2 Characterization of Schiff Base MnO₂-MWCNT composite

Characterization of MnO₂ synthesized via the reaction of aqueous KMnO₄ and 2propanol has been carried out in previous studies [113], [114]. The Schiff base MnO₂-MWCNT composite was investigated using SEM and FTIR. To compare the effectiveness of the Schiff base mixing procedure, MnO₂ and MWCNT were mechanically mixed and also investigated using SEM. The SEM results are shown in Figure 5.2-1 below.



Figure 5.2-1: A, C – Mechanically mixed MnO₂ and MWCNT, B, D – Schiff base MnO₂-MWCNT. MnO₂:MWCNT mass ratio is 4:1 for both composites. 25

Figure 5.2-1-A shows the mechanically mixed MnO₂-MWCNT composite at an original magnification of 15000X. The image shows a large bundle of MWCNT with agglomerates of MnO₂ particles appearing to sit at the surface of the MWCNT bundle or adjacent to it. Figure 5.2-1-C shows the same composite at an original magnification of 50000X. From this image it can be seen that the MnO₂ primary particle size is on the order of \sim 50 nm, consistent with previous investigations [113], [114]. A larger agglomerate of MnO_2 particles, roughly in the center of the image, appears to be resting on the surface of the MWCNT bundle, with little evidence of MnO₂ particle impregnation into the MWCNT bundle. Figure 5.2-1-B shows the Schiff base MnO₂-MWCNT composite at an original magnification of 15000X. The image appears to show a large cluster of agglomerated MnO_2 particles. The MnO_2 agglomerates seem to be on the order of 0.5-1 μ m in size. Careful inspection of this image reveals the presence of MWCNT jutting out from beneath the MnO₂ agglomerates. Figure 5.2-1-D shows the same composite at an original magnification of 50000X. As before, the primary MnO₂ particle size is on the order of ~50 nm with smaller agglomerates hundreds of nanometers in size now more obvious than in the previous image at 15000X. MWCNT are clearly visible and appear intimately mixed with the MnO_2 particles. In some areas, the MWCNT are seen traversing through and between the MnO_2 agglomerates. The quality of the mixing between the MnO_2 and MWCNT in the Schiff base composite is undoubtedly superior when compared to the mechanically mixed composite in Figure 5.2-1-C.

The Schiff base MnO₂-MWCNT composite was also investigated using FTIR. Figure 5.2-2 below was adapted from [115] and shows the FTIR spectra for: a-MnO₂ with adsorbed 3, 4-dihydroxybenzaldehyde and b-the Schiff base MnO₂-MWCNT composite. In the first curve, the adsorption peaks at 1630 and 1576 cm⁻¹ are accounted for by the C-C stretching vibrations of



Figure 5.2-2: FTIR spectra of: a-MnO₂ mixed with 3, 4-dihydroxybenzaldehyde and b-Schiff base MnO₂-MWCNT. Source: [115]. 26

the aromatic ring in 3, 4-dihydroxybenzaldehyde, potentially with some contribution from the C=O group [116], [85]. C-C vibrations and C-O vibrations contributed to the broad adsorption peak centered at 1384 cm⁻¹ [116], [85]. C-H bending vibrations are responsible for the adsorption peak at 1044 cm⁻¹ [116]. In the Schiff base curve, aromatic C-C vibrations are assigned to the adsorption peaks at 1634, 1578 and 1464 cm⁻¹. It is suggested that the broadening of the peak at 1634cm⁻¹ toward larger wavenumbers in the Schiff base curve vs the peak at 1630 cm⁻¹ in the first curve is due to the contribution of C=N stretching vibrations [117]. The peaks at 1329 and 1178 cm⁻¹ may be accounted for by C-N stretching vibrations [118]. The peaks at 1125 and 977 cm⁻¹ can be accounted for by C-H bending vibrations [119].

5.3 Electrochemical performance of Schiff base MnO₂-MWCNT composite.

The Schiff base MnO₂-MWCNT composite was used for the fabrication of single supercapacitor electrodes according to the details in Section 4.8. The electrodes were characterized using cyclic voltammetry and impedance spectroscopy in a three-electrode setup as outlined in Section 4.8. Figure 5.3-1 below shows a series of cyclic voltammograms for one such electrode. The electrode presented had a mass loading of 30.5 mg cm⁻².



Figure 5.3-1: A - Cyclic voltammograms of Schiff base MnO₂-MWCNT composite: $a - 5 \text{ mV s}^{-1}$, $b - 10 \text{ mV s}^{-1}$, $c - 20 \text{ mV s}^{-1}$, B – Gravimetric and C- Areal normalized capacitance vs scan rate. 27

As can be seen from Figure 5.3-1-A at scan rates from 2-10 mV s⁻¹ the cyclic voltammograms are essentially the characteristic box shape indicative of capacitive behaviour as was explained in detail in Section 4.8.1. The slight current inflections at the anodic and cathodic edges of the potential window are indicative of an irreversible process. However, these inflections are minor and tend to disappear after a few cycles as will be seen in the cycling stability voltammograms below. Figure 5.3-1-B is a plot of the calculated gravimetric capacitance vs scan rate for this electrode. The capacitance was calculated according to Eq. 4.8.1-3. At a scan rate of 2 mV s⁻¹ the

gravimetric capacitance was determined to be 144 (+18, -1) F g⁻¹, decreasing to 94 (+12, -1) F g⁻¹ at a scan rate of 100 mV s⁻¹. The corresponding areal normalized capacitance is shown in Figure 5.3-1-C. At 2 mV s⁻¹ the areal capacitance was calculated to be 4.4 (+0.5, -0.4) F cm⁻² decreasing to 2.9 ± 0.3 F cm⁻² at 100 mV s⁻¹. The capacitance clearly decreases with increasing scan rate which is typical of any real capacitive system that has internal resistance. The electrode maintains ~67% of its 2 mV s⁻¹ capacitance at the fast scan rate of 100 mV s⁻¹.



Figure 5.3-2: Impedance data for Schiff base MnO₂-MWCNT composite. 28

Figure 5.3-2 above is a compilation of the measured impedance and capacitive performance calculated using impedance data. Figure 5.3-2-A shows the Nyquist plot for the Schiff base composite electrode. A very small semi-circular feature can be seen at high frequencies, shown magnified in the right-hand corner of the Nyquist plot. At higher frequencies, the plot moves toward an essentially vertical segment indicative of capacitive behaviour. At all frequencies, the real component of the measured impedance, corresponding to classic electrical resistance, is seen to be exceptionally low, < 0.5 Ω . The real component of the complex capacitance, plotted as a function of frequency in Figure 5.3-2-B, shows good agreement with the capacitance calculated using cyclic voltammetry. The capacitance hovers around 4 F cm⁻² at

low frequencies, before falling off to essentially 0 at high frequencies, mimicking the decline in capacitance with increasing scan rate in the cyclic voltammetry measurements. The imaginary component of the complex capacitance is plotted as a function of frequency in Figure 5.3-2-C. The plot exhibits a maximum between the frequencies 0.09 and 0.16 Hz., corresponding to the transition to capacitive behaviour as was discussed in Section 4.8.2.

Figure 5.3-3 below is a plot of the cycling stability of this material at a scan rate of 50 mV s⁻¹ out to 5000 cycles along with three selected cyclic voltammograms during cycling. As can be seen from Figure 5.3-3-A the material retains 82% of its initial capacitance on the 5000th cycle. There is virtually no capacitance fade until the 2500th cycle where there is a drop of ~7%.



Figure 5.3-3: A – capacitance retention versus cycle number and B – 1^{st} , 2500th and 5000th cyclic voltammogram for the Schiff base MnO₂-MWCNT composite. Arrow indicates increasing cycle number 29

After this abrupt drop the capacitance fades a further 7% over the remaining 2500 cycles to the final retention of 82%. Figure 5.3-3-B shows the cyclic voltammograms for the 1st, 2500th and 5000th cycle. There is some change between the 1st and 2500th cycle with the 2500th voltammogram being slightly wider, but with a decreased peak current response. These two

features evidently cancel out since the integrated area (and thus capacitance) is unchanged between the 1st and 2500th cycle. The 5000th voltammogram, however has a noticeably reduced width and peak current response compared to the 1st and 2500th voltammogram. It is unclear whether the capacitance would stabilize with further cycling, however 82% retention after 5000 cycles is already a promising result.

The CV and galvanostatic curves for an asymmetric device, assembled using Schiff base MnO₂-MWCNT as the positive electrode material and AC-CB as the negative electrode material, is shown in Figure 5.3-4 below. The active area for the positive electrode measured ~1 cm X 1.3 cm with a mass loading of 40.3 mg and the active area of the negative electrode measured ~2 cm X 1.7 cm with a mass loading of 111.5 mg. Based on the measured gravimetric capacitances at 2 mV s⁻¹ of both these materials then, according to Eq. 2.12-1, $C_{+ve} = 5.8$ F and $C_{-ve} = 7.5$ F. These electrodes had a %difference in capacitance of 26%.

As can be seen from Figure 5.3-4-A, at scan rates from 5-20 mV s⁻¹ the asymmetric device displays the characteristic box shape indicative of capacitive performance. The operating voltage was limited to 1.6 V as at greater voltages a prominent current tail was observed on the anodic scan. This is less than the expected 1.8 V voltage window based on the individual potential windows of the positive and negative electrode materials when measured in a three-electrode configuration. The device capacitance decreases from 2.6 F at 2 mV s⁻¹ to 1.1 F at 100 mV s⁻¹, a retention of 42%, as can be seen in Figure 5.3-4-B. Selected galvanostatic curves are shown in Figure 5.3-4-C. Each of the curves is essentially symmetric and triangular in shape which, like the cyclic voltammograms, indicates the device is behaving as a capacitor. A very small voltage drop can be seen on the 5 mA curve which gets progressively larger as the current increases. This is to be expected as energy dissipated through any resistance (in this case the



Figure 5.3-4: Performance composite for Schiff base MnO₂-MWCNT/AC-CB asymmetric device, A- cyclic voltammograms: $a - 5 \text{ mV s}^{-1}$, $b - 10 \text{ mV s}^{-1}$, $c - 20 \text{ mV s}^{-1}$, B - capacitance calculated from CVs vs scan rate, C – galvanostatic curves: a - 30 mA, b - 10 mA, c - 5 mA, D – capacitance calculated from galvanostatic curves vs applied current. E – Energy calculated from galvanostatic curves vs applied current. 30

The capacitance calculated from the galvanostatic curves agrees well with the capacitance calculated from the cyclic voltammograms. At a scan rate of 5 mV s⁻¹ the average current response is ~10 mA and the capacitance was calculated to be 2.5 F, while the capacitance calculated from the 10 mA galvanostatic curve was 2.8 F. At a scan rate of 20 mV s⁻¹ the average

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering current response is ~50 mA with a calculated capacitance of 2.1 F while the capacitance calculated from the 50 mA galvanostatic curve was 2.3 F. The galvanostatic curves make calculation of the device energy relatively simple since the voltage can be read directly from the curve. Using Eq. 2.1-2 (E=0.5*C*V²) where V is the voltage after the initial IR drop, the device energy was calculated and plotted vs current in Figure 5.3-4-E. The device has an energy of 4.3 J at a current of 3 mA, decreasing to 2.2 J at 50 mA. The device energy decays faster than the capacitance since the energy calculation directly accounts for the loss due to the IR drop while the slope of the discharge curve is less sensitive to this drop. For perspective, when compared to the Energizer AX92 AAA alkaline battery [120] on a per volume basis at similar discharge currents and assuming minimal packaging, this device only has approximately 0.5% of the energy density. When compared to the rechargeable Energizer NH12-500 AAA nickel metal hydride battery [121], this device has only approximately 1% of the volumetric energy density.

Figure 5.3-5 below is another performance composite for the Schiff base MnO₂-MWCNT/AC-CB asymmetric device showing the device impedance and cycling stability.



Figure 5.3-5: Second performance composite for Schiff base MnO₂-MWCNT/AC-CB asymmetric device, A – device Nyquist plot, B – cycling stability. 31

As can be seen from Figure 5.3-5-A the near vertical section of the impedance only occurs for very low frequencies. At high frequencies (inset) a semicircular feature is visible, followed by an \sim 45° medium frequency region indicative of diffusion control. The device resistance at the lowest measured frequency of 0.01 Hz was 2.3 Ω , which is a good approximation of the DC resistance of the device, an often-reported feature for supercapacitors. The device was cycled galvanostatically 1000 times at a current of 50 mA. As can be seen in Figure 5.3-5-B the device quickly lost charge storage capacity over the first 500 cycles, followed by a slower decay to a final retention of 50% after 1000 cycles. This degradation may be the result of the positive and negative electrodes having too large a disparity in capacitance during device fabrication. It may also be the result of poor matching of the electrodes at the current density used for cycling stability. Based on the gravimetric capacitances at 20 mV s⁻¹, which closely matches the current density of 50 mA for the device, the positive electrode would have a capacitance of 5.2 F while the negative electrode would have a capacitance of 7.0 F. This corresponds to a 30% difference in the capacitance of the positive and negative electrodes.

5.4 Conclusion

A MnO₂-MWCNT composite was produced using a new colloidal processing strategy. MnO₂ particles were modified with 3,4-dihydroxybenzaldehyde and MWCNT were dispersed with New Fuchsine. An adsorption and dispersion mechanism was suggested for New Fuchsine modified MWCNT based on previous investigations of similarly structured dyes. Both additives were selected for the potential to form a Schiff base linkage between the MnO₂ and MWCNT with the goal of improving the mixing of these components. The composite was studied using FTIR which offered some evidence for the formation of a Schiff base. Imaging using SEM M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering revealed that the Schiff base composite had, qualitatively, far greater mixing of the MnO₂ particles and MWCNT compared with a mechanically mixed composite.

The composite was used as the active material in supercapacitor electrodes. It was tested alone in a three-electrode configuration and displayed the characteristic features of a capacitor in cyclic voltammetry and impedance spectroscopy tests. The individual electrodes displayed excellent capacitive performance with a mass normalized capacitance of 144 (+18, -1) F g⁻¹ and areal normalized capacitance of 4.4 (+0.5, -0.4) F cm⁻² at a scan rate of 2 mV s⁻¹ and mass loading of 30.5 mg cm⁻². The performance decreased to 94 (+12, -1) F g⁻¹ / 2.9 ± 0.3 F cm⁻² at a scan rate of 100 mV s⁻¹, a retention of ~66%. This electrode had between 3-30 times the mass loading, with superior areal capacitance to all and greater rate performance than virtually all of the high mass loading electrodes tabulated by Ramirez-Castro et al. [68] (see Section 2.9).

The composite was used as the active material for the positive electrode in an asymmetric supercapacitor device, paired with an AC-CB negative electrode. The fabricated device displayed the characteristic electrical features of a capacitor in cyclic voltammetry and galvanostatic cycling experiments up to a voltage of 1.6 V. The device had a capacitance greater than 2.5 F at low scan rates/current densities with relatively good agreement in the capacitance values calculated from the cyclic voltammetry and galvanostatic curves. The device stored between 4.3 J and 2.2 J of energy at testing currents of 3 mA-50 mA. The resistance of the device was greater than 2 Ω at low frequencies in impedance spectroscopy tests and only had a capacitance retention of 50% after 1000 galvanostatic cycles at a test current of 50 mA. Unfortunately, all of these metrics make this device inferior to comparable supercapacitor devices that are currently commercially available [122], however not by a wide margin. A dedicated effort towards device optimization might reduce this disparity in performance.

76

Chapter 6: Use of liquid-liquid extraction for the colloidal assembly of MnO₂-MWCNT composites

6.1 Background and details of approach

Colloidal processing strategies using MnO_2 powders that have been dried will inevitably be limited by agglomeration due to the drying process. The final product will be a series of large, hard agglomerates composed of much smaller, densely packed primary particles. The synthesis technique used for MnO_2 in the previous chapter, i.e. reaction of aqueous KMnO₄ with isopropanol, is similar to the common sol-gel procedures for the synthesis of SiO₂ by the condensation reaction of Si-alkoxides with water in that both procedures result in an amorphous oxide gel with pores occupied by solvent. In addition to the morphology of the product oxide after drying, the final porosity and electrochemical properties depends on the drying procedure employed [123], [124], [125]. Harreld, Dong and Dunn [124] proposed that the capillary pressure generated within a pore by the surface tension of the occupying solvent as well as solidliquid interface van der Waals interactions were responsible for the pores collapse, or lack thereof, when the solvent is removed. This is why the greatest porosities are achieved when drying is performed with supercritical CO_2 [125]; it has zero surface tension and theoretically very minimal solid-liquid interfacial van der Waals interactions because of its molecular structure. The proposed limitation is highlighted schematically in Figure 6.1-1 below.

It is suggested that the agglomeration associated with drying will lead to greater inaccessibility of any conductive additive added to the composite. Even with the aid of dispersing agents the hardest of agglomerates may not be broken, due to the formation of

77



Figure 6.1-1: Schematic of primary particle agglomeration due to drying. 32

oxo-bridges during this step, meaning that the region within the hard agglomerate will act as electrochemical dead weight. Improved mixing could theoretically be achieved if all processing was performed prior to the drying step. This reasoning led to the development of a liquid-liquid extraction technique to mix the MnO_2 and MWCNT, shown schematically in Figure 6.1-2 below.



Figure 6.1-2: Schematic of the liquid-liquid extraction and colloidal processing of MnO₂-MWCNT composites. 33

The technique involves the use of two liquids with limited miscibility, in this case water and 1butanol. Aqueous KMnO₄ oxidizes the 1-butanol as with 2-propanol and other primary or secondary alcohols, resulting in the formation of amorphous MnO₂. Because of its lower density, the 1-butanol rich phase sits on top of the water rich phase. Next, an extracting/dispersing agent

is added to the system to break apart the soft gel sitting in the water rich phase and disperse it in the 1-butanol rich phase. The extractor/dispersant in this case is a compound called lauryl gallate, the chemical structure of which can be seen in Figure 6.1-2. A few comments about this compound are warranted to explain its selection and the mechanism for its action in the system. Lauryl gallate is a derivative of gallic acid or 3,4,5-trihydroxybenzoic acid. The three adjacent hydroxyl groups present on the benzene ring of the gallate structure allow for the same kind of adsorption on the surface of oxide particles as compounds with a catechol structure. This was confirmed for gallic acid specifically [81]. The long alkyl chain substituted on the carboxylic acid group of gallic acid in deriving lauryl gallate makes this compound insoluble in water, but soluble in 1-butanol and other alcohols. However, the hydroxyl groups of lauryl gallate remain hydrophilic, independent of the alkyl chain. As a result, when lauryl gallate is added to the 1butanol/aqueous system any lauryl gallate near the 1-butanol/water interface will arrange itself such that the hydrophilic hydroxyl groups face towards the aqueous phase while the hydrophobic alkyl chain faces toward the organic 1-butanol phase. This can be seen schematically in Figure 6.1-2. When the system is agitated using ultrasonication, the MnO₂ particles initially settled in the aqueous phase that find themselves at the 1-butanol/water interface can interact with the hydrophilic hydroxyl groups of the lauryl gallate present at the interface. Subsequently, the lauryl gallate can adsorb onto the surface of the MnO₂ making the surface of the particle now hydrophobic, whereas before it was hydrophilic. The result is that the particles become extracted to the 1-butanol phase. The long alkyl chain of lauryl gallate serves to provide some steric stabilization of the MnO₂ particles now extracted to the 1-butanol phase, forming a relatively stable suspension. The extraction process is somewhat analogous to float-fishing, where the particles are the fish, the hydroxyl groups of lauryl gallate are the hook sitting just below the

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering surface which is prevented from sinking by the floater, the hydrophobic interaction of the alkyl chain. When agitated, without lauryl gallate being present, the oxide particles simply settle back to the aqueous phase and don't pass the 1-butanol/water interface. This is shown in the two images in Figure 6.1-3 below, taken after the extraction process.



Figure 6.1-3: Images showing the extraction of MnO₂ particles from the water rich to the 1butanol phase. Photographs from Source: [126]. 34

After extracting the MnO₂ to the 1-butanol phase MWCNT are added and the system is further ultrasonically agitated to mix both components. The long hydrophobic alkyl chain of lauryl gallate will tend to interact with the graphitic structure of the MWCNTs as with other long chain surfactants. This forms a link between the two components in the 1-butanol phase. Heterocoagulation was observed when dispersions of MnO_2 and MWCNT in an ethanol-water solvent containing lauryl gallate were mixed [127], supporting this idea.

6.2 Characterization of Liquid-Liquid Extraction MnO₂-MWCNT composite

Before mixing with MWCNT, the MnO₂ synthesized via reaction of aqueous KMnO₄ with 1-butanol was characterized by SEM, TEM and XRD. The interaction with lauryl gallate was also determined using FTIR. Figure 6.2-1 below shows a compilation of these four characterization techniques. All images in Figure 6.2-1 are as they appear in [126].

Figure 6.2-1-A below shows a high magnification SEM image of the MnO₂ synthesized via reaction of aqueous KMnO₄ with 1-butanol. Large interconnected agglomerates of what appears to be barely resolved fine particles can be seen in this image. The TEM image in Figure 6.2-1-B shows that the material is composed of fine agglomerates of nanoparticles with the agglomerates being roughly 50nm in size. Darker nano-flakes can be seen within the fine agglomerates. The selected area diffraction pattern is featureless, indicating that the material is amorphous. A high-resolution TEM image of the 1-butanol MnO₂ is shown in Figure 6.2-1-C. The circled areas in Figure 6.2-1-C highlight what appears to be nanocrystals in an otherwise amorphous matrix. These nanocrystals are on the order of 5nm in size. The XRD profile in Figure 6.2-1-D shows very weak diffraction peaks. These peaks can all be indexed to the diffraction card JCPDS 87-1497 for birnessite MnO₂. The weak intensity and broadness of the peaks indicates that the material is essentially amorphous, consistent with the selected area diffraction pattern and TEM observations in Figure 6.2-1-B, Figure 6.2-2.



Figure 6.2-1: A-SEM image of MnO₂, B-TEM image of MnO₂, inset is the selected area electron diffraction pattern, C-High resolution TEM image of 1-butanol MnO₂. Circled areas were used to estimate the size of the MnO₂ nanocrystals, D-XRD of MnO₂, chevrons correspond to JCPDS 87-1497. All images from Source: [126]. 35

The adsorption mechanism of lauryl gallate on the synthesized MnO₂ particles was investigated using FTIR, Figure 6.2-2. All band assignments are based on previous studies of the adsorption of cetyl gallate [128], octyl gallate [129] and lauryl gallate [130] on TiO₂ particles. The red curve in Figure 6.2-2 corresponds to pure lauryl gallate. Four peaks of particular importance occur at 3447, 3343, 2914 and 2847 cm⁻¹. The first two peaks at 3447 and 3343 cm⁻¹ can be assigned to the stretching vibrations of the phenolic -OH groups. The peaks at 2914 and M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering 2847 cm⁻¹ can be assigned to the stretching vibrations of the C-H bonds in the alkyl chain. The black curve of Figure 6.2-2 corresponds to the MnO_2 that was extracted using lauryl gallate. The peaks corresponding to the -OH stretching vibrations in lauryl gallate are absent while the peaks corresponding to the alkyl chain C-H bonds are still present and slightly shifted.



Figure 6.2-2: FTIR spectra of: a-pure lauryl gallate and b-MnO₂ extracted using lauryl gallate. 36

The remaining peaks in the range $1800-800 \text{ cm}^{-1}$ are seen to either disappear or become significantly broadened/shifted in the extracted MnO₂ material compared to pure lauryl gallate. This same behaviour was observed when cetyl [128], octyl [129] and lauryl [130] gallate were adsorbed on the surface of TiO₂ particles. This is consistent with the -OH group mediated adsorption mechanism shown in Figure 6.1-3.

After mixing with MWCNT, the MnO₂-MWCNT composite was investigated using SEM and TEM. Figure 6.2-3 below shows two SEM and two TEM images of the composite. The SEM image in Figure 6.2-3-A is at an original magnification of 30000X. At this magnification, it is just possible to resolve very fine particles of MnO₂. MWCNT are clearly visible.



Figure 6.2-3: A, B – SEM images of L-L extraction MnO₂-MWCNT. Image credit: Patrick Wojtal. C, D – TEM images of L-L extraction MnO₂-MWCNT, Source: [127]. 37

There appear to be areas where the MnO_2 particle surround the MWCNT in what looks almost like a foam, and other areas where the MWCNT appear essentially bare. At the original

magnification of 50000X, Figure 6.2-3-B, individual particles on the order of 10nm can be resolved, clumped together in larger agglomerates on the order of 100 nm. The MnO₂ is far less agglomerated compared to the as-synthesized condition, Figure 6.2-1-A. The TEM images in Figure 6.2-3-C, D support the SEM observation. MWCNT, both within an MnO₂ matrix and bare can be clearly resolved. The MnO₂ particles appear to be 10s of nanometer in size, clustering in larger agglomerates on the order of 100nm around the MWCNT. The arrows in Figure 6.2-3-C indicate MWCNT. The arrows in Figure 6.2-3-D indicate what appears to be fibrous MnO₂. This is based on the absence of a clear hollow structure and the presence of what seems to be lattice fringes through the thickness of the fibre. This morphology was not seen in the TEM image of the pure material (Figure 6.2-1-B) and is thus noted here.

6.3 Liquid-Liquid Extraction MnO₂-MWCNT electrode

characterization

The composite MnO₂-MWCNT materials produced via liquid-liquid extraction were used to fabricate supercapacitor electrodes. The composite prepared using KMnO₄ as the manganese source was investigated at different mass loadings and using different current collectors. This composite was also used in the fabrication of asymmetric devices.

Figure 6.3-1 below shows typical CVs of the L-L extraction composite synthesized using KMnO₄ as well as its cycling stability at a scan rate of 20 mV s⁻¹. The CVs in Figure 6.3-1-A, ranging in scan rate from 5-20 mV s⁻¹, are essentially box-shaped indicating the electrode is behaving electrically as a capacitor. A slight current inflection is seen at potentials more anodic than roughly 0.8 V vs SCE followed by what appears to be a slight reduction peak on the cathodic scan. These features appear to be reduced after cycling. Figure 6.3-1-B shows the
M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering capacitance retention vs cycle number. After 1000 cycles the retention is 99%. The retention is quite stable with each data point only fluctuating by $\pm 2\%$ about 100%. Figure 6.3-1-C shows the cyclic voltammograms for the 1st and 1000th cycle. The only feature of note is the slight reduction in peak anodic current and slight increase in peak cathodic current on the 1000th cycle compared to the 1st. It is unclear if the performance would remain consistently stable after further cycling.



Figure 6.3-1: Performance composite of liquid-liquid extraction MnO_2 -MWCNT composite using KMnO₄ as the manganese source. A – selected cyclic voltammograms: $a - 5 \text{ mV s}^{-1}$, $b - 10 \text{ mV s}^{-1}$, $c - 20 \text{ mV s}^{-1}$, B - cycling stability, $C - a - 1^{st}$ and $b - 1000^{th}$ cyclic voltammogram of cycling stability test. 38

The liquid-liquid extraction MnO₂-MWCNT composite synthesized using KMnO₄ was compared at two different mass loadings and at roughly the same mass loading on two different current collectors, regular nickel foam and graphene coated nickel foam. The gravimetric and areal normalized capacitances for these electrodes are compared in Figure 6.3-2 below. Figure 6.3-2-A, B compare the same material on a regular nickel foam current collector at a mass loading of 28.0 mg cm⁻² (blue) and 48.4mg cm⁻² (red). As can be seen in Figure 6.3-2-A the mass loading has little effect on the gravimetric capacitance at scan rates between 2 mV s⁻¹ and 50 mV s⁻¹ which are indistinguishable within experimental error. However, at the highest scan rate of M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering 100 mV s⁻¹ there is a more significant separation with the 28.0 mg cm⁻² having a gravimetric capacitance of 80 (+9, -1) F g⁻¹ and the 48.4 mg cm⁻² having a gravimetric capacitance of 60 (+7, -1) F g⁻¹ corresponding to capacitance retentions of 54% and 40% respectively. This is consistent



Figure 6.3-2: A - Gravimetric capacitance comparison for different mass loadings on regular nickel foam current collectors (a - 48.4 mg cm⁻², b - 28.0 mg cm⁻²), B - Areal capacitance comparison for different mass loadings on regular nickel foam current collectors (a - 28.0 mg cm⁻², b - 48.4 mg cm⁻²) C, D – Gravimetric: C, and areal: D, capacitance comparison on different current collectors at the similar mass loadings (a – regular nickel foam, 28.0 mg cm⁻², b – graphene coated nickel foam, 31.6 mg cm⁻²). 39

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering with the general trend outlined in the literature review of decreasing gravimetric capacitance with increasing mass loading. However, the performance in this case is exceptional since this effect is only observed at the highest scan rate and very high mass loadings. Generally, the decrease in rate performance due to increasing mass loading would also be seen at lower scan rates, not just the fast scan rate of 100 mV s⁻¹. This effect was described in Section 2.9 of the literature review. Because the gravimetric capacitance does not decrease appreciably with mass loading, remarkably high areal capacitances are possible.

Figure 6.3-2-B show the areal normalized capacitances for the 48.4 mg cm⁻² (red) and 28.0 mg cm⁻² (blue) electrodes. The areal capacitance of the 48.4 mg cm⁻² electrode decreases from the incredibly high value of 7.2 (+0.8, -0.7) F cm⁻² at a 2 mV s⁻¹ scan rate to 2.9 \pm 0.3 F cm⁻² at 100 mV s⁻¹. At the same scan rates, the 28.0 mg cm⁻² electrode has capacitances of 4.2 (+0.5, -0.4) F cm⁻² and 2.2 (+0.3, -0.2) F cm⁻² respectively. The 48.4 mg cm⁻² electrode just barely outperforms the 28.0mg cm⁻² electrode within experimental error at 100 mV s⁻¹, but drastically outperforms it at all lower scan rates in terms of areal capacitance. It is suggested that the small particle size and excellent mixing of the MnO₂ and MWCNT using the liquid-liquid extraction technique is responsible for the unusually high performance at such large mass loadings.

Figure 6.3-2-C, D shows the gravimetric and areal capacitance of the same composite material at roughly the same mass loading on graphene coated (red, 31.6 mg cm⁻²) and regular (blue, 28.0 mg cm⁻²) nickel foam current collectors. The 28.0 mg cm⁻² electrode data in Figure 6.3-2-C, D is the same as that in Figure 6.3-2-A, B. There appears to be a capacitance boost at all scan rates for the graphene coated nickel foam over regular nickel foam, however the boost is only outside of experimental error at the higher scan rates of 50 mV s⁻¹ and 100 mV s⁻¹. At these higher scan rates, the regular nickel foam electrode has capacitances of 120 (+14, -1) F g⁻¹/ 3.4

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering

(+0.4, -0.3) F cm⁻² and 80 (+9, -1) F g⁻¹/ 2.3 (+0.3, -0.2) F cm⁻² while the electrode with the graphene coated nickel foam current collector has capacitances of 142 (+17, -1) F g⁻¹/ 4.5 (+0.5, -0.4) F cm⁻² and 101 (+12, -1) F g⁻¹/ 3.2 (+0.4, -0.3) F cm⁻². This corresponds to a 18% and 26% boost in performance for the graphene coated nickel foam current collector electrode at 50 mV s⁻¹ and 100 mV s⁻¹ respectively. Even more intriguing, this electrode maintains 94% of its 2 mV s⁻¹ capacitance at 50 mV s⁻¹. This drops to 67% at 100 mV s⁻¹, which is still superior to regular nickel foam which only maintains 54% of it 2 mV s⁻¹ performance. It is suggested that the graphene coating on the nickel foam reduces the contact resistance between the active material and current collector [127]. This would naturally lead to an overall reduction in system resistivity and thus a boost in performance, particularly at higher scan rates.



Figure 6.3-3: Comparison of impedance performance for the regular nickel foam and graphene coated nickel foam electrodes. Black/a – regular nickel foam, 28.0 mg cm⁻², Red/b – graphene coated nickel foam, 31.6 mg cm⁻², Blue/c – regular nickel foam 48.4 mg cm⁻². A – Nyquist plots, B – Complex capacitance versus frequency. 40

Figure 6.3-3 above is a comparison of the EIS data for the three electrodes discussed in the previous paragraphs. As can be seen from Figure 6.3-3-A all three electrodes display the low frequency vertical region characteristic of capacitive behaviour. The inset shows that the graphene coated current collector electrode has the smallest diameter for the high frequency faradaic charge transfer semi-circular feature. The real component of its impedance is comparable to the 48.4 mg cm⁻² regular nickel foam electrode. The reduction in real resistance of this electrode over the lower 28.0 mg cm⁻² is likely due to the much higher volume of carbon nanotubes present in the former. Figure 6.3-3-B is a plot of the complex capacitance vs frequency for the three electrodes. For both mass loadings on the regular nickel foam current collector the maximum in complex impedance occurs at essentially the same frequency, ~0.09 Hz. There is a visible shift in this peak to higher frequencies for the graphene coated current in rate performance discussed previously, Figure 6.3.2-C.

The MnO₂-MWCNT composite prepared via liquid-liquid extraction was used as the positive electrode material in the construction of an asymmetric device with AC-CB serving as the negative electrode material. The positive electrode had dimensions of ~1 X 1 cm with a mass loading of 26.4 mg while the negative electrode had dimensions of ~1.3 X 1.3 cm with a mass loading of 44.9 mg. This corresponds to a capacitance of $C_{+ve}=3.6$ F and $C_{-ve}=2.8$ F at a scan rate of 20 mV s⁻¹, a percent difference of 25%. Figure 6.3-4 below is a performance composite for the asymmetric device. As can be seen in Figure 6.3-4-A the galvanostatic curves are essentially triangular and symmetric up to a potential of 1.6 V. As with the Schiff base asymmetric device this is lower than the expected 1.8 V based on the potential windows of the positive and negative electrode materials determined in the three-electrode set-up. The capacitance calculated from the

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering slope of the discharge curves vs set current is presented in Figure 6.3-4-B. The capacitance falls quickly from 1.8 F at a current of 3 mA before becoming relatively stable. At 50 mA the capacitance is still 1.5 F. Figure 6.3-4-C shows the device energy calculated from the

galvanostatic curves vs the set-current. The device registers an energy of 2.3 J at a current of



Figure 6.3-4: Performance composite for the liquid-liquid extraction MnO_2 -MWCNT/AC-CB asymmetric device. A – selected galvanostatic curves, a – 30 mA, b – 10 mA c – 5 mA, B – capacitance and C – energy calculated from galvanostatic curves. 41

3 mA, falling by close to 50% to 1.3 J at a current of 50 mA. As with the Schiff base device, the energy decays far more quickly than the capacitance due to an increased sensitivity to the IRdrop. Figure 6.3-5 below shows that devices constructed from liquid-liquid extraction MnO₂/AC-CB are capable of storing a useable amount of energy. Three ~1 F button cell capacitors were fabricated, charged to 1.5 V and stacked in series to power the 13 blue LED display shown in Figure 6.3-5. The button cell stack powered the display for two hours before it was disassembled.



Figure 6.3-5: 13 blue LED display powered by liquid-liquid extraction MnO_2 -MWCNT/AC-CB button cell stack. A – Initial, B – 1 hr of operation, C – 2 hr of operation. 42

6.4 Conclusion

A new colloidal processing strategy was developed in an attempt to reduce the detrimental effects of particle agglomeration during the production of MnO₂-MWCNT composites. MnO₂, synthesized via the reduction of aqueous KMnO₄ with 1-butanol, was extracted to the 1-butanol phase after synthesis using lauryl gallate as an extracting and dispersing agent. The as-synthesized MnO₂ was investigated using SEM, TEM and XRD. These techniques revealed that the MnO₂ consisted of poorly crystalline agglomerates of very fine primary particles. A mechanism for the adsorption of lauryl gallate onto MnO₂ and its subsequent extraction to the organic 1-butanol phase was proposed. The proposed mechanism was supported by FTIR analysis. MWCNT were added to the extracted MnO₂ colloid to produce a liquid-liquid extraction MnO₂-MWCNT composite. Previous investigations had demonstrated that lauryl gallate was also able to disperse MWCNT through a suggested hydrophobic interaction. Lauryl gallate thus acted as a co-dispersant/linking agent between MnO₂ and MWCNT. The composite material was investigated using SEM and TEM. These techniques revealed significant reduction in the MnO₂ agglomeration over the as-synthesized condition and excellent mixing between MnO₂ and MWCNT.

The composite was used to fabricate supercapacitor electrodes using regular and graphene coated nickel foam current collectors. When tested in a three-electrode configuration in aqueous Na₂SO₄ the electrodes displayed the characteristic electrical response of a capacitor. The composite was found to be relatively stable under cycling, maintaining 99% of initial capacitance after 1000 cycles at a scan rate of 20 mV s⁻¹, with only minor changes in the cyclic voltammograms. The composite also maintained high performance over a large range of mass loadings. The gravimetric capacitance of an electrode with the already high mass loading of 28.0

92

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering $mg cm^{-2}$ was maintained up to a scan rate of 50 mV s⁻¹ even at the markedly high mass loading of 48.4 mg cm⁻². This 48.4 mg cm⁻² electrode displayed an exceptionally high areal normalized capacitance of 7.2 (+0.8, -0.7) F cm⁻² at low scan rates. Graphene coated nickel foam was found to enhance the performance of the composite electrode at elevated scan rates. An increase of 18% and 26% at scan rates of 50 mV s⁻¹ and 100 mV s⁻¹ was registered for a graphene coated nickel foam current collector electrode compared to an electrode of similar mass loading using regular nickel foam as the current collector. A shift in the imaginary capacitance maximum to a higher frequency for the graphene coated nickel foam electrode was also found, and is consistent with the boost in performance observed at elevated scan rates in the cyclic voltammetry tests. At a mass loading between 3-30 times greater, this electrode displayed far superior areal capacitance than all with better rate performance than almost all of the of the high mass loading electrodes compiled by Ramirez-Castro et al. [68]

The liquid-liquid extraction MnO₂-MWCNT composite was used as the positive electrode material for an asymmetric device in combination with an AC-CB negative electrode. The device exhibited relatively symmetric, triangular galvanostatic curves, an indication of capacitive behaviour, up to a voltage of 1.6 V. The device capacitance decreased from 1.8 F at a current of 3 mA to 1.5 F at a current of 50 mA while the energy stored in the device decreased from 2.3 to 1.3 J at the same current levels. Three 1 F button cells were fabricated from the same electrode materials and used to power an LED display, demonstrating that the devices stored a useable amount of energy. However, like the Schiff base asymmetric device, these devices were found to be inferior to commercially available supercapacitors based on activated carbon and organic electrolytes [122]. Device optimization, particularly careful electrode balancing and an operational voltage window increase, would be required to obtain comparable performance.

Chapter 7: Use of V₂O₃ as the electrochemically active material for supercapacitor electrodes

7.1 Background and details of approach

The incredibly low intrinsic electrical conductivity of MnO₂ will always limit performance regardless of efforts to incorporate conductive additives. The high performance pseudocapacitive material RuO₂, mentioned in the literature review section, can partially attribute its superb performance to its high intrinsic electrical conductivity [131]. It thus seems reasonable to explore alternatives that do not have the inherent conductivity disadvantage of MnO₂.

In selecting an appropriate material that satisfies this conductivity criteria, but also demonstrates pseudocapacitance, Conway offered some guidance in his seminal textbook [23]. He pointed out that in order for a material to exhibit pseudocapacitance there must be at least two available, stable redox states. In the case of MnO₂ these are Mn³⁺/Mn⁴⁺, as was discussed extensively in the literature review section, and for RuO₂ there are at least two redox couples, possibly three, corresponding to four stable redox states, Ru²⁺/Ru³⁺, Ru³⁺/Ru⁴⁺ and Ru⁴⁺/Ru⁶⁺ [132]. Quick inspection of a periodic table shows that many of the transition metals satisfy this criterion. Some can be excluded almost immediately such as the platinum group metals due to prohibitively high cost. Others do not have multiple redox states within the electrochemical stability window of water. Nb is one example [91], briefly described in the section on organic electrolytes in the literature review. However, this still leaves a large group of elements such as V, Fe, Co, Mo and W which could exhibit pseudocapacitance simply based on the availability of

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering multiple redox states. Indeed, Conway observed a pseudocapacitive response in hydrous oxide films grown electrochemically on the surface of metallic Co, Mo and W electrodes [23], [133].

Of the various candidate elements, V is particularly promising. It can exist in oxidation states from 2+ to 5+ and has very rich aqueous chemistry. In contrast to elements such as Mo and W, V based compounds have been investigated thoroughly for supercapacitor applications, with demonstrated performance in both positive and negative voltage windows. Indeed, in some of the earlier pseudocapacitor publications, Lee and Goodenough were investigating the capacitive response of amorphous hydrated V_2O_5 [33] within a couple years of their investigations of amorphous hydrated MnO₂ [27]. V_2O_5 unfortunately also has very low intrinsic electrical conductivity, and has already been investigated extensively for supercapacitor applications.

The compound vanadium sesquioxide, V_2O_3 demonstrates the desired high electrical conductivity. This oxide adopts the corundum crystal structure and undergoes a metal-insulator transition from an antiferromagnetic insulator to paramagnetic metal at approximately 150°K [134], well below room temperature. It exhibits electrical conductivity comparable to RuO₂, on the order of $10^3 \Omega^{-1}$ cm⁻¹, which is between 6-7 orders of magnitude greater than that for V₂O₅ [135]. As such, it may be a possible alternative to MnO₂ if it proves to be electrochemically active in positive voltage windows. A limited number of reports investigating it as an active material at small mass loadings seems to indicate this is the case [135], [136].

Because of the demonstrated performance of VN in negative voltage windows, this material was also envisioned as potentially complimentary to MnO₂ in an asymmetric configuration, replacing the standard AC-CB negative electrode. As can be seen in Appendix B, because of the lower gravimetric capacitance of AC-CB compared to the MnO₂-MWCNT composites of the previous two chapters, much greater masses and thus larger electrode

95

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering footprints are required to balance the asymmetric device. The benefit here, if the material had a comparable gravimetric capacitance to MnO_2 but in a negative voltage window, would be ease of mass balancing and similar positive and negative electrode sizes.

Commercially available V_2O_3 powder is mixed with MWCNT using lauryl gallate as a dispersing agent for both components as was previously demonstrated for MnO₂ [127]. In this case the MWCNT were initially envisioned as acting as a matrix for the V_2O_3 particles in order to make the composite more stable when pasted and pressed into nickel foam current collectors. As will be seen in the results below, even in the presence of MWCNT, the V_2O_3 composites have inferior rate performance compared with MnO₂-MWCNT composites, which was unexpected considering its higher intrinsic electrical conductivity. Some explanations are suggested for this observation.

7.2 Electrochemical activation and operational conditions of V₂O₃ MWCNT electrodes

The V₂O₃-MWCNT composite was initially investigated in a negative voltage window in aqueous 0.5 M Na₂SO₄ to assess its suitability as a negative electrode material for an asymmetric device paired with MnO₂. Figure 7.2-1-A shows the initial cycling in the voltage window -0.9-0 V vs SCE. The current response in this voltage window is incredibly small for the mass loading of the electrode indicating no operative pseudocapacitance. The potential window was then adjusted to -0.5-0.4 V vs SCE, shown in Figure 7.2-1-B. A current inflection at roughly 0.3 V is observed in this window on the anodic scan indicating the presence of some redox process. No gas evolution was observed and the potential is well below what would be expected for oxygen evolution. This implies that the current inflection is related to an oxidation of the active material.



Figure 7.2-1: Investigation of a V_2O_3 -MWCNT electrode in various potential windows in an unadjusted 0.5 M Na₂SO₄ electrolyte. A – Potential window -0.9-0 V vs SCE, B – Potential window -0.5-0.4 V vs SCE, C – Potential window 0-0.7 V vs SCE. 43

Changing the potential window to 0-0.7 V vs SCE the current inflection at roughly 0.3 V is again observed and the current rapidly increases past this potential on the anodic scan, as seen in Figure 7.2-1-C.

These observations, together with the observation by Lee and Goodenough [33] that amorphous V_2O_5 operates in the voltage window 0-0.8 V vs SCE in aqueous KCl, led to the decision to test this electrode at more anodic potentials.



Figure 7.2-2: A – first 30 cycles of a V₂O₃-MWCNT electrode in the potential window 0-0.8 V vs SCE, arrow indicates increasing cycle number, B – Nyquist plot after these first 30 cycles. 44

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering

After cycling the electrode in the window 0-0.8 V vs SCE 30 times at 50 mV s⁻¹ something intriguing was observed, shown in Figure 7.2-2-A above. With each successive cycle, the cyclic voltammograms progressively became more box-shaped with an increasing current response and decreasing disparity between the peak currents at the edge of the anodic and cathodic sweeps. The EIS spectra also began to display the characteristics of a capacitive response, i.e. a vertical segment on the Nyquist plot, as seen in Figure 7.2-2-B. After repeated cycling the current response ceased to continuously increase. In fact, with further cycling, the current began to sharply decrease at potentials more anodic than approximately 0.6 V vs SCE as can be seen in Figure 7.2-3-A below. Similar behaviour was observed by Chen et al. [137] for V₂O₅. Their results are shown in Figure 7.2-3-B for comparison. After cycling a further 150 times at 50 mV s⁻¹ the electrolyte took on a yellow discolouration indicative of active material dissolution. This is a common failure mechanism for vanadium based supercapacitors [136].



Figure 7.2-3: A – Cyclic voltammogram at a scan rate of 20 mV s⁻¹ after repeated cycling, B – Cyclic voltammograms of V₂O₅ electrode produced by Chen et al. Source: [137]. 45

Based on the observation of decreasing current response at elevated anodic potentials and the work of Chen et al. [137], the upper anodic limit for subsequent tests was set at 0.7 V vs SCE, the same as Chen et al. However, the issue of vanadium dissolution had to be addressed if this material was to be useful. Inspection of the vanadium Pourbaix diagram, shown below, provided some insight into how this could be achieved. It can be seen from this diagram that vanadium is thermodynamically stable as a series of soluble species in the 5+ oxidation state at anodic potentials and neutral to alkaline pH. However, at pH values more acidic than approximately 4.5 the oxide V_2O_5 becomes at least partially stable reaching its greatest stability at a pH value of ~2.



Figure 7.2-4: Vanadium-water Pourbaix diagram. y-axis potential is vs the standard hydrogen electrode Source: [138]. 46

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering

Unfortunately, due to the amphoteric nature of vanadium in the 4+ oxidation state at pH values more acidic than ~5, V^{4+} becomes progressively more soluble. A balance between the stability of V^{5+} and V^{4+} can be struck at a pH value of ~3.6, which is drawn along with the potential window 0-0.7 V vs SCE (0.244-0.944 V vs SHE) on the Pourbaix diagram. When tested between pH 4-5 the electrolyte was observed to discolour, taking on a yellow-green tinge. It is known that dissolved V^{5+} in the form VO_2^+ will form a yellow coloured solution. When tested at a pH of 3 the electrolyte took on a blue colouration, indicative of the presence of dissolved V^{4+} as VO^{2+} which is known to have a distinct blue colour in solution. Testing at a pH of 3.6 did not cause the electrolyte to discolour even after 1000 successive cycles.

With the operating pH of the electrolyte set, attention was returned to the activation process. An electrode was initially cycled in the range 0-0.7 V vs SCE at a scan rate of 50 mV s⁻¹ to see if the activation process would eventually cease after a large number of cycles. It can be seen in Figure 7.2-5 A that the current response increases most rapidly in the first 20 cycles, but hardly changes between the 80th and 100th cycles. After the 100 cycles at 50 mV s⁻¹ no change is observed in the cyclic voltammograms when the scan rate is increased to 100 mV s⁻¹ as shown in Figure 7.2-5 B. Moving to the lower scan rates of 5 mV s⁻¹ and 2 mV s⁻¹, Figure 7.2-5 C and D respectively, the cyclic voltammograms are observed to change further. After 8 cycles at 5 mV s⁻¹ and 8 cycles at 2 mV s⁻¹, no further change in the cyclic voltammograms with cycling at any of the tested scan rates is observed. The 7th and 8th voltammograms at 2 mV s⁻¹ in Figure 7.2-5 D are virtually perfect boxes, indicating true capacitive behaviour. The activation protocol 50 mV s⁻¹ X 100, 100 mV s⁻¹ X 50, 5 mV s⁻¹ X 8, 2 mV s⁻¹ X 8 presented in Figure 7.2-5 was used for all V₂O₃ electrodes for which performance results are presented in subsequent sections



Figure 7.2-5: Cyclic voltammograms showing the activation procedure. A – Scan rate: 50 mV s⁻¹, B – Scan rate: 100 mV s⁻¹, C – Scan rate 5 mV s⁻¹, D – Scan rate: 2 mV s⁻¹. Arrows indicate increasing cycle number. 47

7.3 Proposed explanation for the observed electrochemical activation

The activation process shows similar behaviour to that of hydrous oxide growth during the cycling of Ru metal electrodes in an acidic electrolyte [139]. For Ru, the metal undergoes dissolution and re-deposition as a hydrous oxide during potential cycling with the increasing area of the cyclic voltammogram related to the thickness of the deposited oxide [139]. Other metals such as Au, Pt and Ir undergo a different, complex growth mechanism that does not involve M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering

dissolution and re-deposition [139], [140], but the end product of potential cycling, i.e. a hydrous amorphous oxide film, is the same. The cyclic voltammograms for the deposited Ru oxide are also box-shaped indicating capacitive behaviour. Indeed, it was these observations that spurred the initial research on RuO₂ as a material for supercapacitors [23].

Burke and O'Sullivan [141] proposed a model for the structure of the oxide layer formed by the potential cycling of metallic electrodes in aqueous electrolytes. This model is shown in a visually updated form produced by Rebouillat et al. [140] in Figure 7.2-6 below.



Figure 7.2-6: Burke-O'Sullivan model for oxide formed by potential cycling of a metal electrode in an aqueous environment. Source: [140]. 48

In the case of V_2O_3 , there is no metallic layer and the hydrous oxide would hypothetically be formed directly on the surface of the V_2O_3 particle. Rebouillat el al. [140] point out that hydrous oxides formed through potential cycling often contain electrolyte species and loosely bound water molecules. The boundary between the hydrous oxide and solution is thus somewhat diffuse. In addition, the hydrous oxide layer tends to be amorphous due to the deposition M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering following the most kinetically favourable instead of thermodynamically favourable pathway under the rapidly changing conditions of potential cycling.

Figure 7.2-7 schematically shows the formation of this proposed hydrous oxide layer on the surface of a spherical V_2O_3 particle. The composition is represented as being nonstoichiometric and hydrated to reflect the arguments of Rebouillat el al. mentioned in the previous paragraph. This schematic is similar to the model proposed by Pan et al. [135] who suggested that the V₂O₃ in their electrodes was encapsulated in a naturally formed VO_x surface.



Figure 7.2-7: Schematic showing the formation of an amorphous hydrous oxide layer on the surface of a V_2O_3 particle due to potential cycling. 49

7.4 Evidence of the proposed explanation for the electrochemical activation of V_2O_3 -MWCNT electrodes

In the case of metallic iron, the inhibition of hydroxide ion and water transfer within the growing hydrous oxide layer will eventually cause the layer to reach a maximum thickness [142]. This results in the thickness of the oxide layer obeying a relationship of the form:

$$Q = a(1 - \exp(bN))$$
 (Eq. 7.4-1)

Where Q is the integrated voltammetric charge, i.e. the area of the cyclic voltammogram which is directly related to the hydrous oxide film thickness, N is the number of cycles and a and b are fitted constants [142]. This function will tend towards a maximum value, implying a maximum film thickness and decreasing growth rate as the film increases in thickness. Indeed, as was mentioned for Figure 7.2-5 A the rate of increase in the current response/area of the cyclic voltammogram with every 20-cycle increment progressively decreases with cycling to the point where there is little difference between the 80th and 100th cyclic voltammograms. This does not mean the same mechanism is operative for V_2O_3 as with iron electrodes, i.e. hydroxide ion transfer, especially considering that they were tested in an acidic or neutral environment compared to the alkaline environment for the cited iron electrodes. However, it does imply that the thicker film impedes the growth mechanism responsible for the formation of the hydrous vanadium oxide. After 100 cycles at 50 mV s⁻¹ the cyclic voltammograms at 100 mV s⁻¹ show no change while the cyclic voltammograms at 5 mV s⁻¹ and 2 mV s⁻¹ still show some activation. This is somewhat consistent with the observation that the efficiency of oxide growth for metals such as iron is scan rate dependent [143]. It may also be consistent with a dissolution/redeposition mechanism for the hydrous oxide layers growth. The slowest scan rates would provide the longest amount of time for the diffusion of the necessary reactant species, leading to the thickest film.

Two general observations during the activation of various V_2O_3 -MWCNT electrodes seem to suggest a dissolution mechanism is in fact involved. The first is that during the first few cycles of the activation process in either Na₂SO₄ or NaNO₃ electrolytes, a clear stream can be seen coming off the bottom of the electrode, indicative of a solution of differing composition to the electrolyte. The appearance is akin to mixing ethanol and water or adding stock acid to water;

104

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering

before mixing both clear phases are visible due to differing refractive indices. It is known that many of the oxovanadate anions shown in Figure 7.2-4 are in fact colourless in solution [138], and this may be what is observed coming off the electrode. The second observation was made during the attempted activation of a V₂O₃ electrode in 1 M NaCl adjusted to pH 3.6 using 1 M HCl. During the first few cycles the electrolyte started to become cloudy. With progressive cycling, there was an increasing disparity between the peak anodic and cathodic currents compared to the decreasing disparity in Na₂SO₄ and NaNO₃. The activation was terminated after a few tens of cycles. A yellow tinged precipitate eventually settled to the bottom of the electrochemical cell as can be seen in the photograph Figure 7.2- below.



Figure 7.2-: Photograph showing the precipitate formed after the attempted activation of a V_2O_3 electrode in 1 M NaCl at pH=3.6. 50

This is in stark contrast to the observed behaviour in Na_2SO_4 and $NaNO_3$ electrolytes, adjusted to pH=3.6 with their respective acids. Both electrolytes remained precipitate free over the course of activation, electrochemical testing and cyclic stability. The formation of a precipitate seems to imply material dissolution is occurring. However, why the precipitate forms in a NaCl electrolyte and not Na_2SO_4 or $NaNO_3$ is not immediately clear.

The initial current inflection at increasingly *anodic* potentials during CV cycling implies an oxidative process. Based on the position of the inflection with respect to the vanadium Pourbaix diagram it is likely an oxidation to the V^{5+} oxidation state. As stated previously, the proposed explanation for the activation process is the formation of a hydrous vanadium oxide on the *surface* of the particle which, based on the Pourbaix diagram, would be predominantly in the V^{5+} state. Taken together, a number of predictions can be made. The first is that there should be an enrichment of the V^{5+} oxidation state on the surface after the activation process. The second is that the bulk crystal structure and particle morphology should remain intact if just the surface is involved as depicted in Figure 7.2-7.

Figure 7.2-8 below shows the XPS profiles for pure V_2O_3 , V_2O_3 -MWCNT before the activation procedure and V_2O_3 -MWCNT after the activation procedure.



Figure 7.2-8: XPS results for: A-pure V_2O_3 , B- V_2O_3 -MWCNT before activation and C- V_2O_3 -MWCNT after activation. 51

The pure V_2O_3 is seen to have the highest proportion of the V^{3+} oxidation state on its surface, however the higher oxidation states of V^{4+} and V^{5+} make up more than 80% of the vanadium oxidation state. This is not unexpected, as lower oxidation state vanadium oxides are known to immediately begin oxidizing upon exposure to ambient air with the oxidation being accelerated M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering via exposure to moisture [144]. This also explains the enrichment of the V⁴⁺ oxidation state prior to the activation process as the V₂O₃ and MWCNT were processed in an aqueous environment and dried under ambient humidity at elevated temperatures. After the activation process, it is seen that there is significant enrichment of the V⁵⁺ oxidation state as was expected based on the consideration of the Pourbaix diagram and cyclic voltammograms. The V⁵⁺ oxidation state now accounts for more than 85% of the total signal. This also implies that the observed pseudocapacitance likely results from the V⁵⁺/V⁴⁺ redox couple, which is consistent with the position of the operating potential window on the Pourbaix diagram.

Figure 7.2-9 below shows a collection of SEM images for pure V₂O₃, V₂O₃-MWCNT before the activation procedure and V₂O₃-MWCNT after the activation procedure. The pure V₂O₃ material, seen in Figure 7.2-9 A at an original magnification of 2000X, is a collection of large blocky particles that range in size from microns to tens of microns. Clear evidence of necking between particles can be seen at the original magnification of 5000X, Figure 7.2-9 B, indicative of exposure to high temperatures. This is not unexpected as V₂O₃ is often produced using high temperature sintering techniques in reducing atmospheres. The V₂O₃-MWCNT composite before activation is seen in Figure 7.2-9 C at an original magnification of 5000X. The particle morphology and size appears to be the same as the pure V₂O₃ material. MWCNT are clearly visibly coating the surface of some of the particles, however there appear to be large areas that are completely devoid of MWCNT. Figure 7.2-9 D shows the same material at an original magnification of 15000X. The surfaces of the exposed particles in the image appear smooth and the MWCNT appear to surround other adjacent particles. Figure 7.2-9 E shows the V₂O₃-MWCNT composite after activation at an original magnification of 5000X. The particle

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering



Figure 7.2-9: SEM images for: A, B-pure V_2O_3 , C, D- V_2O_3 -MWCNT before activation and E, F- V_2O_3 -MWCNT after activation. Arrow indicates a particle with noticeable surface texture. 52

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering morphology and size does not appear to have changed compared to the unmodified V₂O₃ or the V₂O₃-MWCNT composite. Particles surrounded by MWCNT are clearly visible while, again, large areas appear to lack any coverage by MWCNT. At an original magnification of 10000X, Figure 7.2-9 F, a particle in the center of the image, indicated by the red arrow, appears to have visible surface texture. This contrasts with the smooth particle surfaces observed in the composite prior to activation, Figure 7.2-9 D. It has been observed previously that the oxide formed via potential cycling of an Fe electrode exhibits significant surface roughness [142], which may also be the case for the indicated particle in Figure 7.2-9 F.

Figure 7.2-10 below shows the XRD results for pure V_2O_3 , V_2O_3 -MWCNT before the activation procedure and V_2O_3 -MWCNT after the activation procedure.



Figure 7.2-10: XRD results for: A-pure V₂O₃, B-V₂O₃-MWCNT before activation and C- V₂O₃-MWCNT after activation. 53

For the pure V_2O_3 , all the peaks can be indexed to the V_2O_3 phase (JCPDS 34-187). After mixing with MWCNT the V_2O_3 structure remains intact. All major peaks can be indexed to the V_2O_3 phase with a minor peak at ~25° corresponding to the graphitic structure of the MWCNT. After activation, all the major peaks for the V_2O_3 phase are still present. However, the overall intensity of the signal for the V_2O_3 phase is reduced while the peak at 25° corresponding to the MWCNT.

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering

is far more prominent compared to the material prior to activation. In addition, one minor peak at ~80° seen in the pure V_2O_3 and V_2O_3 -MWCNT composite prior to activation could not be distinguished from the background signal in the post activation V_2O_3 -MWCNT material. A shoulder peak can also be seen at ~50° which was not previously present. The loss of signal intensity could imply significant loss of the V_2O_3 phase due to the activation process. However, if this was the case, one would not expect to see the majority of the peaks so sharply defined, particularly all of the minor peaks with the exception of the peak at ~80°. A more likely explanation is that the minimal amount of material that could be retrieved for XRD analysis via scraping of the activated electrode surface was significantly less than the amount tested for the other two materials. Despite the lower intensity the collected pattern can still be readily indexed to the V_2O_3 phase indicating that the bulk structure remains intact through the activation process.

7.6 Results of electrochemical testing

After the activation procedure was completed the V₂O₃-MWCNT composite was tested for its capacitive performance in a three-electrode configuration. Figure 7.6-1 below is the cyclic voltammetry performance composite for the V₂O₃-MWCNT electrode. The electrode represented in Figure 7.6-1 had a mass loading of 29.1 mg cm⁻² and was tested in 0.5 M Na₂SO₄ adjusted to a pH of 3.6 using 1 M H₂SO₄. As can be seen from Figure 7.6-1-A the cyclic voltammograms are virtually symmetric and box shaped in the potential window 0-0.7 V vs SCE. Even at 10 mV s⁻¹ it appears that the voltammograms are tilting, which is indicative of high resistance. A slight current decrease on the anodic scan at potentials greater than 0.6 V can be seen, however it is minor. It is possible this is being caused by overoxidation of the active vanadium sites in the hydrous oxide. If no sites are available for oxidation then this would show up as a drop in current response. Figure 7.6-1-B shows the cycling stability of the electrode, conducted at a scan rate of M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering 50 mV s^{-1} in the same electrolyte that the activation and CV/EIS tests were performed. The capacitance does not stay perfectly static with cycling, fluctuating by a few percent around the initial value. After 1000 cycles the measured capacitance was 107% of the initial value.



Figure 7.6-1: Performance composite for V₂O₃-MWCNT in 0.5 M Na₂SO₄ electrolyte at pH=3.6. A – selected cyclic voltammograms: $a - 5 \text{ mV s}^{-1}$, $b - 10 \text{ mV s}^{-1}$, $c - 20 \text{ mV s}^{-1}$, B – cycling stability, C – gravimetric and D – areal capacitance vs scan rate. Mass loading: 29.1 mg cm⁻². 54 The electrolyte was also perfectly clear after the cycling stability test This result is uncharacteristic for vanadium based supercapacitors tested in aqueous electrolytes, which tend to

degrade very rapidly due to active material dissolution, even over the course of a couple hundred

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering

cycles [136], [145]. The fluctuations in capacitance seem to imply that the active surface layer is not completely static, which could be a performance problem at even greater cycle numbers. Figure 7.6-1-C, D show, respectively, the gravimetric and areal normalized capacitance vs scan rate of the V₂O₃-MWCNT electrode. The gravimetric capacitance decreases from 150 (+18, -2) F g^{-1} at a scan rate of 2 mV s⁻¹ to 32 (+4, -0.3) F g^{-1} at a scan rate of 100 mV s⁻¹. This corresponds to a high areal capacitance of 4.4 (+0.5, -0.4) F cm⁻² at 2 mV s⁻¹ and 0.9 ±0.1 F cm⁻² at 100 mV s⁻¹, a retention of only 21%.

Figure 7.6-2 below is the EIS performance composite for the same electrode as Figure 7.6-1. The Nyquist plot in Figure 7.6-2-A has the characteristic low frequency vertical section indicative of capacitive behaviour with very low real resistance at all frequencies. A high frequency semi-circular feature associated with charge transfer resistance and a medium frequency inflection associated with diffusion resistance can also be seen in the inset of Figure 7.6-2-A.



Figure 7.6-2: EIS performance composite for V_2O_3 -MWCNT in 0.5 M Na₂SO₄ electrolyte at pH=3.6. A – Nyquist plot with low real resistance inset, B – Real capacitance vs frequency, C – Imaginary capacitance vs frequency. 55

The calculated real capacitance vs frequency is plotted in Figure 7.6-2-B. The capacitance decreases from 3.85 ± 0.5 F cm⁻² at 0.01 Hz, which is relatively close to the low scan rate areal capacitance calculated from the CV data, to essentially 0 past approximately 0.1 Hz. The imaginary capacitance vs frequency plot shows a maximum at a frequency of ~0.05 Hz. The location of the maximum is shifted towards lower frequencies compared with the MnO₂-MWCNT composites presented in the previous two chapters, and is consistent with the notably reduced rate performance of the V₂O₃-MWCNT composite compared to the MnO₂-MWCNT composites.

Figure 7.6-3 below shows the performance of a V₂O₃-MWCNT electrode activated and tested in a 1 M NaNO₃ electrolyte at pH=3.6. The electrode had a mass loading of 33.6 mg cm⁻². As can be seen from Figure 7.6-3-A, at scan rates up to 20 mV s⁻¹ the cyclic voltammograms display the characteristic box shape indicative of capacitive performance. However, as with the electrode tested in Na₂SO₄, tilting of the voltammograms is evident even at a scan rate of 10 mV s^{-1} , indicating relatively high resistance. Figure 7.6-3-B shows the cycling stability of the electrode. The capacitance retention does not remain perfectly static, however after 1000 cycles there is no reduction in charge storage capacity. The fluctuating retention, as with the Na_2SO_4 electrode, could be a sign that the active surface layer is not totally stable, which could become an issue at larger cycle numbers. Unlike the Na₂SO₄ electrode, the NaNO₃ electrolyte had a light green colouration after cycling. The colour did not qualitatively match that of any vanadium species, however did appear very similar to dissolved nickel (II). It is possible that the acidic environment caused some dissolution of the nickel current collector. This might have been exacerbated in the NaNO₃ electrolyte compared to the Na₂SO₄ electrolyte as nitrate is known to accelerate the corrosion of nickel [146], [147].



Figure 7.6-3: Performance composite for V₂O₃-MWCNT in 1 M NaNO₃ electrolyte at pH=3.6. A – selected cyclic voltammograms: $a - 5 \text{ mV s}^{-1}$, $b - 10 \text{ mV s}^{-1}$, $c - 20 \text{ mV s}^{-1}$, B - cycling stability, C – gravimetric and D – areal capacitance vs scan rate. Mass loading: 33.6 mg cm⁻². 56 Figure 7.6-3-C, D show the gravimetric and areal capacitance respectively for the electrode. The capacitance drops from 142 (+16, -1) F g⁻¹/4.8 (0.6, -0.5) F cm⁻² at a scan rate of 2 mV s⁻¹ to

merely 26 (+3, -0.3) F g⁻¹/0.9 \pm 0.1 F cm⁻² at a scan rate of 100 mV s⁻¹, a retention of only 19%.

Figure 7.6-4 below is the EIS performance composite for the V_2O_3 -MWCNT electrode tested in a 1 M NaNO₃ electrolyte at a pH of 3.6. As for the electrode tested in the Na₂SO₄ electrolyte the Nyquist plot, Figure 7.6-4-A shows a suppressed semi-circular feature at high frequencies followed by a transition through a diffusion controlled region and finally a low

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering

frequency vertical section characteristic of capacitive performance. The real part of the capacitance calculated from the impedance data is 3.75 ± 0.5 F cm⁻² at the lowest frequency of 0.01 Hz and decreases rapidly with increasing frequency as can be seen in Figure 7.6-4-B. The capacitance calculated from the impedance data has a greater discrepancy with the capacitance calculated from the cyclic voltammetry data compared to the electrode tested in the Na₂SO₄ electrolyte. The maximum in the imaginary component of the capacitance occurs at approximately 0.05 Hz, the same position as the electrode tested in the Na₂SO₄ electrolyte. This is consistent with the virtually identical rate performance calculated from the cyclic voltammetry data for both electrodes.



Figure 7.6-4: Figure 7.6-2: EIS performance composite for V_2O_3 -MWCNT in 1 M NaNO₃ electrolyte at pH=3.6. A – Nyquist plot with low real resistance inset, B – Real capacitance vs frequency, C – Imaginary capacitance vs frequency. 57

7.7 Conclusion

A V₂O₃-MWCNT composite was produced using colloidal processing. Both V₂O₃ and MWCNT were dispersed using lauryl gallate. The composite material was impregnated into nickel foam current collectors and tested in Na₂SO₄ and NaNO₃ electrolytes. Based on consideration of the vanadium Pourbaix diagram, the electrolytes were set to a pH of 3.6. An electrochemical activation process was observed when the electrodes were tested in the voltage window 0-0.7 V vs SCE. However, during the initial cycles, the composite did not exhibit any notable capacitance. In Na₂SO₄ and NaNO₃, the activation appeared to involve the partial dissolution of the active material. When tested in a NaCl electrolyte, a precipitate formed during initial cycling and the activation process would not proceed. After activation involving many consecutive cycles at progressively lower scan rates, the electrodes exhibited the characteristic electrical response of a capacitor (i.e. box-shaped cyclic voltammograms and vertical Nyquist plots) with a dramatically enhanced current response compared to the initial cycles. XPS analysis revealed that the activation process resulted in an enrichment of the V^{5+} oxidation state on the surface of the material. XRD analysis indicated that the bulk V₂O₃ crystal structure remains intact during colloidal processing as well as after the activation process. SEM images show that the general particle morphology remains intact with potentially some evidence of surface etching/roughening after the activation process.

After the electrochemical activation process, there is no discernible difference in performance between electrodes tested in Na₂SO₄ or NaNO₃. This implies the identity of the electrolyte anion is not a performance limiter. The gravimetric and areal capacitance at low scan rates is comparable to previously tested MnO₂-MWCNT composites. However, the rate performance is significantly lower. It is suggested that the large particle size prevents adequate

116

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering mixing of the conductive carbon nanotubes, leading to poor rate performance despite the high electrical conductivity of V_2O_3 in comparison to other oxides.

Despite some promising characteristics such as high intrinsic electrical conductivity and high capacitance after electrochemical activation, the V_2O_3 -MWCNT composite appears inferior to MnO₂-MWCNT composites. The poor rate performance and smaller potential window are serious drawbacks. In addition, due to acidic pH used to make the material more stable during cycling, it would be difficult to use this material in an asymmetric configuration. The acidic pH would result in hydrogen evolution at less cathodic potentials on the negative electrode, leading to a reduction in the operational voltage window for the device. The requirement that the material be activated would also complicate device fabrication.

Chapter 8: Final Conclusions and Future Work

Two different colloidal processing strategies were developed to produce MnO₂-MWCNT composite materials for supercapacitors. Both composites allowed for the fabrication of electrodes with very high areal capacitance and good capacitance retention at high scan rates. However, when combined with an AC-CB negative electrode, the resulting asymmetric devices failed to outperform commercially available supercapacitors. Comparatively little time was spent on the fabrication of the asymmetric device, even though the MnO₂-MWCNT composites are not particularly useful outside of this configuration. In a future project, a dedicated effort would be made to the general optimization of the asymmetric device. Parameters such as separator, current collector size, distance between the positive and negative electrodes and even a re-investigation of the operating potential windows of the positive and negative electrodes would all be systematically explored. Investigation of different negative electrode materials would also be undertaken, with the aim of better matching the positive and negative capacitances at all scan rates, instead of just one. This would make the resulting device far more flexible in its potential application.

 V_2O_3 was investigated both as a potential negative electrode material and as a replacement for MnO₂ due to its advantage of high electrical conductivity. The V₂O₃-MWCNT composite failed to live up to the desired expectations. However, with very little optimization, it performed at levels comparable to the far more developed MnO₂-MWCNT composites. Future work would involve modification of the V₂O₃ particle size and the processing strategy for mixing V₂O₃ and MWCNT. Further attention would be given to other vanadium based compounds, as there still seems to be a great deal of promise for development.

Appendix A

Electrode Error Analysis

Error Source: Measurement of electrode area and overcoating of active material with epoxy.

The final electrode dimensions were measured using an office ruler with millimeter hashmarks. Each electrode measured ~1 X 1 cm according to the office ruler. A reading error of ± 0.5 mm was assigned to these measurements. For each electrode, some of the impregnated nickel foam was overcoated with epoxy. Overcoated active material was thus not available during the measurement of electrode capacitance, but was accounted for in the measured active material mass. The spatial extent of the epoxy overcoat was never observed to exceed 1 mm (measurement using the aforementioned office ruler). Thus, the epoxy overcoat was varied between 0-1 mm. In the schematic below the dimensions *a* and *b* correspond to the final electrode length and width. The dimension *c* corresponds to the extent of epoxy overcoating the electrode active material.



Table A-1: Various cases accounting for the error in the areal and gravimetric capacitance due to electrode area measurement and overcoating with epoxy. 3

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering

For each of the four cases presented the following areal and gravimetric capacitances can be calculated. In the formulae below, C is the capacitance calculated according to Eq. 4.8.1-3 or Eq. 4.8.2-8 and M is the mass of impregnated active material calculated by taking the difference in the measured mass of the bare and impregnated nickel foam. A constant linear density of active material in the impregnated nickel foam was assumed in order to calculate the amount of active mass coated by epoxy in Case 2 and Case 4. Of the four cases, Case 1 will yield the minimum value and Case 4 will yield the maximum value for both areal and gravimetric capacitance.

Case 1 (min)	Case 2
$C_{areal} = \frac{C}{1.1025 cm^2}$	$C_{areal} = \frac{C}{1.1025 \ cm^2}$
$C_{grav} = \frac{C}{M}$	$C_{grav} = \frac{C}{M - (\frac{M}{1.05cm * 1.15cm} * (0.1cm * 1.05cm))} = \frac{C}{0.913 * M}$
Case 3	Case 4 (max)
$C_{areal} = \frac{C}{0.9025 cm^2}$	$C_{areal} = \frac{C}{0.9025 \ cm^2}$
$C_{grav} = \frac{C}{M}$	$C_{grav} = \frac{C}{M - (\frac{M}{0.95cm * 1.05cm} * (0.1cm * 0.95cm))} = \frac{C}{0.905 * M}$

Table A-2: Adjusted areal and gravimetric capacitance due to error in electrode area measurement and overcoating with epoxy. 4

Error Source: Current measurement by ParaSTAT 2273 and mass measurement by Mettler Toledo AX105 scale.

The maximum rated error for current measurement by the ParaSTAT 2273 is 0.75% of the current measurement. Eq. 4.8.1-3 will thus yield a maximum C_{max} and minimum C_{min} depending on whether the raw current measurement is increased or decreased by 0.75%. A schematic is shown in Figure A-1 below for the case of a simple box cyclic voltammogram. It can easily be

M.A.Sc. Thesis – Cameron Jon Wallar; McMaster University – Materials Science & Engineering seen how increasing or decreasing the current measurement will affect the integrated area of the box. It should be noted that an accuracy for applied voltage could not be found for the ParaSTAT 2273. It is thus assumed that the measured voltage was the true voltage.



Figure A-1: Schematic showing the effect the current measurement error has on the integrated area of a hypothetical cyclic voltammogram. 58

The maximum rated error for the measured electrode impedance is 1%. This error was used to adjust the relevant quantities in Eq. 4.8.2-8,9 to obtain C_{max} and C_{min} values. The following is a detailed error analysis for the real part of the complex capacitance calculated using Eq. 4.8.2-8.

$$|Z(\omega)|^{2} = Z'(\omega)^{2} + Z''(\omega)^{2}$$

= $(Z' \pm 1\%)(Z' \pm 1\%) + (Z'' \pm 1\%)(Z'' \pm 1\%)$
= $(Z')^{2} \pm 2\% + (Z'')^{2} \pm 2\%$
= $(Z')^{2} \pm 0.02(Z')^{2} + (Z'')^{2} \pm 0.02(Z'')^{2}$
= $[(Z')^{2} + (Z'')^{2}] \pm 0.02[(Z')^{2} + (Z'')^{2}]$
= $[Z'(\omega)^{2} + Z''(\omega)^{2}] \pm 2\%$
 $C'(\omega) = \frac{1}{\omega} \left[\frac{-Z''(\omega) \pm 1\%}{|Z(\omega)|^{2} \pm 2\%} \right] = \frac{-Z''(\omega)}{\omega |Z(\omega)|^{2}} \pm 3\%$

$$C'(\omega)_{max} = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} + 0.03 \left(\frac{-Z''(\omega)}{\omega |Z(\omega)|^2}\right), C'(\omega)_{min} = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} - 0.03 \left(\frac{-Z''(\omega)}{\omega |Z(\omega)|^2}\right)$$
The Mettler Toledo AX105 scale has an accuracy of ±0.015 mg and linearity of ±0.03 mg in the range of masses measured. Assuming an extraordinarily unfavourable linearity curve, the calculated active mass would have an error of ±(0.015+0.015+0.03+0.03) mg = ±0.09 mg = $\pm 9*10^{-5}$ g.

Final error determination

Based on the above analysis, the final upper and lower bounds for the areal and gravimetric capacitance are calculated as follows:

Minimum	Maximum
$C_{areal,min} = \frac{C_{min}}{1.1025 \ cm^2}$	$C_{areal,max} = \frac{C_{max}}{0.9025 \ cm^2}$
$C_{grav,min} = \frac{C_{min}}{\left(M + (9 * 10^{-5})\right)g}$	$C_{grav,max} = \frac{C_{max}}{\left(0.905 * (M - 9 * 10^{-5})\right)g}$

Table A-3: Final minimum and maximum areal and gravimetric capacitances used to determine the error bars of electrodes measured in a three-electrode configuration. 5

Error in calculation of capacitance for asymmetric devices

As can be seen in the above error analysis, the bulk of the error in the calculation of capacitance is the result of mass or area normalization. If the capacitance is not normalized, then the error only arises due to instrument inaccuracy and linear fitting error for galvanostatic cycling. Instrument errors are merely $\pm 0.75\%$ of measured current for cyclic voltammograms, $\pm 1\%$ of measured impedance for impedance plots and $\pm 0.05\%$ of measured voltage for galvanostatic cycling. In the case of galvanostatic cycling it was found that all discharge curves approximated a straight line with a very high R² value so that even a 99% confidence interval for the upper and lower bound of the fitted linear slope yielded error bars that were not actually visible against the thickness of the plotted data points. This error is tabulated for the capacitance

M.A.Sc. Thesis - Cameron Jon Wallar; McMaster University - Materials Science & Engineering

values of both the asymmetric devices presented in Chapter 5 and Chapter 6 and is presented in Table A-4 and Table A-5 below. Because of how small the error is, error bars were not plotted on the capacitance vs current figures for the devices presented in Chapter 5 and Chapter 6.

Current (mA)	Slope (mV/s)	99% CI upper capacitance slope (mV/s)	99% CI lower capacitance slope (mV/s)	Capacitance (F)	+ve cap error (F)	-ve cap error (F)	Max error (%)
3	0.8738	0.8676	0.88	3.43	0.025	0.024	0.7
5	1.55	1.54	1.56	3.22	0.025	0.024	0.8
7.5	2.52	2.5	2.53	2.98	0.020	0.019	0.7
10	3.56	3.54	3.58	2.81	0.015	0.015	0.5
30	11.78	11.69	11.88	2.55	0.021	0.021	0.8
50	21.53	21.1	21.97	2.37	0.048	0.046	2.0

Table A-4: Tabulated error in capacitance calculation due to linear fitting of discharge curve for

the Schiff base MnO₂-MWCNT/AC-CB device presented in Chapter 5.6

Current (mA)	Slope (mV/s)	99% CI upper capacitance slope (mV/s)	99% CI lower capacitance slope (mV/s)	Capacitance (F)	+ve cap error (F)	-ve cap error (F)	Max error (%)
3	1.65	1.63	1.66	1.82	0.021	0.020	1.2
5	2.96	2.94	2.99	1.69	0.014	0.014	0.8
8	4.98	4.97	5.00	1.60	0.006	0.006	0.4
10	6.26	6.24	6.29	160	0.006	0.006	0.4
20	13.03	12.99	13.08	1.53	0.006	0.006	0.4
30	19.69	19.52	19.85	1.52	0.013	0.012	0.9
40	26.38	26.04	26.71	1.52	0.019	0.019	1.2
50	33.15	32.52	33.77	1.51	0.029	0.028	1.9

Table A-5: Tabulated error in capacitance calculation due to linear fitting of discharge curve for

the liquid-liquid extraction MnO2-MWCNT/AC-CB device presented in Chapter 6.7

Appendix B

AC-CB performance

In order to balance an asymmetric device, the capacitance of both the positive and negative electrode must be known. The AC-CB composite used as the negative electrode material was tested in a three-electrode configuration in order to determine its gravimetric capacitance. This was then used in conjunction with Eq. 2.12-1 to attempt to balance the capacitance of the electrodes in the asymmetric device. Figure B-1 below shows selected cyclic voltammograms and the gravimetric capacitance vs scan rate for an AC-CB electrode at a mass loading of ~24 mg cm⁻².



Figure B-1: Performance of AC-CB negative electrode material. A – selected cyclic voltammograms, arrow indicates increasing scan rate, B – gravimetric capacitance vs scan rate. 59

The gravimetric capacitance was 67 (+7.8, -0.8)F g⁻¹ at 2 mV s⁻¹, 63 (+7.4, -0.7) F g⁻¹ at 20 mV s⁻¹ and 58 (+6.8, -0.7) F g⁻¹ at 100 mV s⁻¹.

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