

Synthesis and Characterization of Layered Materials for Electrochemical Capacitors and Batteries

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A thesis submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy.

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Declaration

I, Sharona Ashira Melchior, declare that this thesis is my own unaided work. It is being submitted for the Degree of Doctor of Philosophy to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other university.

..... Sharona Melchior

Signature

..... 21 day of September Year 2018

Abstract

The energy storage performance of one of the lightest but less researched MXenes, Ti_2CT_x , combined with other materials, was investigated for improved electrodes in electrochemical capacitors (ECs) and lithium-ion batteries (LIBs). This work investigated: (i) Ti_2CT_x combined with carbon nanospheres (CNS) as a symmetric electrode system in an aqueous electrolyte (1M Li_2SO_4); (ii) Ti_2CT_x combined with electrolytic manganese dioxide (EMD) as an anode for LIB. The structure, composition, morphology and electrochemical properties of the synthesized materials were studied. The combined MX/CNS material demonstrated a higher specific capacitance compared to the individual components. The material was fabricated with relatively high ($1.87 \text{ mg}\cdot\text{cm}^{-2}$) and low ($0.17 \text{ mg}\cdot\text{cm}^{-2}$) mass loadings and assembled into a symmetric device. Specific capacitance, power and energy for the lower electrode mass loading of $180 \text{ F}\cdot\text{g}^{-1}$, $37.6 \text{ kW}\cdot\text{kg}^{-1}$ and $14.1 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ were all higher than $86 \text{ F}\cdot\text{g}^{-1}$, $20.1 \text{ kW}\cdot\text{kg}^{-1}$ and $6.7 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$ for the higher mass loading. A wide voltage window of 1.5 V, which is larger than the window reported in works involving MXene as symmetric supercapacitor electrodes in an aqueous electrolyte ($<1.0 \text{ V}$), was obtained, but with limited long-term cycling behaviour. Mathematical modelling and simulation of the supercapacitor showed good correlation with the experimental results, validating the model. The cell performance was demonstrated by lighting an LED. This reveals the potential of the Ti_2CT_x to be employed as a viable energy storage system for applications requiring low mass. In the study of MXene combined with EMD, three different ratios were examined

as anodes for LIB in a half-cell configuration. Results showed that the combined MXene/EMD material has a greater capacity, rate capability and cycling stability compared to the EMD. The best ratio was found to be MXene:EMD=80:20. The capacity obtained for this material after 200 cycles is $460 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$. The Li-ion accessibility was found to improve with cycling. This study provides a first insight into the viability of using a light-weight MXene/EMD composite for improved LIB anodes. EMD is a low cost and abundant material, thus provides great opportunities for improved capabilities for light-weight applications at an affordable cost.

Dedication

*To my beloved husband Itai and children Maytal, Ophir, Yotam, Harel, Arbel and
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To my mother Ana and father Alexander for their love and support throughout my
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List of Abbreviations and Symbols

A	Area
A	Ampere
$\text{\AA}$	Ångström
AC	Alternating current
Ag/AgCl	Silver/Silver Chloride
Al	Aluminium
Ar	Argon
Be	Berilium
BE	Binding energy
BET	Brunauer-Emmet-Teller
BS	British Standards
BSE	Backscattered electrons
C	Carbon
C	Coulomb
C	Capacitance
C_{elec}	Electrode capacitance
C_1	Capacitance of electrode 1
C_2	Capacitance of electrode 2
C_{sp}	Specific capacitance
C_{sp1}	Specific capacitance of electrode material 1
C_{sp2}	Specific capacitance of electrode material 2
$C_{th,g}$	Theoretical specific capacitance
$C_{th,sp}$	Theoretical specific capacity
$C_{p,final}$	Capacity of the final cycle
$C_{p,sp}$	Practical specific capacity
$C_{p,2}$	Capacity of the second cycle
CB	Carbon Black
CCD	Charge-Coupled-Device
CD	Charge-Discharge
CE	Counter electrode
Co	Cobalt

CPE	Constant Phase Element
CPE_f	Constant Phase Element of the surface film
CPE_{dl}	Constant Phase Element of the double layer capacitance
Cu	Copper
CV	Cyclic Voltammetry
d	Distance
DEC	Diethyl Carbonate
DMC	Dimethyl Carbonate
E	Energy
E_{sp}	Energy density
EC	Electrochemical Capacitor
EC	Ethylene Carbonate
EDLC	Electrical Double Layer Capacitor
EDS	Energy Dispersive X-ray Spectroscopy
EDX	Energy Dispersive X-ray Spectroscopy
EEC	Electric Equivalent Circuit
EIS	Electrochemical Impedance Spectroscopy
EMD	Electrolytic Manganese Dioxide
EN	European Norms
ESCA	Electron Spectroscopy for Chemical Analysis
ESR	Equivalent series resistance
eV	Electron-volt
F	Farad
F	Faraday's constant ($9.64853 \times 10^4 \text{ C}$)
F	Fluorine
f	Frequency
FEG-SEM	Field Emission Gun Scanning Electron Microscope
g	Gram
GCPL	Galvanostatic Cycling with Potential Limitation
h	Hour
h,k,l	Miller indices
Hz	Hertz

I	Current
I_t	Current response signal at time t
I_0	Amplitude of the current signal at $t=0$
ICDD	International Centre for Diffraction Data
IEC	International Electrotechnical Commission
KCl	Potassium Chloride
keV	Kiloelectron-volt
kg	Kilogram
kV	Kilovolt
LaB ₆	Lanthanum hexaboride
LED	Light emitting diode
LFP	Lithium-Ferro-Phosphate
Li	Lithium
Li ₂ SO ₄	Lithium Sulphate
LIB	Lithium-Ion Battery
LiPo	Lithium Polymer
Li-S	Lithium-Sulphur
LMO	Lithium-Manganese-Oxide
LTO	Lithium-Titanite-Oxide
m	Meter
m	Active material mass
m_1	Active material mass of electrode 1
m_2	Active material mass of electrode 2
mA	Milliampere
min	Minute
MnO ₂	Manganese Dioxide
mV	Millivolt
M_w	Molecular weight
mW	Milliwatt
MX	MXene
NMP	N-Methyl-2-Pyrrolidone
n	Integer

N	Nitrogen
NH ₄ OH	Ammonium hydroxide
nm	Nanometer
O	Oxygen
P	Phosphorus
PEO	Poly (Ethylene Oxide)
P_{max}	Maximum power
$P_{max,sp}$	Maximum power density
P_{sp}	Power density
PVDF	Polyvinylidene Fluoride
PXRD	Powder X-ray Diffraction
Q	Constant -phase element (CPE)
q_1	Charge on electrode 1
q_2	Charge on electrode 2
R	Resistance
R_{ct}	Charge transfer resistance
R_f	Surface film resistance
R_s	Ohmic resistance of the solution
RE	Reference electrode
Redox	Reduction-Oxidation
S	Mass, volume or geometric area
s	Second
S_{elec}	Mass, volume or area of an electrode
S_1	Mass, volume or area of electrode 1
S_2	Mass, volume or area of electrode 2
SDS	Sodium dodecyl sulfate
SE	Secondary electrons
SEI	Solid Electrolyte Interphase
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SSA	Specific surface area
T	Temperature

t	Time
t_c	Charge time
t_d	Discharge time
T_x	Surface functional groups in x quantity
TEM	Transmission Electron Microscopy
Ti	Titanium
TiC	Titanium Carbide
U	Uranium
V	Volt
V	Voltage
V_t	Potential difference at time t
V_0	Amplitude of the potential signal at $t=0$
V_1	Potential range of electrode 1
V_2	Potential range of electrode 2
vs	Versus
W	Tungsten
W	Watt
W_c	Warburg impedance
WE	Working electrode
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
Z	Impedance
Z_0	Impedance magnitude
Z'	Resistance – the real part of the complex impedance
Z''	Reactance – the imaginary part of the complex impedance
ZrO	Zirconium oxide
Δt	Time window
ΔV	Voltage window
ΔV_{iRdrop}	Voltage drop
ΔV_{max}	Maximum voltage region
ϵ_0	Permittivity of free space
ϵ_r	Relative permittivity / dielectric constant

η	Coulombic efficiency
θ	Diffraction angle
λ	Wavelength
μm	Micro-meter
ν	Scan rate
φ	Phase shift angle
Ω	Ohm
ω	Angular frequency
2D	Two-dimensional
3D	Three-dimensional
$^{\circ}$	Degree
$^{\circ}\text{C}$	Degree Celsius
%	Percent

1. Chapter 1: Introduction

1.1 Background and motivation

In today's world, the advancement and sophistication of technology require greater energy in smaller and lighter packages, entwined with the call for a safer and cleaner environment. A huge amount of research, as well as investments, are put into developing environmentally-friendly energy systems. Two such systems, that are relatively clean, safe and produce high energy density or high power are Lithium-ion batteries (LIBs) and Electrochemical capacitors (ECs) as compared to other types of batteries (e.g., lead-acid and nickel-cadmium batteries). They both play important roles in transportation (electric vehicles for example), portable tools, toys and more, completing each other according to their properties (high energy for LIBs and high power for ECs). However, they both have their own advantages and disadvantages. Therefore, a huge effort is devoted to development in both areas.

Electrochemical Capacitors (ECs) are an emerging technology that is becoming a significant component in electronic apparatuses and systems. ECs are not projected to replace batteries but rather take their unique place, with their specific properties, as complementary and sometimes standalone energy storage devices.

An EC is an electrical apparatus that stores electrical energy physically, rather than chemically, by a nano-size charge separation in the electrochemical interface between an electrolyte and a solid electrode with a high surface area.

ECs are also known as electric double-layer capacitors (EDLC), Supercapacitors (SCs), Ultracapacitors (UCs), gold capacitors, or pseudocapacitors, indicating (but not always) different types or manufacturers [1]. So, the terms EC or supercapacitors may be used alternatively during this document referring to the technology.

Their present and potential uses are vast. Several examples of such usages include [2], [3]: DC power applications (e.g., backup power for computer memory, short-term backup power for systems against interruptions in the utility grid, all-EC powered bus, flashlights, screw guns, toys and more); Energy conservation and harvesting applications (e.g., restoring braking energy of hybrid vehicles, storage of wind and solar power when available and release when they are not available); Combination with other energy technology (such as batteries, fuel cells, combustion engines or other), for more efficient and compact systems, where the EC takes the peak loads and the other energy source provides the average power load, therefore, enabling it to be smaller (e.g., digital cameras, portable computers, motor starters, etc.).

Supercapacitors have high specific power, very high cycle life, high energy efficiency, the ability to operate in extended temperature range and rapid charging-discharging compared to batteries [1], [4]. However, one of their biggest disadvantages is very low energy densities (commonly $1\text{-}10\text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) compared to batteries ($\sim 20\text{-}180\text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) [1]. Therefore, tremendous research efforts are currently being devoted to increasing their energy densities and performance. As these properties greatly depend on the materials used, significant resources are

dedicated to improving electrode and electrolyte materials and understanding their behaviour [5].

Lithium-ion batteries (Li-ion batteries or LIBs), since first being introduced in 1980 are extensively used in many types of electrical applications, continue to capture attention and are predicted to continue dominating the electronic market. LIB is a type of rechargeable device that enables the conversion of chemical energy into electrical energy and its storage within the battery. The charge-discharge process involves Li-ions moving across from the anode to the cathode and vice versa via an electrolyte and through a separator that enables their movement but prevents direct contact of the electrodes.

LIBs are used in a plethora of applications which include: portable electronics like cell phones, cameras, toys and laptops; larger devices like electric cars, radio-controlled aircraft; backup power and storage and many more uses.

LIBs have a high energy density, no “memory” effect and low self-discharge (2% loss per month at 20 °C) [6]. However, development is still needed in areas of safety, cost, charging speed, power density, energy density, life cycle and more [7]. Here also, these properties greatly depend on the materials used. Therefore, significant research is conducted to improve electrode and electrolyte materials and to understand their behaviour.

Manganese oxide is an environmentally friendly and safe material that has a relatively low cost, long storage life and is abundant in nature. It potentially also has a high reduction-oxidation (redox) potential and a high rate capability.

Therefore, it is an attractive material for electrode applications and is extensively used as such and researched for improved properties [8].

Atomically layered materials are also currently being researched as candidates for improved supercapacitor electrodes and batteries (as well as other electrochemical applications). Their two-dimensional (2D) structure demonstrates unique properties that are in many cases very different from the properties of their three dimensional (3D) equivalents and are predicted to enhance the performance of both supercapacitors and batteries [9], [10]. Such layered materials being studied at present are graphene and its derivatives, hexagonal BN, layered metal dichalcogenides (LMDCs) (such as MoS_2 and WS_2), metal oxides and hydroxides, as well as clays. Many of these materials have been known to exist only in theory and have been synthesized only recently, therefore there is much yet to discover about their actual properties and potential applications, as well as the mastering of large-scale production and thickness and structural control [9], [11].

In 2011, Gogotsi and co-workers [12], first synthesized a 2D layered material called MXene, by selectively etching aluminium (Al), using hydrofluoric acid (HF) from the MAX phase material. MAX phase materials are layered ternary carbide and nitride materials with the general chemical formula of $\text{M}_{n+1}\text{AX}_n$ (where 'M' represents an early transition metal, 'A' represents a group IIIA or IVA element, 'X' is C and/or N, and n may equal 1, 2, or 3). There are more than 70 different MAX phase compositions currently known [13], [14]. MXenes are formed when the 'A' element is etched out of the MAX phase material, and subsequently have a general formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$ (where T represent surface

functional groups such as **F**, OH or O, and x is the number of functional groups that are attached to the surface following the etching process) [15]. This newly discovered family of materials has similar properties to graphene with good electronic conductivity and different surface terminations enabling the possibility to manipulate their properties to fit different applications. 2D materials are single or few atoms thin with more exposure of surface atoms than their bulk lamellar counterpart materials, therefore have larger surface areas. Additionally, they have a higher utilization of their active sites and they possess gaps which enable electrolyte ion intercalation [16], [17]. As a result, they potentially have larger electroactive surfaces than traditional electrode materials and therefore attract research attention. MXenes are currently studied, both theoretically and experimentally, as potential electrode materials for energy storage devices such as batteries [18]–[28] and ECs [21], [26], [29]–[44] as well as other uses [45]–[47].

Much research and work are carried out on MXenes as electrodes both for batteries and ECs. Nevertheless, as they are relatively new materials, there is still room for more work on improving the properties of MXene for these applications and more room for understanding their behaviour. For instance, the most studied MXene is $\text{Ti}_3\text{C}_2\text{T}_x$ and not much work is done on the lighter MXene (Ti_2CT_x). Ti_2CT_x is expected to have a higher gravimetric capacitance and therefore is an attractive material for further investigations. There is a need to improve the electrochemical properties, such as the specific capacitance, specific capacity, energy density and power density of the light Ti_2CT_x MXene, in a simple and affordable way, to make it appealing for use in the industry for light-weight energy demanding applications.

This research is aimed at synthesizing and characterizing composites of layered material as enhanced electrodes for supercapacitor and battery applications. This work is focused on: (i) tuning the synthesis of MXene Ti_2CT_x and modifying it with carbon nanospheres (CNS) for enhanced symmetric supercapacitor performance in the aqueous electrolyte; (ii) improving the performance of the lithium-ion battery by using a MXene Ti_2CT_x / electrolytic manganese dioxide (EMD) composite as anode material.

1.1.1 Research objectives

- To synthesize MXene Ti_2CT_x /CNS composite
- To synthesize MXene Ti_2CT_x /EMD composites with three different MXene/EMD ratios
- To study the structure, morphology and composition of the synthesized materials
- To investigate the electrochemical properties and performance of the MXene Ti_2CT_x /CNS composite for symmetric supercapacitor in a neutral aqueous electrolyte
- To demonstrate the performance of the supercapacitor by lighting an LED
- To validate the model and simulation developed by Ike [48] using the parameters obtained in this work for the symmetric supercapacitor
- To investigate the electrochemical properties and performance of the MXene Ti_2CT_x /EMD composites with different ratios as anode materials for lithium-ion batteries

Hypothesis

When combining Ti_2CT_x with CNS or EMD, the electrochemical properties of the combined materials, such as specific capacitance for supercapacitor electrodes or specific capacity for LIB anodes, improve as compared to these properties for each of the individual components.

Contribution to knowledge

The following are contributions of this work to the field:

- Better knowledge and understanding of the morphological, structural and electrochemical properties of the less investigated, lightest Ti_2CT_x MXene and the Li intercalation process which occurs during charging and discharging both for EC electrodes and LIB anodes
- This work shows that adding a small amount of CNS, by simple mixing, to Ti_2CT_x , can improve the capacitance of the material when used as an electrode for aqueous symmetrical EC
- A wide voltage window of 1.5 V was achieved for a symmetrical EC in a neutral aqueous electrolyte using the MXene Ti_2CT_x /CNS composite. This voltage window is larger than the decomposition voltage of water (~ 1.23 V) and significantly larger than the voltage window reported in works on MXene-based symmetric supercapacitor electrode in an aqueous electrolyte (usually < 1.0 V)
- The model and simulation of a symmetric EC developed by Ike et al. [49] is validated using the experimental data obtained in this work

- This study demonstrates that combining EMD, which is a low cost and abundant material, with Ti_2CT_x MXene improves the capacity of the material as an anode for LIB and provides great opportunities for improved capabilities for light-weight applications at an affordable cost
- The results presented here reveal the potential of the Ti_2CT_x to be employed as an electrode in an energy storage system for applications requiring low mass

1.1.2 Structure of the thesis

The thesis is divided into 5 chapters as follows:

- Chapter 1 is the introductory chapter giving the problem statement, the research background, the motivation for the study, aim, objectives, hypothesis and contribution to knowledge. Further, it details the literature review that gives the background and core principles of energy storage devices, and particularly EC and LIB. Materials for electrodes are also reviewed, and particularly MXene and manganese oxide.
- Chapter 2 describes the characterization techniques, equipment and experimental procedures that were used in this work.
- Chapter 3 provides the results and discussion of the MXene/CNS symmetric supercapacitor work.
- Chapter 4 reports the results and discussion for the MXene/EMD materials for LIB anode work.
- Chapter 5 gives the concluding remarks showing the significance of this study and recommendations for future work.

1.2 Literature review

This section of the work reviews the main characteristics of the energy storage devices. The focuses are on electrochemical capacitors and lithium-ion batteries involved in this work. The electrode materials reviewed here are limited to the materials used in this work, namely MXene and manganese oxide.

1.2.1 Energy storage devices

An energy storage device is an apparatus designed to capture energy in order to release it at a desirable time. A variety of energy storage types exist. These include: mechanical (like in flywheels), thermal (such as a solar pond), chemical (e.g., hydrogen storage), electrochemical (such as batteries), electrical (like in capacitors) and more. These energy storage devices have different mechanisms and different properties. In this chapter, two types of energy storage devices will be introduced: the electrochemical capacitor and the battery. Their main properties, advantages and limitations will be reviewed as well as relevant theory related to this research.

Since different types of ECs and different types of batteries vary greatly in their characteristics and applications, standardized testing protocols are needed. Standards, issued by the International Electrotechnical Commission (IEC), the European Norms (EN), the British Standards (BS) and many more standard bodies, issue specifications setting a base for testing the electrical properties and setting the testing conditions and requirements for the devices. A list of some of these specifications, generic and for special applications, can be found in

Appendix A. The testing procedures used in this work do not necessarily follow a specific procedure but are defined in the relevant sections 2.2, 3.2.2 and 4.2.2.

Electrochemical Capacitor (EC)

Capacitors are passive electrical devices for energy storage. The energy is stored electrostatically rather than by chemical reactions like batteries. Electrochemical Capacitors (ECs) are a special kind of capacitors. Their advantages compared to batteries are: high power in a relatively small volume or weight ($0.5\text{-}20.0 \text{ kW}\cdot\text{kg}^{-1}$), rapid charging (seconds to minutes) and fast release of energy (seconds to minutes), very high life cycle ($>10^6$ cycles or >10 years), high cycle efficiency ($0.85\text{-}0.99\%$), a wide range of operating temperatures (-40 to $+70$ °C), and they are usually simple to construct [50]. They are also environmentally friendly, safe, reliable and usually non-toxic. Their disadvantages, as compared to batteries, are limited energy densities ($1\text{-}10 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$), relatively high self-discharge (several μA to several mA), require balancing if more than 2 cells are stacked together, and linear sloping voltage during charge and discharge, therefore, requiring electronic control in many applications [3], [4], [50].

The ability of ECs to store great amounts of charge and release them at short times, their high cycling rate and reliability make them invaluable for many applications. Some of the vast applications of EC's are power for emergency applications (e.g., emergency evacuation doors and slides in planes), backup for short power interruptions (e.g., computers), transportation (e.g., an all capacitor powered bus, capture and reuse of brake energy in vehicles, improve power

efficiency for peak use by combining with battery or fuel cell), short-term applications (such as led flashlights, toys) and more [50].

A simple conventional capacitor is built of two parallel metal plates separated by a dielectric. When the plates are charged with a potential difference, negative charges attach physically to the positive electrode, and positive charges attach to the negative electrode. When this device is connected to an electrical circuit, this energy ($< 0.1 \text{ W}\cdot\text{h}\cdot\text{kg}^{-1}$) can be released in a very short time (10^{-6} - 10^{-3} s), as the process is entirely physical [1]. The EC is a derivative of the simple capacitor. The typical EC cell (Figure 1.1) is built of two parallel electrodes, usually of porous material with a very high surface area (e.g., $1000\text{-}3000 \text{ m}^2\cdot\text{g}^{-1}$ for activated carbons), separated by a dielectric porous material and attached to metallic substrates called current collectors. The cell is saturated with a liquid electrolyte [1]. The dielectric separator is a porous layer of electric non-conductive material which is inserted between the electrodes to prevent short-circuiting but allows diffusion of the ions of the electrolyte between both sides. When an electric potential difference is applied between the two electrodes, positive ions are attracted to the negatively charged electrode, and negative ions are attracted to the positively charged electrode. Consequently, a very thin electric double layer (first conceptualized by Helmholtz [51], [52]) is formed at the surface of the electrodes [1], [53].

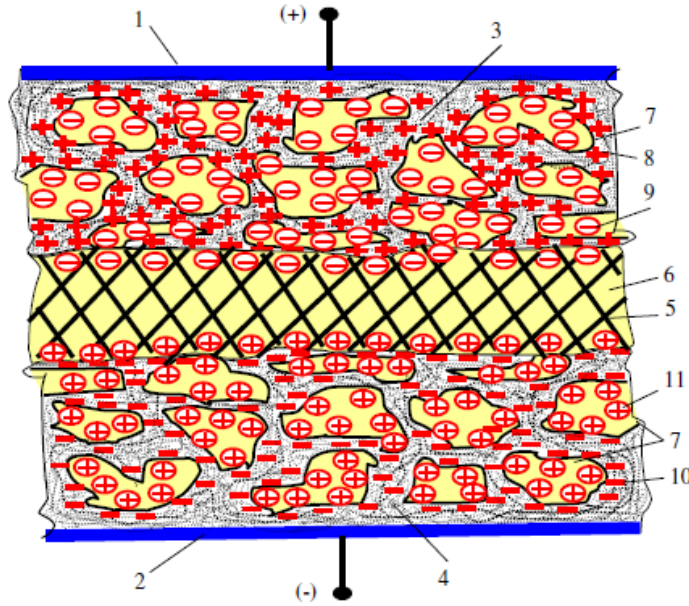


Figure 1.1: Schematic illustration of a charged EC with porous electrodes and separator: 1 and 2—current collectors; 3 and 4—porous electrodes; 5—separator; 6—electrolyte; 7—pores in the electrode material; 8—positive charge in electrode; 9—negative ion in electrolyte; 10—negative charge (electrons) in electrode; 11—positive ion in electrolyte [53].

One important parameter of an EC is the capacitance. The capacitance, C (F), for any capacitor, is proportional to the accessible surface area, A (m^2), and the inverse of the distance, d (m), between the charges, as given by the equation (1.1) [4], [50]:

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} \quad (1.1)$$

where ε_0 ($\text{F}\cdot\text{m}^{-1}$) is the permittivity of free space and ε_r is the relative permittivity (i.e., dielectric constant). As the electrode surface area is very high, and as the distance between the charges in the electrode-electrolyte interface is in the atomic scale (thus, very low) the capacitance values reached in ECs are extremely high in comparison with conventional capacitors.

Two other important features of a supercapacitor are the power and energy. The Energy, E , is defined as [4], [50]:

$$E = \frac{CV^2}{2} \quad (1.2)$$

where V is the potential difference. From this relationship stems that the energy is strongly dependant on the voltage window and the maximum energy is reached when the potential is maximal. The Power, P , is defined as the rate of energy per the time it takes to deliver it. The maximal power that can be delivered is dependent on the resistance of the cell components. This resistance causes a voltage drop during discharge and therefore limits the maximal voltage that can be gained. It is termed the Equivalent Series Resistance (ESR). The maximal power, P_{max} , is calculated using equation (1.3) [4], [50]:

$$P_{max} = \frac{V^2}{4ESR} \quad (1.3)$$

In real cells (consisting of two electrodes and an electrolyte and may contain current collectors and a separator) and systems (consisting of two or more cells connected in series and/or parallel), the highest power that is actually delivered is lower than the maximal power possible [50].

Summarizing the above depictions, the factors that determine the EC capacitance, power and energy are the electrode properties (i.e., material conductivity, electric field across the electrode, electrode surface area, controlled porosity and accessibility of ions to the surface) and the electrolyte/solvent properties (i.e., interactions between ions and solvents, sizes of ions and molecules, the effectivity

of solvents as electron-pair donors, and dipole moments) [1]. Thus, the choice of electrode material and electrolyte are very important, and specific consideration should be given to matching the material pore size to ion size for better accessibility. The different types of electrodes and electrolytes are discussed below.

The ECs can be classified into 3 main types according to the electrode materials used [1]:

- *Electric double layer capacitors (EDLC)*, where the charge storage mechanism is electrostatic – non-faradic (i.e., Helmholtz layer). The EDLC electrode material is usually highly porous such as activated carbon, carbon aerogels, carbon nanotubes and graphene.
- *Pseudocapacitive electrochemical capacitors*, where the charge storage mechanism is electrochemical – faradic (i.e., fast and reversible redox reactions or sorption). Electrode material, in this case, is usually transition metal oxides or conducting polymers.
- *Hybrid capacitors*, where the charge storage mechanism is a combination of the electrostatic and the electrochemical mechanisms. They can be further divided into two types:
 - a. *Composite*, where electrodes consist of combined materials or features. Therefore, the same electrode will contain a pseudocapacitive as well as a double layer capacitance component. Examples are functionalized porous carbons, compositions of conducting polymers with carbons, CNTs or metal oxides.

- b. *Asymmetric*, where one electrode is EDLC type (e.g., activated carbon) and the other is pseudocapacitive “battery-like” type (e.g., intercalating metal oxide).

The electrolytes used in ECs can also be classified into 3 types [1]:

1. *Aqueous* electrolytes (e.g., acids or alkali) have high ionic conductivity (up to $\sim 1 \text{ S}\cdot\text{cm}^{-1}$), the specific capacitances of carbons in them is higher (e.g., for activated carbons $200 - 400 \text{ F}\cdot\text{g}^{-1}$ as compared to $100 - 150 \text{ F}\cdot\text{g}^{-1}$ in organic and ionic liquids), do not require special assembly conditions, are environmentally friendly and are less costly. However, the breakdown voltage of water is low ($\sim 1.23 \text{ V}$) and typically, aqueous designs don't exceed 1 V . Consequently, they are attractive at low cost – high power applications.
2. *Organic* electrolytes have higher dissociation voltage ($2.0\text{-}2.7 \text{ V}$). Hence the specific energy achieved is higher. Thus, the number of cells needed for assembling in systems is lower raising reliability and reducing the need for balancing the voltage of cells in series.
3. *Ionic liquid* electrolytes, which are salts that are liquid at room temperature, have a high electrochemical window ($3.0\text{-}7.5 \text{ V}$), are stable electrochemically and at higher temperatures, non-volatile and non-flammable. However, at room temperature, their ionic conductivity is very low due to low ionic mobility ($0.1\text{-}15.0 \text{ mS}\cdot\text{cm}^{-1}$).

Besides the electrodes and the electrolytes, another part of the EC is the separator. The role of the separator is to prevent electrical short, but at the same time be permeable to the ions that move from one side of the cell to the other. The separator should have the properties of high electric resistance, high ionic conductance (to relevant ions), and should have low thickness without impairing the stability of the cell. The separator material depends on the type of electrolyte used. The separator is usually made of polymer or paper if the electrolyte is organic or made of ceramic or glass if the electrolyte is aqueous.

The ECs can be classified into two types of cell constructions: Symmetric and Asymmetric. They are defined herein:

Symmetric EC

A symmetric cell is an electrochemical cell where both the positive and the negative electrodes are of the same material, size, mass, thickness and ionic radius [50]. In a general case, the capacitance of a cell, C , can be expressed as [50]:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1.4)$$

where C_1 and C_2 are the capacitances of the opposite electrodes (namely, the positive and the negative). In the case of a symmetric cell, the capacitance of both the cell electrodes is identical ($C_1=C_2=C_{elec}$). Subsequently, the capacitance of the whole cell, C , can be expressed as [50]:

$$C = \frac{C_{elec}}{2} \quad (1.5)$$

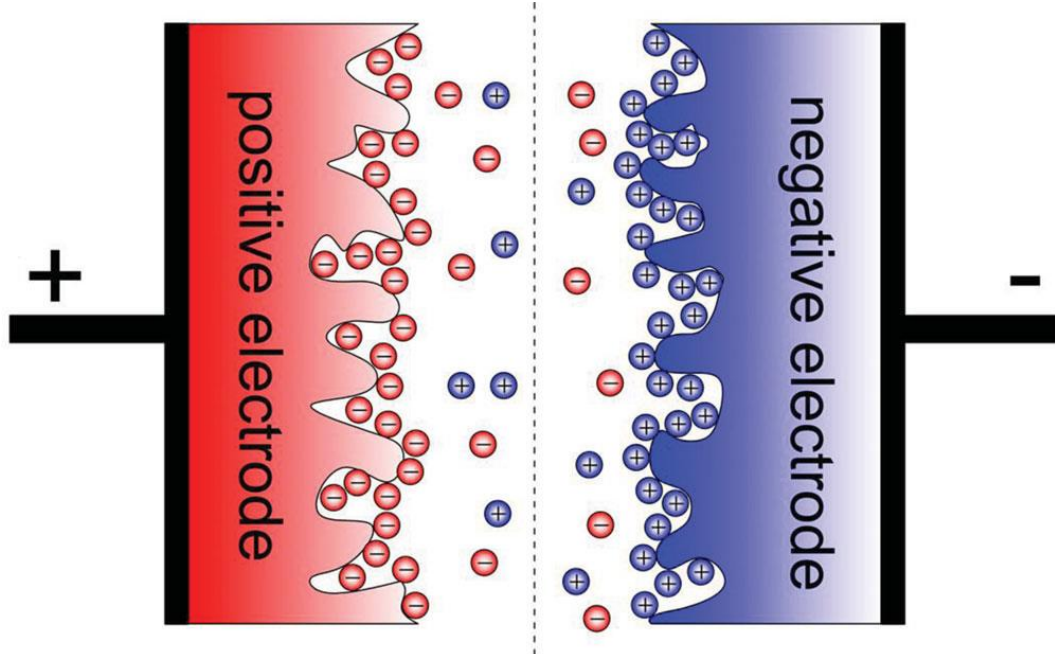


Figure 1.2: A schematic representation of a symmetric EDLC [54].

In reported data, it is common to describe the results in terms of a single electrode, as in this form it is convenient to compare to data from other sources. This reporting style stems from works on three-electrode systems, where the behaviour of a single electrode or half-cell is studied (see description in later section 2.2). It is also customary to express the results as ‘specific’ values, namely per unit of mass, volume or area (S) of the active material in the investigated unit, also for comparative purposes. Hence, the specific capacitance, C_{sp} , of an electrode will be [50]:

$$C_{sp} = \frac{C_{elec}}{S_{elec}} \quad (1.6)$$

where S_{elec} is the mass, volume or area of the active material in each electrode. In the symmetric cell, $S_{elec} = S_1 = S_2$, thus for the whole cell:

$$S = S_1 + S_2 = 2S_{elec} \quad (1.7)$$

Combining equations (1.5), (1.6) and (1.7) and expressing as specific capacitance per electrode gives equation (1.8) [4], [50]:

$$C_{sp} = \frac{4 C}{S} \quad (1.8)$$

Asymmetric EC

An asymmetric cell is an electrochemical cell where the positive and negative electrodes differ in material or in size (i.e., mass and thickness). A common type of asymmetric EC is where one electrode is an electrostatic non-faradic type electrode (usually carbon) and the other is a faradic type, pseudocapacitive electrode (Figure 1.3). In such a cell both charge storage mechanisms are combined. Other asymmetric configurations where the two electrodes are both pseudocapacitive or both EDLC with different properties also exist. The two asymmetric electrodes often have a close, but a different potential window. This way, the cell operational window can be extended, leading to larger energy densities. These asymmetric cells have the potential to bridge the gap between the current conventional common ECs and batteries [50]. However, careful planning needs to be employed when deciding on materials and operation voltages in an asymmetric configuration. Choosing incorrectly may lead to unwanted irreversible reactions, changes in the micro and macro structure of the materials during cycling which may lead to poor cyclability and instability. Therefore, a study of the combined properties is needed.

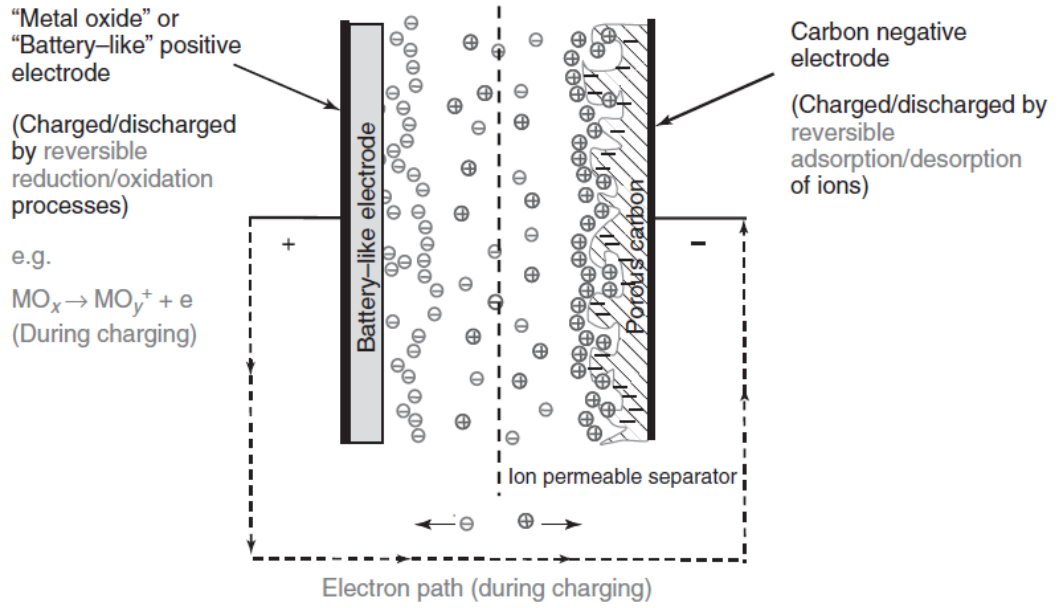


Figure 1.3: Schematic drawing of an asymmetric EC [50].

In an asymmetric cell, in many cases, the capacitance of one electrode (e.g., the faradic) is much higher than the other (e.g., non-faradic), so $C_1 \gg C_2$. In this case, the general equation (1.4) mentioned above becomes [50]:

$$C \cong C_2 \quad (1.9)$$

Hence, the capacitance of the asymmetric cell, in this case, is almost double the capacitance of a symmetric device with a non-faradic electrode in the same size, for which the capacitance of the cell is half the capacitance of the electrode (equation (1.5)). Another approach in asymmetric design is to compensate for the large difference in capacities between the electrodes by balancing their masses.

For any cell, the changes in the charge on the positive electrode, the charge on the negative electrode and the charge derived from ions in the electrolyte during charge/discharge, are the same and limited by the smallest accessible of the three [55]. In a case where excess available ions exist in the electrolyte, such as in this study, the charge exchanges can be expressed by equation (1.10) [56].

$$q_1 = q_2 \quad (1.10)$$

where q_1 and q_2 are the charges accumulated on the opposite electrodes. This charge $q_{1/2}$ depends on the electrode active material mass $m_{1/2}$, the potential range of the charge/discharge $\Delta V_{1/2}$, and the specific capacitance of the electrode material $C_{sp1/2}$ and can be expressed by equation (1.11) [56]:

$$q_{1/2} = m_{1/2} \times C_{sp1/2} \times \Delta V_{1/2} \quad (1.11)$$

In the case of a symmetric cell where both negative and positive electrodes, as described above, are of the same material, mass and thickness, the voltage splits evenly between the two. However, when the electrodes' materials are different, as in the case of an asymmetric cell, the voltage splits according to the materials' specific capacitances. To achieve optimum cell voltage 'mass balancing' is needed. When we combine equations (1.10) and (1.11) we get [56]:

$$q_1 = m_1 \times C_{sp1} \times \Delta V_1 = m_2 \times C_{sp2} \times \Delta V_2 = q_2 \quad (1.12)$$

or

$$\frac{m_1}{m_2} = \frac{C_{sp2} \times \Delta V_2}{C_{sp1} \times \Delta V_1} \quad (1.13)$$

$C_{sp1/2}$ and $\Delta V_{1/2}$ are derived from Cyclic Voltammetry (CV) experiments (explained in later section 2.2.1) of the relevant electrode material in a three-electrode system (described in later section 2.2). When the cell is balanced, and the optimum cell voltage is achieved, we can calculate the parameters of the asymmetric cell with the same equations we use for the symmetric cell, thereby using equation (1.8) given above to also calculate the specific capacitance in the asymmetric case. This enables us, once again, to compare results between different designs and different reference sources. The behaviour of the asymmetric cell will resemble the behaviour of the limiting electrode [50].

When pseudocapacitive reactions occur the theoretical gravimetric capacitance $C_{th,g}$ ($\text{C} \cdot \text{g}^{-1}$) of an EC can be calculated using equation (1.14) [57]:

$$C_{th,g} = \frac{\delta F}{M_w} \quad (1.14)$$

where δ is the number of electrons participating in the electrochemical reaction, F is Faraday's constant ($96,485.3 \text{ C} \cdot \text{mol}^{-1}$) and M_w ($\text{g} \cdot \text{mol}^{-1}$) is the molecular weight of the active material. The practical specific capacity of an operating cell can be different from the theoretical one.

Battery

A battery is an electrochemical device that converts chemical energy into electrical energy using electrochemical oxidation-reduction (redox) reactions. Batteries can store energy for long periods of times and release it when connected to an electric circuit. The main parts of the battery are the anode, the cathode, the electrolyte and the separator. During discharge of the battery, the electrode that has the stronger reducing potential (driving force to give up electrons) is the anode (negative), while itself becoming oxidized. In the process, cations move from anode to cathode, and anions from the cathode towards the anode. The cathode (positive) itself accepts the electrons and is reduced. The process is reversed when charging occurs. The separator allows ions to move between the two halves of the cell without physical contact between the electrodes. A very wide variety of batteries with different capacities and discharge rates exist, applicable to different and vast uses. Some uses of batteries are for car ignition and electronics or for all electric vehicles, smartphones, toys, laptops, hearing aids, for storing wind or sun energy for later use, as an emergency backup in case of electricity failure for different uses, for electronic applications in space and many more. Batteries can be classified into primary and secondary categories. In primary batteries, the processes are irreversible and therefore they are for one-time use. They are commonly used in emergency applications, or for low current portable applications such as watches and hearing aids. In secondary batteries, processes are reversible, and they can be used for several charge and discharge cycles. Mostly, they are charged by applying current, which reverses the reactions and processes that occur during discharge. They are the more commonly

used today, utilised in cell phones, computers, cars and many more applications. Devices using batteries continue to develop and are increasingly complex and powerful in their functionality. Concurrently there is a need for lighter weight and smaller volume. Therefore, corresponding battery technology is required. As can be seen in Figure 1.4, Lithium (Li) ion batteries have higher gravimetric and volumetric energy densities than other types of secondary batteries. They also have better power densities as compared to other battery types. Their advantages result from the use of compounds containing Li which is light in weight in combination with a non-aqueous electrolyte that enables a larger potential window (and thus higher energy densities). These advantages make them an attractive choice for many applications.

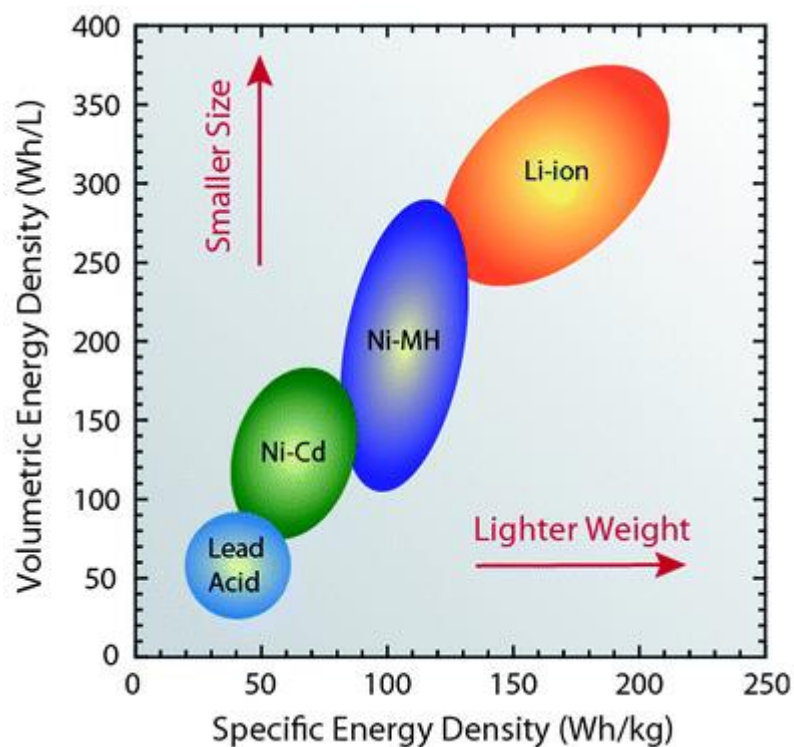


Figure 1.4: Energy density volume versus weight comparison of common secondary battery systems [58].

Lithium-ion batteries (LIB)

The Li element has a standard reduction potential of -3.04 V vs Standard Hydrogen Electrode (SHE), thus it is the strongest reductant on the periodic table. Li is also the lightest metal, therefore the theoretical specific capacity of Li is very high ($3860\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$). These factors make it very attractive as the negative electrode in batteries. However, in its metallic form, it is highly reactive and flammable when it comes in contact with water or moisture. Another potential problem is dendrites, which are outgrowths of Li formed because of inhomogeneity in the deposition of Li, formed during repetitive cycling. These dendrites react with the electrolyte, causing loss of active material and electrolyte. This creates a potential risk of short-circuiting when they penetrate through the separator [59].

There are two kinds of Li related secondary batteries, Lithium-ion battery (LIB) and Li metal battery. In LIB both negative and positive electrodes are based on an intercalation compound (Figure 1.5). Both electrode materials need to be able to insert and extract Li ions in a reversible process. In the second kind, the more common secondary Li metal battery is Li metal polymer battery, in which the negative electrode is the metal lithium, the positive is an intercalation material and the electrolyte is made of poly (Ethylene Oxide) (PEO) saturated with a lithium salt. Two other types of novel Li-metal batteries are Li-air and Lithium-Sulphur (Li-S) batteries. In both cases, the negative is Li metal. In Li-air, the positive is oxygen. In Li-S the positive is liquid sulphur forming Li polysulphide during

discharge. They both potentially have very high specific energy of above 500 $\text{W}\cdot\text{h}\cdot\text{kg}^{-1}$ [59].

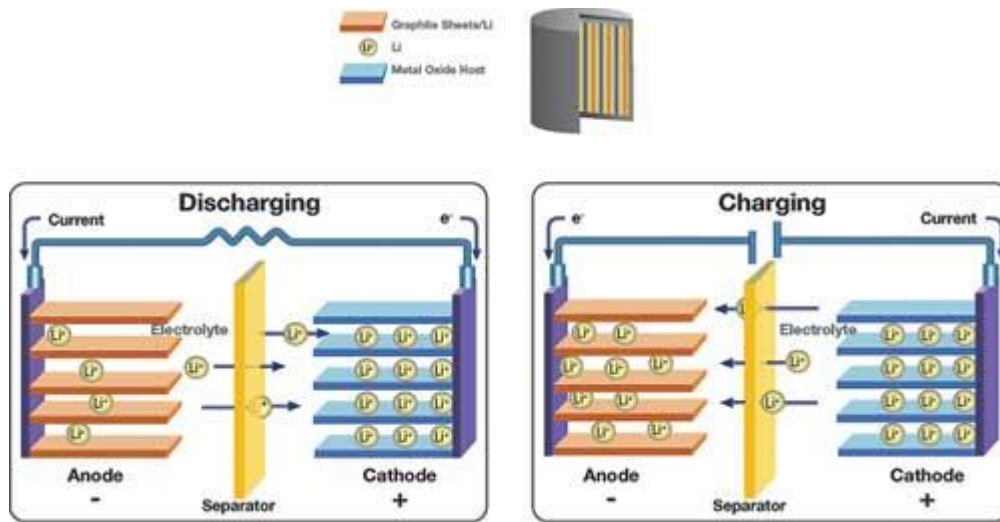


Figure 1.5: Schematic illustration of LIB operation [60].

The positive electrode in LIB can be a lithiated transition metal oxide, $\text{Li}_{(1-x)}\text{MO}_2$, where M is Co, Ni, Mn, V, etc., that can also be doped with Al. These materials have a layered structure. Other options for cathode material are spinel Lithium-Manganese-Oxide $\text{Li}_{(1-n)}\text{Mn}_2\text{O}_4$ (LMO) or Lithium-Ferro-Phosphate $\text{Li}_{(1-n)}\text{FePO}_4$ (LFP). The negative electrodes are usually carbonaceous compounds such as graphite. Another optional material is Lithium-Titanate-Oxide (LTO).

Two types of electrolytes are used in LIB: liquid electrolytes and solid electrolyte. The liquid electrolyte is an organic solvent with a Li salt. The solvents are generally Ethylene Carbonate (EC), Dimethyl Carbonate (DMC) or Diethyl Carbonate (DEC). The salt is the Li source. Examples are LiPF_6 , LiAsF_6 or LiClO_4 . Another option for liquid electrolyte is polymer electrolyte (LiPo). Here again, the source of Li is the Li salt in PEO.

The main advantages of LIB as compared with other secondary batteries are high energy density and stability for relatively long cycling. The important features in a battery are the capacity, energy density and power density. The capacity of a battery, according to Faraday's law, is related to the number of electrons transferred in a reaction. In LIB, one electron is transferred for every Li^+ . To calculate the theoretical capacity of an electrode we need to know the stoichiometry of the active lithiated material. If the reaction between Li-ion and a component A forming the lithiated component Li_nA is given by:



then the specific theoretical gravimetric capacity, $C_{th,sp}$ ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$), can be calculated from equation (1.16) [59]:

$$C_{th,sp} = \frac{1000nF}{3600M_w} \quad (1.16)$$

where n is the number of Li in Li_nA , F is Faraday's constant ($96,485.3 \text{ C}\cdot\text{mol}^{-1}$), and M_w ($\text{g}\cdot\text{mol}^{-1}$) is the molecular weight of the active material Li_nA . The practical specific capacity of an operating cell can be different from the theoretical one.

Another parameter that sheds information on processes in the battery is the coulombic efficiency η (%) that is calculated by equation (1.17) [59]:

$$\eta = \frac{t_d}{t_c} \cdot 100\% \quad (1.17)$$

where t_d and t_c are the discharge and charge times, respectively. When the coulombic efficiency is 100% the lithiation process is totally reversible. If η is

lower than 100%, then there is some charge being diverted to processes other than the reversible lithiation/de-lithiation reaction. It is common that the first charge/discharge cycle for the negative electrode has a low efficiency. This is caused by the irreversible reactions creating a Solid Electrolyte Interphase (SEI) due to electrolyte decomposition at low potentials. After the first cycle, the SEI layer passivates the electrode surface and SEI does not continue to grow. This layer contributes to the stabilization of the lithiation/de-lithiation process. Subsequently, the efficiency improves in the following cycles and very little irreversible capacity loss occurs.

Development of LIBs is directed at enhancing the electrochemical properties in general and specifically improving their energy density and storage capacity. The LIB's energy density depends on operating potentials and capacities of their electrodes. Research of new materials is directed to three main methods: (i) reversible intercalation/de-intercalation of Li-ions to 2D or 3D material; (ii) anode material that performs conversion or reduction/oxidation (redox) with Li; or (iii) elements forming alloys with Li metal. MXene is the type (i) material and Manganese oxide is type (ii) material currently being investigated for LIB use.

1.2.2 Electrode materials

MXene

Considerable research efforts are currently being invested in finding new materials and combinations, as well as enhancing materials for improved supercapacitive properties as well as battery properties and specifically their capacitance, capacity, energy density and power density. One new type of such a material is MXene, which was synthesized by exfoliation from MAX phase materials [12], [15], [61]-[69].

The family of MAX Phase materials consists of over 70 ternary carbides and nitrides which hold combined and favourable properties of both ceramics and metals. Their general formula of MAX phase materials is $M_{n+1}AX_n$ (see Figure 1.6), where **M** is an early transition metal, **A** is an A-group element (mostly IIIA and IVA), **X** is carbon and/or nitrogen and $n = 1-3$. They are generally divided into 3 groups according to their formula, where M_2AX , M_3AX_2 , and M_4AX_3 groups are named 211, 312, and 413, respectively [13].

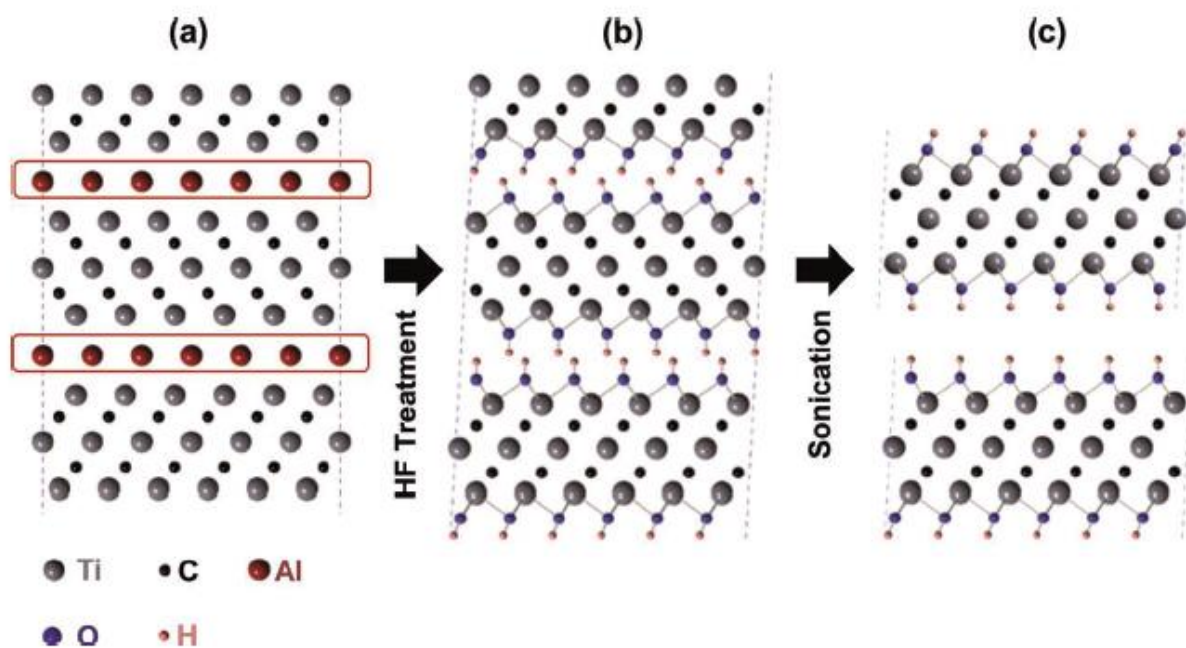


Figure 1.7: Schematic of exfoliation of Ti_3AlC_2 [12]: (a) Ti_3AlC_2 before treatment; (b) After etching of Al and replacement by OH group; (c) separation of layers after sonication.

The separation of the layers is then achieved by sonication (as illustrated in Figure 1.7 above) [12] or by intercalation of ions between the layers (as illustrated in Figure 1.8 below) [69].

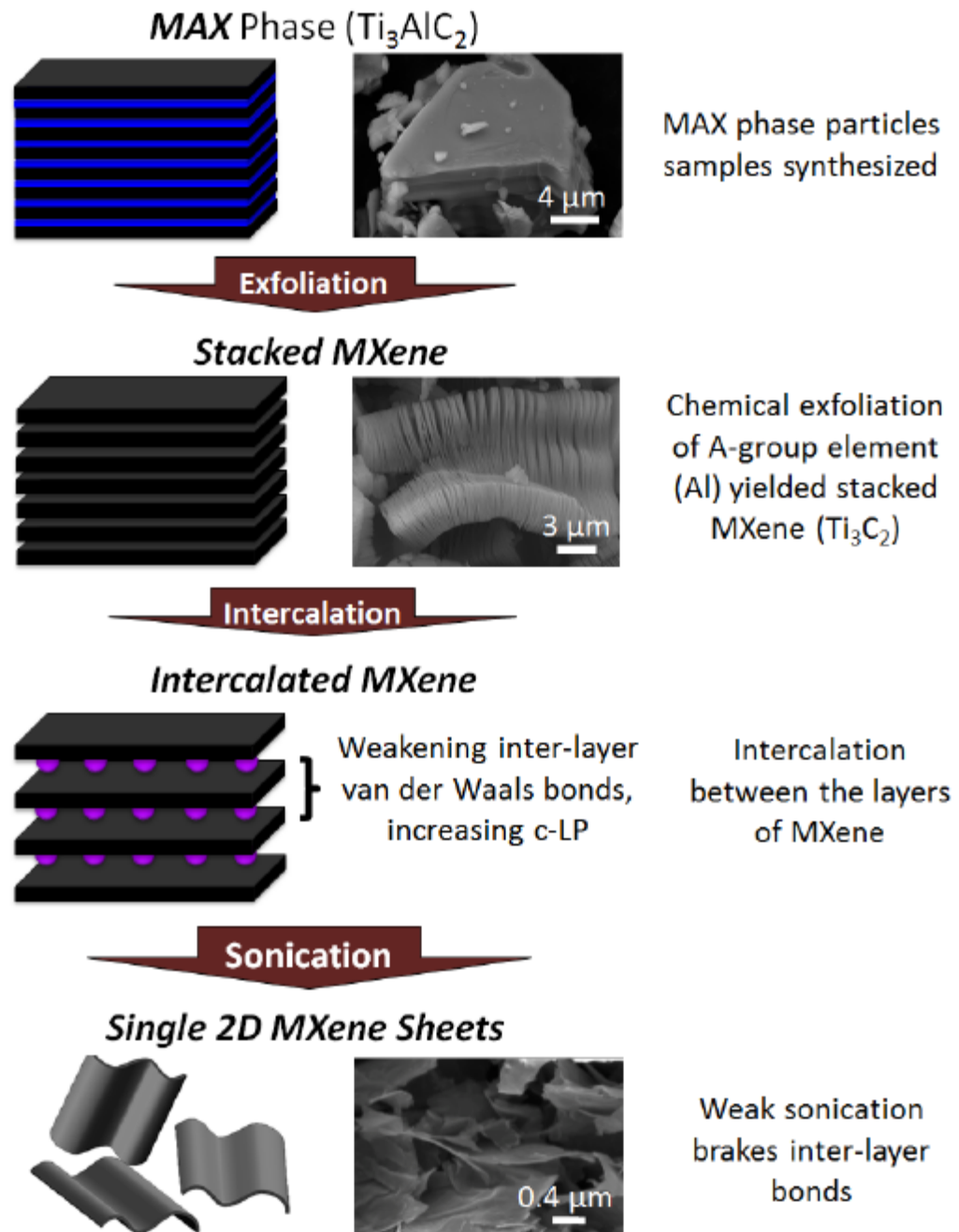
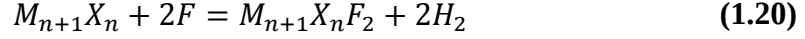
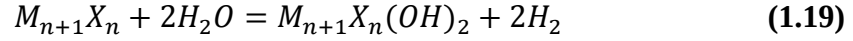
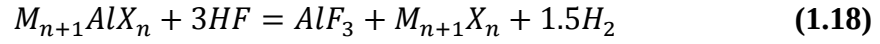


Figure 1.8: Schematic of delamination of MXene flakes. (from the supplementary information of paper by Mashtalir, O. et al. [69])

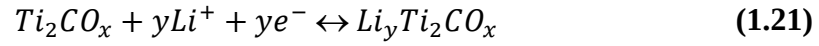
Based on their results, Naguib, M. et al., came to the conclusion that the following reactions take place [62]:



The MXenes have a general formula of $M_{n+1}X_nT_x$ (where T represent surface elements or groups that are attached to the surface as a result of the etching process, such as F, OH or =O, and x represents the number of these attached functional groups) [15]. The properties of these new materials are being explored, both experimentally and theoretically [12], [15], [61]–[69], [82]–[94]. It was demonstrated that a large number of MAX phases can be exfoliated into MXenes [12], [62] and that they can be intercalated with different ions [88], [69]. Their use as potential electrodes for batteries [18]–[28] and ECs [21], [26], [29]–[44] as well as other uses was demonstrated [45]–[47] [63], [69], [84], [86], [88]. It was also shown that by changing and controlling the surface groups and introducing selected impurities, or by combining with other materials, the properties of the MXenes can be selectively altered for favourable use in different applications [15], [65], [82], [92], [93], [95].

The MXene materials do not possess such a high surface area as electric double-layer capacitor (EDLC) materials [18], [23], [36], [79], [87]. Nevertheless, they are suggested to employ the energy storage through a pseudocapacitive ion intercalation route giving rise to high capacitance and attractive electrochemical properties without the need for a high surface area [88]. Ghidui *et al.* [31] obtained an excellent capacitance of $245 \text{ F} \cdot \text{g}^{-1}$ ($900 \text{ F} \cdot \text{cm}^{-3}$) at $2 \text{ mV} \cdot \text{s}^{-1}$ in $1 \text{ M H}_2\text{SO}_4$ for $\text{Ti}_3\text{C}_2\text{T}_x$ films at a window of 0.55 V . The coulombic efficiency was

close to 100% with no measurable capacitance losses even after 10,000 cycles. Lukatskaya *et al.* [57] indicated that the capacitance comes mainly from pseudocapacitive redox reactions of the Titanium. Gogotsi and co-workers [87], [63] studied MXene as an anode material for Li-ion batteries (LiBs) and asymmetric cells and suggested the following lithiation and delithiation reactions taking place when Li^+ ions are inserted into the MXene matrix as described in equation (1.21) [87], [63]:



Ling *et al.* [35] and Zhao *et al.* [42] also showed that expanding the inter-layer gaps improves the capacity by facilitating ion transport. MXene combined with nanocarbons [24], [26], [35], [42], [78], [96] and polymers [29], [35] were shown to yield better capacitance than pristine MXene but in a narrow voltage window (< 1.0 V) in aqueous electrolytes [29], [38], [40]–[42], [96] or higher voltage window (> 1.0 V) in organic electrolyte [26], [78].

Manganese oxide

Manganese Oxide (MnO_2) is a low-cost non-toxic material that is a promising material for both ECs and LIBs. It is environmentally friendly, safe, inexpensive and is abundant in the world generally and in South Africa specifically. According to the mineral commodity summaries 2018 study, South Africa accounts for about 30% of the world's reserve [97]. MnO_2 has several crystallographic forms

including type α , β , γ , ε , and δ - MnO_2 . Manganese oxide has a high rate capability, long shelf life, low cost and a high theoretical specific capacity of $1232 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ and theoretical capacitance of $1370 \text{ F}\cdot\text{g}^{-1}$. Therefore, it is used for alkaline batteries, Zinc-carbon batteries, lithium manganese primary batteries, magnesium, lithium and sodium ion rechargeable batteries and supercapacitors. However, the actual capacities reached are significantly lower than the theoretical. It also has a low electrical conductivity, a low repetitive cycling ability and a low rate capability. Electrolytic manganese dioxide (EMD) is named after its production method. When produced commercially it is generally composed of several crystallographic phases, possesses a low surface area and does not exhibit good capacity. Therefore a lot of research is devoted to improving its capabilities of EMD, and the properties of MnO_2 for energy storage devices in general [7], [8].

2. Chapter 2: Characterisation

In this section, the material characterization and electrochemical characterisation methods and equipment are discussed.

2.1 Materials characterization

This chapter outlines and describes the basic principles of material characterization. Several techniques used for characterization of the materials in this work, namely composition, structure, morphology, chemistry and electrochemical properties are detailed. The materials' characterization techniques described here are Powder X-Ray Diffraction (PXRD), X-Ray Photoelectron Spectroscopy (XPS), Raman Spectroscopy, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS) and surface area and porosity analysis. The electrochemical characterization techniques described here are Cyclic voltammetry (CV), Galvanostatic Cycling with Potential Limitation (GCPL), Electrochemical Impedance Spectroscopy (EIS) and Voltage holding and cycling.

2.1.1 Powder X-Ray Diffraction (PXRD)

The Powder X-ray Diffraction (PXRD) is a popular technique for general material characterization. It enables fast, non-destructive analysis of powders containing several components without the need for extensive sample preparation. It is used to uniquely identify phases of bulk crystalline materials by comparing their unique X-ray signature to a huge database which practically contains XRD

fingerprints of every phase of every known material. This technique can also be used for amorphous materials if it can be compared to a suitable reference pattern. It can be used qualitatively to identify compositions and phases and quantitatively to determine relative amounts of these components and phases from diffraction peak intensities. It is utilised, apart from phase identification, also to determine the purity of materials, crystallinity, lattice parameters and more.

The XRD instrument consists of an X-ray tube, a sample holder and a detector. The tube produces a monochromatic X-ray beam which bombards the sample. When these waves reach the sample, the sample atoms diffract them, producing spots at particular angles on the detector plate that are constructive interferences [98]. By measuring the angle where these spots occur, the spacing between the atoms can be determined using Bragg's law [99] given in equation (2.1):

$$n\lambda = 2d \sin\theta \quad (2.1)$$

where n is an integer (i.e., 1, 2, 3, etc.), λ (Å) is the wavelength of the incident X-ray radiation (1.54 Å for Copper (Cu) or 1.79 Å for Cobalt (Co)), d (Å) is the interplanar distance between lattice planes (the interatomic spacing) and θ (°) is the diffraction angle.

In powder diffraction, every possible crystalline orientation of the material analysed is represented equally and randomly. Consequently, a statistically significant number of atoms exist in the powder in every orientation of each plane of the crystal structure, diffracting the X-rays in all angles. As a result, the pattern on the detector plate appears as rings around the beam axis rather than discrete

spots. These rings are translated to peaks in a diffractogram plotting peak intensity vs 2θ angle or d -spacing. The diffraction peaks are represented by Miller indices (h,k,l) to identify the different planes of atoms.

PXRD was used here to confirm material phase identities and learn about changes in their structure and was performed on as-synthesised powder samples, using Bruker D2 Phaser Desktop Diffractometer or Ultima IV Rigaku Diffractometer. Large aggregates of the examined powders were crushed gently using mortar and pestle, transferred to a sample holder and the powder surface was gently levelled. The holder was placed in the XRD machine. The Bruker D2 Phaser Desktop Diffractometer (Bruker AXS, Karlsruhe, Germany) was equipped with Lynxeye detector using Co $K\alpha$ radiation of wavelength $\lambda = 1.78897 \text{ \AA}$. The diffraction angles ranged between $2\theta = 7^\circ$ to $2\theta = 100^\circ$, with a step size of 0.0260° . The generator settings were 30 kV and 10 mA. The Ultima IV Rigaku Diffractometer (Rigaku Co., Tokyo, Japan) was equipped with D/tex Ultra detector with a monochromatized Cu $K\alpha$ radiation of wavelength $\lambda = 1.54059 \text{ \AA}$. The diffraction angles ranged from $2\theta = 3^\circ$ to $2\theta = 90^\circ$, with a step size of 0.010° at a speed of $10^\circ/\text{min}$. The Bruker DIFFRAC.SUITE EVA software with International Centre for Diffraction Data (ICDD) PDF-4+ database (2014/2015/2016) was used to identify the phases from the patterns acquired on both instruments.

Note: When comparing results of $2\theta_1$ spectrum obtained with an incident wavelength of λ_1 to $2\theta_2$ spectrum results obtained with a different incident wavelength of λ_2 , we need to remember that there will be a shift in the angles for

the same d spacing. Since d and n are the same, we can derive from Bragg's law in equation (2.1) the following equation to calculate the new angle $2\theta_2$:

$$2\theta_2 = 2 \sin^{-1} \left(\frac{\lambda_2}{\lambda_1} \sin \left(\frac{2\theta_1}{2} \right) \right) \quad (2.2)$$

2.1.2 X-Ray Photoelectron Spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS), known also as Electron Spectroscopy for Chemical Analysis (ESCA), is a spectroscopic technique suitable for investigating the surfaces of materials. It gives quantitative information on the different elements present on the sample's thin surface layers (can be between 1- 5 nm in depth), their empirical formula and their chemical and electronic state. The material can be analysed as received without a need for treatment. XPS spectra are obtained when the material is bombarded with X-ray photons, which interact with core electrons present around the nucleus of the atoms of the sample. The electrons that escape the sample, are emitted at a specific kinetic energy (Figure 2.1). This kinetic energy depends on the photoelectron energy and the binding energy required to remove the electron. As this binding energy depends on the atom type, the orbital in which it is situated and its bonding neighbours, it can be plotted and analysed, and the type of atom, chemical state and abundance can be determined [100]. The XPS consists of a monochromatic X-ray source, a sample holder and electron analyser, all situated in a high vacuum chamber.

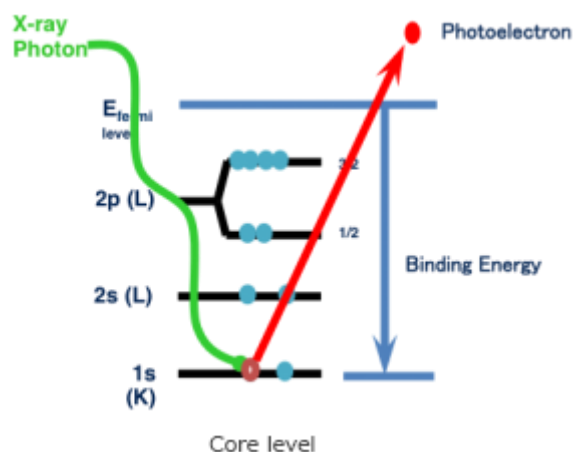


Figure 2.1: Schematic diagram of XPS operation [101].

XPS measurements in this work were performed using an AXIS ultra DLD spectrometer (Kratos Analytica) equipped with a monochromatic AlK α excitation source (1486.6 eV) to investigate the oxidation states of the elements in the samples. The deconvolution of the obtained XPS high-resolution core-levels was carried out using CasaXPS Version 2.3.16.

2.1.3 Raman Spectroscopy

Raman spectroscopy is a technique that provides information about molecular vibrations and crystal structure and can be used for sample identification and quantification owing to fingerprint patterns of known materials. It can also be a useful tool in evaluating local crystallinity orientation and stress in polymorphs. This technique is very fast, non-destructive, and no special sample preparation is needed. In this technique, a monochromatic laser light source is projected on a sample. A cooled Charge-Coupled-Device (CCD) camera detects the scattered light. Most of the light that passes through the sample interacts with the molecule and distorts the cloud of electrons to form a “virtual state”, but the electrons

immediately “fall” back and do not change in energy in an elastic process called Rayleigh scattering. A minuscule amount of the scattered light is shifted in energy from the laser incident frequency in an inelastic process. This shift is caused by interactions between the electromagnetic waves and the sample molecules’ vibrational energy levels (Figure 2.2). This shifted light is plotted versus the shift in wavenumber in a Raman spectrum and can be analysed [102].

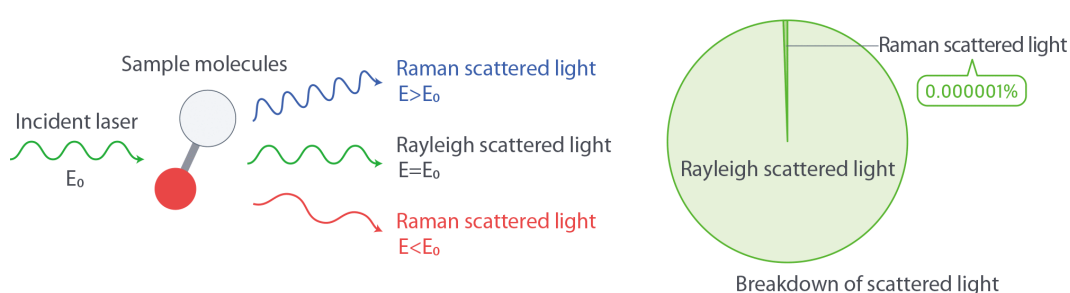


Figure 2.2: Scattering of Rayleigh and Raman light by molecules [103].

To help determine the structural composition of the materials in this work Raman spectra were collected using a Horiba LabRAM HR micro-Raman spectrometer equipped with an Ar (Argon) ion laser (514.5 nm, 0.5 mW at the sample) as the excitation source. Backscattered spectra were collected using an Olympus BX41 microscope attachment (100x objective), and the light was dispersed with 600 lines per millimetre gratings onto a liquid nitrogen–cooled CCD detector. Spectra were processed using LabSpec v5 software.

2.1.4 Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (SEM) is a popular imaging tool that utilizes a focused high-energy electron beam to generate a range of signals by interacting

with the atoms on the surface of a sample. These signals can be gathered by different detectors and can be translated to information about the sample including macro and micromorphology, chemical composition, crystalline structure and orientation of the materials in the sample. Different instruments may have different detectors. The most common use is producing an image from secondary electrons (SE). These electrons have very low energy, therefore when emitted are gathered near the sample surface and can give a very detailed high-resolution image of the sample surface. The beam is very narrow, giving the produced image a large effective focus range. Subsequently, the 2D image has an appearance of a 3D image, enabling the visualization of the topography. Some SEM instruments have two SE detectors. A conventional SE detector and an in-lens SE detector. The in-lens detector is located inside the column and due to its electron collection method images with high contrast can be obtained. This may be advantageous in some cases, especially when low voltages and small working distances are involved. Backscattered electrons (BSE) also produced are elastic scattering beams reflected from the sample with higher energy. They emerge from deeper regions in the sample, giving an image with less resolution. The BSE signal intensity is strongly related to atomic numbers. Therefore, along with characteristic X-ray scattering from the sample that is used to identify the chemical composition, they can map the abundance of the atoms in the sample. Other signals generated that can also be analyzed include plasmons, non-characteristic x-rays, cathodoluminescence, and electron-beam-induced current [104]. Sample preparation for the SEM is usually minimal. Electrons from the beam must pass through the sample and be evacuated into the metallic

mounting plate to prevent electrostatic build-ups. These charge build-ups can cause image distortion or saturation. Therefore, samples are attached or dispersed on a conducting double-sided tape made of carbon, copper or other metals or alloys. In case of a sample that is partially or totally insulating, coating with a thin layer of conducting material is also needed. Common coating materials are graphite, gold, or some other metals or alloys.

The SEM's major parts, as presented in Figure 2.3, are an electron gun, an electron lens system, electron-beam deflection coils, various electron detectors, and display and recording devices. The electron gun is situated on a thermionic filament cathode, or a field-emission needle tip and emits an electron beam. The electron gun is often made of Tungsten (W). Another type of electron emitter is the lanthanum hexaboride (LaB_6) cathode. This cathode enables higher brightness levels but also needs a better vacuum system. Field emission guns can be made of a zirconium oxide (ZrO) cathode which needs heating or W single crystal emitters that can function at room temperature. The W single crystal field-emission gun has a much smaller source size (5 - 10 nm) as compared to the W filament (1 - 10 μm) with much higher current density and brightness. The electron beam is usually in the range of 0.5 to 40 keV. An electron-condenser lens system usually focuses the electron source forming a small probe on the sample. The beam passes through pairs of scanning coils and a final objective lens, which deflects the beam in the x and y axes so that it scans over a chosen area of the sample surface in a raster fashion. The column is under vacuum, which helps to evacuate unwanted atoms and molecules from the column so that they will not interact with the electron beam. The electron detector improves the signal-to-noise ratio [104].

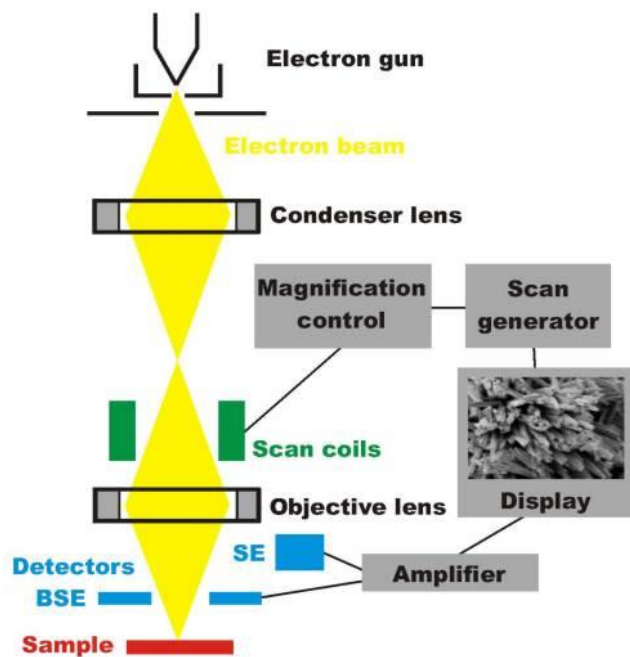


Figure 2.3: Schematic representation of an SEM operation [105].

SEM images in this work were collected using an FEI Nova Nanolab 600 FIB/SEM instrument operating at 30 kV or using a Carl Zeiss Sigma Field Emission Gun Scanning Electron Microscope (FEG-SEM) instrument operated at varying accelerating voltages between 5 and 20 kV. The elemental composition on the SEM was obtained using an Oxford INCA Energy Dispersive X-ray Spectroscopy (EDS) system (see section 2.1.6). Charging or partially charging samples were coated with a thin coat (~10 nm) of gold/palladium alloy.

2.1.5 Transmission Electron Microscopy (TEM)

The Transmission Electron Microscopy (TEM) is an imaging tool that uses a focused high-energy electron beam that is transmitted through a very thin sample.

The electrons interact with the sample atoms and the transmitted image is then magnified and focused onto an imaging device, such as a fluorescent screen or a CCD. The TEM consists of an electron source, a condenser system, an objective lens, and a projector system (Figure 2.4). Many TEM instruments have in addition an X-ray detector and/or an energy loss spectrometer for elemental analyses. The electron gun is composed of a cathode and an accelerating system. The cathode can be a thermal cathode, a Schottky emitter or a cold field emission cathode. In the thermal cathode, the electrons are emitted at high temperatures from tungsten or LaB₆. In the Schottky emitter, a strong electrostatic field is applied to a tip, thereby lowering the emission barrier. In the cold field emission cathode, a stronger electrostatic field at a sharp tip is used to extract electrons by means of the quantum mechanical tunnel effect. This type of cathode requires an ultra-high vacuum to avoid destruction of the tip by atoms present in the chamber. The electrons then pass through an accelerating system towards the anode. Most transmission electron microscopes operate at voltages of 100–300 kV. The condenser system transfers the electrons onto the specimen, by the use of two to five electron lenses. These lenses enable altering the illumination angle and controlling the size of the illuminated area on the sample. The electrons are then transmitted through the sample, focused and then magnified and obtained as an image [106].

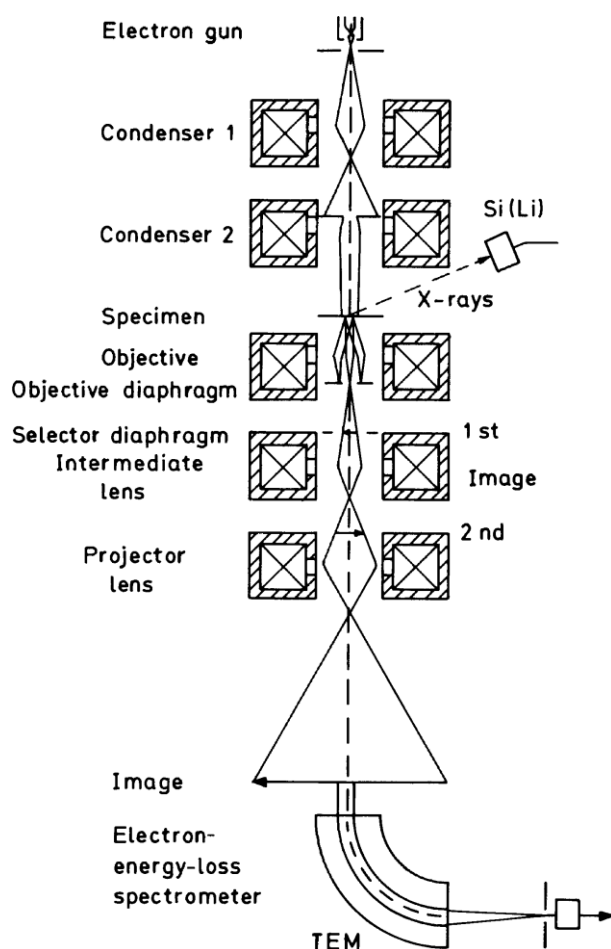


Figure 2.4: Schematic diagram of a typical TEM [107].

The TEM can be used to see thin layers, crystal structure, orientation and more.

TEM images were collected, in this work, using an FEI Tecnai T12 Spirit electron microscope (FEI Co., Hillsboro, OR, USA), operated at an accelerating voltage of 120 kV. The samples were ultra-sonicated in ethanol and loaded onto a carbon-coated copper grid. Elemental composition was obtained using an Oxford INCA Energy Dispersive X-ray Spectroscopy (EDS) system (see section 2.1.6) on the TEM.

2.1.6 Energy Dispersive X-ray Spectroscopy (EDS)

Energy Dispersive X-ray Spectroscopy (EDS or EDX) is an analytical technique used in conjunction with the SEM or the TEM for elemental analysis. The X-ray spectrum is emitted by a sample bombarded with a focused beam of electrons of the SEM or the TEM. The analysis can be qualitative or quantitative, by identifying the lines in the spectrum and measuring their intensities in comparison to calibration standards of known compositions. This is done by recording the number of electron-hole pairs created after absorption of the X-ray photon in a semiconductor detector [106]. Point analysis or scanning of a selected area in a raster fashion producing an element distribution image or 'map' can be carried out. Basically, all elements between Be and U (Atomic number 4 and 92, respectively) can be detected, although some overlap of intensity may occur making it difficult to separate the lines [107].

Elemental composition analysis and identifying the phases observed in SEM and TEM images was performed using an Oxford INCA EDS on the respective SEM or TEM instrument.

2.1.7 Surface area and porosity analysis

Specific Surface Area (SSA) and porosity can be measured by a gas absorption method. The Brunauer-Emmet-Teller (BET) technique most commonly used, named after the three who first published the theory [108], is based on the concept that inert gas is physically adsorbed on the surface of a solid without reacting, in a single monolayer. This is applicable to liquid nitrogen (N_2) which has a boiling

temperature of -196°C . Nitrogen gas is most commonly used as it is inert, and the molecule is small therefore tracing the surface roughness best and enabling entering small pores. The sample is weighed and pre-treated by heating and flowing an inert gas to remove any adsorbed water or other contaminants. The sample is then cooled, and the inert measuring gas allowed to adsorb on the surface. The quantity of adsorbed gas is measured and is directly proportional to the area it adsorbed on therefore allowing the calculation of the sample surface area.

The SSA and porosity were measured using a Micromeritics TriStar II 3000 area and porosity analyser instrument. Prior to testing, a sample of about 0.2 g was degassed in N_2 at 150°C for 4 hours or 90°C overnight and the surface area measurements were performed via N_2 adsorption/desorption at -196°C and calculated by the BET analysis method in the relative pressure range $P/P_0=0.05\text{--}0.35$. Total pore volumes of the samples were calculated at a relative pressure of $P/P_0=0.99$.

2.2 Electrochemical characterisation

To assess the electrochemical characteristics and behaviour of investigated materials for ECs and batteries, several techniques are employed as described below in this section. The data is acquired on electrochemical cells in three-electrodes or two-electrode systems. A three-electrode system (Figure 2.5a) is employed when studying the half-cell behaviour of the analysed material separately. This cell configuration has three components. (i) The investigated material is integrated into the working electrode (WE), where the measured electrochemical activity occurs. (ii) A reference electrode (RE), made of materials with a known reduction potential that passes no current, serves as a reference point for determining the voltage of the WE. (iii) The counter electrode (CE), made of a stable non-reactive material with a high surface area, completes the circuit and carries the current. All three electrodes are immersed in an electrolyte and connected to a potentiostat/galvanostat/EIS (Electrochemical Impedance Spectroscopy) component in an electrochemical analysis system on the other end. The voltage is controlled or measured between the WE and RE and the current is controlled or measured between the WE and CE. A two-electrode system (Figure 2.5b) is used when studying the behaviour of a full cell and is a better representation of how the cells will behave as seen by the consumer. The potential measured in this case is the voltage of the whole electrochemical cell. This configuration consists of a WE and a CE. The RE cable is connected to the CE.

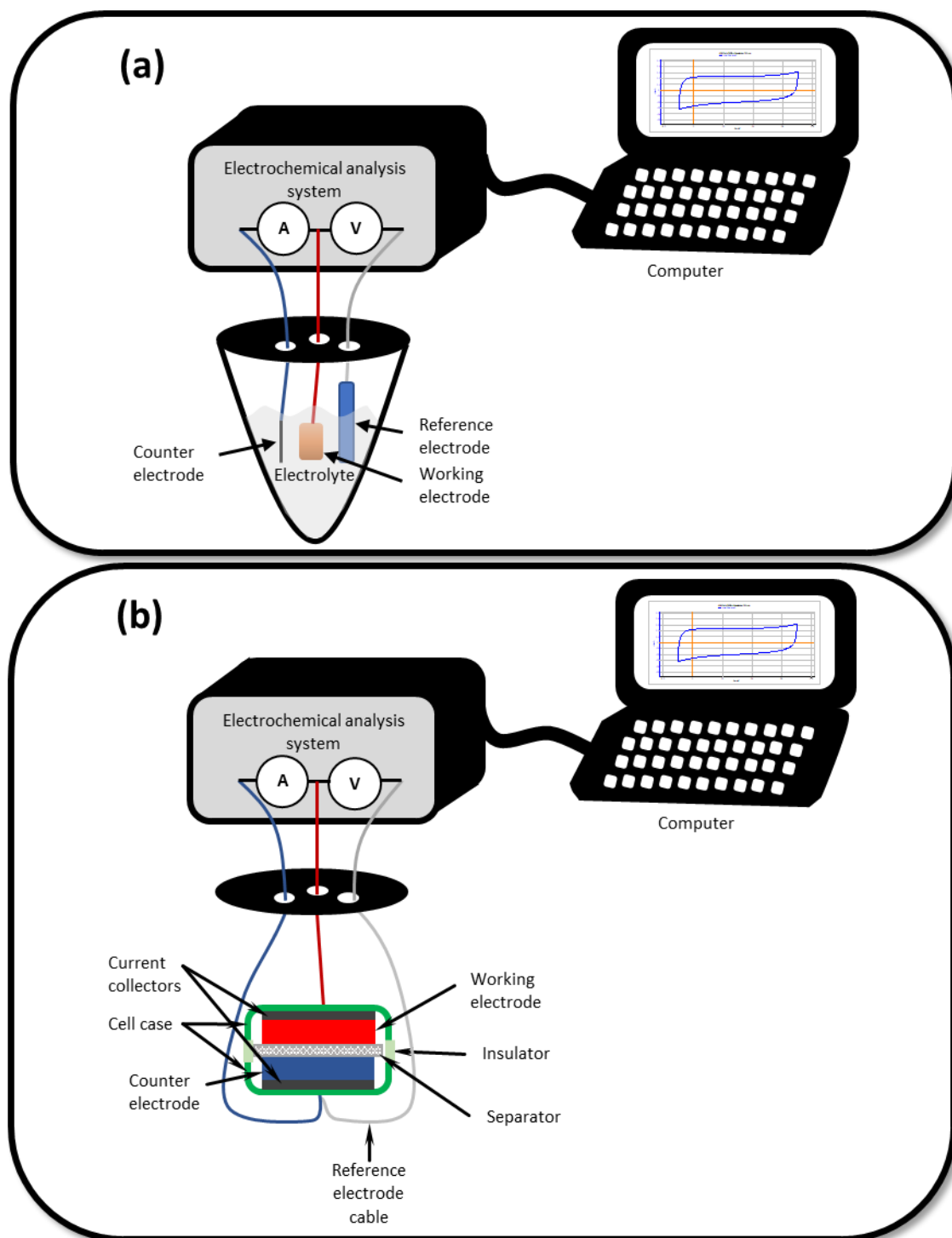


Figure 2.5: A schematic diagram representing a three-electrode system (a) and a two-electrode system (b).

2.2.1 Cyclic voltammetry

Cyclic voltammetry (CV) is a popular technique used to acquire qualitative information on the kinetics of reactions and processes happening at the electrode/electrolyte interphase in electrochemical systems. In this technique, the potential of the working electrode is changed linearly from one potential to another and then back again, at a specific scan rate (Figure 2.6), and the resulting current is measured. The current is plotted vs the voltage for each scan rate in a plot termed voltammogram. The resulting curve depends on the kinetics of the physical and chemical reactions taking place within the voltage range. The upper half of the curve represents oxidation and the lower half represents reduction (in accordance with standard IUPAC convention). This technique provides information on the thermodynamics of redox reactions, kinetics of electron-transfer reactions and charge separation. It can be used to analyse coupled electrochemical reactions and adsorption processes [109].

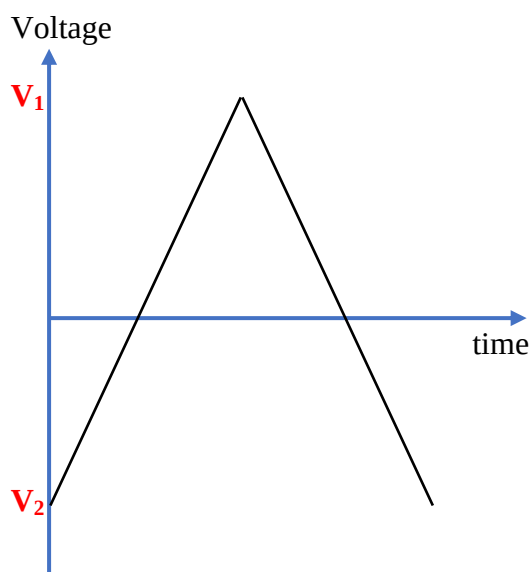


Figure 2.6: A triangular potential waveform.

For an ideal double-layer capacitor, the charge is electrostatic with no resistivity, therefore the current is independent of the potential yielding a rectangular-shaped voltammogram (Figure 2.7a). For a double-layer capacitor that is affected by resistive losses, the current is dependent on the voltage applied, therefore the curve on the voltammogram will be similar to a parallelogram (Figure 2.7b). Electrodes with kinetically slow faradic processes exhibit distinctive peaks and the electrical charge stored in the capacitor is strongly dependent on the potential (Figure 2.7c) [110].

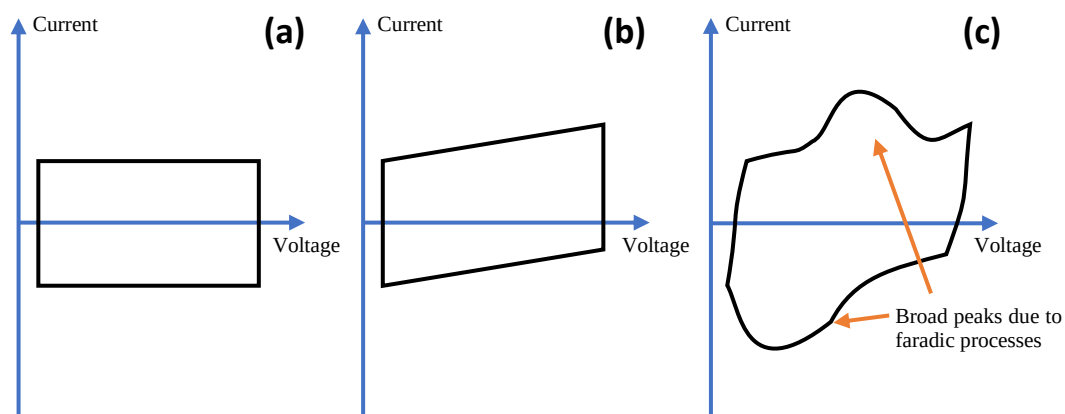


Figure 2.7: A representation of cyclic voltammograms of an ideal capacitor (a), a capacitor with resistivity (b) and influences of faradic reactions (c). (After Frackowiak & Béguin [110])

Unique voltammogram curve profiles are obtained depending on whether the electronic transfer processes at the material surface are reversible (Figure 2.8a), quasi-reversible (Figure 2.8b) or irreversible (Figure 2.8c) [109]. When the process is reversible the positive potential sweep will be a mirror image of the negative sweep. Conversely, when the process is irreversible, a different range of potentials is obtained for the oxidation and for the reduction.

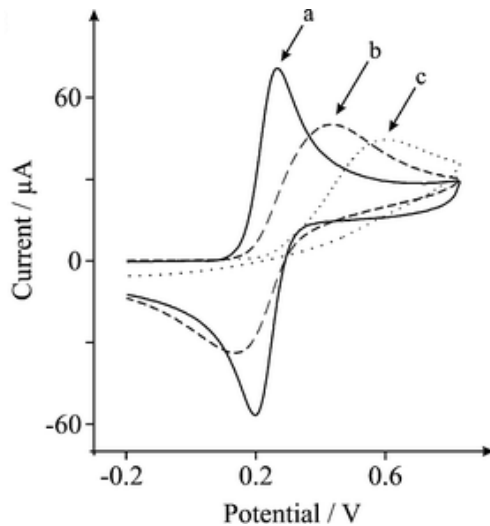


Figure 2.8: A representation of cyclic voltammograms of Cyclic voltammograms for reversible (a), quasi-reversible (b) and irreversible (c) electron transfer processes [109].

When calculating the capacitance, C (F) from a voltammogram, the well-established equation (2.3) can be used [4], [111].

$$C = \frac{(\int I(t)dt)/_2}{V} = \frac{(\int I(V)dV)/_2}{\nu \cdot V} \quad (2.3)$$

where $\int I(t)dt$ (A·s) is the charge integrated from a current vs time diagram, $\int I(V)dV$ (A·V) is the integration of the area enclosed by the CV, when near rectangular, divided by 2 to account for the discharge part, ν (mV·s⁻¹) is the scan rate and V (V) is the voltage window for the CV curve. The specific capacitance, C_{sp} (F·g⁻¹, F·cm⁻³ and F·cm⁻² for gravimetric, volumetric and geometric specific capacitances, respectively) for the three-electrode systems or half-cells is calculated by equation (2.4) in a similar way to equation (1.6) detailed in section 1.2.1.

$$C_{sp} = \frac{C}{S} \quad (2.4)$$

where S is the mass (g) or the volume (cm³) or the geometric area (cm²) of the active material. In the case of a symmetric EC cell, where both the working and counter electrodes are of the same material, size, mass and thickness, the specific capacitance, C_{sp} per electrode (F·g⁻¹, F·cm⁻³ and F·cm⁻² for gravimetric, volumetric and geometric specific capacitances, respectively) is evaluated by equation (1.8).

$$C_{sp} = \frac{4 C}{S} \quad (1.8)$$

where S is the mass (g) or the volume (cm³) or the geometric area (cm²) of the active material of both electrodes.

The CV testing was performed using a computer controlled multi-channel Potentiostat/Galvanostat Bio-Logic VMP3, driven by EC-Lab[®] v10.40 software.

2.2.2 Galvanostatic Cycling with Potential Limitation (GCPL)

Galvanostatic Cycling with Potential Limitation (GCPL) is an extensively used electrochemical analysis and characterization method for batteries and ECs. In this test, as can be seen in Figure 2.9, constant currents for charge and discharge are imposed in a cycling fashion and the voltage is recorded increasing or decreasing, while the potential is limited for both charge and discharge. The obtained plot of voltage versus time provides information on the behaviour of the tested cell. For a cell, where the reactions and resistances are constant and reversible over the

whole tested voltage range, such as in the case of an EDLC, the curve will be linear and often an isosceles triangle will be obtained (Figure 2.9a). If humps or non-linearity in the slope appear at specific voltages during charge or discharge, it is an indication of pseudocapacitive or other reactions existing (Figure 2.9b).

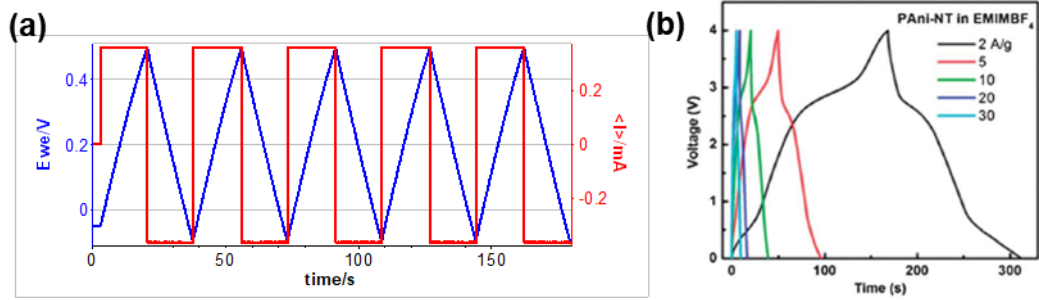


Figure 2.9: GCPL test plots of (a) the current versus time (red) and the corresponding voltage versus time (blue) for an EC; (b) voltage versus time for an EC with humps owing to a pseudocapacitive effect [112].

GCPL testing is one of the most used cycling methods for determining capacitance, capacity and cycle life in supercapacitors and batteries. The properties of the EC cells and electrodes, i.e., specific capacitance, energy density, power density and maximum power density are calculated from the discharge part of the GCPL curves. The capacitance, C (F) of an EC is given by the well-established equations (2.5) [4], [111].

$$C = \frac{I\Delta t}{\Delta V} \quad (2.5)$$

where I (A) is the applied current, ΔV (V) is the discharge voltage window excluding the IR drop, Δt (s) is the corresponding discharge time. Specific capacitance, C_{sp} ($F \cdot g^{-1}$, $F \cdot cm^{-3}$ and $F \cdot cm^{-2}$ for gravimetric, volumetric and

geometric specific capacitances, respectively) for the three-electrode systems or half-cells is calculated by equation (2.4) given above in section 2.2.1. In the case of a symmetric cell, where both the working and counter electrodes are of the same material, size, mass and thickness, the specific capacitance, C_{sp} per electrode ($F \cdot g^{-1}$, $F \cdot cm^{-3}$ and $F \cdot cm^{-2}$ for gravimetric, volumetric and geometric specific capacitances, respectively) is evaluated by equation (1.8) given above in section 1.2.1. The energy density, power density and maximum power density for an EC are calculated from GCPL results. Gravimetric energy density, E_{sp} ($W \cdot h \cdot kg^{-1}$), in correlation with equation (1.2) that was given in section 1.2.1 for the energy, is calculated using equation (2.6) [111].

$$E_{sp} = \frac{C \Delta V_{max}^2}{2m} \cdot \frac{1000}{3600} \quad (2.6)$$

where ΔV_{max} (V) is the maximum voltage region applied and m (kg) is the mass of the active material in both electrodes. The gravimetric power density, P_{sp} ($W \cdot kg^{-1}$), is calculated according to equation (2.7) [50].

$$P_{sp} = \frac{E_{sp} \cdot 3600}{\Delta t} \quad (2.7)$$

The maximum power density, $P_{max,sp}$ ($W \cdot kg^{-1}$), in correlation with equation (1.3) that was given in section 1.2.1 for the maximal power, is evaluated by equation (2.8) [111].

$$P_{max,sp} = \frac{\Delta V_{max}^2 \cdot 1000}{4m \cdot ESR} \quad (2.8)$$

where ESR (Ω) is the equivalent series resistance of the system, determined from the initial voltage drop between the first two points at the beginning of the discharge curve. In the case where discharge comes immediately after charge by switching the current, it is determined by equation (2.9) [113].

$$ESR = \frac{\Delta V_{iRdrop}}{2I} \quad (2.9)$$

where ΔV_{iRdrop} (V) is the voltage drop between the first two points after the switch to discharge.

For a battery, the practical specific capacity, $C_{p,sp}$ ($\text{mA}\cdot\text{h}\cdot\text{g}^{-1}$), can be calculated from the GCPL test using the following equation (2.10) given below [6]. This is different from the theoretical value, $C_{th,sp}$, that was presented in equation (1.16) in section 1.2.1.

$$C_{p,sp} = \frac{I\Delta t}{3600m} \quad (2.10)$$

where I (A) is the applied current, Δt (s) is the discharge time and m (g) is the active material weight. The gravimetric energy density, E_{sp} ($\text{W}\cdot\text{h}\cdot\text{kg}^{-1}$), for the battery, is calculated using equation (2.6) [6].

$$E_{sp} = \Delta V C_{p,sp} \quad (2.11)$$

where ΔV is the voltage window.

When batteries are tested in GCPL at different currents for comparison purposes they are referred to as C -rates. C -rate is the measure of the rate at which the battery is discharged relative to the theoretical capacity $C_{th,sp}$ (given in equation

(1.16)) $1C$ is the current needed to discharge the battery fully in one hour. It is calculated by [6]:

$$1C = mC_{th,sp} \quad (2.12)$$

For example, for a battery of 100 mA·h, $1C$ is 100 mA. For a rate 5 times slower, the current would be $0.2C$, which in the example case be 20mA, and the battery will be fully discharged in 5 h. For a rate 5 times faster, $5C$, the current will be 500mA and the battery will be fully discharged in 12 min.

The coulombic efficiency η (%) for both ECs and batteries is calculated by equation (1.17) that was presented in section 1.2.1.

$$\eta = \frac{t_d}{t_c} \cdot 100\% \quad (1.17)$$

where t_d and t_c are the discharge and charge times, respectively.

Capacity retention (%) for batteries is calculated by comparing the capacity in the final cycle ($C_{p,final}$) to the capacity of the second cycle ($C_{p,2}$):

$$Capacity\ retention = \frac{C_{p,final}}{C_{p,2}} \cdot 100\% \quad (2.13)$$

The GCPL testing for the ECs was performed using a computer controlled multi-channel Potentiostat/Galvanostat Bio-Logic VMP3, driven by EC-Lab v10.40 software. For the batteries, the GCPL tests were conducted using a MACCOR series 4000 tester.

2.2.3 Voltage holding and cycling

One of the advantageous features of ECs is their stability during high charge-discharge (CD) cycling periods. Therefore, new materials and designs for EC need to demonstrate that ability. One possible option is to cycle for thousands of cycles, but it is highly resources consuming because of the need to use the testing apparatus for long periods. Weingarth *et al.* [114] demonstrated that constant voltage-holding (floating) tests are more demanding than cycling tests and therefore are a more suitable method for determining the long-term stability of ECs in a shorter time span. In this work, cycling was performed for hundreds of cycles for batteries and thousands of cycles for ECs. Constant voltage-holding experiments were performed by holding for 10 h at a specific voltage, then three charge-discharge cycles were carried out. This process was repeated five times for a total of 50 h. The CD cycling and voltage holding testing were performed using a computer controlled multi-channel Potentiostat/Galvanostat Bio-Logic VMP3, driven by EC-Lab v10.40 software.

2.2.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a powerful technique for electrical characterization of electrochemical devices including electrodes as well as electrolytes. This technique is often used to obtain bulk conductivity, but additional information related to the motion of charged particles could also be obtained as well as investigating interfaces. In this technique, the impedance of a system is measured. The impedance is the ability of a circuit to resist the flow of an electrical current and is a more complex parameter than simple resistance.

The relationship between current and voltage in an EC cell is highly non-linear. But when considering a small part of the I - V curve, Pseudo linearity can be considered. The impedance (Z) can be measured by applying a low-amplitude alternating excitation potential, E , and measuring the phase shift, ϕ , in the obtained current, I (Figure 2.10). This phase shift depends on the impedance to the current electron flow originating from electrode kinetics, the electrolyte, diffusion, and chemical reactions in the cell [115].

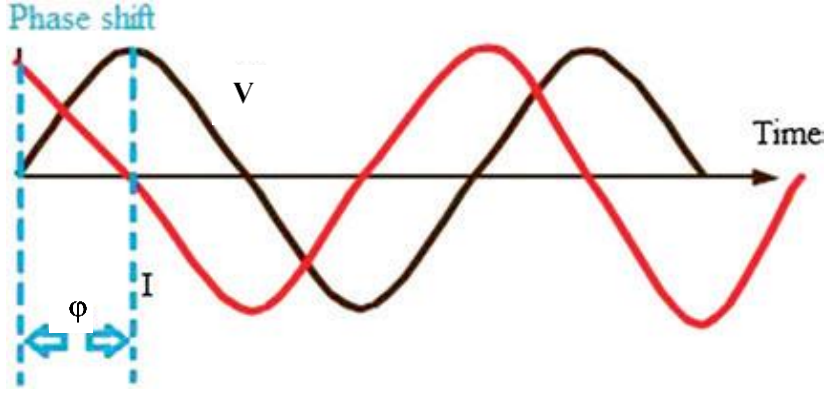


Figure 2.10: Phase shift φ in the current I as a response to a sinusoidal perturbation-potential V in a pseudo-linear system [115].

The impedance Z (Ω) is expressed mathematically as a complex number comprising of resistance (Z') and reactance (Z''). The resistance is the real part of the complex number and is a property of the system that is independent of the incident Alternating Current (AC). The reactance is the imaginary part and is frequency dependent and appears in capacitors and conductors when an incident AC frequency is applied.

The excitation potential V (V) can be expressed as a function of time as in equation (2.14), while the response signal I (A) can be expressed similarly, but with a phase shift φ (rad) as in equation (2.15) [115]:

$$V_t = V_0 \sin \omega t \quad (2.14)$$

$$I_t = I_0 \sin(\omega t - \varphi) \quad (2.15)$$

where V_t (V) is the potential difference at time t (s), V_0 (V) is the amplitude of the potential signal at $t=0$, I_t (A) is the current response signal at time t , I_0 (A) is the

amplitude of the current signal at $t=0$ and ω ($\text{rad}\cdot\text{s}^{-1}$) is the angular frequency, where $\omega = 2\pi f$. f (Hz) is the frequency. The impedance can be expressed in terms of magnitude Z_0 (Ω) and time t using an expression following Ohm's law by equation (2.16) [115]:

$$Z = \frac{V_t}{I_t} = \frac{V_0 \sin \omega t}{I_0 \sin(\omega t - \varphi)} = Z_0 \frac{\sin \omega t}{\sin(\omega t - \varphi)} \quad (2.16)$$

Using Euler's law relationship, the impedance can be expressed as a complex expression by equation (2.17) [115]:

$$Z(\omega) = \frac{V_t}{I_t} = \frac{V_0 e^{j\omega t}}{I_0 e^{j(\omega t - \varphi)}} = Z_0 e^{j\theta} = Z_0 (\cos \varphi + j \sin \varphi) \quad (2.17)$$

where $j = \sqrt{-1}$. The impedance is now in the form of a real part and an imaginary part as expressed in equations (2.18) and (2.19) [115]:

$$Z' = Z_0 \cos \varphi \quad (2.18)$$

$$Z'' = Z_0 \sin \varphi \quad (2.19)$$

The data can be plotted in different format types for data analysis purposes. One such plot format is the Bode plot, where the impedance magnitude $|Z(\omega)|$ and the phase shift $\varphi(\omega)$ are both plotted versus $\log f$. In this plot, the electrical response of the material can be separated into three main regions. At low frequencies (long times), electrical relaxation may be attributed to charge transfer and/or diffusion-controlled reactions at the electrode-electrolyte surface. At intermediate frequencies, relaxations are associated with long-range ion migration/conduction within the bulk of the electrolyte. At high frequencies (short times), electrical

relaxations are associated with short-range ion migrations. Another efficient plot format is a Nyquist plot, known also as Cole-Cole. In this plot type, the imaginary part of the impedance $Z''(\omega)$ is plotted versus the real part $Z'(\omega)$ and each point represents the impedance at one frequency. An Electric Equivalent Circuit (EEC) can be fitted to the data on this plot, representing the different components of the system (e.g., resistors, capacitors and inductors) and their values can be evaluated. Some of these possible components are: (i) The solution resistance which is affected by the solution's ionic concentration, type of ions, temperature, and the area where the conductance occurs; (ii) The double layer capacitance on the interface between the electrode and the electrolyte. The resistance depends on the ionic concentration, type of ions, temperature, electrode surface layer roughness, content and more; (iii) Polarization resistance controlled by the diffusion and kinetics of reactants on the electrode-electrolyte interface; (iv) Charge transfer resistance formed by a single kinetically controlled electrochemical reaction that depends on the reaction kinetics, reactants and products' concentration, etc.; (v) Diffusion, creating an impedance called Warburg impedance, which depends on the frequency. On a Nyquist plot, the Warburg impedance appears as a line with a 45° slope; (vi) The Constant Phase Element (CPE) is a component which was invented to represent a capacitor that does not behave ideally and therefore is treated as empirical. This impedance element can be attributed to non-uniform current distribution, surface roughness or other factors. The impedance of this component is represented by equation (2.20) [116]:

$$Z_{CPE} = \frac{1}{[Q(j2\pi f)^n]} \quad (2.20)$$

where Q is a frequency-independent constant that relates to the interface and n is derived from the slope of $\log Z(\omega)$ plotted versus $\log f$ (with values $-1 \leq n \leq 1$). When $n \cong 1$, the CPE is equivalent to a capacitor and when $n \cong 0$ it resembles a resistor. For $n \cong 0.5$ the CPE impedance resembles the Warburg impedance and $n \cong -1$ it resembles an inductor [50].

The capacitance of a cell can be calculated from EIS using equation (2.21) [4], [111]:

$$C = -\frac{1}{2\pi f z''} \quad (2.21)$$

The specific capacitance, C_{sp} ($F \cdot g^{-1}$, $F \cdot cm^{-3}$ and $F \cdot cm^{-2}$ for gravimetric, volumetric and geometric specific capacitances, respectively) for the three-electrode systems or half-cells is calculated by equation (2.4) given above in section 2.2.1. In the case of a symmetric cell, where both the working and counter electrodes are of the same material, size, mass and thickness, the specific capacitance, C_{sp} per electrode ($F \cdot g^{-1}$, $F \cdot cm^{-3}$ and $F \cdot cm^{-2}$ for gravimetric, volumetric and geometric specific capacitances, respectively) is evaluated by equation (1.8) given above in section 1.2.1.

The EIS testing was performed using a computer controlled multi-channel Potentiostat/Galvanostat Bio-Logic VMP3, driven by EC-Lab[®] v10.40 software.

3. Chapter 3: MXene/CNS Symmetric Electrochemical Capacitor*

3.1 Introduction

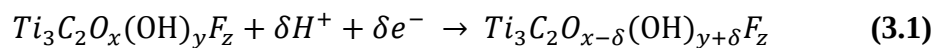
In contrast to EDLC materials, MXene materials, generally, do not possess a high surface area. However, their energy storage mechanism was found to be complex and utilises a pseudocapacitive ion intercalation route giving rise to high capacitance and attractive electrochemical properties [88]. Theoretical calculations have shown that it is influenced, among other factors, by the MXene surface groups [84], [117], [118]. It was also shown that the capacitance can be improved through facilitating ion transport, by expanding the interlayer gaps [35], [96]. MXene combined with nanocarbons [24], [26], [35], [42], [78], [96] and polymers [29], [35] were shown to yield better capacitance than pristine MXene but in a narrow voltage window (< 1.0 V) in aqueous electrolytes [29], [38], [40]–[42], [96] or higher voltage window (> 1.0 V) in organic electrolytes [26], [78]. For further details see section 1.2.2.

To date, nearly all reported works on MXene-based supercapacitors have been on the heavy MXene ($\text{Ti}_3\text{C}_2\text{T}_x$) rather than on the MXene type Ti_2CT_x , usually referred to as the lightest MXene [36], [87]. It is known that the performance of the heavier MXene as a supercapacitor is higher than that of the lightest MXene.

* A substantial part of this chapter has been published in a peer-reviewed journal: **Melchior, S. A., Raju, K., Ike, I. S., Erasmus, R. M., Kabongo, G., Sigalas, I., Iyuke, S. E. and Ozoemena, K. I.** High-Voltage Symmetric Supercapacitor Based on 2D Titanium Carbide (MXene, Ti_2CT_x)/Carbon Nanosphere Composites in a Neutral Aqueous Electrolyte. *J. Electrochem. Soc.* **165**, A501–A511 (2018).

For example, in a recent work by Rakhi *et al.* [37], the authors reported the specific capacitance of the symmetric $Ti_3C_2T_x$ as $79.9 \text{ F}\cdot\text{g}^{-1}$ which is about twice that of the Ti_2CT_x ($32.3 \text{ F}\cdot\text{g}^{-1}$) obtained under the same experimental conditions (i.e., 30% wt KOH aqueous electrolyte, at a maximum voltage of 0.7 V and a constant current density of $1 \text{ A}\cdot\text{g}^{-1}$). Irrespective of the type of MXene studied as symmetric supercapacitor in an aqueous electrolyte, electrochemical data are limited to a very narrow voltage window (usually $< 1.0 \text{ V}$). That being said, a recent report by Zhu *et al.* [119] showed an MXene based electrode that gave a large voltage window (-1.2 to 0.2 V vs SCE) in a three-electrode system, or larger as an asymmetric cell.

Considering the huge interest in developing MXene-based ultra-light and flexible supercapacitors for electronic applications, it goes without saying that similar (if not more) research attention should be paid towards the development of the lightest MXene (Ti_2CT_x) for enhanced supercapacitance. Theoretically, Ti_2CT_x should have a higher gravimetric capacitance than $Ti_3C_2T_x$ as it has $\sim 50 \%$ more theoretical surface area per gram (because Ti_3C_2 has one inaccessible TiC layer) [79]. For example, Lukatskaya *et al.* [120] calculated the theoretical gravimetric capacitance for the pseudocapacitive reaction of $Ti_3C_2T_x$ in sulfuric acid presented in equation (3.1):



For calculation purposes, the MXene was assumed as $Ti_3C_2O_{0.85}(OH)_{0.06}F_{0.25}$. The theoretical capacitance, using equation (1.14) and assuming full reaction ($\delta=0.85e^-$), is estimated to be $\sim 438.6 \text{ C}\cdot\text{g}^{-1}$. Assuming the same reaction extent

($\delta=0.85e^-$) and surface terminations for Ti_2CT_x (i.e., $Ti_3C_2O_{0.85}(OH)_{0.06}F_{0.25}$) the maximal theoretical capacitance can be estimated as $645.2\text{ C}\cdot\text{g}^{-1}$. Motivated by this understanding, this work is focused on tuning the synthesis of Ti_2CT_x and modifying it with carbon nanospheres (CNS) for enhanced supercapacitor performance in 1 M Li_2SO_4 aqueous electrolyte.

3.2 Experimental procedure / Methodology

3.2.1 Materials and methods

The MXene Ti_2CT_x was prepared from the commercially available Ti_2AlC MAX phase powder (Maxthal 211, Kanthal AB, Sandvik Materials Technology, Sweden; >90%wt. purity; <45 μm particle size) by selective exfoliation of the aluminium following a slight modification of the procedure developed by Naguib *et al.* [12], [62]. In summary, 10 g of Ti_2AlC MAX phase powder was slowly added into 100 ml of 40% Hydrofluoric (HF) acid solution (Gold line, CP, Associated Chemical Enterprises Pty Ltd) in a plastic container and stirred with a magnetic stirrer for 2.5 h at room temperature. The obtained suspension was washed several times with copious amounts of de-ionized water; each time, the suspension was left to settle, and the supernatant liquid decanted. After several washing cycles to dilute the acid solution using this settling and decanting process, the suspension was finally subjected to more washing with de-ionized water, separated each time by centrifugation. The process was continued until a pH of 5-6 was reached. The resultant MXene Ti_2CT_x powder (denoted herein as **MX**) was then oven-dried at 70 °C for 4 days.

Carbon Nano-Spheres (**CNS**) were synthesized by direct pyrolysis of hydrocarbon gas in the Chemical Vapour Deposition (CVD) method. Acetylene (C_2H_2) gas (AFROX, Instrument grade N2.0, 508103-DC-C, $\geq 99.0\%$ purity) as the carbon source, and Argon (Ar) (AFROX, Baseline 5.0, 512203-SE-C, $\geq 99.999\%$ purity) as carrier gas, were passed through a tubular quartz reactor (5 cm inner diameter and 100 cm length), which was placed vertically in a furnace. The heating rate and reaction temperature in the furnace was electronically controlled. The gases' flow rates were controlled using Cole-Parmer n082-03 rotameters (reading of the scale was translated to the flow rate of the relevant gas [121]). Prior to the synthesis and during heating to the required reaction temperature of $1000\text{ }^{\circ}\text{C}$, the quartz tube was flushed with Ar, to remove all air, at a flow rate of $330\text{ ml}\cdot\text{min}^{-1}$. When the reaction temperature was reached, C_2H_2 at a constant flow rate of $290\text{ ml}\cdot\text{min}^{-1}$ was added to the Ar carrier gas. The product was deposited on the inner wall of the quartz tube and carried by the gas flow to the product collection chamber. The reaction was held at these conditions for 30 min, after which the flow of C_2H_2 was stopped and the system was allowed to cool to room temperature (about 6 hours) under Ar gas flow. After cooling, the product was collected from both the quartz tube and the collection chamber.

PXRD patterns for the materials in this chapter were obtained using a Bruker D2 Phaser Desktop Diffractometer (Bruker AXS, Karlsruhe, Germany), equipped with Lynxeye detector using Co $K\alpha$ radiation of wavelength $\lambda = 1.78897\text{ \AA}$.

3.2.2 Fabrication and evaluation of cells

Electrochemical performance was investigated for the conventional three-electrode system (half-cell) and two-electrode symmetric system (full or single cell) configurations. The active electrode material was obtained by thoroughly mixing MX, CNS, carbon black (CB) (PRINTEX[®] XE-2-B, Degusa[®]) as a conducting agent and Polyvinylidene fluoride powder (PVDF) (Sigma-Aldrich) as a binder in a weight ratio of 76:4:15:5, respectively, using mortar and pestle. A few ml of *N*-Methyl-2-pyrrolidone (C₅H₉NO) (NMP) (ReagentPlus[®], 99%, Sigma-Aldrich) were added as a wetting agent, to produce a homogeneous slurry. For the three-electrode configuration, the slurry was coated on to a Ni foam which acted as a current collector (Celmet[®]: thickness = 1.6 mm) using a spatula at an active material mass loading range of 1-2 mg·cm⁻² and dried at 90 °C in a vacuum oven for 15 h. The mass loading was chosen to lower ion transport resistance and ohmic losses due to electric conductivity problems on one hand, but to have enough mass for reliability on the other hand. The Ni foam was cleaned, prior to use, by sonication for 30 min in a 1 M HCl solution and washing with a copious amount of de-ionized water. The process was repeated twice, after which the Ni foam was dried overnight in a vacuum oven. An over-sized platinum net was used as the counter electrode, Ag|AgCl (3 M KCl) as the reference electrode, and 1 M Li₂SO₄ (ACS reagent, ≥ 99.0% wt., Sigma-Aldrich) aqueous solution as the electrolyte. The cell was allowed to equilibrate for 2 h prior to electrochemical testing. For the two-electrode symmetric cells, slurries were pasted on Al foil current collector and dried at 90 °C in a vacuum oven for 18h,

after which electrodes with a diameter of 15 mm were cut out. Two symmetric MX/CNS electrodes, separated by a glass microfiber filter (Whatman GF/F) in a 1M Li₂SO₄ aqueous solution were sandwiched in supercapacitor coin-type cells (CR 2032) or Swagelok cells (MTI, Inc., USA). A stainless-steel spacer and spring were inserted between the case and the negative electrode for better fitting. After assembly, the coin cells were pressed at 500 psi and left for complete soaking of all components in the electrolyte for 18 h, prior to testing. Electrochemical measurements on both three-electrode and two-electrode symmetric cells were performed at room temperature and using cyclic voltammetry (CV), galvanostatic cycling with potential limitation (GCPL), and electrochemical impedance spectroscopy (EIS). The testing was performed using a computer controlled multi-channel Potentiostat / Galvanostat Bio-Logic VMP3, driven by EC-Lab[®] v10.40 software. The CV tests were conducted at scan rates varying from 5 to 1000 mV·s⁻¹. The GCPL tests were carried out at varying current densities from 0.1 to 10 A·g⁻¹. EIS measurements were carried out in the frequency ranging from 200 kHz to 10 mHz at an open circuit voltage with an AC voltage amplitude of 3 mV and the Z-fit tool was used for data analysis. Constant voltage-holding (floating) experiments were performed by holding for 10 h at a specific voltage, then three charge-discharge cycles were carried out. This process was repeated five times for a total of 50 h.

3.3 Results and discussion

3.3.1 Material characterization

Figure 3.1 shows the PXRD patterns of the Maxthal 211 powder before and after exfoliation. The as-received Maxthal 211 powder before etching (Figure 3.1a) consists mainly of Ti_2AlC (JCPDS 01-081-8106), with minor quantities of Ti_3AlC_2 (JCPDS 04-012-0632), TiC (JCPDS 01-089-3828) and Ti_xAl_y (JCPDS 04-007-2382, 01-074-4925, 04-007-2383 and 01-081-9785). These phases were also observed by other researchers who worked with the same material obtained from the same source [122]–[126]. After treatment with HF (Figure 3.1b), the intensity of the main peaks of Ti_2AlC and Ti_3AlC_2 decreases. The (002) peak broadens and a shift to lower angles - higher d -spacing is observed. This correlates with the formation of MXene, i.e., replacement of Al with =O, OH or F [12], [62], [64], [69], [71], [79], [127], [128]. TiC (JCPDS 01-089-3828) and TiO_2 (JCPDS 00-021-1272) can also be identified in the samples as also observed by others [36], [44]. The other unknown peaks may be related to some MXene surface oxides arising from prolonged drying of MXene in the air. However, further studies are needed to understand the origin of these peaks.

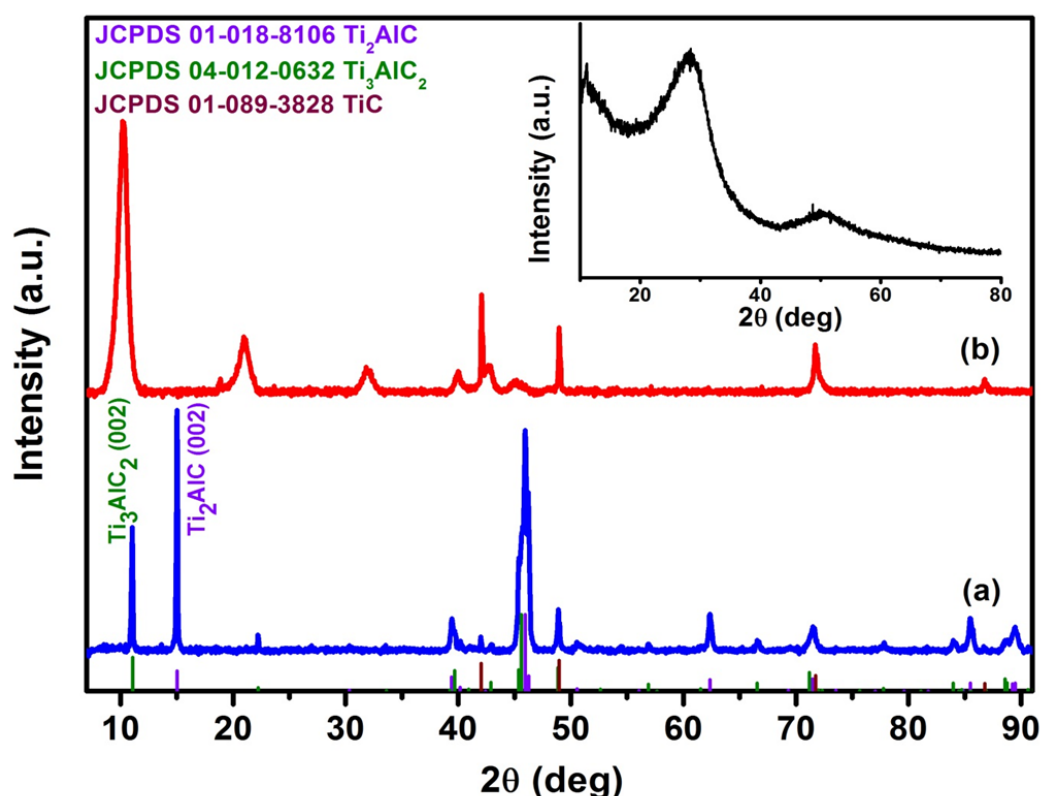


Figure 3.1: XRD patterns of Ti_2AlC powder (Maxthal 211) before treatment with HF (a) and after etching with 40% HF for 2.5h (b). Inset: XRD patterns of CNS.

The PXRD pattern of CNS can be seen in the inset of Figure 3.1. Two wide diffraction peaks can be clearly identified, centred at $\sim 29^\circ$ and $\sim 51^\circ$. These peaks can be indexed to the (002) and (100) graphite planes (JCPDS 00-041-1487). The relatively low and broad shape of the (002) peak implies that the CNS is composed of turbostratic carbon with weakly ordered graphene layers that are randomly rotated with respect to each other [129], [130].

Figure 3.2 displays the Raman spectra of the Maxthal 211 powder before and after exfoliation. The peaks ω_1 , ω_2 & ω_3 and ω_4 in the spectrum (a) are at 149.3, 267.8 and 360 cm^{-1} , respectively. These peaks, are the main characteristic peaks of

Ti₂AlC and are in good agreement with the literature [79], [131]–[134] where they are assigned to the shear and longitudinal vibrations of the Ti and the Al atoms [135]. Specifically, ω_1 is associated with vibrations of the Al, and its disappearance in the spectrum (b) correlates with the removal of the Al and the formation of MXene. The peaks in the spectrum (b) are upshifted and broadened as compared to the peaks in the spectrum (a). The upshift can be attributed to intercalation of surface groups due to the etching process [136]. The broadening of the peaks in the spectrum (b) corresponds with a decrease in order, as is expected by the exfoliation process and was also observed in the XRD spectrum discussed above (Figure 3.1b) [136]. The broad peak at $\sim 630 \text{ cm}^{-1}$ may be attributed to non-stoichiometric TiC_x [18], [137]. The broad weaker bands ω_5 and ω_6 at around 1350 cm^{-1} and 1580 cm^{-1} , respectively, are likely the characteristic D- and G-bands of carbon, associated with the presence of some free carbon and disorder in the samples. Both G and D peaks are due to sp^2 sites. The G-band peak is associated with the stretching of the C-C bond in carbon materials and is common to all sp^2 carbon systems, both rings and chains. The D peak depends on sp^2 fraction and order and appears only if the sp^2 is in disordered rings [138], [139].

Figure 3.2 inset displays the Raman spectra of the synthesized CNS. As expected, the obtained peaks are the D and G bands at 1337.2 , and 1595.4 cm^{-1} , respectively, as discussed above. The relative intensities of the D and G peaks (I_D/I_G) are commonly used to evaluate the graphitic character. The value of I_D/I_G obtained here is 0.84 and was measured by dividing the relevant intensities of the

peaks. This value is within the range of obtained ratios in literature denoting that the degree of graphitization is not high [130], [140]. These results corroborate the observations from the XRD results above.

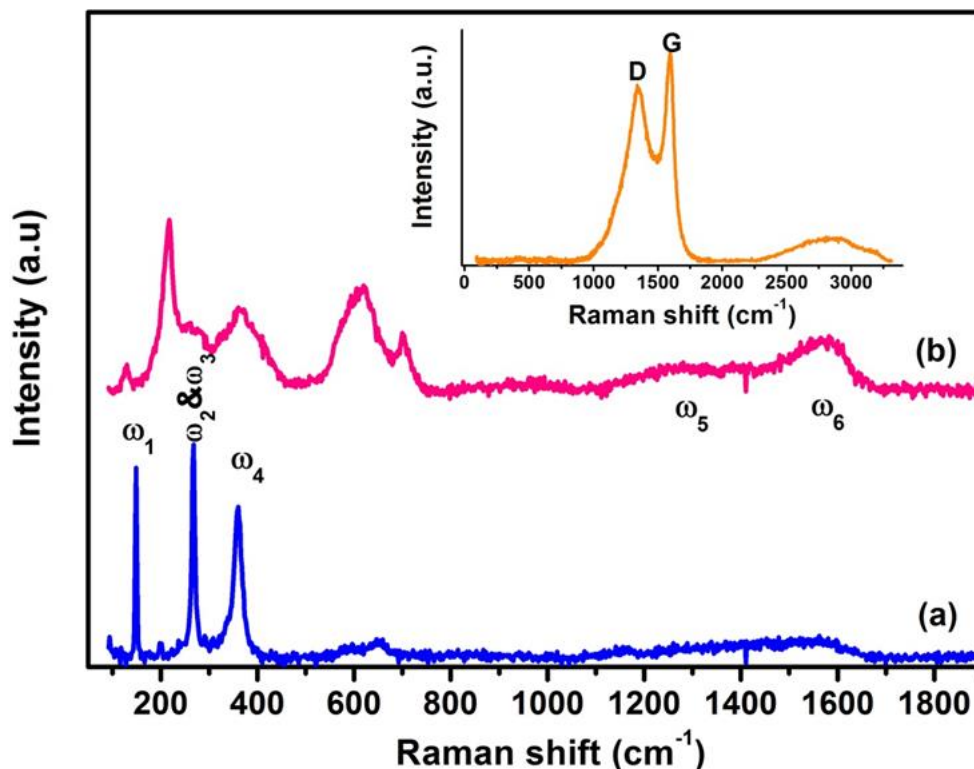


Figure 3.2: Raman spectra of Ti_2AlC powder (Maxthal 211) before treatment with HF (a) and after etching with 40% HF for 2.5h (b). Inset: Raman spectrum of the CNS.

The SEM and TEM images of the Ti_2AlC powder (Maxthal 211) before and after treatment with HF as well as of the CNS are presented in Figure 3.3. The gaps left by the successful etching of the Al layer can be clearly seen in the SEM picture in Figure 3.3b as compared to Figure 3.3a. Additionally, there is a sharp decrease in Al and appearance of F that can be seen in the relevant EDS elemental analysis in the insets, while the intensity of the Ti in the precursor MAX phase is the same as in the final MXene. This is also supported by the rise in magnitude in the

calculated BET specific surface area (SSA) from $1.7 \text{ m}^2\cdot\text{g}^{-1}$ in the MAX phase to $20.2 \text{ m}^2\cdot\text{g}^{-1}$ in the MXene, which are in agreement with literature [18], [23], [36], [79], [87]. These findings strongly support the results obtained above in the XRD and Raman spectroscopy indicating the rise in the disorder of the obtained materials. In Figure 3.3d the randomly oriented graphene planes comprising the CNS are evident, supporting the conclusions from the XRD and Raman data.

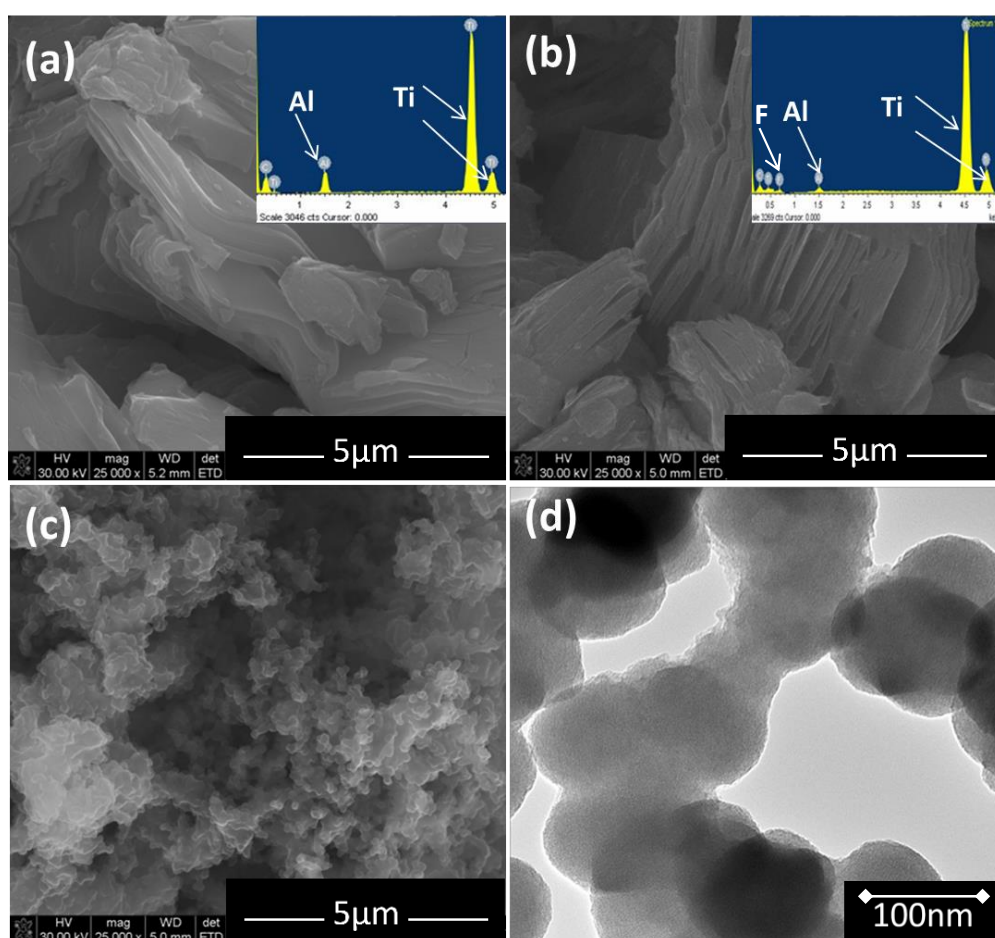


Figure 3.3: SEM images of Ti₂AlC powder (Maxthal 211) before treatment with HF (a) and after etching with 40% HF for 2.5h (b). The insets are the EDS analysis of both samples. SEM image of the CNS (c) and TEM image of the CNS (d).

3.3.2 Electrochemical characterization

Figure 3.4a shows the CV behaviour of the individual CNS, MX and combined MX/CNS electrodes in a three-electrode system in the 1M Li_2SO_4 electrolyte at $20 \text{ mV}\cdot\text{s}^{-1}$. These results show that the combination of MX and CNS has an improved capacitance ($70 \text{ F}\cdot\text{g}^{-1}$) as compared to the individual components MX ($61 \text{ F}\cdot\text{g}^{-1}$) and CNS ($0.13 \text{ F}\cdot\text{g}^{-1}$).

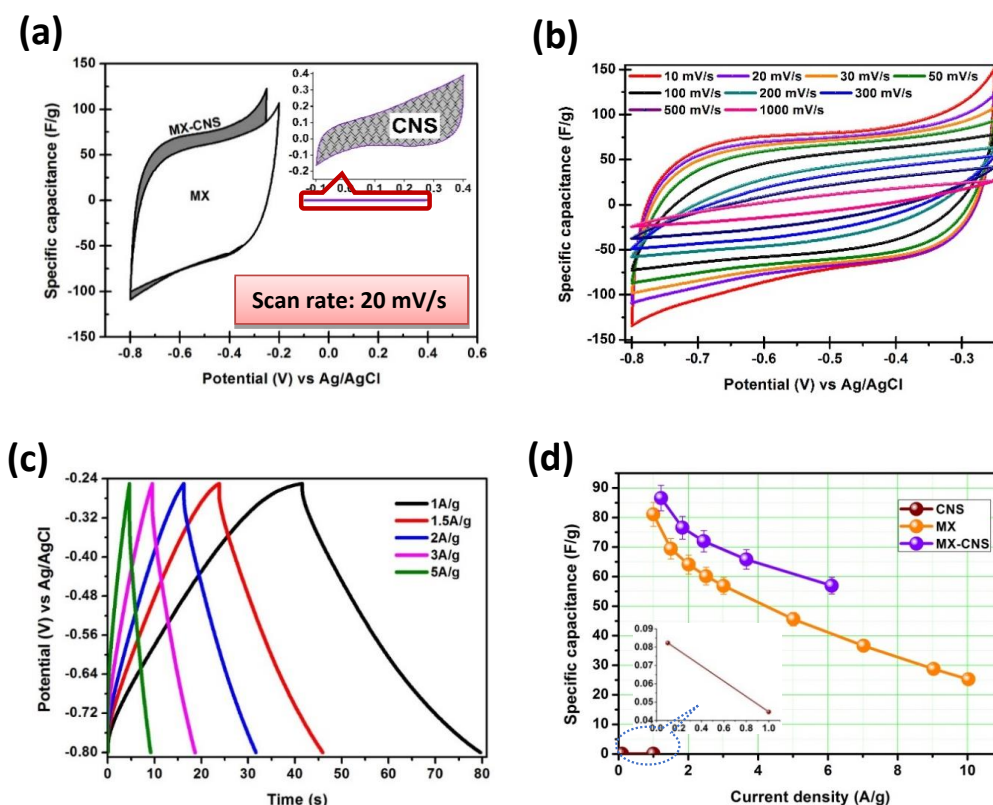


Figure 3.4: Cyclic Voltammetry (CV) compared curves of MX, CNS and MX/CNS at (a) $20 \text{ mV}\cdot\text{s}^{-1}$; (b) CV curves of MX/CNS at various scan rates; (c) GCPL curves of MX/CNS at various gravimetric current densities and (d) GCPL compared results of specific capacitance at varying gravimetric current densities of MX, CNS and MX/CNS. All data acquired in a three-electrode system with 1 M Li_2SO_4 electrolyte. In CV curves (a, b), the measured current is normalized by the scan rate and working electrode active material mass, resulting in the virtual $\text{F}\cdot\text{g}^{-1}$ unit.

It is clearly observed that the capacitance of CNS alone is extremely low ($0.13 \text{ F}\cdot\text{g}^{-1}$). It can also be seen that at lower voltage change rates the additional effect of the added CNS is more significant. Figure 3.4b and c display the CV curves at different scan rates and GCPL curves at different gravimetric current densities of the combined MX/CNS composite materials. The CV curves in Figure 3.4b have a shape that is approximately rectangular, which corresponds to good reversible capacitive behaviour but still differ from the ideal rectangular shape for the EDLC. This is also demonstrated by the nearly isosceles triangle shape of the CD curves in Figure 3.4c, indicating good coulombic efficiency calculated as between 95-97% above $1.5 \text{ A}\cdot\text{g}^{-1}$. These results suggest that pseudocapacitive Li^+ intercalation reactions occur at the electrodes as described in equation (1.21). Above $100 \text{ mV}\cdot\text{s}^{-1}$, the CV curves in Figure 3.4b become less rectangular indicating a more resistive character. This distortion may be because of greater difficulty for Li^+ ions to diffuse into or out of the materials' structure as the rate increases, therefore limiting effective interaction of the cations with the electrode surface to shallower adsorption sites [31], [141]–[143]. This behaviour can also explain the line becoming rounded during charging at the higher voltages for the lower current density of $1 \text{ A}\cdot\text{g}^{-1}$. Both the CV scans and the GCPL curves show no peaks. The absence of peaks suggests that the same pseudocapacitive behaviour, probably lithiation and de-lithiation as in equation (1.21), occurs over the entire cycle.

Figure 3.4d presents the comparative results of the specific gravimetric capacitance of the individual components MX and CNS, and their combination

MX/CNS, at different gravimetric current densities. As can be seen from these results, the capacitance of the MX material and MX combined with CNS decreases with the increase of the gravimetric current density. It can also be observed here, as was seen in Figure 3.4a, that the capacitance of the CNS is extremely low ($0.045 \text{ F}\cdot\text{g}^{-1}$ at $1.0 \text{ A}\cdot\text{g}^{-1}$) as compared to the MX ($81 \text{ F}\cdot\text{g}^{-1}$ at $1.0 \text{ A}\cdot\text{g}^{-1}$). However, the combination of the MX with the CNS yields improved capacitance ($87 \text{ F}\cdot\text{g}^{-1}$ at $1.2 \text{ A}\cdot\text{g}^{-1}$). This finding can be clearly observed when comparing the GCPL curves of the combined MX/CNS material to the MX alone (Figure A. 1 in Appendix B). For the MX material alone, at $2.5 \text{ A}\cdot\text{g}^{-1}$, the capacitance is $60 \text{ F}\cdot\text{g}^{-1}$ while for the combined MX/CNS material the capacitance is $72 \text{ F}\cdot\text{g}^{-1}$, which is an improved of more than 15%. This is quite significant if one considers that CNS constitutes a mere *ca.*4% of the active electrode materials. Such an improvement may be ascribed to (i) increased content of the high-surface-area CNS on the surface of the MXene (as discussed later, XPS data show that MXene is mainly carbon) and / or (ii) the ability of the CNS to assist in expanding the interlayer spacing of the MXene for improved ion transport (exemplified in Figure 3.5). Although the MXene/CNS electrode was obtained by a simple mixing of MXene and CNS, Figure 3.5 clearly shows that the possibility that some of the CNS ($\sim 100 \text{ nm}$) and other additives used in this work got between the large MXene sheets (micron-sized) cannot be completely ruled out.

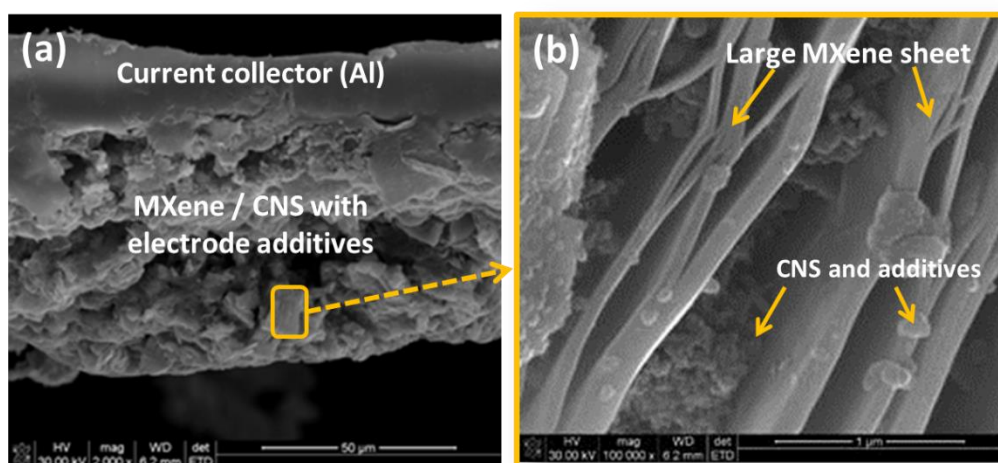


Figure 3.5: (a) Typical SEM image of MX/CNS composite electrode fabricated on an aluminium current collector using the same method described in the experimental section, (b) is the expanded portion of the SEM image showing the long sheets of MXene where CNS and other electrode additives such as the carbon black are deposited on the surface or buried in the interlayer spacing of the MXene sheet.

The symmetric MX/CNS electrodes were tested at increasing voltage ranges from 0.6 up to 1.8 V as can be seen in Figure 3.6a. Up to a voltage range of 1.5 V, the curves sustain a semi-rectangular shape, pertaining to good capacitive behaviour. Above 1.5 V, oxidation of the electrolyte starts to occur thus, 1.5 V is the optimal supercapacitor voltage for this device. The wide voltage range obtained stems from the use of the Li_2SO_4 electrolyte in a cell with a contained amount of water. It has been reported that symmetric supercapacitors with wide voltage range, higher than the theoretical limit of water, can be overcome with pH-neutral electrolytic solutions of inorganic salts such as Li_2SO_4 , Na_2SO_4 and K_2SO_4 with the Li_2SO_4 being the most promising salt to date [144]. As explained by Fic *et al.* [144], the Li^+ and SO_4^{2-} ions are strongly solvated in the water molecules. The energy needed to decompose the water competes with the solvating energy. Since the number of water molecules is limited, it can be assumed that they are all

bonded to the ions, resulting in water decomposition being delayed to 1.6 – 2.2 V instead of the expected 1.23 V theoretical limit for water. In addition to that, Srimuk *et al.* [145] demonstrated that the distribution of voltage in the symmetric MXene cell between anode and cathode is not symmetric as in the case of an EDLC based symmetric cell (e.g., activated carbon). In such a case, the MXene electrodes may behave as in an asymmetric cell, enabling the wider range of cell voltage, as observed in our results. To the best of our knowledge, it is the first time that such a wide voltage has been reported in a symmetric aqueous system with MXene-based electrode materials. At this juncture, it should be mentioned that many other researchers [41], [88], [141] have studied the performance of Ti_3C_2 in the same electrolyte (Li_2SO_4) used in this work.

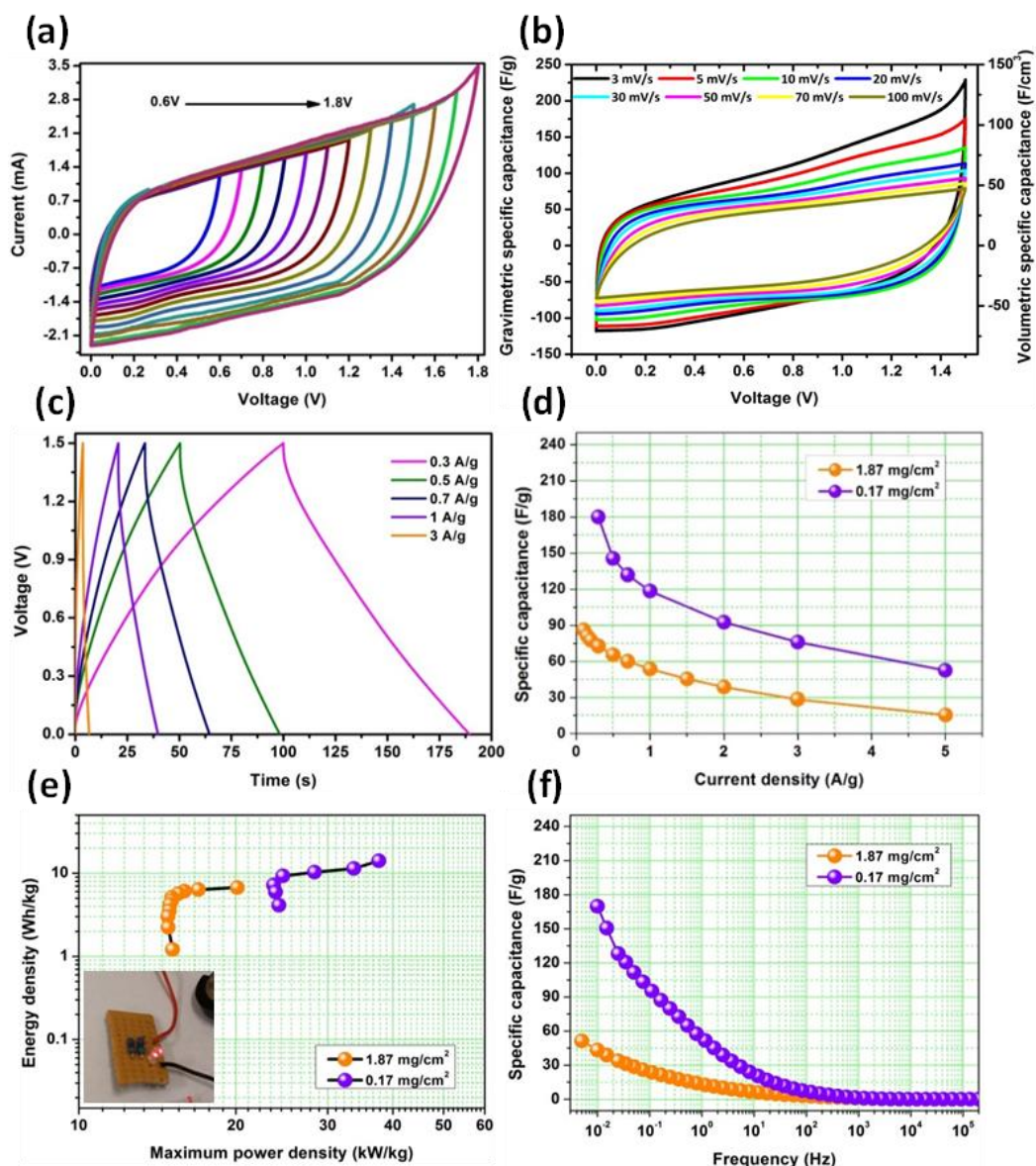


Figure 3.6: CV curves (a) at different voltage ranges at $20 \text{ mV}\cdot\text{s}^{-1}$ and (b) at various scan rates; (c) GCPL curves at various gravimetric current densities; (d) specific gravimetric capacitance from GCPL at various gravimetric current densities for different electrode material mass loading; (e) gravimetric energy density vs maximal power density for different electrode material mass loading; The inset showing demonstration of LED lighting by coin cells (f) specific gravimetric capacitance from EIS data at various frequencies for different electrode mass loading. All data acquired for MX/CNS symmetric coin cells with $1 \text{ M Li}_2\text{SO}_4$ electrolyte. Data for (b) and (c) attained with an electrode mass loading of $1.87 \text{ mg}\cdot\text{cm}^{-2}$. In (b), the measured current is normalized by the scan rate and the active material mass or volume of both electrodes and multiplied by 4, resulting in the virtual $\text{F}\cdot\text{g}^{-1}$ or $\text{F}\cdot\text{cm}^{-3}$ unit.

Figure 3.6b shows the CV obtained for the MX/CNS symmetric cell at various scan rates. At $20 \text{ mV}\cdot\text{s}^{-1}$ the curve has an almost rectangular shape. As the rate becomes higher, the shape becomes less rectangular, possibly because of diffusion limitations of Li^+ into the MXene structure. At lower scan rates, oxidation is evident at the higher voltages. No other peaks are evident, indicating again that the only processes occurring are the highly reversible lithiation and de-lithiation suggested in equation (1.21). This is also reinforced by the nearly linear charge-discharge profiles in Figure 3.6c. These CD curves show minor IR drop and coulombic efficiency of 67.7% at $0.1 \text{ A}\cdot\text{g}^{-1}$, above 82% for $0.15\text{-}0.3 \text{ A}\cdot\text{g}^{-1}$ and between 95 and 98.5% for $0.5 \text{ A}\cdot\text{g}^{-1}$ and higher.

Figure 3.6d shows the specific gravimetric capacitance for two symmetric MX/CNS cells with different electrode material mass loading obtained at different current densities. The capacitance decreases with the increase of gravimetric current density with a capacitance loss of 82% between $0.1 \text{ A}\cdot\text{g}^{-1}$ and $5 \text{ A}\cdot\text{g}^{-1}$. It can be seen from this figure that a smaller mass loading yields a higher specific capacitance of $180 \text{ F}\cdot\text{g}^{-1}$ at $0.3 \text{ A}\cdot\text{g}^{-1}$, while $86 \text{ F}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$ is obtained for the higher mass loading. CV data also follow a similar trend (Figure A. 2 in Appendix B). The phenomenon of the dependence of the specific capacitance on the mass loading or electrode thickness was demonstrated by others [31], [32], [146], [147] who also attained a similar trend. This can be explained by the fact that when the mass is higher, the thickness is higher, and the penetration of the Li^+ ions to the deeper electrode layers and intercalation, which directly involves the surface of the material, is more difficult. As a result, resistance increases. In addition, part of

the electrode mass is ineffective and does not contribute to the overall capacitance, therefore, leading to a lower specific capacitance.

Figure 3.6e shows energy density vs maximum power density of the two symmetric MX/CNS cells with different electrode material mass loading obtained at different current densities. The maximal power and energy achieved are 37.6 kW·kg⁻¹ and 14.1 W·h·kg⁻¹, respectively, at 0.3 A·g⁻¹ for the lower mass loading electrodes and 20.1 kW·kg⁻¹ and 6.7 W·h·kg⁻¹, respectively, at 0.1 A·g⁻¹ for the higher mass loading electrodes. These values are in the range or even higher than usually seen for symmetric aqueous EC [37], [148]–[151]. The picture in the inset of Figure 3.6e demonstrates the lighting of a red light emitting diode (LED) using EC coin cells.

Figure 3.6f shows a typical plot of the specific capacitance as a function of frequency, obtained from electrochemical impedance spectroscopy (EIS) at different mass loadings. As expected, the specific capacitance increases with a decrease in frequency response. At high frequencies, the cells behave as absolute resistors. Interestingly, however, the result is in excellent agreement with charge-discharge data (Figure 3.6b).

Considering that several researchers have shown that carbon-based symmetric supercapacitors can be operated in a neutral aqueous electrolyte in high voltage, we decided to conduct XPS experiments to provide some insights into the electronic structures and carbon contents of the MXene used in this work. The results (Figure 3.7, Table 3.1 and Table 3.2) demonstrate the co-existence of the

main expected functional groups, namely, oxide (-O-), hydroxyl (-OH) and fluoride (-F) [152]. The survey scan spectra (Figure 3.7a) show the expected core levels, namely, F 1s, O 1s, C 1s, Ti 2p for MXene, and O 1s, C 1s, Si 2p for CNS. Analysis of these spectra reveals the atomic percentage for each element. The obtained values for the MX sample are O 1s (32.9 at.%), C 1s (48 at.%), Ti 2p (2.6 at.%) and F 1s (16.5 at.%), clearly showing that the MXene used in this work is mostly carbon. For the CNS the atomic percentages are C 1s (88.8 at.%), O 1s (8.4 at.%) and Si 2p (2.8 at.%). Gaussian deconvolution with $\chi^2 \leq 1$ was used to fit the components in the high-resolution XPS core-level spectra for the MX sample (Figure 3.7b-e) and the CNS sample (Figure 3.7f-h), giving a more detailed picture of the materials' surface structure. The obtained values of the binding energy (BE) after deconvolution are comparable with previous studies [152]–[154]. For the MXene, the O 1s core level consists of three photoelectron peaks (Figure 3.7b). The lower BE, located at 529.38 eV, which comprises 57.59 % of the photoemission in the O 1s core level is assigned to TiO₂ formed by oxidation of the MXene surface [153]–[155]. The medium BE, located at 530.84 eV is assigned to C-Ti-O_x and comprises 7.73 % of the O 1s photoemission [155]. The higher BE detected at 531.9 eV which account for 34.67 % of the photoemission is related to C-Ti-(OH)_x [23], [153], [155]. These last two BEs can be assigned to -O_x/(OH)_x terminations on the MXene surface [12]. The C 1s core level was also successfully fitted using four Gaussian components (Figure 3.7c) located at 280.47 (12.38 % of C 1s photoemission), 283.58 (74.25 %), 285.44 (6.58 %) and 287.5 eV (6.78 %) corresponding to C-Ti, C-C, C-N, O-C=O bonds, respectively. The large amount of C-C and the O=C-O peaks may arise from hydrocarbons

formed during the etching [152] remaining after washing or formed during oxidation [18], [36]. The Ti 2p core level (Figure 3.7d) was fitted with five components which consist of two doublets ($2p_{3/2}$ and $2p_{1/2}$). The deconvoluted peaks at BE 453.76 (9.6 % of Ti 2p photoemission), 454.91 (20.22 %), 458.27 (12.98 %), 459.23 (42.03 %) and 464.11 eV (15.8 %) can be assigned to Ti-C, Ti^{2+} , Ti^{3+} , Ti-O and C-Ti-F_x, respectively [72], [152], [156]. The Ti-C signal may be ascribed to Ti atoms coming from the interior and can also come from TiC [155] which was evidenced by the XRD results to be present as an impurity in the original MAX phase material. Ti signals with oxidation states 2+ and 3+ indicate the formation of different mixed oxides and carboxides on the MXene surface. The Ti-O signal, which represents a large amount of 42.03 %, may be due to oxidation of the MXene at the edges, forming TiO terminations and TiO₂ aggregates [12], [23]. This may be a result of the material being exposed to air during drying. For F 1s core level (Figure 3.7e), two components were obtained after Gaussian fitting and can be respectively assigned to C-Ti-F_x (683.87 eV which is 64.16 % of F 1s photoemission) and AlF_x (684.44 eV which is 35.84 %). C-Ti-F signals observed both from the Ti 2p and F 1s can arise from the F termination on the MXene surface due to HF etching. A considerable amount of AlF_x is also detected, probably stemming from the etching residues which were not washed away [157]. The results are in good agreement with the literature [72], [152]–[156]. Indeed, the XPS results show the existence of the expected functional groups and oxidation of the surface and also prove that MXene is made up of mostly carbon. If we consider that the electrode was constructed with extra carbons (4% CNS and 15% carbon black), it can easily be inferred that the

high-voltage operation of this supercapacitor may be partly related to the high carbon content. It should be noted that several works show that carbon-based symmetric supercapacitors in aqueous electrolyte (e.g., Li_2SO_4) can be operated at high voltages. For example, Beguin's group [158] reported that seaweed-derived carbons can be operated at 1.6 V in a neutral aqueous electrolyte. So, it should perhaps not be completely surprising that our MXene materials gave a high voltage of 1.5 V.

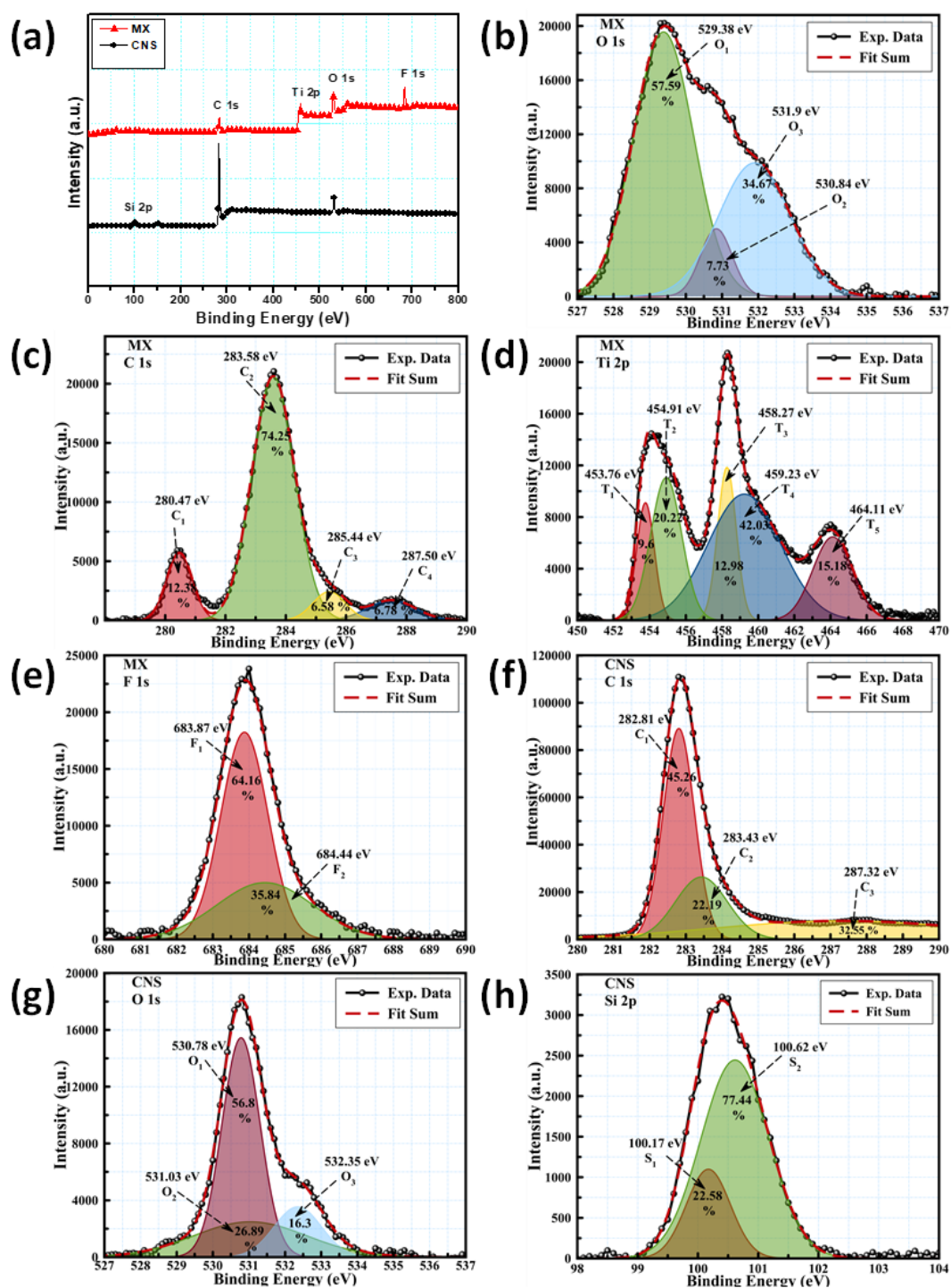


Figure 3.7: (a) XPS survey spectra of MX and CNS samples. (b),(c),(d) and (e) are the MX deconvoluted high-resolution O 1s, C 1s, Ti 2p and F 1s core levels, respectively. (f), (g) and (h) are the CNS deconvoluted high-resolution C 1s, O 1s and Si 2p core level spectra, respectively.

Table 3.1: Detailed high-resolution XPS core-levels atomic percentages and Gaussian fitting results for MX sample.

Core Level	Overall at. %	BE (eV)	Component at. %	Origin
Ti 2p3/2 (2p1/2)	(2.6 %)	453.76	9.60	Ti-C
		454.91	20.22	Ti ²⁺
		458.27	12.98	Ti ³⁺
		459.23	42.03	Ti-O
		464.11	15.18	C-Ti-F _x
C 1s	(48.0 %)	280.47	12.38	C-Ti
		283.58	74.25	C-C
		285.44	6.58	CH _x -CO
		287.50	6.78	O-C=O
O 1s	(32.9 %)	529.38	57.59	TiO ₂
		530.84	7.73	C-Ti-O _x (and/or VO)
		531.90	34.67	C-Ti-(OH) _x
F 1s	(16.5 %)	683.87	64.16	C-Ti-F _x
		684.44	35.84	AlF _x

Table 3.2: Compiled XPS high-resolution core-levels atomic percentages and Gaussian fitting results for CNS sample.

Sample ID	Core Level	Overall At%	BE (eV)	Component at. %
CNS AR 70	C 1s	(88.8 %)	282.81	45.26
			283.43	22.19
			287.32	32.55
	O 1s	(8.4 %)	530.78	56.8
			531.03	26.89
			532.35	16.3
	Si 2p	(2.8 %)	100.17	22.58
			100.67	77.44

Weingarth et al. [114] demonstrated that constant voltage-holding (floating) tests are more demanding than cycling tests and therefore are a more suitable method for determining the long-term stability of ECs in a shorter time span. A floating test was performed on an MX/CNS symmetric cell with the electrode material mass loading of $0.18 \text{ mg}\cdot\text{cm}^{-2}$. The results of the obtained specific capacitance and efficiency of the cell as a function of time are shown in Figure 3.8a. The specific capacity after the first 10 hours decreases vastly to about 33% of the initial capacity, probably related to the degradation due to high voltage operation and/or oxidation of the MXene [141], but thereafter remains constant for 40 hours, with

an effective efficiency higher than 110%, which means that the charge time is shorter than the discharge time. As with the voltage-holding experiment, long-term repetitive galvanostatic charge-discharge cycling showed similar deterioration with time (not shown here). The unstable cycling data may be related to the use of the high voltage and/or oxidation of the MXene. This phenomenon was also observed by Levi et al. [141] who noted that in long-time CV cycling, at potential sweeps beyond 1.1 V, there is a deterioration due to changes in the mechanical properties of the electrodes related to electrode oxidation and associated with hydrodynamic dissipation phenomena occurring at the solid-liquid interface.

EIS is employed to better understand the characteristics of the electrode-electrolyte interface and the charge transfer between them. For that purpose, the impedance data obtained over a range of frequencies is fitted with an electrical equivalent circuit (EEC). Figure 3.8b compares the Nyquist plots prior to and after the 50-hour voltage-holding experiment, fitted with the EEC shown in Figure 3.8b inset. This EEC comprises of the elements R_s , C_{dl} , R_{ct} and Q described here. R_s , which is the intercept of the curve with the real axis at the high-frequency region (low impedances seen in the enlarged area in the figure), represents the solution's ohmic resistance of the electrode system due to electric resistivity of the electrolyte, separator and electrodes. It is also known as the Equivalent Series Resistance (ESR). At the high-frequency region, the semicircle is formed by the double layer capacitance (C_{dl}), while the diameter of the semicircle represents the charge transfer resistance (R_{ct}) due to the electrolyte-accessible electrode surface area as well as the electrical conductivity

of the electrode material (i.e., R_{ct} decreases as the electroactive surface and conductivity of the electrode increase). Q , in the lower-frequency region, represents the constant-phase element (CPE) referring to the capacitance arising due to the heterogeneous nature of the MXene/CNS composites and the possible Faradaic (redox) activities occurring within the cell, which may corroborate the hypothesis that a symmetric MXene/CNS system may behave like an asymmetric cell. The impedance of CPE is represented by equation (2.20) which was given in section 2.2.4:

$$Z_{CPE} = \frac{1}{[Q(j2\pi f)^n]} \quad (2.20)$$

where $j = \sqrt{-1}$, Q is a frequency-independent constant that relates to the interface, n is derived from the slope of $\log Z$ plotted vs. $\log f$ (with values $-1 \leq n \leq 1$). When n takes a value close to 1, the CPE is equivalent to a capacitor and when n is close to 0 it resembles a resistor. For a value close to 0.5 the CPE impedance resembles the Warburg impedance which represents ion diffusion, and when close to -1, it resembles an inductor. It is well known that CPE is a consequence of any one of the following or a combination of them: (i) the nature of the electrode material (such as porosity, roughness, or polycrystallinity), or (ii) the differences arising from the manner in which the relaxation times are distributed as a result of the heterogeneous nature of the electrode/electrolyte interface, or (iii) the fluctuations in the rate of diffusion of ions (i.e., dynamic disorder) at the electrode/electrolyte interface. The values of R_s (ESR), C_{dl} , R_{ct} , Q and n obtained from the fitting of the EEC are given in Table 3.3. The low values of the ESR and R_{ct} indicate the efficient electrode-electrolyte interfacial resistance

of the MXene/CNS cell. The values of n here (0.58 before and 0.65 after the holding test) are greater than 0.5 confirming the pseudocapacitive behaviour of the electrodes, becoming more capacitive in nature after the 50-hour voltage-holding test. From the total series resistance ($R_s + R_{ct}$) in Table 3.3, the total resistance prior to voltage-holding is $1.22\ \Omega$, while at the end of the 50-hour experiment it is $1.61\ \Omega$. The increase in impedance along with the decrease in the double layer capacitance and CPE capacitance (0.17 and 6.31 decreasing to 0.03 and 2.35 after the holding test, respectively) may be due to a gradual deformation of the Mxene/CNS-electrolyte interface during voltage-holding experiments.

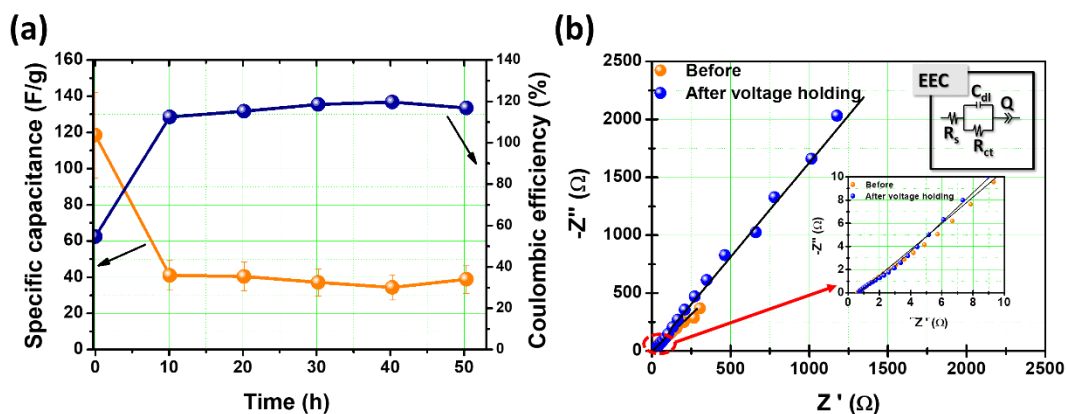


Figure 3.8: Electrochemical test data for MX/CNS symmetric cells with electrode material mass loading of 0.18mg cm^{-2} : (a) Specific capacitance and efficiency as a function of time for 50 hours voltage holding experiment, capacitance measured at $0.7\text{ A}\cdot\text{g}^{-1}$; (b) Nyquist plots before and after the 50 hours voltage-holding experiment, with the electrical equivalent circuit (EEC), used to fit the experimental EIS data. The arrow-indicated inset is the expanded portion of the high-frequency region. Data acquired in a Swagelok type cell with $1\text{ M Li}_2\text{SO}_4$ electrolyte.

Table 3.3: Comparative fitting parameters for the EIS data for MX/CNS symmetric Swagelok cell with the electrode material mass loading of 0.18mg cm⁻² before and after 50 h voltage holding experiment fitted using the EEC.

Parameter	Before holding test	After holding test
R_s / Ω	0.67±0.38	0.71±0.38
C_{dl} / mF	0.17±0.75	0.03±0.07
R_{ct} / Ω	0.55±0.46	0.90±0.43
$Q / \text{mF s}^{(n-1)}$	6.31±0.03	2.35±0.00
n	0.58±0.50	0.65±0.50

3.3.3 Mathematical modelling and simulation

The performance of the MXene/CNS symmetric ECs was modelled and simulated by Ike et al. [49]. This model displays the effects of specified physical and electrical material parameters and design (i.e., electrodes and separator porosity, conductivity and thickness) on EC electrochemical properties such as specific capacity, power density and energy density. It allows for examining these properties at different cell operation conditions (namely charging times and current densities) while taking into consideration the self-discharge. The model equations were derived based on the work of Kazaryan et al. [159], representing the charge conservation and mass transfer of ECs during charge and discharge [49]. The experimental parameters of the present work were entered into the simulation along with data extracted from the literature. Details of the mathematical derivations and simulation details are described elsewhere [49].

Using the simulation, the cell specific capacitance $C_{spec,cell}$ ($F \cdot g^{-1}$) was calculated using equation (3.2):

$$C_{spec,cell} = \frac{\int_0^{t_{dis}} i_{cell} dt}{M_{sy} \cdot V_{cell}} = \frac{i_{cell} \cdot \Delta t_{dis}}{M_{sy} \cdot V_{cell}} \quad (3.2)$$

where i_{cell} (A) is the cell current, V_{cell} (V) is the cell voltage, t_{dis} is the time of discharge and M_{sy} is the mass of the cell which includes the mass of the two electrodes, separator, and electrolyte in the cell.

The energy density ED_{sy} ($W \cdot h \cdot kg^{-1}$) and power density PD_{sy} ($W \cdot kg^{-1}$) were calculated according to equations (3.3) and (3.4):

$$ED_{sy} = \frac{E_{Sdis}}{M_{sy}} \quad (3.3)$$

$$PD_{sy} = \frac{E_{Sdis}}{M_{sy} \cdot t_{dis}} \quad (3.4)$$

where E_{Sdis} ($W \cdot h$) is given by equation (3.5):

$$E_{Sdis} = \frac{C(U_{Sbdis}^2 - U_{Sedis}^2)}{2} \cdot \frac{1000}{3600} \quad (3.5)$$

where C is the capacitance of the cell, U_{Sbdis} is the cell voltage before the beginning of discharging process and U_{Sedis} is the cell voltage at the end of the discharging process.

Figure 3.9 shows the results of the simulation as compared to the experimental results obtained for (a) specific gravimetric capacitance for a whole cell vs current density and (b) gravimetric energy density vs gravimetric power density at different electrode material mass loadings and corresponding simulation results. It can be seen that there is an excellent correlation between the experimental results and the simulation. Similar correlations were observed for energy and power densities vs current densities (Figure A. 3 in Appendix B). The differences arise from the fact that in the experimental results, only the mass of the active material is taken into consideration in the calculations, while in the modelling the mass includes the mass of the electrodes, separator and electrolyte. Moreover, the porous electrode theory used for deriving the model equations does not account for heterogeneous microstructure of electrodes like morphology, pore size, and pore connections. Furthermore, the 1-D model employed will cause a slight deviation of the experiment results from the modelling. Nevertheless, the results show a good correlation.

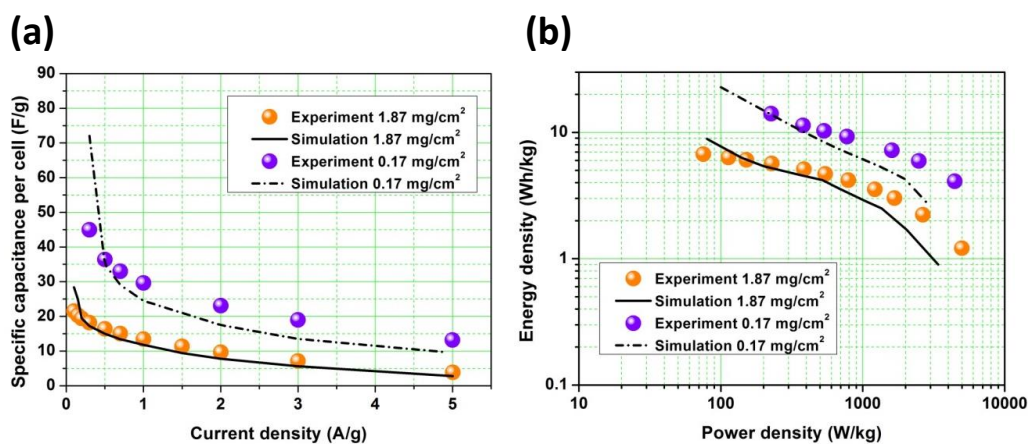


Figure 3.9: (a) Specific gravimetric capacitance for a cell vs current density for different electrode material mass loadings and corresponding simulation results; (b) Gravimetric energy density vs gravimetric power density for different electrode material mass loadings and corresponding simulation results. All data acquired for MX/CNS symmetric coin cells with 1 M Li₂SO₄ electrolyte.

3.4 Conclusions and recommendations

The electrochemical performance of one of the lightest MXene (Ti₂CT_x) materials, modified with a small amount of carbon nanospheres (CNS) to slightly open up the interlayer spacing, has been investigated. When assembled into symmetric cells and operated in an aqueous electrolyte, a relatively high voltage window of 1.5 V was obtained, which is the first such observation for MXene containing electrodes in an aqueous electrolyte. The ability to undergo long-term cycling is found to be limited, suggesting the need for future improvement. Electrodes were fabricated with relative high (1.87 mg·cm⁻²) and low (0.17 mg·cm⁻²) mass loading and performance results were compared. Specific capacitance, maximal specific power and specific energy for the lower electrode mass loading were all higher (180 F·g⁻¹, 37.6 kW·Kg⁻¹ and 14.1 W·h·Kg⁻¹) than for the higher mass loading (86 F·g⁻¹, 20.1 kW·Kg⁻¹ and 6.7 W·h·Kg⁻¹). This phenomenon can be explained by the Li⁺ ions' greater difficulty to penetrate the

electrode materials and intercalate, in the thicker electrode, thus resulting in a higher ion transport resistance and lower electrochemical properties (i.e., Specific capacitance, maximal specific power and specific energy). Modelling and simulation of the EC correlate well with the experimental results, validating the model. The performance of the cell was demonstrated by the lighting of an LED. The use of a light-weight MXene to fabricate high-voltage symmetric supercapacitors gives promise for the realisation of next-generation light-weight portable and flexible electronics. Opportunities in this area should constitute the future research direction of this work.

4. Chapter 4: MXene/EMD anode material for Battery

4.1 Introduction

Expanding the interlayer gaps is one of the strategies employed for enhancing the electrochemical properties of MXenes, because it facilitates the mobility of ions to the MXene's active surfaces, as was discussed in the introduction (section 1.2.2) and in chapter 3 [35], [96]. Different types of dopants and fillers have been introduced for that purpose [24], [26], [29], [35], [42], [78], [96]. Manganese based oxides are attractive as LIB electrode materials due to their low cost, abundance and non-toxicity along with high theoretical capacity. For example, the theoretical capacity of MnO is $756 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ [160], of MnO₂ is $1233 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ [161] and of Mn₃O₄ is $937 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ [7]. However, these materials have low conductivity (i.e., $\sim 10^{-5}$ - $10^{-6} \text{ S}\cdot\text{cm}^{-1}$ for birnessite MnO₂ [162] and $\sim 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ for Mn₃O₄ [163]), poor cycling stability, poor rate capability and reduced power handling capability [164].

Recently, Liu et al. [165] stacked MXene sheets with MnO₂ sheets, obtaining a hybrid flexible film with superior supercapacitive properties. The MnO₂ sheets were the main electroactive ingredient, while the MXene served as the completing conductive component. In other works, Tang et al. [38] and Rakhi et al. [37] demonstrated that combining MXene with MnO₂ yields excellent electrodes for supercapacitors. The combination of MXene acting as the conductive matrix, providing stability for expansion and shrinkage, while the MnO₂ enlarged the MXene interlayer spacing, exhibited outstanding electrochemical properties.

EMD is a low cost, environmentally friendly and abundant material. It was previously investigated as a precursor for manganese-based materials designed for ECs[151], [166], [167], LIBs[168]–[171] and other uses [172].

Driven by this knowledge, MXene Ti_2CT_x , one of the lightest MXenes, that is expected to show higher gravimetric capacities than the heavier but more extensively studied $\text{Ti}_3\text{C}_2\text{T}_x$ and EMD, as a locally sourced low-cost MnO_2 are combined to improve the properties of LIB anodes. In this work, three combinations of MXene and EMD with three different ratios were studied and compared.

4.2 Experimental procedure / Methodology

4.2.1 Materials and methods

MXene Ti_2CT_x (**MX**) was fabricated, as detailed in section 3.2.1. The prepared MX powder and commercially available Electrolytic Manganese Dioxide (**EMD**) (from a local South African resource) were used to produce **MX/EMD** compositions at different mass ratios of 20:80, 50:50 and 80:20 of MX to EMD. The desired weight ratio of MX and EMD (see Table 4.1 for weights used) were dispersed in 40 ml of 5% NH_4OH (diluted with de-ionized water from 25% Platinum line (AR), Associated Chemical Enterprises (PTY) LTD) aqueous solution. Sodium Dodecyl Sulfate (SDS) ($\geq 98.5\%$ (GC), *ReagentPlus*®, Sigma-Aldrich) was added in a 1:1 mass ratio to the EMD as a dispersion agent (Table 4.1). The solution was stirred overnight, ultrasonicated for 30 min, and heated in a Teflon-lined stainless-steel beaker in an autoclave to 130°C for 24 h.

The material was cooled to room temperature, washed four times with copious amounts of de-ionized water via centrifugation and dried overnight at 50 °C in a vacuum oven. The final product was further heated at 300 °C for 3 h under Ar gas flow in a horizontal tube furnace.

Table 4.1: Starting compositions of MXene and EMD used in this work

MX: EMD mass ratio	MX weight (g)	EMD weight (g)	SDS weight (g)
20:80	0.30	1.20	1.20
50:50	0.75	0.75	0.75
80:20	1.2	0.30	0.30

PXRD patterns for the materials in this chapter were obtained using an Ultima IV Rigaku Diffractometer with a Cu K α incident radiation of wavelength $\lambda = 1.54059 \text{ \AA}$.

4.2.2 Electrodes and cells fabrication and evaluation

The electrochemical performance was studied at room temperature by performing GC (Galvanostatic cycling), CV (Cyclic voltammetry) and EIS (electrochemical impedance spectroscopy). The electrodes for testing were prepared by thoroughly mixing the MX/EMD composition (e.g., 50:50 MX:EMD, active material) with carbon black (CB) (PRINTEX[®] XE-2-B, Degusa[®]) as a conducting agent and Polyvinylidene fluoride powder (PVDF) (Sigma-Aldrich) as a binder in a weight

ratio of 70:15:15, respectively, using mortar and pestle. The mixed powders were then stirred overnight (14 h) using a magnetic stirrer in a glass vial, with a few ml of *N*-Methyl-2-pyrrolidone (C_5H_9NO) (NMP) (ReagentPlus[®], 99%, Sigma-Aldrich) as a solvent to produce a homogeneous slurry. The slurry was pasted on a Cu foil current collector by using the Doctor Blade Technique (DBT) and dried at 80 °C in a vacuum oven for 16 h, after which electrodes with a diameter of 15 mm were cut out. The mass of the active material on the electrodes varied between 3-4 mg. The fabricated MX/EMD electrodes were assembled in an Ar-filled glove box (MBraun MB 150B-G, Germany - maintaining the concentrations of O₂ and H₂O < 1 ppm) into coin-type cells (CR 2032) serving as the anode, separated by polymer microfiber filter (Cellgard 2300) from Li metal (Hohsen Corp., Japan) which served both as the counter electrode and the reference electrode and filled with 1 M LiPF₆ in Ethylene Carbonate (EC), Diethyl Carbonate (DEC) and dimethyl carbonate (DMC) (1: 1 :1 by volume, Merck) as the electrolyte. After assembly, the coin cells were pressed at 750 psi and left for complete soaking of all components in the electrolyte for 18 h, prior to testing. The GCPL tests were conducted at varying current densities from 100 to 5000 mA·g⁻¹ at a potential range of 0.005–3.000 V. The CV tests were performed at a scan rate of 0.1 mV·s⁻¹ and potential range of 0.005–3.000 V. The EIS measurements were carried out in the frequency ranging from 100 kHz to 10 mHz at an open circuit voltage with an AC voltage amplitude of 10 mV. Z-view software (version 2.2, Scribner Assoc. Inc. USA) was used for the data analysis. The choice of 100 kHz to 10mHz as the frequency range for EIS study on metal oxide electrodes for LIB is very common (for example: Park et al. [173], Zheng,

et al. [174], Wang, et al. [175], Amine et al. [176] and many more). In the very high frequencies, above 20 kHz, an inductive behaviour is measured that is mainly attributed to the cables used for the measurement. This is in addition to the real part of the impedance (resistance, capacitance and inductance (that is negligible)) which is attributed to conduction through the electrolyte and the porous separator [177]. However, the electrolyte conductivity, which is the resistance to the Li-ion transport, is determined by the pure ohmic resistance. In the Nyquist plot, this is obtained at the lower real impedances part of the semicircle where the imaginary part of the impedance is zero. These data points are in the high-frequency range. Therefore, we start at 100 kHz to obtain a more accurate result [178].

4.3 Results and discussion

4.3.1 Material characterization

The PXRD patterns of the samples before and after loading the MXene with different ratios of EMD are presented in Figure 4.1. The results of the MXene (red line) are very similar to the XRD results obtained and analysed in section 3.3.1. It should be noted that the peaks in the MXene spectrum seen here are shifted in the location on the 2θ spectrum, as compared to Figure 3.1. This shift stems from the change from Co $K\alpha$ incident radiation of wavelength $\lambda = 1.78897 \text{ \AA}$ in section 3.3.1 to Cu $K\alpha$ incident radiation beam of wavelength $\lambda = 1.54059 \text{ \AA}$ here. For further information on the relation between θ and λ see section 2.1.1. For further information on the MXene XRD pattern analysis see section 3.3.1.

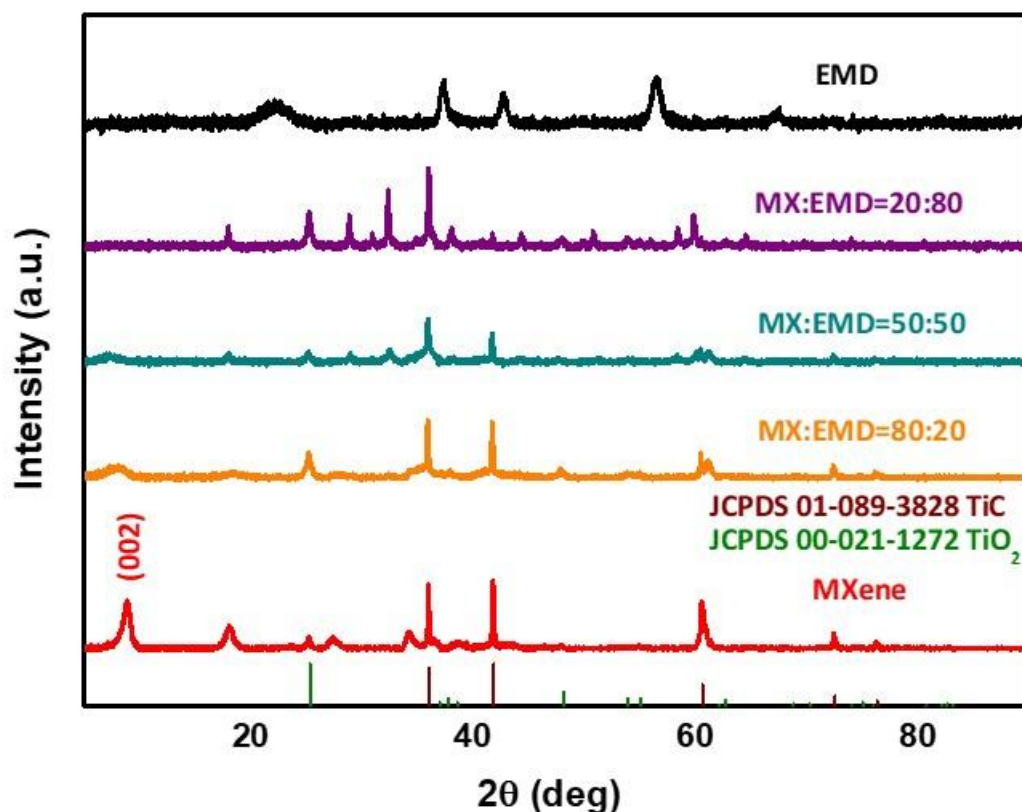


Figure 4.1: XRD patterns of MXene, EMD and MX/EMD compositions with different mass ratios.

In Figure 4.1 the EMD diffraction peaks (black line) can be indexed to mixed γ [179], [180] and ε phases of MnO_2 (see Figure A. 4 in Appendix C). The broad peaks indicate a lack of order and a lack of crystallinity. The XRD patterns of the combined MX/EMD materials show an apparent shift of the (002) diffraction peak of the MXene towards lower 2θ angles (higher d -spacing), as well as peak broadening and a decrease in intensity, with a decrease in MXene ratio. This (002) plain peak, located at 8.9° (0.992nm d -spacing) in the MXene pattern (red line), shifts to $\sim 8^\circ$ (1.10nm d -spacing) in the MX:EMD=80:20 composition pattern (yellow line) and further to $\sim 7^\circ$ (1.26nm d -spacing) in the composition with 50:50 ratio pattern (light blue line). For the mixture with the least amount of MX

(MX:EMD=20:80, purple line), the (002) diffraction peak disappears. The shifting of the (002) peak to a higher d -spacing represents an increase in the c -lattice parameter. The decrease in intensity of this (002) peak suggests less order. These changes may imply the trapping of MnO_2 particles between the MXene layers [38] and/or removal of functional groups by the composition synthesis process [37]. With the MX:EMD ratios of 80:20 and 50:50, the higher the ratio of EMD to MX, the more material is successfully intercalated into the MX structure. But, when the ratio of EMD is too high (MX:EMD=20:80) the (002) peak disappears implying that the features of the MXene are less noticeable. Some peaks present in the MXene sample, such as the peak at 41.76° related to TiC, decrease with the reduction in contents of MX, while other peaks appear. The peaks that appear mainly in the MX:EMD=20:80 composition can be indexed to Mn_3O_4 Hausmannite (JCPDS card # 00-024-0734), TiO_2 Anatase (JCPDS card # 00-021-1272), Titanium Manganese Oxide (JCPDS card # 04-008-6706) and small amounts of TiC (JCPDS card # 04-003-3780) as can be seen in Appendix C. These changes (decrease or appearance of peaks) are related to the varying contents of the MX and EMD as peaks become more or less pronounced, depending on their relative quantity in the material. The changes may also be associated with: (i) the decrease in structural order; (ii) possible oxidation of TiC and the MXene, due to the synthesis processes; (iii) exchange of MX functional groups with manganese oxide molecules and (iv) the transformation of the EMD to different phases of manganese oxide, due to the synthesis procedure [166], [167]. Other peaks that were not identified may be related to some other MXene surface oxides arising from the synthesis process or to other Mn_xO_y phases

formed. However, further studies are needed to understand the origin of these peaks.

The morphology of the samples was investigated using SEM and TEM analysis. SEM images of MXene and EMD alone with different mass ratios as well as MX/EMD compositions are presented in Figure 4.2 and Figure 4.3, respectively. The layered nature of the MXene material before loading is clearly seen in Figure 4.2a. When comparing the images of the MXene before combining with EMD (Figure 4.2a and b) with the images of the composites (Figure 4.3a-f) it is notable that the particle surface has changed, while the basic layered appearance still exists. The MXene particles of the composition with the higher EMD ratio (MX:EMD=20:80), as can be observed both in higher and lower magnifications (Figure 4.3a and b), seem to be covered with a larger number of smaller particles resembling the EMD material (Figure 4.2c and d).

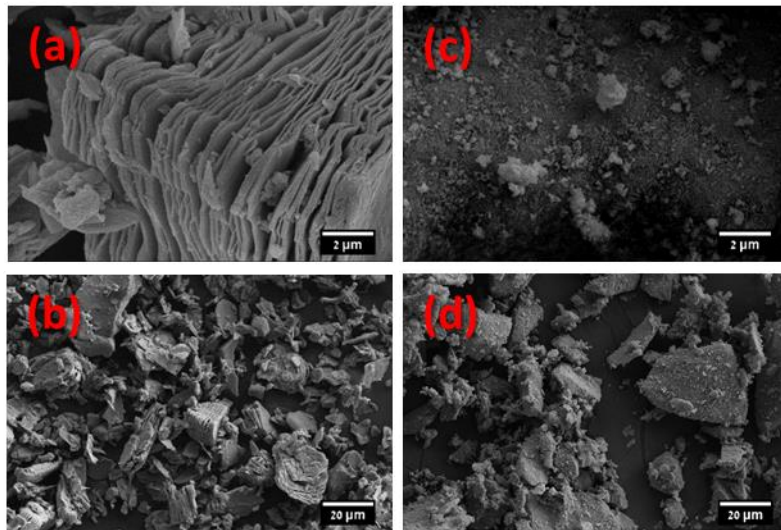


Figure 4.2: SEM images of MXene (a,b) and EMD (c,d) at different resolutions.

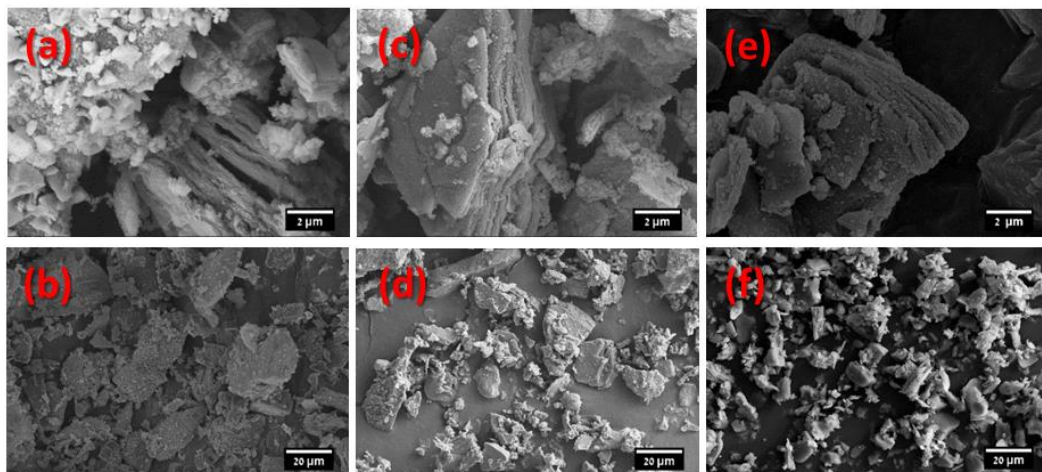


Figure 4.3: SEM images of MX/EMD compositions with different mass ratios of MX:EMD=20:80 (a,b), 50:50 (c,d) and 80:20 (e,f) at different resolutions.

Figure 4.4 shows the TEM images of the MXene particles before loading with EMD (Figure 4.4a) and of the different MX/EMD compositions (Figure 4.4b-d). The layered structure of the MXene can be clearly seen (red arrows) for all particles. The Manganese oxide can be seen covering the layers. The EDS analysis in the respective insets shows the Mn that is detected and is pointed out by the green arrows. It can be observed that Mn content increases with increase in EMD ratio. For example, the intensity of the Mn peak for the MX:EMD=80:20 composite (Figure 4.4b) is very low compared to the Ti peak, whereas in the MX:EMD=20:80 composite, the intensity of the Mn peak is much higher than the Ti peak. However, particles with a higher content of Ti and not covered with Mn could also be observed in the MX:EMD=20:80 composite (see Figure A. 6 in Appendix D).

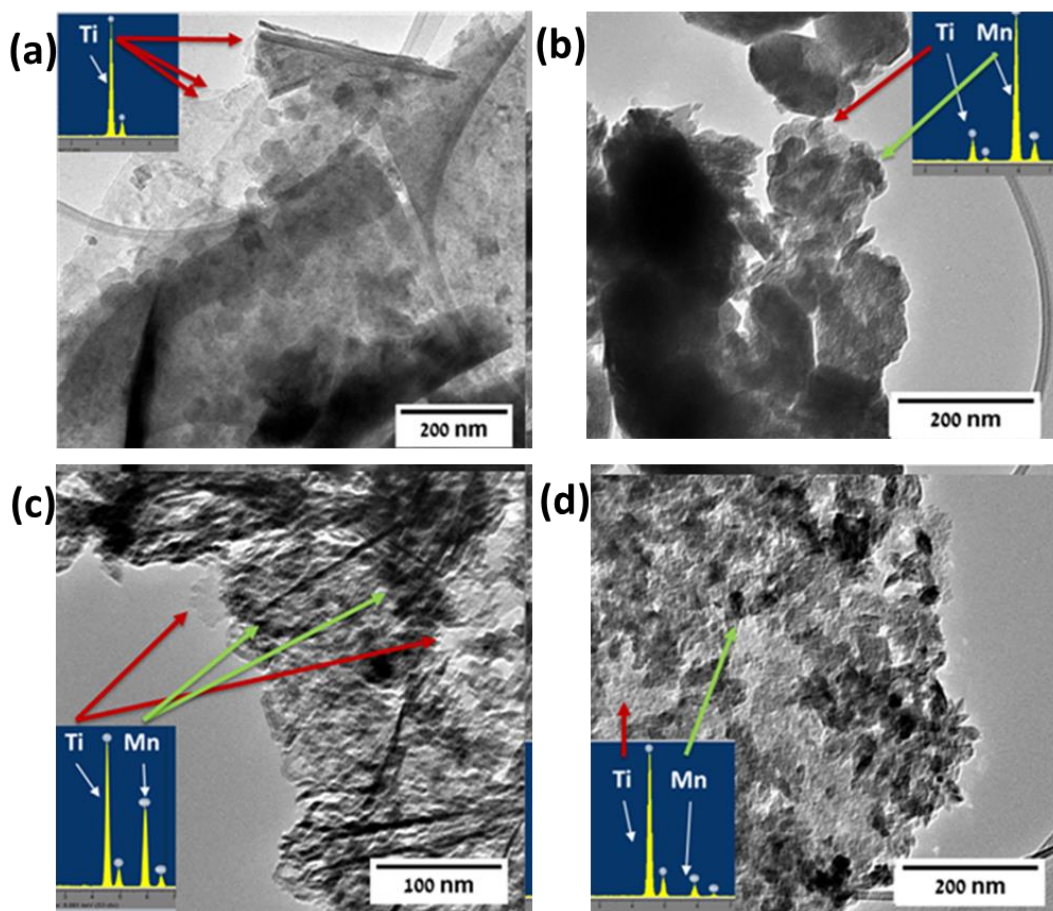


Figure 4.4: TEM images of MXene (a) and MX/EMD compositions with mass ratios of 80:20 (b);50:50 (c); and 20:80 (d); insets showing the EDS analysis of all samples. Red arrows point out the MXene thin layers and green arrows point to manganese oxide.

Figure 4.5 below, as well as Figure A. 7-9 in Appendix D, show the EDS elemental mapping analysis of Mn and Ti for the MX:EMD=80:20, 50:50 and 20:80, respectively. It can be observed from Figure 4.5 for the MX:EMD=80:20 ratio composition, that small Mn particles are distributed all over the sample; however, larger denser manganese oxide aggregates also exist. In Figure A. 7-9, for the MX:EMD=80:20, 50:50 and 20:80 ratios, respectively, which show a lower magnification, several large particles can be noticed. However, it can be clearly noticed that there are far more particles in the compositions with higher

EMD concentrations as compared to the composition with the MX:EMD=80:20 ratio. EDS quantitative analysis carried out on an area of 120 X 120 μm with several particles, for the three composites reveals that the weight ratio of Ti/Mn for the compositions with MX:EMD=20:80, 50:50 and 80:20 ratios, is: 1.1, 2.5 and 7.5, respectively. Clearly, the Ti/Mn ratio affects the physicochemical properties (e.g., the lattice parameters seen with the XRD) and, as will be seen later, in the electrochemical properties of the MX/EMD composites. This corresponds well with the XRD and mapping results discussed above. In summary, the material characterisation results suggest that manganese oxide covers the MXene samples. Nevertheless, a surplus of the material settles as manganese oxide aggregates alongside the MXene particles.

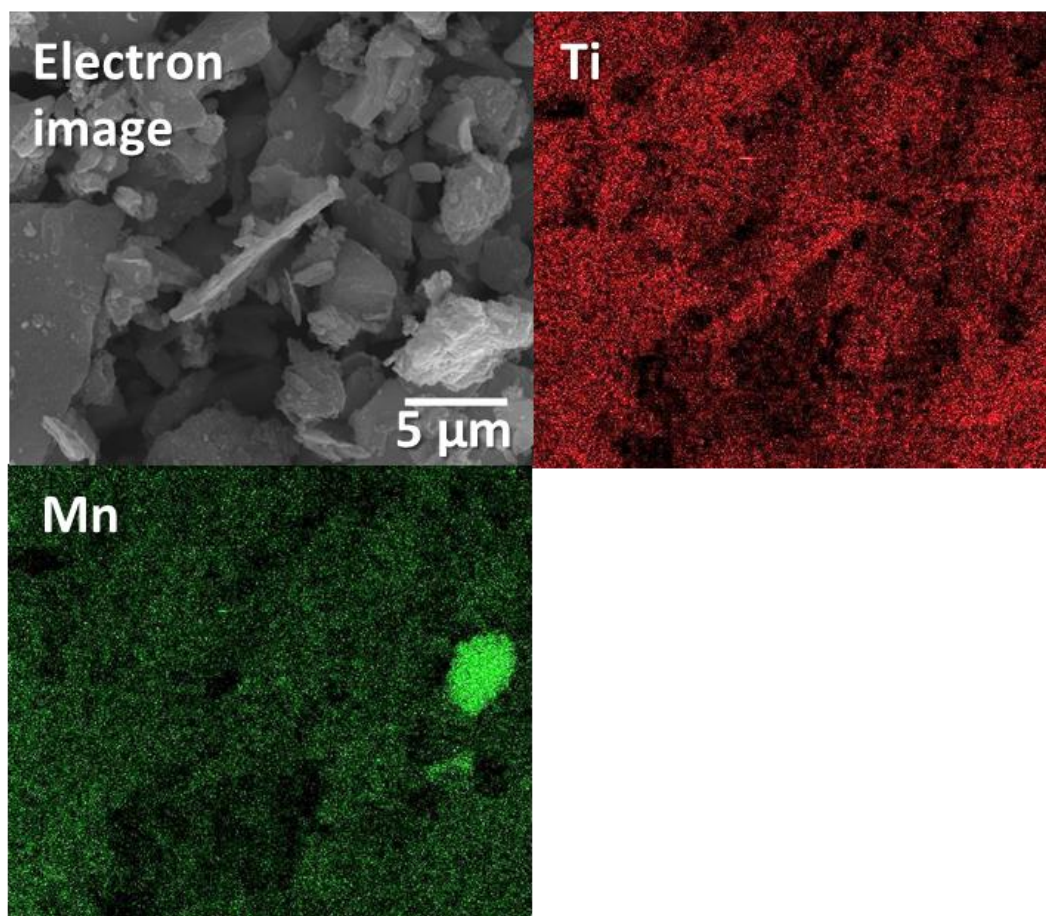


Figure 4.5: EDS mapping of Ti and Mn for the sample with MX:EMD=80:20 composition.

4.3.2 Electrochemical characterization

Cyclic voltammetry analysis

Figure 4.6 compares the obtained cyclic voltammetry (CV) curves of EMD and of the three different mass ratio composites at selected cycles. The CV was performed on coin cells containing the materials at a scan rate of $0.1 \text{ mV} \cdot \text{s}^{-1}$, with a potential window of 0.005-3.000 V.

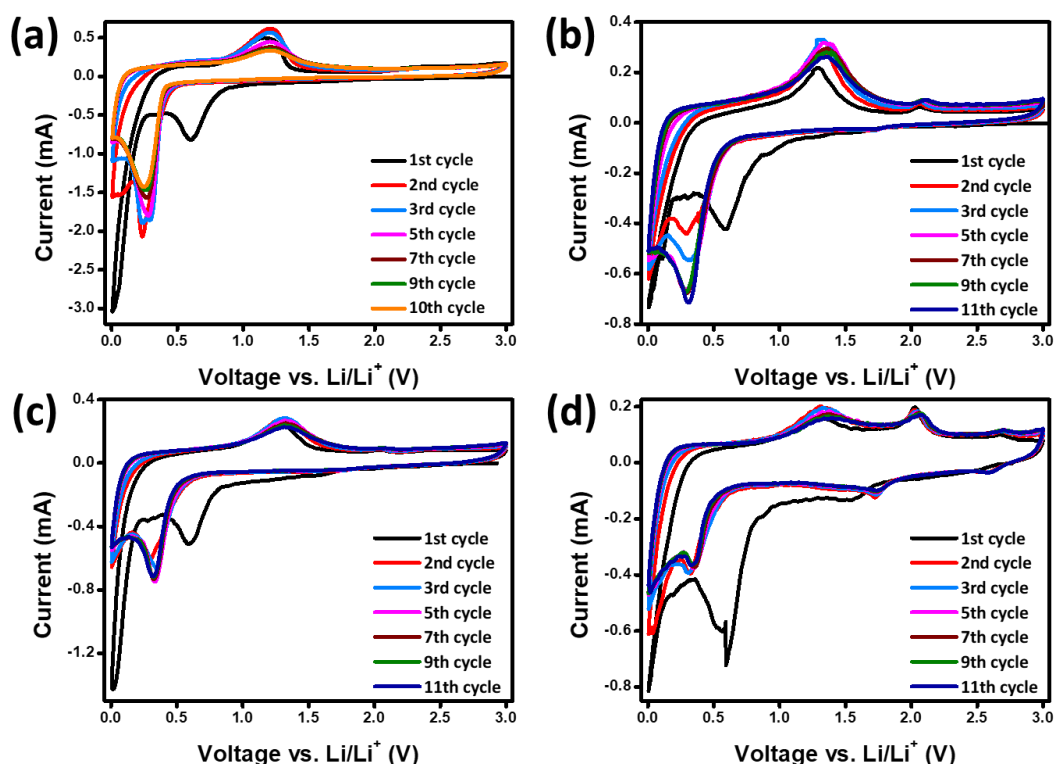
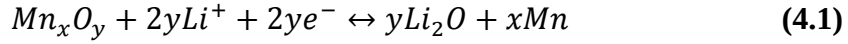


Figure 4.6: CV curves of (a) EMD and (b-d) MX/EMD compositions with different mass ratios: (b) MX:EMD = 20:80; (b) MX:EMD = 50:50; and (c) MX:EMD = 80:20. All data acquired at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$, with a potential window of 0.005-3.000 V.

The decomposition of the electrolyte and subsequent formation of a solid-electrolyte interface (SEI) film on the surface of the electrode can be linked to the irreversible cathodic peaks observed at ~ 0.01 and $\sim 0.6 \text{ V}$ vs. Li/Li^+ , which appear in all samples, in the first cycle only. Additionally, these peaks may be associated with irreversible reactions of the Li ions with the surface groups on the MXene surface (i.e., OH or F) [18], [87], [117], [181], [182]. The narrow peak at $\sim 0.01 \text{ V}$ can be specifically assigned to an irreversible reduction reaction of Li with manganese oxide forming Li_2O and metallic manganese [173] according to the reaction in equation (4.1) [173], [183], [184]:



The intensity of the peak at ~ 0.6 V vs. Li/Li^+ increases with the increase in MXene percentage, indicating that reactions of the Li with the surface groups on the MXene have a greater influence on the formation of the SEI. It should be noted that in the case of the EMD alone, the intensity of this peak at ~ 0.6 V vs. Li/Li^+ , in the first cycle is high, indicating that the SEI formation there is greater than the one observed in the other samples. This is consistent with the XRD analysis, indicating that the composite synthesis procedure generated a change in the manganese oxide phases.

After the first cycle, the cathodic peaks at ~ 0.6 V and at ~ 0.01 V disappear and a reversible broad cathodic peak at ~ 0.33 V vs Li/Li^+ is observed in all samples. Additionally, an anodic broad peak at ~ 1.34 V vs Li/Li^+ can be clearly seen in all samples. The cathodic peak is due to the reduction of the manganese oxide, while the anodic peak is assigned to the oxidation to manganese ion of the metallic manganese as described in the electrochemical conversion in equation (4.1) above [173]. In the three composites, two other reversible peaks are located at ~ 1.7 V (cathodic) and ~ 2 V vs Li/Li^+ (anodic). These peaks are associated with the MXene related to lithiation (cathodic) and de-lithiation (anodic) by way of intercalation according to the reaction presented in the following equation [63], [87]:



The area of the peaks for the MX/EMD compositions increases or remains approximately the same after the second cycle, while the EMD peaks are clearly decreasing, which denotes capacity fading. These results imply that the MX/EMD compositions are more stable and have better cycling capabilities than the EMD material.

Charge-discharge analysis

To further test the materials, the coin cells with the composites were subjected to galvanostatic charge-discharge cycling with potential limitation (GC) at the current density of $100\text{mA}\cdot\text{g}^{-1}$ with a voltage range of 0.005-3.000 V.

Figure 4.7 compares the first discharge-charge cycle curves of MX/EMD compositions with different mass ratios as well as selected cycles' curves (cycles: 1, 2, 5, 10, 50, 100, 200 and 300) of the composites with three different ratios. A substantial capacity loss in the first discharge of all three compositions is again seen here. The first cycle capacity is 1090, 622 and $570\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ for the composites with ratios of MX:EMD=20:80, 50:50 and 80:20, respectively. The capacity decreases to 459, 256 and $220\text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ in the second cycle, respectively. The capacity loss in the first discharge (Figure 4.7a), occurring between 2.80 and 0.25 V vs. Li/Li^+ with a plateau at $\sim 0.8\text{ V}$, is attributed in all three compositions to (i) an irreversible SEI layer formation; (ii) possible irreversible reactions with the MXene surface groups; (iii) possible formation of $\text{Li}_2\text{Mn}_x\text{O}_y$ [185]; and (iv) intercalation of Li^+ into the MX matrix.

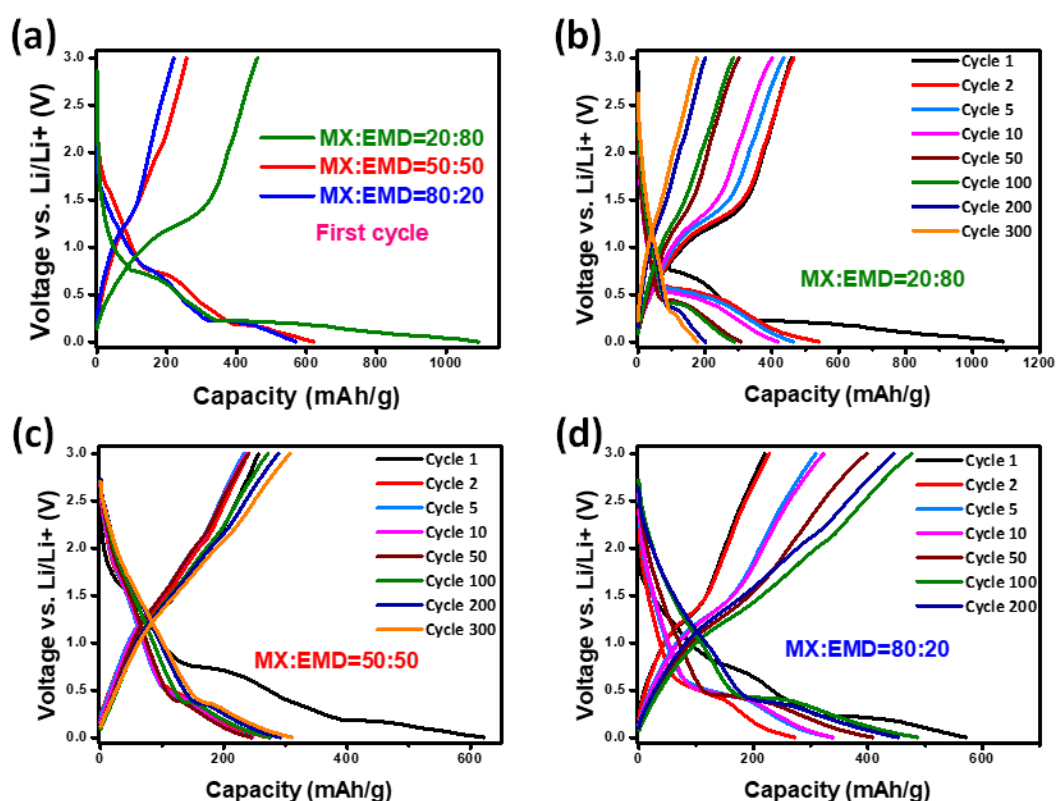


Figure 4.7: (a) First discharge-charge cycle curves of MX/EMD compositions with different mass ratios and selected cycles' curves of (b) MX:EMD = 20:80; (c) MX:EMD = 50:50; and (d) MX:EMD = 80:20. All data acquired at a current density of $100 \text{ mA} \cdot \text{g}^{-1}$, with a potential window of 0.005-3.000 V.

The plateau at 0.25 V is due to the reduction of the manganese to metal and the formation of Li_2O [185]. In the charge curve of the first cycle, two inflexion points can be observed, at $\sim 1.1 \text{ V}$ and at $\sim 2 \text{ V}$ vs Li/Li^+ corresponding to the reversible reactions of Mn oxidation and formation of Li_2O and de-lithiation of the MXene, respectively. At subsequent cycles (Figure 4.7b-c) the discharge plateau at $\sim 0.8 \text{ V}$ disappears, confirming it is related to irreversible reactions. Another inflexion point can be observed at around 1.6 V, assigned to the reversible lithiation of the MXene. The wide plateau associated with the reversible reduction of Mn and Li shifts to $\sim 0.4 \text{ V}$. On the charge side, as the reactions are all reversible, the peaks remain for all cycles.

Cycling analysis

The cycling performance of the various MX/EMD compositions cycled at $100 \text{ mA}\cdot\text{g}^{-1}$ is shown in Figure 4.8a. The capacity for the composition with MX:EMD=20:80 drops from $1090 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ in the first cycle to $540 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ in the second cycle. Gradual capacity fading was observed from the initial cycles until the end of the 300 cycles, reaching $178 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at the 300th cycle, with a coulombic efficiency of 99%. Conversely, for the two other compositions, after the initial drop, the capacity increases. For the MX:EMD=80:20 composition, the capacity drops from 570 to $272 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ in the first two cycles, and immediately picks up, increases and reaches $490 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at around a hundred cycles. After two hundred cycles, the capacitance is $460 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ with a coulombic efficiency of 98% throughout. The capacity for the MX:EMD=50:50 composition drops from 621 to $274 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$. After another 30 cycles of moderate decrease, the capacity also starts increasing and reaches $315 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at three hundred cycles, with a coulombic efficiency of 99%. For comparison, the capacity of EMD at the same current density of $100 \text{ mA}\cdot\text{g}^{-1}$ (not shown), reaches $270 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after one hundred cycles and fades quickly. The capacity drop in LIBs, during the first cycle and the later fade, is attributed to the loss of lithium to the SEI [186], [187]. The SEI film is formed as a result of electrolyte decomposition due to reduction with the anode at the high negative voltages. The film formed protects from further massive electrolyte decomposition [6]. Although the main formation of the SEI layer is during the first cycle, it continues to grow in the next few cycles, until

it is fully developed, and capacity loss is greatly reduced. The gradual thickening of the layer continues throughout the electrode life, at a much slower rate, due to electrolyte diffusion to the anode surface, causing continual lithium, solvents and salts consumption and leading to the capacity fade [188]. However, the phenomenon of the capacity's gradual increase was seen here for the compositions with MX:EMD=80:20 and 50:50, was observed by others and is attributed to improvement in the accessibility of Li-ions to the MXene active sites and reduced diffusion barriers with cycling [182], [189], [190]. It is probable, from the trend of the composite with a ratio of MX:EMD=50:50 that if cycling continued it would reach an even higher capacity. But the composition with a lower EMD content (MX:EMD=80:20), achieves a better capacity. It can be inferred that loading the MXene matrix with EMD contributes to opening the gaps between the layers enabling better accessibility for the Li-ions, as was seen in the XRD analysis. But above a certain ratio, the high EMD content inhibits the properties.

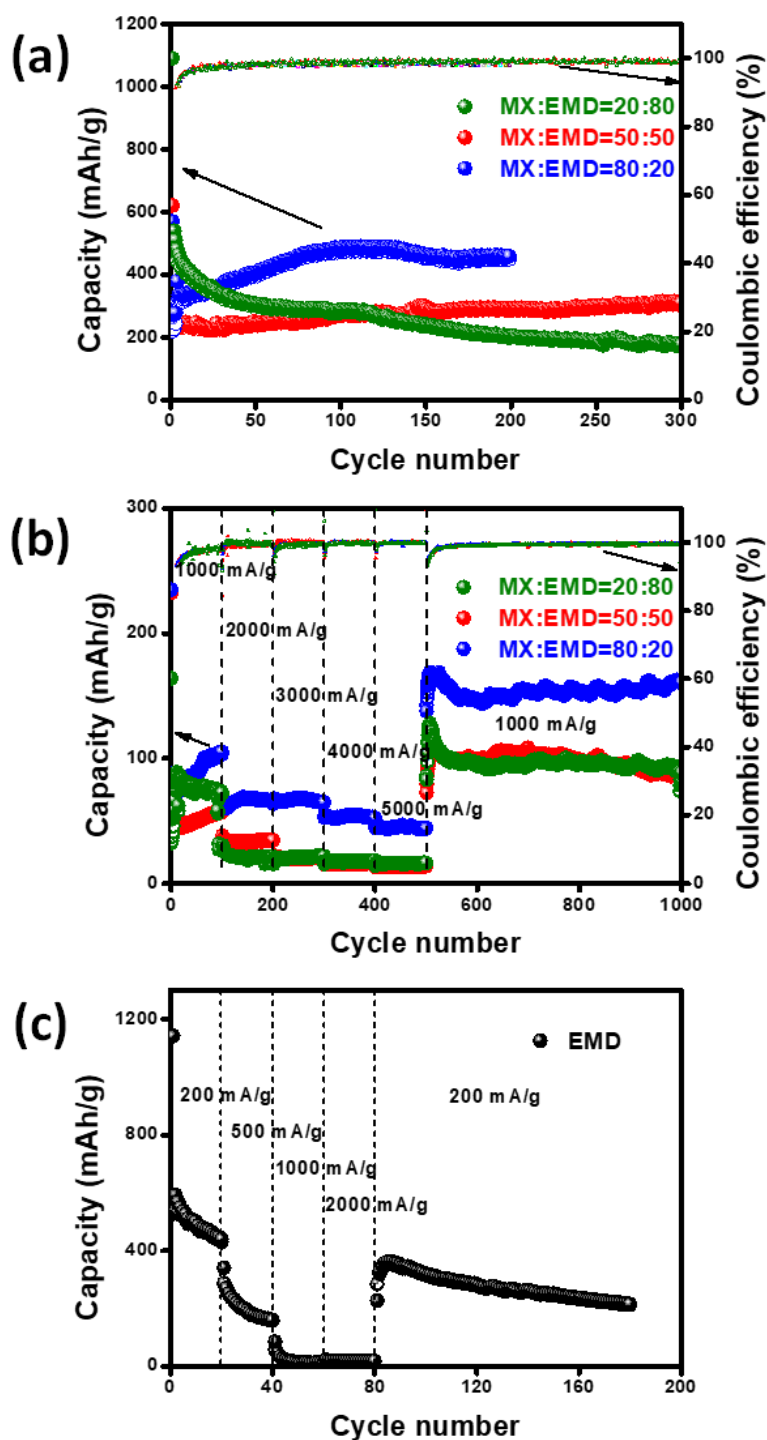


Figure 4.8: (a) Cycling performance and coulombic efficiency of different MX/EMD compositions, cycled at a current density of 100 mA·g⁻¹. (b-c) Rate capability performance and coulombic efficiency of different MX/EMD composition cycled at current densities of 1000, 2000, 3000, 4000 and 5000 mA·g⁻¹ (b) and EMD cycled at current densities of 200, 500, 1000 and 2000 mA·g⁻¹ (c). All tests performed at a potential window of 0.005-3.000 V.

Rate performance

Figure 4.8b shows the rate capability performance of the MX/EMD compositions at current densities of 1000, 2000, 3000, 4000, 5000 and back to 1000 mA·g⁻¹ and the EMD rate capability performance of 200, 500, 1000, 2000 and back to 200 mA·g⁻¹ (Figure 4.8c) in comparison. The EMD capacity fades quickly and continuously at all rates, drops to 10-20 mA·h·g⁻¹ at current densities of 1000-2000 mA·g⁻¹, and continues to fade when the current density goes back to 2000 mA·g⁻¹. On the other hand, MX/EMD compositions hold capacities that are considerably higher. The phenomenon, where the capacity increases with the cycling in the two compositions with higher MX ratio, while it decreases for the composition with the high EMD ratio, is seen here again. In all three compositions, once the current density is stabilised when back to 1000 mA·h·g⁻¹, the capacity reached is substantially higher than the capacity attained after the first 100 cycles at 1000 mA·h·g⁻¹. This implies that there is a continuous Li⁺ insertion process and excellent reversible capacity. For the MX:EMD=20:80 ratio composition, the capacity at the 100th cycle is 73 mA·h·g⁻¹, reaches 128 mA·h·g⁻¹ at cycle ~510, and 90 mA·h·g⁻¹ after 1000 cycles. The MX:EMD=50:50 ratio composition capacity at the 100th cycle is 58 mA·h·g⁻¹, reaches 108 at cycle ~510, and 86 mA·h·g⁻¹ after 1000 cycles. The MX:EMD=80:20 ratio composition's capacity at the 100th cycle is 105, reaches 98 at cycle ~510, and continues to grow steadily to 160 mA·h·g⁻¹ after 1000 cycles. These results indicate that the composition with the higher MXene percentage has a better ability to handle high currents as compared to the other two compositions. Moreover, it has a far better

capability to manage high currents as compared to EMD alone. Efficiency for all materials is close to 100% indicating their stability. It was demonstrated in the material characterization part, that the EMD settles on the MXene surface. But if contents are too high EMD aggregates also form. Here again, it may be stipulated that the high percentage of EMD takes a greater effect in inhibiting the capacity. Therefore, the composition with a higher MXene ratio exhibits far better capacity abilities as compared to the other two compositions and as compared to EMD alone. It is evident that the performance of the EMD-doped Ti_2C -MXene cells favourably compares or even out-performs some related works (see Table A. 1 in Appendix E). For example, doping with EMD has allowed the light Ti_2C -MXene cells to operate at very high C-rates (11 – 20 C). Indeed, even at such high rates (such as 12 C) the cell achieved about the same capacity (71 mAh.g^{-1}) as for lower C-rate (10 C) for the undoped Ti_2C -MXene cell (70 mAh.g^{-1}) [63], [87] or even compared the DMSO-intercalated Ti_3C_2 -MXene cell (69 mAh.g^{-1}) [73]. This work shows the possibility of achieving a scalable process route to obtain EMD-modified MXene materials for high-performance anodes for LIBs.

Electrical impedance spectroscopy

For a further understanding of the Li-ion kinetics as affected by the morphology, EIS tests were conducted. The Nyquist plots of the MX/EMD composites for fresh cells and after cycling are given in

Figure 4.9. The Nyquist plots (Z' vs. Z'') of all the composites were fitted using an electrical equivalent circuit (EEC) given in the inset of Figure 4.9a. In the figure, the dots represent the experimental data and the lines denote the calculated

data. The fitted data parameters obtained for $\chi^2 < 0.001$ are given in Table 4.2. The circuit consists of the elements R_s , R_f , R_{ct} , CPE_f , CPE_{dl} and W_c described here. R_s represents the ohmic resistance of the electrolyte solution, R_f represents the surface film resistance caused by the resistance of the SEI to transport of the Li^+ , and R_{ct} represents the charge transfer resistance through the electrode-electrolyte interface [191]. The CPE_f and the CPE_{dl} represent the constant phase elements of the surface film and double layer capacitance, respectively, instead of pure capacitances. CPE is chosen here due to the heterogeneous nature of the electrode surface. W_c represents the Warburg impedance which is resistance due to the diffusion of Li^+ ions through the solid state of the electrode material. The Nyquist plots of all compositions consist of one semicircle in the high-mid frequency region, represented by R_f and R_{ct} , and an inclined line in the low-frequency region, represented by W_c . The surface film and charge transfer resistance of all three composites are lower after cycling (108, 74, 11 and 120, 100, 32, respectively) as compared to the fresh cells (139, 147, 56 and 515, 312, 289, respectively). The decrease in the resistance after cycling indicates an improvement in the insertion of Li^+ to active sites during cycling and is in agreement with the phenomenon of the increase in capacitance with increased cycling. Moreover, compared to all the compositions, the composition with MX:EMD=80:20 ratio exhibits lower surface film and charge transfer resistance and provides superior performance. This is in agreement with the better capacitance obtained for this composition. The low W_c values indicate very low resistance due to the diffusion of Li^+ ions through the electrode material. The values of n (0.51-0.76) validate the choice of CPE instead of pure capacitance and indicate a pseudo-capacitive behaviour. In conclusion, it

can be seen from the higher impedances before cycling, that the interfacial properties of the aged cells are improved, probably related to better insertion of the Li^+ ions into the matrix.

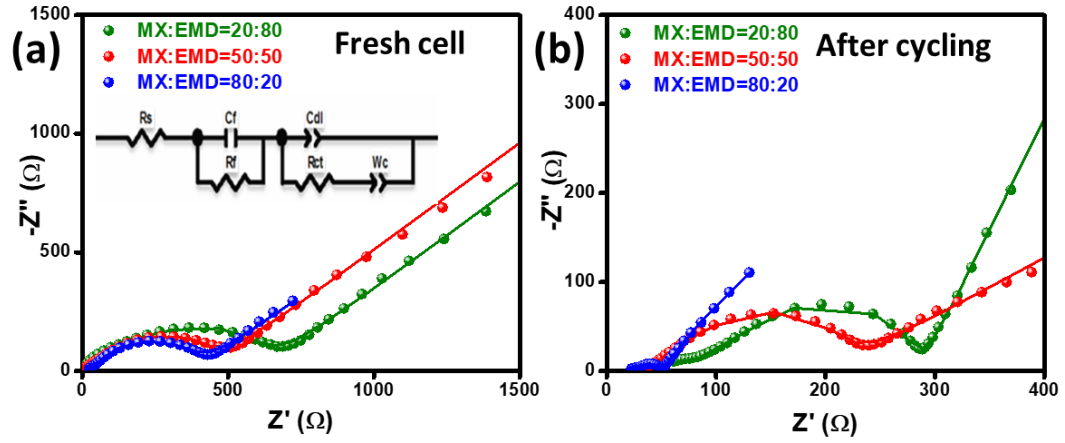


Figure 4.9: Nyquist plots of MX:EMD = 20:80, MX:EMD = 50:50 and MX:EMD = 80:20 compositions for (a) fresh cell and (b) after 200 cycles. The inset of (a) showing the fitted electrical equivalent circuit. The dots and straight line denote experimental results and calculated data, respectively. All data acquired at the open circuit of ~ 2.9 V.

Table 4.2: EIS data parameters fitted using the EEC compared for MX/EMD compositions before (fresh cell) and after testing.

Material	Before/ after testing	R_s ($\pm 5\Omega$)	R_f ($\pm 5\Omega$)	R_{ct} ($\pm 3\mu F$)	n (± 0.02)	W_c ($\pm 0.02\Omega$)
MX:EMD =20:80	Fresh cell	3	139	515	0.58	0.07
	After cycling	54	108	120	0.51	0.08
MX:EMD =50:50	Fresh cell	4	147	312	0.57	0.06
	After cycling	16	74	100	0.58	0.07
MX:EMD =80:20	Fresh cell	11	56	289	0.73	0.04
	After cycling	13	11	32	0.76	0.06

4.4 Conclusions and recommendations

The energy-storage properties of MXene (Ti_2CT_x) material, combined with low-cost EMD in three different ratios, were studied. Results showed that the combined MXene/EMD material has a greater capacity, rate capability and cycling stability as compared to the EMD. The best ratio of MXene to EMD was found to be 80:20, respectively. At this ratio, the added EMD helped in the opening of the MXene layers and reducing stacking, which improved performance as compared to EMD alone and pristine MXene. The capacity obtained is $460 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 200 cycles at a current density of $100 \text{ mA}\cdot\text{g}^{-1}$ as compared to $270 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ after 100 cycles for EMD at the same current density. At higher EMD contents, the performance of the composite was hindered, owing to excess manganese oxide aggregation. The Li-ion accessibility was found to improve with

cycling. Further studies to understand the exact materials that are formed during the synthesis process and the process that allows for the improved Li-ion accessibility are suggested as future research.

This study also provides a first insight into the viability of using a light-weight MXene and EMD composite for improved anodes for lithium-ion batteries. As EMD is a low cost and abundant material, it provides great opportunities for improved capabilities for lightweight applications at an affordable cost, which will probably appeal to industry. Future research work should be directed to this area.

5. Chapter 5: Conclusions and recommendations

5.1 Conclusions

The synthesis and characterization of layered material composites as enhanced electrodes for supercapacitor and battery applications were studied in this work. The work focused on the layered MXene (Ti_2CT_x), as one of the lightest MXenes, combined with other materials for improved electrodes in ECs and LIBs. The work included: (i) tuning the synthesis of MXene Ti_2CT_x and modifying it with carbon nanospheres (CNS) for enhanced symmetric supercapacitor performance in an aqueous electrolyte; (ii) synthesizing and characterizing MXene Ti_2CT_x , combined with a low-cost electrolytic manganese dioxide (EMD), as an anode material for LIBs. The MXene electrode was modified by adding a small amount of CNS to open up the interlayer spacing for testing as an EC electrode. MXene Ti_2CT_x /EMD composites with three different MXene/EMD ratios were synthesized for testing as an anode for LIBs. The structure, morphology and composition of both the MXene/CNS and the MXene/EMD materials were studied using scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM) techniques, energy dispersive X-ray (EDS), X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and Brunauer-Emmett-Teller (BET) surface area analysis. The MXene Ti_2CT_x /CNS composite's electrochemical properties and performance for symmetric supercapacitor in a neutral aqueous electrolyte were investigated by using cyclic voltammetry (CV), galvanostatic charge-discharge, voltage holding and impedance measurements. The results show that when the composite's electrode was assembled into a symmetric cell and operated in an aqueous electrolyte (1 M

Li₂SO₄), a relatively high voltage window of 1.5 V was obtained, which is the first such observation for MXene containing electrodes in an aqueous electrolyte symmetric cell. The ability to undergo long-term cycling was found to be limited. Electrodes were fabricated with relatively high (1.87 mg·cm⁻²) and low (0.17 mg·cm⁻²) mass loading and performance results were compared. Specific capacitance, maximal specific power and specific energy for the lower electrode mass loading were all higher (180 F·g⁻¹, 37.6 kW·Kg⁻¹ and 14.1 W·h·Kg⁻¹) than for a higher mass loading (86 F·g⁻¹, 20.1 kW·Kg⁻¹ and 6.7 W·h·Kg⁻¹). This phenomenon can be explained by the Li⁺ ions' greater difficulty in penetrating the electrode materials and intercalate, in the thicker electrode, thus resulting in a higher resistance and lower electrochemical properties. Modelling and simulation of the EC correlate well with the experimental results, thus, the model used was validated. The performance of the cell was demonstrated by the lighting of an LED.

The energy-storage properties of MXene (Ti₂CT_x) combined with low-cost EMD in three different ratios were also studied using cyclic voltammetry (CV), galvanostatic charge-discharge and impedance measurements. Results showed that the combined MXene/EMD material has a greater capacity, rate capability and cycling stability as compared to the EMD. The best ratio of MXene to EMD was found to be 80:20, respectively. At this ratio, the added EMD helped in the opening of the MXene layers and reducing stacking, which improved performance as compared to EMD alone and pristine MXene. The capacity obtained is 460 mA·h·g⁻¹ after 200 cycles at a current density of 100 mA·g⁻¹ as compared to

270 mA·h·g⁻¹ after 100 cycles for EMD at the same current density. At higher EMD contents, the performance of the composite was hindered, owing to excess manganese oxide aggregation. The Li-ion accessibility was found to improve with cycling.

In summary, the MXene/EMD composition study provides a first insight into the viability of using a light-weight MXene and EMD composite for improved lithium-ion battery anodes. As EMD is a low cost and abundant material, it provides great opportunities for improved capabilities for lightweight applications at an affordable cost, which will probably appeal to the industry. The study for combined MXene/CNS shows that by adding a small amount of CNS to the MXene the properties of symmetric ECs in aqueous neutral electrolytes can be enhanced and a relatively high voltage of 1.5V can be obtained. The use of light-weight MXene to fabricate high-voltage symmetric supercapacitors and enhanced lithium-ion battery anodes gives promise for the realisation of next-generation light-weight portable and flexible electronics.

5.2 Recommendations for future work

Additional research is necessary to further explore the properties of the investigated materials with an aim to improve them. These future studies should include:

- Investigation of the exact causes of instability during cycling of the MXene/CNS composite in order to eliminate them.

- Examination of the origins of the unknown peaks seen in the XRD patterns for the MXene and the understanding of their effects on the performance results.
- Study of the MXene/CNS composite with a suitable counter electrode in an asymmetric configuration to further enlarge the cell's potential window.
- Enhancing the MXene composite using CNS with special additional features, such as N-doped CNS and higher surface area CNS, e.g., treated CNS or hollow CNS, to further improve the capacitance and energy density.
- Fabricating the composite as a thin film electrode and further study their properties for use in lightweight portable and flexible applications.
- Investigation of the unknown peaks in the XRD measurement of the MX:EMD material that originates from the synthesis of the MXene/EMD and understanding of their effects on the performance of the anode for LIBs
- Fine tuning of the exact optimal MXene/EMD ratio for better performance as an anode for LIBs
- Interrogation of the exact cause of improvement in the accessibility of the lithium ion during cycling of the MXene/EMD and exploring the possibility to accelerate it to reach the high capacity in less time without compromising stability and performance.

List of publications

Melchior, S. A., Raju, K., Ike, I. S., Erasmus, R. M., Kabongo, G., Sigalas, I., Iyuke, S. E. and Ozoemena, K. I., ‘High-Voltage Symmetric Supercapacitor Based on 2D Titanium Carbide (MXene, Ti_2CT_x)/Carbon Nanosphere Composites in a Neutral Aqueous Electrolyte’, *J. Electrochem. Soc.*, 165, A501–A511 (2018).

Melchior, S. A., Palaniyandy N., Sigalas, I., Iyuke, S. E. and Ozoemena, K. I., ‘Probing the electrochemistry of MXene (Ti_2CT_x) / electrolytic manganese dioxide (EMD) composites as anode materials for lithium-ion batteries’, submitted.

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Appendix A

Listed herein are a few standards for ECs and for batteries in general and LIBs.

Standards for Electrochemical Capacitors:

- IEC 62391-1, Fixed electric double-layer capacitors for use in electric and electronic equipment. Part 1: Generic specification
- IEC 62391-2, Fixed electric double-layer capacitors for use in electronic equipment. Part 2: Sectional specification - Electric double-layer capacitors for power application
- IEC 62576, Electric double-layer capacitors for use in hybrid electric vehicles - Test methods for electrical characteristics
- BS/EN 61881-3, Railway applications - Rolling stock equipment - Capacitors for power electronics. Part 3: Electric double-layer capacitors
- IEC 62813, Lithium ion capacitors for use in electric and electronic equipment - Test methods for electrical characteristics

General standards for batteries:

- EC 60050, International electrotechnical vocabulary. Chapter 486: Secondary cells and batteries.
- IEC 60086-1, BS 387, Primary Batteries - General
- IEC 60086-2, BS, Batteries - General

- ANSI C18.1M, Portable Primary Cells and Batteries with Aqueous Electrolyte - General and Specifications
- ANSI C18.2M, Portable Rechargeable Cells and Batteries - General and Specifications
- IEEE 1625, Standard for Rechargeable Batteries for Mobile Computers

Standards for Lithium batteries:

- BS 2G 239, Specification for primary active lithium batteries for use in aircraft
- BS EN 50604-1, Secondary lithium batteries for light EV (electric vehicle) applications. Part 1: General safety requirements and test methods
- BS EN/IEC 60086-4, Primary batteries. Safety standard for lithium batteries
- BS EN/IEC 61960-1, Secondary lithium cells and batteries for portable applications. Part 1: Secondary lithium cells
- BS EN/IEC 61960-2, Secondary lithium cells and batteries for portable applications. Part 2: Secondary lithium batteries
- BS EN/IEC 61960-4, Secondary cells and batteries containing alkaline or other non-acid electrolytes. Part 4: Coin type secondary lithium cells and batteries
- IEC 62281, Safety of primary and secondary lithium cells and batteries during transport
- BS EN/IEC 62660-1, Secondary lithium-ion cells for the propulsion of electric road vehicles. Part 1: Performance testing

- ISO/DIS 18243, Electrically propelled mopeds and motorcycles — Test specification and safety requirements for lithium-ion battery system

Appendix B

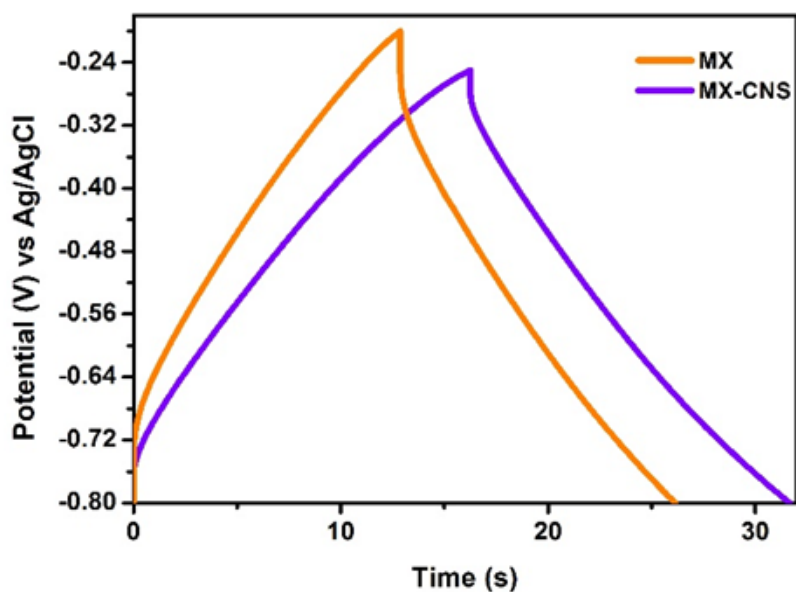


Figure A. 1: Comparative GCPL data of the MX and MX/CNS. All data acquired in a three-electrode system with 1 M Li_2SO_4 electrolyte at $2.5 \text{ A} \cdot \text{g}^{-1}$.

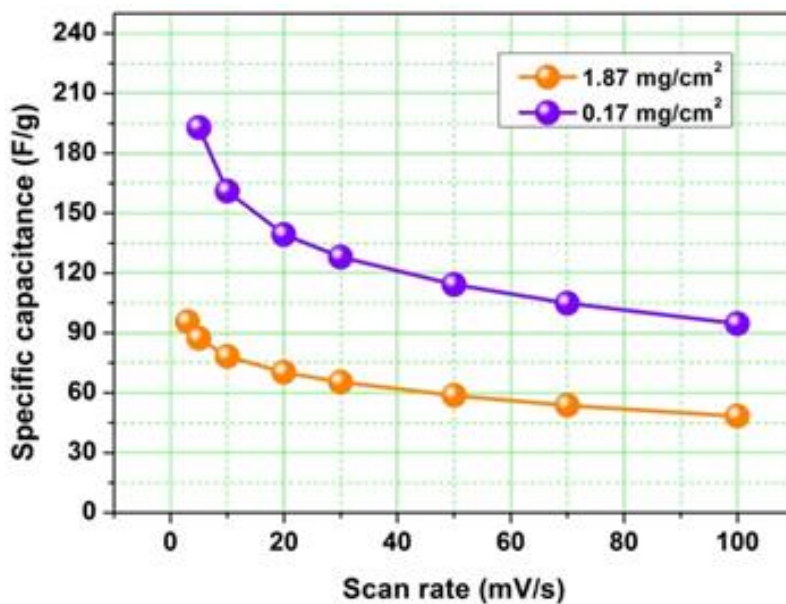


Figure A. 2: Specific gravimetric capacitance from CV at various scan rates for different electrode material mass loading. Data acquired for MX/CNS symmetric coin cells with 1 M Li_2SO_4 electrolyte.

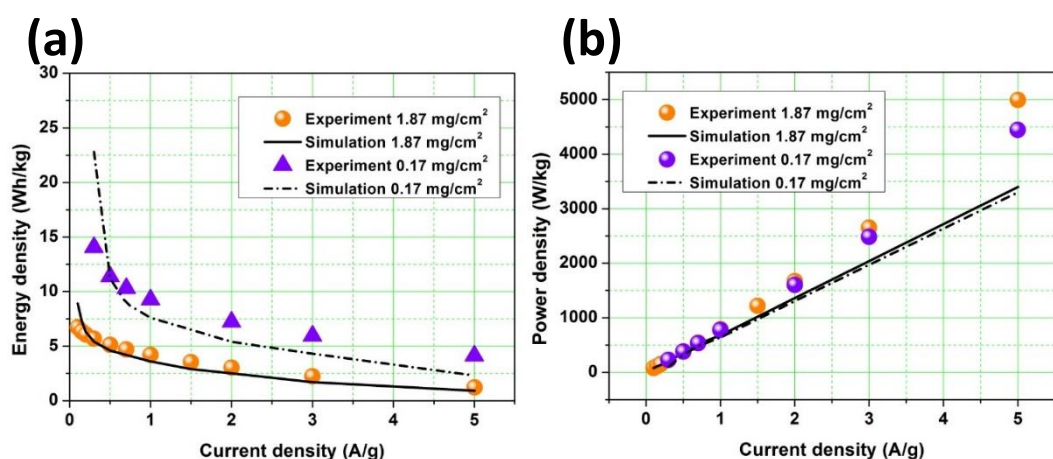


Figure A. 3: (a) Energy density vs current density plot at different mass loadings and corresponding simulation results; (b) Power density vs current density at different electrode material mass loading and corresponding simulation results. All data acquired for MX/CNS symmetric coin cells with 1 M Li_2SO_4 electrolyte.

Appendix C

The identification of the as-received EMD was performed using the Bruker DIFFRAC.SUITE EVA software with the ICDD PDF-4+ database (2016). The EMD was found to consist of a mixture of phases, including (see Figure A. 4 below): Akhtenskite (ϵ -MnO₂ JCPDS 04-005-4883 and 00-030-0820), Ramsdellite (JCPDS 00-044-0142 and 04-005-4334), and JCPDS 00-012-0713.

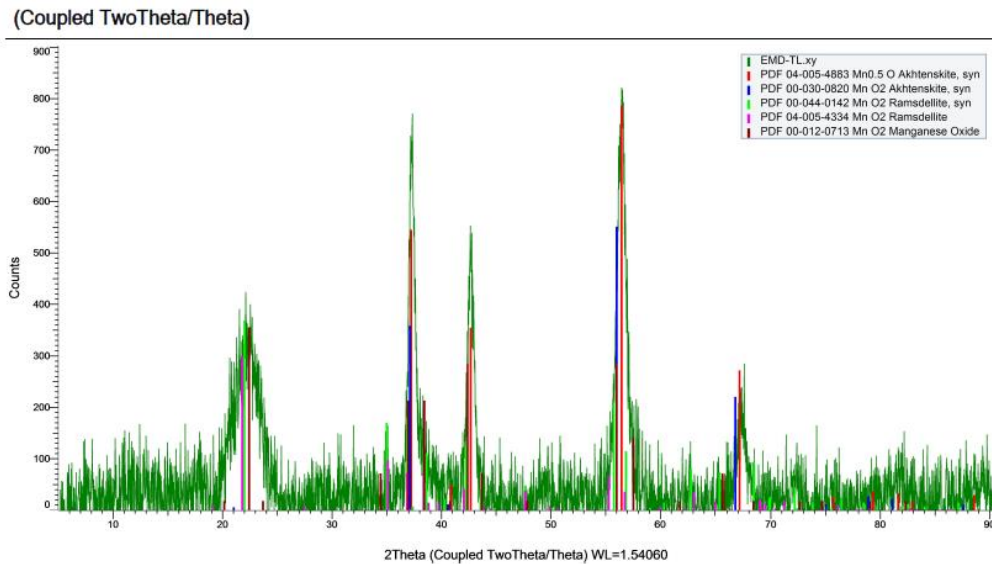


Figure A. 4: XRD pattern of EMD and identified phases.

Several phases can be identified in the XRD diffraction peaks of the MX:EMD=20:80 composition. One identified material is TiC (JCPDS 04-003-3780) as can be seen in Figure A. 5a below, that originates from the MXene sample. In this composition, it can be clearly seen (from Figure 4.1) that the peak at 41.76 ° has decreased as compared to the original MXene and the other compositions. As can be seen from Figure A. 5b, two additional phases that

can be identified are Mn_3O_4 Hausmannite (JCPDS card # 00-024-0734) and TiO_2 Anatase (JCPDS card # 00-021-1272). Another phase that correlates well with the sample peaks is Titanium Manganese Oxide (JCPDS card # 04-008-6706).

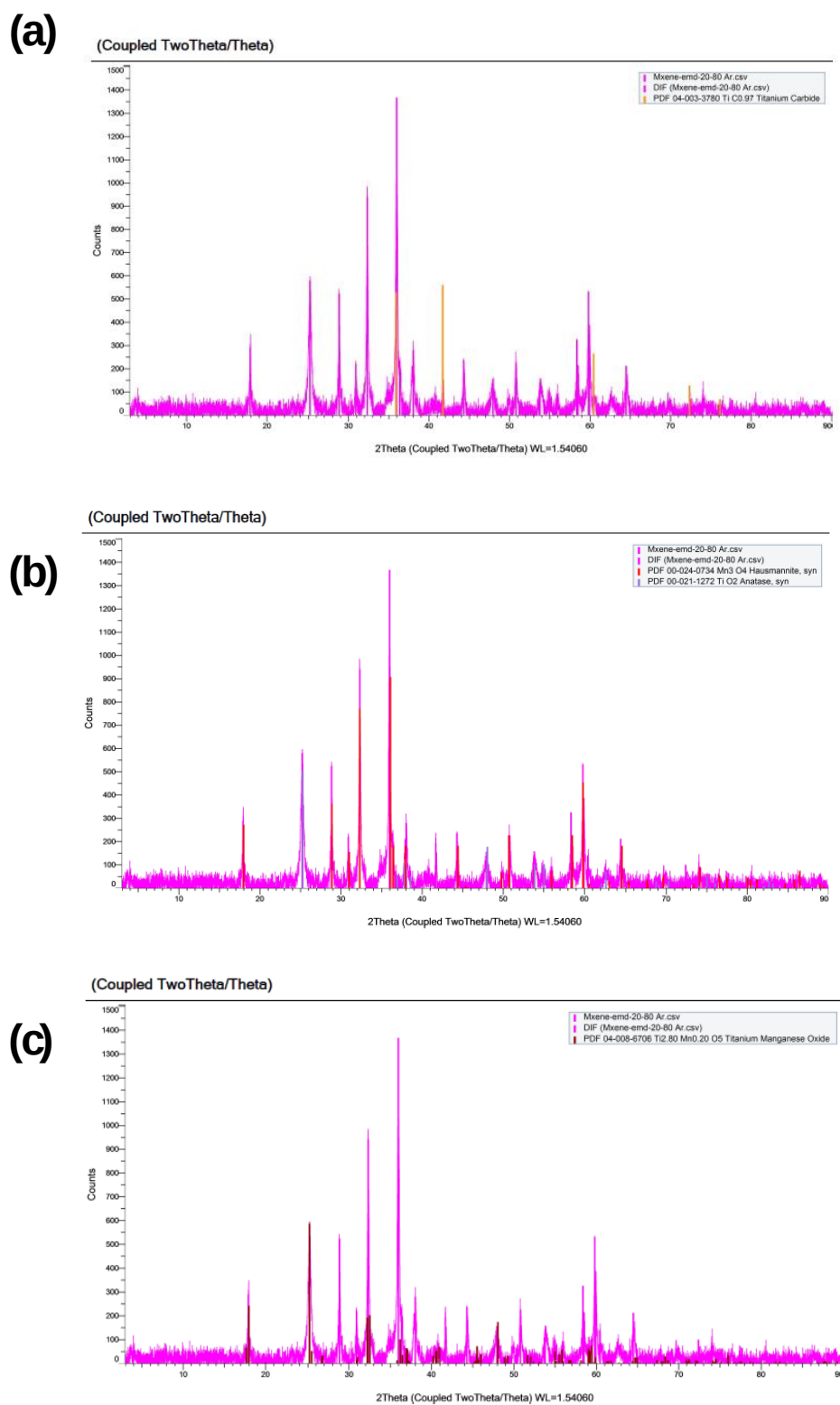


Figure A. 5: XRD pattern of MX:EMD=20:80 composition and identified phases.

Appendix D

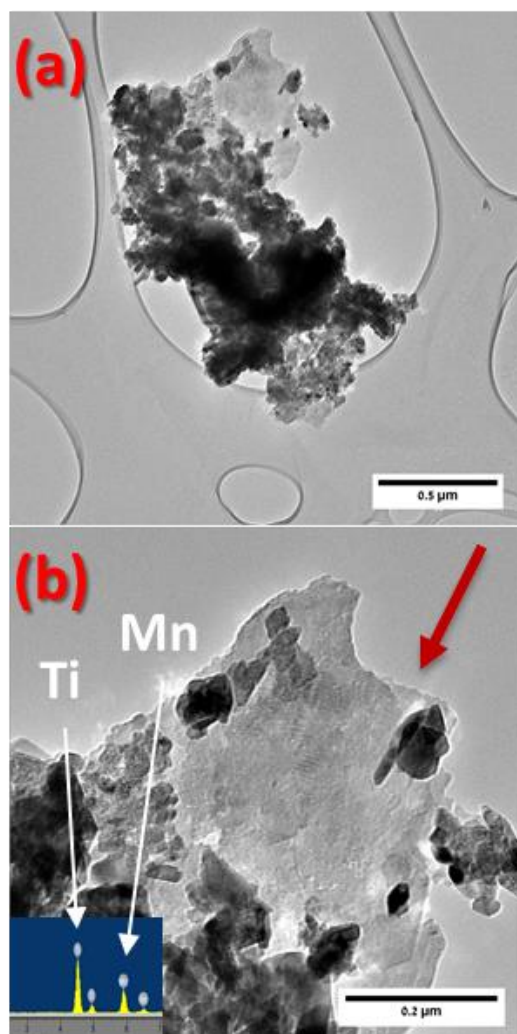


Figure A. 6: TEM images of MX/EMD composition with mass ratios of 20:80 in (a) lower resolution and (b) higher resolution. Inset showing the EDS analysis of the sample. The red arrow points out the MXene thin layers.

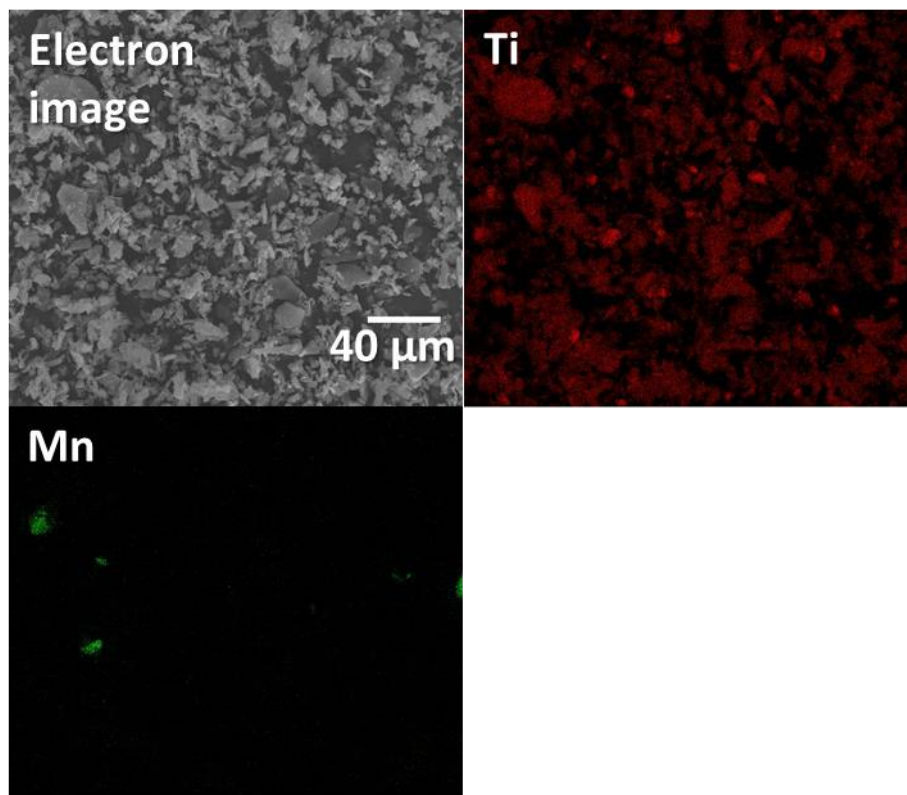


Figure A. 7: EDS mapping of Ti and Mn for the sample with MX:EMD=80:20 composition at low magnification.

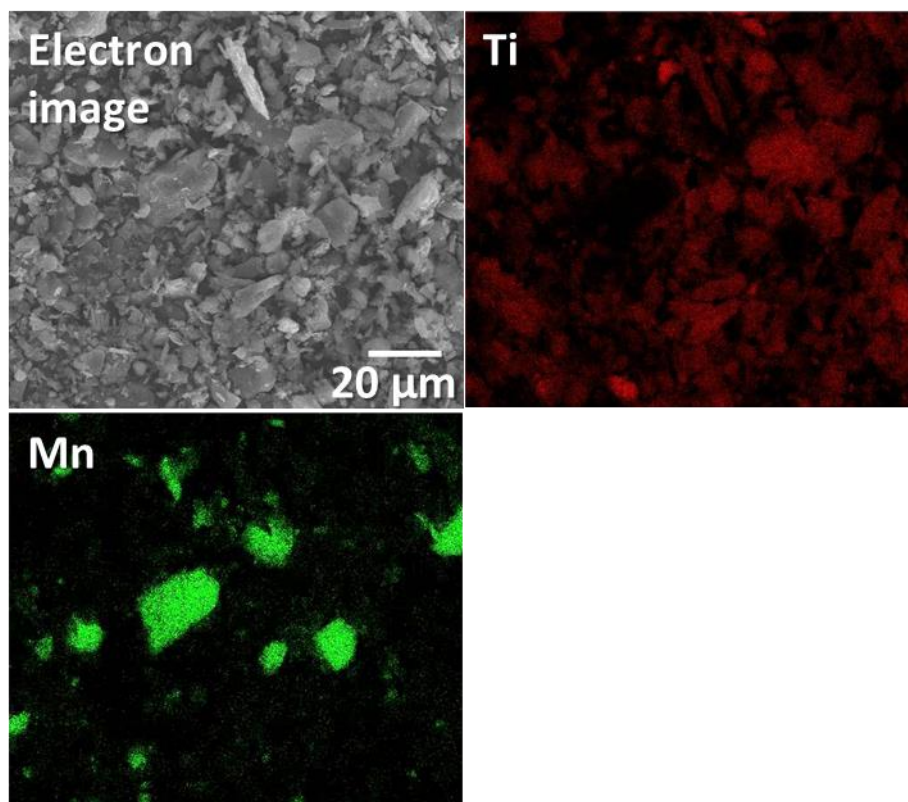


Figure A. 8: EDS mapping of Ti and Mn for the sample with MX:EMD=50:50 composition.

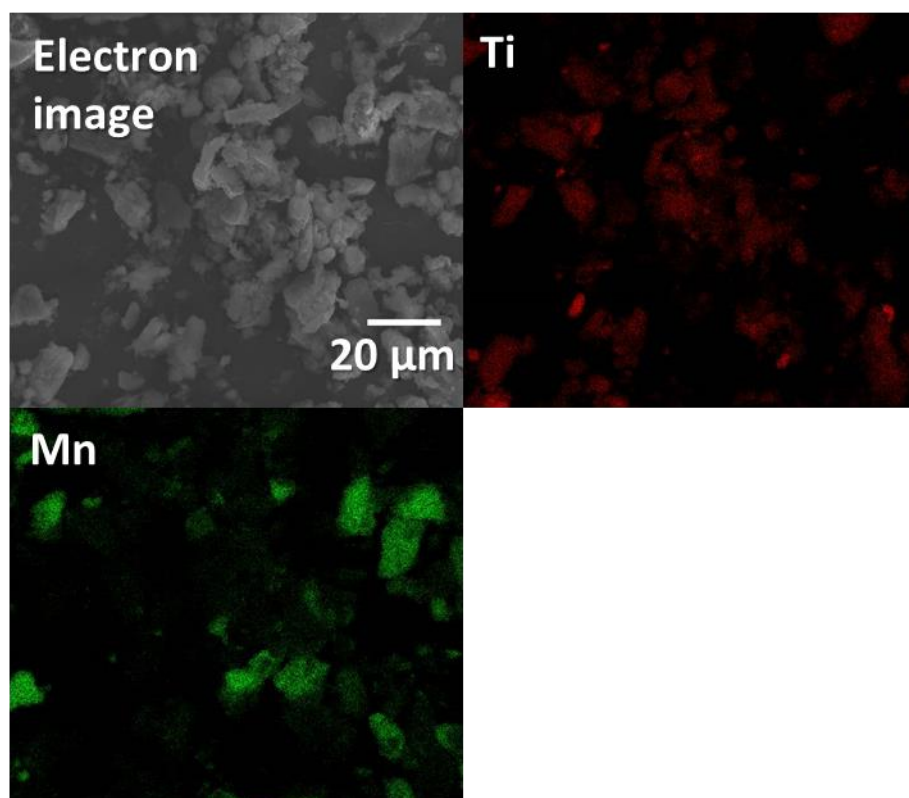


Figure A. 9: EDS mapping of Ti and Mn for the sample with MX:EMD=20:80 composition.

Appendix E

Table A. 1: Electrochemical results of various MXene materials as LIB anodes in a half-cell configuration.

Material	Capacity [mA·h·g ⁻¹]	Current density or C-rate	Cycle no.	Voltage window [V]	Reference no.
Ti ₂ C MXene/EMD composite with mass ratio of MX:EMD=80:20 (HF etched, multi-layered)	460	100 mA·g ⁻¹ (0.4 C)*	200	0.005-3.000	This work
	160	1000 mA·g ⁻¹ (4 C)*	1000		
	71	2000 mA·g ⁻¹ (8 C)*	101-200		
	71	3000 mA·g ⁻¹ (12 C)*	201-300		
	55	4000 mA·g ⁻¹ (16 C)*	301-400		
	46	5000 mA·g ⁻¹ (20 C)*	401-500		
Ti ₂ C MXene (HF etched, multi-layered)	225	0.04 C	5	0.05-2.50	[87]
	160	0.10 C	25		
	~180	0.17 C	10		
	110	1 C	80		
	80	3 C	120		
	70	10 C	200		
H ₂ O ₂ treated Ti ₂ C MXene (HF etched, multi-layered)	389	100 mA·g ⁻¹	50	0.005-3.000	[18]
	297	1000 mA·g ⁻¹	100		
	280	1000 mA·g ⁻¹	1000		
	150	5000 mA·g ⁻¹	400-500		
Ti ₂ C MXene (HF etched, multi-layered)	~250	100 mA·g ⁻¹	50	0.005-3.000	
	~150	1000 mA·g ⁻¹	100		
Ti ₂ C MXene (HF etched, multi-layered)	~150	0.1 C	80	0.5-2.7	[63]
	~140	0.5 C	21-30		
	~130	1 C	31-40		
	~90	5 C	51-60		
	~65	10 C	61-70		
	~100	1 C	150		
Ti ₃ C ₂ MXene (HF etched, multi-layered)	90	1 C (260 mA·g ⁻¹)	75	0.0-2.5	[69]
Ti ₃ C ₂ MXene (HF etched, multi-layered)	121	0.5 C (130 mA·g ⁻¹)	30-35	0.05-3.00	[73]
	179	0.1 C (26 mA·g ⁻¹)	35-40		
Ti ₃ C ₂ MXene intercalated with DMSO (HF etched, multi-layered)	119	1 C (260 mA·g ⁻¹)	75	0.05-3.00	
	88	3 C (780 mA·g ⁻¹)	100		
	69	10 C (2600 mA·g ⁻¹)	100		
Ti ₃ C ₂ MXene cold pressed disc with CB and no binder	97	0.33 C (30 mA·g ⁻¹)	50	0.005-3.000	[22]
Porous Ti ₃ C ₂ MXene	~110	0.5 C	100	0.01-3.00	[182]
Pristine Ti ₃ C ₂ MXene/CNT	~220	0.5 C	70		
Porous Ti ₃ C ₂ MXene /CNT	~790	0.5 C	100		
Ti ₃ C ₂ MXene	~80	1000 mA·g ⁻¹	200	0.01-2.50	[190]
Li ₄ Ti ₅ O ₁₂ -Ti ₃ C ₂	~200	1000 mA·g ⁻¹	200		

* For capacity calculation, 1C based on M_w of Ti₂C (107.7 g·gmol⁻¹):

$$\text{Theoretical gravimetric capacity: } C_{th} = \frac{1000nF}{3600M_w}$$

where n here is the one Li⁺ ion reacting to form the lithiated component, F is Faraday's constant (96485 C·gmol⁻¹), and M_w is the molecular weight of the active material.

$$C_{th} = \frac{96485 \frac{C}{gmol} \times 1 Li^+}{107.7 \frac{g}{gmol} \times 3600 \frac{s}{h}} \times 1000 \frac{mA}{A} = 250 mA \cdot h \cdot g^{-1} = 1 C$$